

qXNMR references

1. Improved Characterization of the Botanical Origin of Sugar by Carbon-13 SNIF-NMR Applied to Ethanol

ByThomas, Freddy; Randet, Celia; Gilbert, Alexis; Silvestre, Virginie; Jamin, Eric; Akoka, Serge; Rемаud, Gerald; Segebarth, Nicolas; Guillou, Claude

From Journal of Agricultural and Food Chemistry (2010), 58(22), 11580-11585.Language:English, Database: CAPLUS, DOI: 10.1021/jf102983v

Until now, no anal. method, not even isotopic ones, had been able to differentiate between sugars coming from C4-metab. **plants** (cane, maize, etc.) and some crassulacean acid metab. **plants** (e.g., pineapple, agave) because in both cases the isotope distributions of the overall carbon-13/carbon-12 and site-specific deuterium/hydrogen isotope ratios are very similar. Following recent advances in the field of **quant.** isotopic carbon-13 **NMR** measurements, a procedure for the anal. of the positional carbon-13/carbon-12 isotope ratios of ethanol derived from the sugars of pineapples and agave using the site-specific natural isotopic fractionation-**NMR** (SNIF-**NMR**) method is presented. It is shown that reproducible results can be obtained when appropriate anal. conditions are used. When applied to pineapple juice, this new method demonstrates a unique ability to detect cane and maize sugar, which are major potential adulterants, with a detection limit in the order of 15% of the total sugars, which provides an efficient mean of controlling the authenticity of juices made from this specific fruit. When applied to tequila products, this new method demonstrates a unique ability to unambiguously differentiate authentic 100% agave tequila, as well as misto tequila (made from at least 51% agave), from products made from a larger proportion of cane or maize sugar and therefore not complying with the legal definition of tequila.

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2. Chemical Structure and Heterogeneity Differences of Two Lignins from Loblolly Pine As Investigated by Advanced Solid-State NMR Spectroscopy

ByHoltman, Kevin M.; Chen, Na; Chappell, Mark A.; Kadla, John F.; Xu, Ling; Mao, Jingdong

From Journal of Agricultural and Food Chemistry (2010), 58(18), 9882-9892.Language:English, Database: CAPLUS, DOI: 10.1021/jf101258x

Advanced solid-state **NMR** was employed to investigate differences in chem. structure and heterogeneity between milled wood lignin (MWL) and residual enzyme lignin (REL). Wiley and conventional milled woods were also studied. The advanced **NMR** techniques included ¹³C **quant.** direct polarization, various spectral-editing techniques, and two-dimensional ¹H-¹³C heteronuclear correlation **NMR** with ¹H spin diffusion. The ¹³C chem. shift regions between 110 and 160 ppm of two lignins were quite similar to those of two milled woods. REL contained much more residual carbohydrates than MWL, showing that MWL extn. more successfully sepd. lignin from cellulose and hemicelluloses than REL extn.; REL was also of higher COO, arom. C-C, and condensed aroms. but of lower arom. C-H. At a spin diffusion time of 0.55 ms, the **magnetization** was equilibrated through the whole structure of MWL lignin, but not through that of REL, indicating that REL is more heterogeneous than MWL.

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3. Medullosalean fusain trunk from the roof rocks of a coal seam: Insight from FTIR and NMR (Pennsylvanian Sydney Coalfield, Canada)

ByZodrow, Erwin L.; Mastalerz, Maria; Werner-Zwanziger, Ulrike; D'Angelo, Jose A.

From International Journal of Coal Geology (2010), 82(1-2), 116-124.Language:English, Database: CAPLUS, DOI:

Reported for the first time from the Sydney Coalfield, Canada, is a fragmentary fusain (**R_o** = 2.51%) specimen, 41 cm long, of a medullosalean trunk or massive petiole that originated from the roof rocks of the

banded bituminous Hub Seam (**R_o** ~ 0.65%). Megascopic characteristics of the flat-preserved specimen

include an irregular-cracked fusain surface with secretinite-rodlet structures and sclerenchymatous strands some of which still embedded in the shaly matrix, and locally preserved vitrain (**R_o** = 0.69%). Co-occurrence with a compression **flora** composed virtually of only the seed-fern taxon *Macroneuropteris scheuchzeri* (Hoffmann) is noted. The goal of this study is to provide a framework for the phytophysicochem. taphonomic history which includes the perspective on vitrinite/fusinite relationship, formation of fusinite, and on the significance the only fusinized identifiable **plant**-fossil specimen in the Sydney Coalfield. We use state-of-the-art solid-state FTIR, ¹³C, ¹H **NMR** CP/MAS techniques, and std. reflected-light microscopy and SEM methods as investigative tools. Results indicate that the fusinite is characterized by long and narrow xylem fibers, without fungal signals, and cell structures infilled with pyrite and carbonate. FTIR spectra of the fusinite and secretinite are similar particularly in respect to high absorbance of arom. and low absorbance of aliph. compds., and absorbance of Si-O functionalities relating to kaolinite. ¹³C **NMR** expts. with direct carbon excitation **quantify** the arom. to aliph. ratio as being 20 ± 3:1. As part of the taphonomic history, the evidence favors a hot, > 400 °C, directional surface-fueled flame palaeofire of local extent that charred trunks of growing arborescent seed ferns on only one side, and that these trunks were transported to comprise part of the roof rocks of the Hub Seam.

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4. Biochars from fast pyrolysis and gasification of switchgrass and corn stover

ByBrewer, Catherine E.; Unger, Rachel; Brown, Robert C.

From Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010 (2010), ENVR-438.Language:English, Database: CAPLUS

Seventeen chars with known prodn. conditions were selected for chem. and phys. characterization from fast pyrolysis and gasification of switchgrass and corn stover. Slow pyrolysis chars of the same feedstocks, as well as several hardwood chars, were included for comparison. The methods used to characterize the chars included proximate anal., CHNS elemental anal., BET surface area, higher heating value (HHV), particle d., photo-acoustic Fourier transform IR spectroscopy (FTIR-PAS), cation exchange capacity (CEC), and **quant.** ¹³C solid-state **NMR (NMR)** spectroscopy. Special attention was paid to the types of carbon and degree of aromaticity present in the char in relation to pyrolysis temp. A follow-on soil incubation study was also conducted to relate char properties to soil fertility (**plant**-available nutrients, CEC, etc) **responses**.

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5. Solubility of wood and wood biopolymers in ionic liquids

ByKing, Alistair W.; Jarvi, Paula; Olszewska, Anna; Kilpelainen, Ilkka; Argyropoulos, Dimitris S.

From Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010 (2010), CELL-328.Language:English, Database: CAPLUS

The reported ability of certain ionic liqs. to dissolve wood is often attributable to their efficiency in solubilising cellulose, as a major constituent of **plant** material. A recently developed process of phosphorylation, followed by **quant.** ³¹P **NMR** anal., of wood and purified wood biopolymers from a given media can afforded semi-empirical evidence of their soly. in that media. Advanced information and discussion on the soly. of native and refined wood biopolymers (wood, cellulose, lignin, xylan and galactoglucomannan) in certain ionic liqs.

is consequently presented. Significant soly. differences are obsd. suggesting new avenues for non-destructive and potentially environmentally benign fractionation. Addnl., valuable information about the reactivity and structure of wood biopolymers has been uncovered, including such simple concepts as total no. of hydroxyls per mass unit of material. It is expected that this information be used for the continued realization of the ionic liq.-based biorefinery concept and assocd. materials science.

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6. Quantitative ^{13}C NMR of whole and fractionated Iowa Mollisols for assessment of organic matter composition

ByFang, Xiaowen; Chua, Teresita; Schmidt-Rohr, Klaus; Thompson, Michael L.

From *Geochimica et Cosmochimica Acta* (2010), 74(2), 584-598. Language: English, Database: CAPLUS, DOI: 10.1016/j.gca.2009.10.008

Do the amts. of recalcitrant components of soil org. matter (SOM) vary with landscape position. To address this question, we studied four Mollisols in central Iowa, two developed in till and two developed in loess, were studied. Two of the soils were well drained and two were poorly drained. Surface-horizon samples were collected and the org. matter studied in the particulate org. matter (POM) fraction, the clay fractions, and the whole, unfractionated samples. The soil samples were treated with 5 M HF at ambient temp. or at 60 °C for 30 min to conc. the SOM. To assess the compn. of the SOM, solid-state NMR spectroscopy, in particular, quant. ^{13}C DP/MAS (direct-polarization/magic-angle spinning), was used with and without recoupled dipolar dephasing. Spin counting by correlation of the integral NMR intensity with the C concn. by elemental anal. showed that NMR was $\geq 85\%$ quant. for the majority of the samples studied. For untreated whole-soil samples with < 2.5 wt.% C, which is considerably less than in most previous quant. NMR analyses of SOM, useful spectra that reflected $\geq 65\%$ of all C were obtained. The NMR analyses led to the conclusion that (1) the HF treatment (with or without heat) had low impact on the org. C compn. in the samples, except for protonating carboxylate anions to carboxylic acids, (2) most org. C was observable by NMR even in untreated soil materials, (3) esters were likely to compose only a minor fraction of SOM in

these Mollisols, and (4) the arom. components of SOM were enriched to $\sim 53\%$ in the poorly drained soils,

compared with $\sim 48\%$ in the well drained soils; in plant tissue and particulate org. matter (POM) the

aromaticities were $\sim 18\%$ and $\sim 32\%$, resp. Nonpolar, nonprotonated arom. C, interpreted as a proxy for

charcoal C, dominated the arom. C in all soil samples, composing 69-78% of arom. C and 27-36% of total org. C in the whole-soil and clay-fraction samples.

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7. Accurate Quantitative Isotopic ^{13}C NMR Spectroscopy for the Determination of the Intramolecular Distribution of ^{13}C in Glucose at Natural Abundance

ByGilbert, Alexis; Silvestre, Virginie; Robins, Richard J.; Remaud, Gerald S.

From *Analytical Chemistry* (Washington, DC, United States) (2009), 81(21), 8978-8985. Language: English, Database: CAPLUS, DOI: 10.1021/ac901441g

In order to understand ^{13}C isotope distributions in glucose and its metabolites, it is necessary to measure

the internal ^{13}C distribution at natural abundance. These data, however, are not directly accessible, even by **quant.** isotopic ^{13}C **NMR** spectrometry, due to anomerization at the C-1 position. A strategy has been developed that overcomes this difficulty by converting glucose via a three-step synthesis into 3,5,6-triacetyl-1,2-O-isopropylidene- α -D-glucofuranose (TAMAGF). This compd. provides a satisfactory mol. probe to measure the site-specific $^{13}\text{C}/^{12}\text{C}$ ratios in glucose by ^{13}C **NMR**. It is shown that the isotopic ^{13}C **NMR** signal gives sufficient precision (repeatability std. deviation ≤ 0.8 0/00, V-PDB scale) for routine use for the detn. of the ^{13}C abundance of each carbon atom position in glucose. Thus, it can be seen that the internal ^{13}C distribution of glucose biosynthesized by the C3 and C4 metabolic pathways differs markedly. Furthermore, the method is suitable for detg. the isotope ratio in the glucose moiety of sucrose and, possibly, in free fructose and the fructose moiety of sucrose.

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8. Phosphorus speciation in temperate basaltic grassland soils by solution ^{31}P NMR spectroscopy

ByMurphy, P. N. C.; Bell, A.; Turner, B. L.

From European Journal of Soil Science (2009), 60(4), 638-651.Language:English, Database: CAPLUS, DOI: 10.1111/j.1365-2389.2009.01148.x

Phosphorus (P) speciation in 21 basaltic and four non-basaltic Irish grassland soils was detd. by NaOH-EDTA extn. and ^{31}P **NMR** spectroscopy. Org. P in basaltic soils ranged between 30 and 697 mg P kg⁻¹ and consisted of phosphate monoesters (84-100%), DNA (0-16%) and phosphonates (0-5%). Inorg. P was mainly phosphate (83-100%) with small concns. of pyrophosphate (0-17%). Phosphate monoesters were more important as a proportion of extd. P in basaltic soils, probably because of their greater oxalate-extractable Fe and Al contents. Phosphate monoesters appeared to be strongly assocd. with non-cryst. Al and increased with total soil P concn., indicating that they do accumulate in grassland soils. In non-basaltic soils myo-inositol hexakisphosphate constituted between 20 and 52% of org. P, while scyllo-inositol hexakisphosphate constituted between 12 and 17%. These compds. were not **quantified** sep. in basaltic soils because of poor **NMR** resolu. in the phosphate monoester region, but appeared to represent a considerable proportion of the org. P in most samples. DNA concns. were greater in basaltic soils compared with non-basaltic soils and were assocd. with acidic pH and large total C contents. The inability of the Olsen P test to assess effectively the P status of basaltic soils may result from strong phosphate sorption to Fe and Al oxides, inducing **plant** utilization of soil org. P. Phosphorus nutrient management should account for this to avoid **over**-application of P and assocd. financial and environmental costs.

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9. Characterization of bright tobaccos by multivariate analysis of ^{13}C CPMAS NMR spectra

ByWooten, Jan B.; Kalengamaliro, Newton E.; Axelson, David E.

From Phytochemistry (Elsevier) (2009), 70(7), 940-951.Language:English, Database: CAPLUS, DOI: 10.1016/j.phytochem.2009.04.015

Univariate and multivariate statistics were applied to characterize cured bright tobacco samples on the basis of their ^{13}C CPMAS **NMR** spectra and leaf constituent anal. **NMR** spectra were obtained for 55 samples selected from a set of 134 samples of graded bright tobacco leaves from crop year 1999. Historical leaf constituent analyses were available for total alkaloids, reducing sugars, total nitrogen, and insol. ash. In addn., HPLC was applied to **quantify** the two abundant **plant** polyphenols, chlorogenic acid, and rutin. Principal component anal. (PCA) and partial least squares (PLS) of the **NMR** spectra revealed systematic relationships between groups of samples related to these substances and afforded predictive **quant.** models for the analyzed constituents. Anal. of the PLS significant variables showed that leaf polysaccharides, alkaloids, and minerals are major determinants influencing the grading of cured bright tobacco leaves.

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10. Characterization of Various Fast-Pyrolysis Bio-Oils by NMR Spectroscopy

ByMullen, Charles A.; Strahan, Gary D.; Boateng, Akwasi A.

From Energy & Fuels (2009), 23(5), 2707-2718. Language: English, Database: CAPLUS, DOI: 10.1021/ef801048b

NMR spectroscopy, including ^1H , ^{13}C , and DEPT spectra, was used to characterize fast-pyrolysis oils from numerous energy crops and other agricultural feedstocks. The bio-oils studied were produced from switchgrass, alfalfa stems, corn stover, guayule (whole **plant** and latex-extd. bagasse), and chicken litter. The ^1H and ^{13}C **NMR** spectra were integrated **over** spectral regions to **quantify** classes of carbon and hydrogen atoms in each bio-oil sample. DEPT spectra were used to **quantify** by protonation, and the no. of the carbon atoms in each of those classes was used to give further information on the types of mols. that are found in the bio-oil. The **NMR** spectra of the bio-oils varied greatly. The percentage of carbons and protons in the upfield regions of the **NMR** spectra tracked with the energy content of the bio-oil as well as the feedstock type, but there was no such consistent trend for the arom. content. Degrees of branching in the aliph. portions of the bio-oils were inferred from percentages of CH₁, CH₂, and CH₃ groups. Arom. portions were extremely complex, with substituted arom. carbons outnumbering unsubstituted arom. carbons >2:1 in most cases. Fully substituted carbons represented 27-37% of all the carbons in the sample.

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11. Analytical pyrolysis and thermally assisted hydrolysis and methylation of EUROSOIL humic acid samples - A key to their source

ByBuurman, P.; Nierop, K. G. J.; Kaal, J.; Senesi, N.

From Geoderma (2009), 150(1-2), 10-22. Language: English, Database: CAPLUS, DOI: 10.1016/j.geoderma.2008.12.012

Humic acids have been widely investigated by spectroscopic methods, esp. **NMR** and FTIR, and they are known to show significant differences according to their origin. Low resolu. methods such as **NMR** and FTIR, however cannot easily distinguish different input sources or establish relations between SOM chem. and **vegetation** or land use in general. High resolu. methods, such as anal. pyrolysis and pyrolysis combined with methylation do offer such possibilities. Therefore, HAs from five ref. soils called the Eurosoils, including a Vertic Cambisol (E1, Italy), a Rendzina (E2, Greece), a Dystric Cambisol (E3, Great Britain), an Orthic Luvisol (E4, France) and an Orthic Podzol (E5, Germany), that were previously characterized a.o. by **NMR**, FTIR and ESR, were also analyzed by pyrolysis-gas chromatog./mass spectrometry (Py-GC/MS) and thermally assisted hydrolysis and methylation (THM) and subsequent anal. by GC/MS. The Orthic Podzol sample showed the largest aliphaticity, and the strongest degrdn. of aliphatics and lignin. The Dystric Cambisol featured the least decompd. HA, which was reflected by a large content of long-chain alkanes, and little lignin degrdn. Both the Dystric Cambisol and the Orthic Luvisol HAs contained a significant amt. of microbial org. matter. Polyaroms., which indicate the presence of charred material, were most abundant in the Vertic Cambisol and the Podzol HAs and lowest in the Dystric Cambisol and the Rendzina HAs. THM was able to distinguish between the various vegetations/land uses. Although **quantifications** by **NMR** and py-GC/MS are essentially different, the general results largely coincided. **NMR** appears to underestimate aromaticity and overestimate aliphaticity, but a mol. mixing model yielded reasonable correlations between **NMR** and pyrolysis data. Classification by degrdn. state' based on py-GC/MS largely coincided with acidity detd. by titrn., but FTIR data did not coincide. Py-GC/MS, with its much larger resolu., is a better tool to distinguish effects of **vegetation**, microbial input, and degrdn. HA's produce the same variety of compds. upon pyrolysis as total SOM exts. and are therefore chem. not more simple than SOM. HA chem., however can be understood in the light of land use history and SOM dynamics.

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12. Effect of alkali-activation on aluminosilicate-based cementitious materials

ByYang, Xiaoguang; Ni, Wen; Zhang, Xufang; Wang, Yali

From Journal of University of Science and Technology Beijing (2008), 15(6), 796-801. Language: English, Database: CAPLUS, DOI: 10.1016/S1005-8850(08)60290-X

High-performance aluminosilicate-based cementitious materials were produced with fly ash from a coal power **plant** as one of the major raw materials. The structures of fly ash contg. aluminosilicate-based cementitious materials were compared before and after treatment by the methods of **NMR** and SEM. During the 28 d curing time, the compressive strength of water glass and fly ash samples increased from 9.08 MPa to 26.75 MPa. The results show that most of the stiff shells are destroyed after mech. grinding and chem. activation. Magic angle spinning (MAS) **NMR** of ^{27}Al shows that the wide peak becomes narrow and the main peak shifts to the direction of low field, indicating the decrease of polymn. degree, the enhancing of activity, the decrease of six-coordination structure, and the increase of small and sym. four-coordination polyhedron structure within the aluminum-oxygen polyhedron network. Comparisons between MAS **NMR** of ^{29}Si with different treatments suggest that Q0 disappears, the **quantity** of Q2 increases, and the **quantity** of Q4 decreases. The polymn. degree of silicon-oxygen is reduced, and the potential activity of fly ash is increased.

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13. Quantitative high-resolution online NMR spectroscopy in pharmaceutical reaction and process monitoring

ByMaiwald, M.; Steinhof, O.; Sleight, C.; Bernstein, M.; Hasse, H.

Edited byHolzgrabe, Ulrike; Wawer, Iwona; Diehl, Bernd

From NMR Spectroscopy in Pharmaceutical Analysis (2008), 471-491. Language: English, Database: CAPLUS, DOI: 10.1016/B978-0-444-53173-5.00020-2

A review. **Quant.** high-resoln. online **NMR** spectroscopy is the method of choice for investigating complex reacting mixts. We describe the use of **NMR** flow cells for pharmaceutical reaction and process monitoring where reactions and processes can be covered from several hours down to minutes.

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14. Biomass Characterization of Buddleja Davidii: a Potential Feedstock for Biofuel Production

ByHallac, Bassem B.

From Abstracts, 60th Southeast Regional Meeting of the American Chemical Society, Nashville, TN, United States, November 12-15 (2008), SERM-252. Language: English, Database: CAPLUS

Many researchers are focusing on developing alternative and sustainable sources of energy, esp. transportation fuels. One of the promising sustainable sources of energy is biofuels, including bioethanol from lignocellulosic materials such as wood, agricultural or forest residues. These materials do not directly compete with food and can be grown on non-agricultural lands. Buddleja davidii is a shrub that originated in China, but has been naturalized in different parts of the world, including the U.S. As a potential bioresource for biofuels this **plant** has several attractive agro-energy features. It exhibits a very wide range of growth habitat and is well adapted to growing in poor soil conditions. The **plant** is perennial, has moderate growth dimensions, and has very few pests or diseases. These attributes suggest that this **plant** could be a valuable future agro-energy crop. Further, it has no food-value which eliminates the concerns of todays starch based biofuels feedstocks. This research project constitutes the first detailed characterization of this novel biomass feedstock and the results will help det. the appropriate chem. and enzymic pathways for its conversion to biofuels. Results from the biomass characterization of B. davidii, which includes the detn. of lignin, hemicellulose, and cellulose contents, as well as, detailed elucidation of the chem. structures of both lignin and cellulose by **NMR** will be presented. Solid-state CP/MAS ^{13}C **NMR** has been used to study the structure of cellulose, in terms of the relative amts. of cellulose I α , cellulose I β , para-cryst. cellulose, and celluloses at accessible and inaccessible surfaces. Structural characterization of lignin has been performed

using **quant.** ^{13}C **NMR** and ^{31}P **NMR** spectroscopy.

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15. A simplified method for the quantification of pyrogenic organic matter in grassland soils via chemical oxidation

ByKnicker, Heike; Wiesmeier, Martin; Dick, Deborah P.

From Geoderma (2008), 147(1-2), 69-74. Language: English, Database: CAPLUS, DOI: 10.1016/j.geoderma.2008.07.008

The elucidation of the impact of pyrogenic org. carbon (PyOC) on soil ecol. functions and its role within geobiochem. cycles requires a **quantification** that is not restricted to a certain window of the Black Carbon continuum. In the present study the method of chem. oxidn. with acid dichromate was modified to allow for the detn. of the whole range of PyOC in soil systems frequently subjected to prescribed fires with a fairly homogenous intensity distribution. After confirming the reproducibility of the technique, top and subsoils of Leptosols and Umbrisols from a grassland (Campo) landscape in the Planalto region, Southern Brazil were demineralized with hydrofluoric acid and subsequently the residues were chem. oxidized. Solid-state ^{13}C **NMR** spectroscopy was applied to distinguish between chem. oxidn. resistant elemental C (COREC) of pyrogenic org. carbon (PyOC) and lipid components surviving the harsh treatment because of their hydrophobic properties. Correlation of the arom. COREC content of the samples with their arom. C content resulted in a pos. correlation with $R^2 = 0.74$ for the topsoils and $R^2 = 0.53$ for the subsoils. The correlation functions allowed the development of an equation that yields in a correction factor f , which is necessary to account for the C-losses of PyOC caused by the chem. oxidn. and thus for the estn. of its original contribution to the soil. For the topsoils this correction factor was comparable to that detd. for a model char derived from the Campo **vegetation** after charring for 4 min at $350\text{ }^\circ\text{C}$. Applying this factor to Campo **plant-char/soil** mixts. resulted in recoveries between 93 and 125%, indicating that it should be possible to elucidate the PyOC content of soils by the detn. of COREC_{arom} and subsequent multiplication with f . In soil systems with char input of fairly consistent chem. compn., as they occur in prescribed grassland fires, f may be directly obtained from model chars produced from the resp. **vegetation** cover.

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16. Influence of animal manure application on the chemical structures of soil organic matter as investigated by advanced solid-state NMR and FT-IR spectroscopy

ByMao, Jingdong; Olk, Dan C.; Fang, Xiaowen; He, Zhongqi; Schmidt-Rohr, Klaus

From Geoderma (2008), 146(1-2), 353-362. Language: English, Database: CAPLUS, DOI: 10.1016/j.geoderma.2008.06.003

Annual application of cattle manure to a farmer's field in eastern Nebraska for 5 yr caused improved soil **N** and **P** supply and increased corn (*Zea mays* L.) yield in less productive portions of the field compared to another field treatment receiving the same amt. of **N** as inorg. fertilizer. As a first step toward identifying the soil processes that led to these changes, the effects of manure addn. on the chem. nature of soil org. matter were investigated by extg. two humic fractions-mobile humic acid (MHA) and calcium humate (CaHA)-from the field soil for subsequent anal. by solid-state ^{13}C **NMR** spectroscopy and Fourier Transform-IR (FT-IR) spectroscopy. Functional groups were selectively identified and **quantified** through **NMR** techniques that included **quant.** direct polarization, cross polarization/total suppression of sidebands, ^1H - ^{13}C heteronuclear correlation **NMR**, ^{13}C chem. shift anisotropy filtering, CH-signal selection, and other spectral-editing techniques. The CaHAs exhibited high aromaticity and line shapes typical of Mollisols rich in oxidized charcoal, while the MHAs had lower aromaticity and greater contributions from lignin arom. ethers. Results show that the chem. nature of each humic fraction did not differ significantly between an unfertilized control and the treatment receiving **N** as inorg. fertilizer. The FT-IR results were consistent with all these findings. The **NMR** results further showed that the CaHA fraction from the manure treatment was clearly depleted in arom. rings and enriched in nonpolar alkyl compds., most likely fatty acids, compared to the other two fertilizer treatments. Selective spectra further show strong indications of enhanced peptide contributions in

the manure CaHA, consistent with the improved soil N supply assocd. with the manure treatment. The peptide enrichment was partially masked in unselective spectra by a simultaneous decrease in overlapping signals for OCH₃ and COO groups that are assocd. with arom. components, demonstrating the improved accuracy of the selective spectral-editing NMR techniques.

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17. Estimation of the available free energy in a LOV2- α photoswitch

ByYao, Xiaolan; Rosen, Michael K.; Gardner, Kevin H.

From Nature Chemical Biology (2008), 4(8), 491-497. Language: English, Database: CAPLUS, DOI: 10.1038/nchembio.99

Protein photosensors are versatile tools for studying ligand-regulated allostery and signaling. Fundamental to these processes is the amt. of energy that can be provided by a photosensor to control downstream signaling events. Such regulation is exemplified by the phototropins-plant serine/threonine kinases that are activated by blue light via conserved LOV (light, oxygen and voltage) domains. The core photosensor of oat phototropin 1 is a LOV domain that interacts in a light-dependent fashion with an adjacent α -helix ($J\alpha$) to control kinase activity. We used soln. NMR measurements to **quantify** the free energy of the LOV domain-

$J\alpha$ -helix binding equil. in the dark and lit states. These data indicate that light shifts this equil. by ~ 3.8 kcal

mol⁻¹, thus **quantifying** the energy available through LOV- $J\alpha$ for light-driven allosteric regulation. This study provides insight into the energetics of light sensing by phototropins and benchmark values for engineering photoswitchable systems based on the LOV- $J\alpha$ interaction.

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18. Methods for detection and quantification of polyphosphate and polyphosphate accumulating microorganisms in aquatic sediments

ByHupfer, Michael; Gloess, Stefanie; Schmieder, Peter; Grossart, Hans-Peter

From International Review of Hydrobiology (2008), 93(1), 1-30. Language: English, Database: CAPLUS, DOI: 10.1002/iroh.200610935

A review. It has been speculated that the microbial P pool is highly variable in the uppermost layer of various aquatic sediments, esp. when an excessive P accumulation in form of polyphosphate (Poly-P) occurs. Poly-P storage is a universal feature of many different organisms and has been tech. optimized in wastewater treatment **plants** (WWTP) with enhanced biol. phosphorus removal (EBPR). In the recent past, new insights into mechanisms of P elimination in WWTP almost exclusively depended on the development and application of novel methods like ³¹P-NMR spectroscopy and mol. methods for identifying Poly-P accumulating microorganisms (PAO). The aim of the present review is to compile current methods potentially available for detection and **quantification** of Poly-P in sediments and to complement it with yet unpublished results to validate their application in natural sediments. The most powerful tool for reliable Poly-P **quantification** in sediments is the liq. ³¹P-NMR technique which has been successfully used for Poly-P measurements in a variety of aquatic sediments. But the microorganisms as well as mechanisms involved in Poly-P storage and cycling are largely unknown. Therefore, we also intend to stimulate future studies focusing on these encouraging topics in sediment research via the implementation of novel methods.

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19. **Quantification of free and protein-bound trans-resveratrol metabolites and identification of trans-resveratrol-C/O-conjugated diglucuronides - two novel resveratrol metabolites in human plasma**

ByBurkon, Alexander; Somoza, Veronika

From Molecular Nutrition & Food Research (2008), 52(5), 549-557. Language: English, Database: CAPLUS, DOI: 10.1002/mnfr.200700290

The polyphenol trans-resveratrol (t-RES) is present as t-RES-3-O- β -D-glycoside (piceid) in several **plant**-derived foods. Although data on the metab. and on in vivo effects of t-RES have been reported, **quant.** data on the metabolites formed after dietary intake of piceid are lacking. In this study, 85.5 mg piceid per 70 kg body wt. were taken by 9 healthy men (23-41 yr, BMI 21-29 kg/m²) in a bolus dose. The t-RES metabolites formed in blood plasma and urine were identified and **quantified** by LC-MS/MS, **NMR**, and HPLC-DAD anal. using chem. synthesized t-RES conjugate stds. The amt. of t-RES metabolites bound noncovalently to plasma proteins was detd. The metabolites identified and **quantified** were t-RES-3-sulfate, t-RES-3,4'-disulfate, t-RES-3,5-disulfate, t-RES-3-glucuronide, and t-RES-4'-glucuronide, with t-RES-sulfates being the dominant conjugates in plasma and urine. Two novel t-RES-C/O-conjugated diglucuronides were identified and **quantified** in plasma and urine. Up to 50% of plasma t-RES-3-sulfate, t-RES-disulfates, and the novel t-RES-C/O-diglucuronides were bound to proteins. The total recovery of the dietary piceid dose in urine ranged 13.6-35.7%.

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20. **Biosynthesis of β -sitosterol and stigmasterol proceeds exclusively via the mevalonate pathway in cell suspension cultures of *Croton stellatopilosus***

ByKongduang, Damrong; Wungsintaweekul, Juraithip; De-Eknamkul, Wanchai

From Tetrahedron Letters (2008), 49(25), 4067-4072. Language: English, Database: CAPLUS, DOI: 10.1016/j.tetlet.2008.04.049

Cell suspension cultures of *Croton stellatopilosus* were fed with [1-¹³C]glucose and [2-¹³C]sodium acetate and cultured under control conditions. β -Sitosterol and stigmasterol were isolated and their ¹³C-labeling patterns examd. using **quant. NMR** spectroscopy. Anal. of the patterns of ¹³C-enrichment revealed that all the isoprene units in the mols. of both phytosterols originated exclusively from the mevalonate pathway. These results were in contrast with our previous study using callus cultures of *C. stellatopilosus*, which showed that the isoprene units of β -sitosterol and stigmasterol were supplied equally from both the deoxyxylulose phosphate (DXP) pathway and the mevalonate pathway. Observation by transmission electron microscopy of sub-cellular structures of both cell types revealed that the callus cells contained partially differentiated chloroplasts, whereas the suspension cultured cells did not. Since the DXP pathway is known to be located in the chloroplasts, it was suggested that the presence of chloroplasts is essential for expression of the DXP pathway. Therefore, the sole operation of the phytosterol biosynthesis by the mevalonate pathway obsd. in this study was likely to be the result of non-expression of the DXP pathway in the chloroplast-free cell suspension cultures of *C. stellatopilosus*.

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21. **Identification and quantitative determination of carbohydrates in ethanolic extracts of two conifers using ¹³C NMR spectroscopy**

ByDuquesnoy, Emilie; Castola, Vincent; Casanova, Joseph

From Carbohydrate Research (2008), 343(5), 893-902. Language: English, Database: CAPLUS, DOI: 10.1016/j.carres.2008.01.001

The authors developed a method for the direct identification and **quantification** of carbohydrates in raw vegetable exts. using ¹³C **NMR** spectroscopy without any preliminary step of pptn. or redn. of the components. This method has been validated (accuracy, precision and **response** linearity) using pure compds. and artificial mixts. before being applied to authentic ethanolic exts. of pine needles, pine wood and pine cones and fir twigs. The authors detd. that carbohydrates represented from 15% to 35% of the crude exts. in which pinitol was the principal constituent accompanied by arabinitol, mannitol, glucose and fructose.

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22. Evaluation of Characteristic Deuterium Distributions of Ephedrines and Methamphetamines by NMR Spectroscopy for Drug Profiling

ByMatsumoto, Teruki; Urano, Yasuteru; Makino, Yukiko; Kikura-Hanajiri, Ruri; Kawahara, Nobuo; Goda, Yukihiro; Nagano, Tetsuo

From Analytical Chemistry (Washington, DC, United States) (2008), 80(4), 1176-1181.Language:English, Database: CAPLUS, DOI: 10.1021/ac701639j

The authors have established a method for **quant.** anal. of the deuterium contents (D/H) at the Ph, methine, benzyl, **N**-Me and Me groups of L-ephedrine/HCl, D-pseudoephedrine/HCl and methamphetamine/HCl by ²H **NMR** spectroscopy. Comparison of the 5 position-specific D/H values of L-ephedrine/HCl and D-pseudoephedrine/HCl prepd. by three methods (chem. synthesis, semichem. synthesis, and biosynthesis) showed that chem. synthesized ephedrines and semisynthetic ephedrines have highly specific distributions of deuterium at the methine position and at the benzyl position, compared with the other positions. The classification of several methamphetamine samples seized in Japan in terms of the D/H values at these two positions clearly showed that the methamphetamine samples had been synthesized from ephedrines extd. from Ephedra **plants** or semisynthetic ephedrines but not from synthetic ephedrine. This isotope ratio anal. should be useful to trace the origins of seized methamphetamine in Southeast Asia.

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23. Biosynthetic origin of isoprene units in chromenes of Piper aduncum (Piperaceae)

ByLeite, Ana C.; Lopes, Adriana A.; Kato, Massuo J.; Bolzani, Vanderlan da S.; Furlan, Maysa

From LabCiencia con Noticias Tecnicas del Laboratorio (2007), 15(3), 16-17.Language:Spanish, Database: CAPLUS

Metabolic studies involving the incorporation of [1-¹³C]-D-glucose into intact leaves of Piper aduncum (Piperaceae) have indicated that both the mevalonate (MVA) and the pyruvate-triose (MEP: 2-C-methyl-D-erythritol-4-phosphate) non-mevalonate pathways are implicated in the biosynthesis of isoprene moieties present in Me 2,2-dimethyl-2H-1-chromene-6-carboxylate (1) and Me 2,2-dimethyl-8-(3'-methyl-2'-butenyl)-2H-1-chromene-6-carboxylate (2). The pattern of incorporation of label from [1-¹³C]-D-glucose into these chromenes was detd. by **quant.** ¹³C **NMR** spectroscopy. The results confirmed that biosynthetic compartment of 1 and 2 could either be the plastid and/or the cytosol or, possibly, an addnl. compartment such as the plastid inter-membrane space.

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24. A metabolic flux analysis to study the role of sucrose synthase in the regulation of the carbon partitioning in central metabolism in maize root tips

ByAlonso, Ana Paula; Raymond, Philippe; Hernould, Michel; Rondeau-Mouro, Corinne; de Graaf, Albert; Chourey, Prem; Lahaye, Marc; Shachar-Hill, Yair; Rolin, Dominique; Dieuaide-Noubhani, Martine

From Metabolic Engineering (2007), 9(5-6), 419-432.Language:English, Database: CAPLUS, DOI: 10.1016/j.ymben.2007.06.002

In order to understand the role of sucrose synthase (SuSy) in carbon partitioning, metabolic fluxes were analyzed in maize root tips of a double mutant of SuSy genes, sh1 sus1 and the corresponding wild-type, W22. [U-¹⁴C]-glucose pulse labeling expts. permitted the **quantification** of unidirectional fluxes into sucrose, starch and cell wall polysaccharides. Isotopic steady-state labeling with [1-¹³C]-, [2-¹³C]- or [U-¹³C]-glucose followed by the **quantification** by ¹H-**NMR** and ¹³C-**NMR** of enrichments in carbohydrates and amino acids was also performed to det. 29 fluxes through central metab. using computer-aided modeling. As a consequence of the suppression of SUS1 and SH1 isoenzymes, maize root tip diam. was significantly decreased and respiratory metab. reduced by 30%. Our result clearly established that, in maize

root tips, starch is produced from ADP-Glc synthesized in the plastid and not in the cytosol by sucrose synthase. Unexpectedly, the flux of cell wall synthesis was increased in the double mutant. This observation indicates that, in maize root tips, SH1 and SUS1 are not specific providers for cellulose biosynthesis.

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25. How useful is chemical oxidation with dichromate for the determination of "Black Carbon" in fire-affected soils?

ByKnicker, Heike; Mueller, Petra; Hilscher, Andre

From Geoderma (2007), 142(1-2), 178-196. Language: English, Database: CAPLUS, DOI: 10.1016/j.geoderma.2007.08.010

A common approach for the **quantification** of Black Carbon (BC) in soils and sediments represents the chem. oxidn. with acid potassium dichromate. Because this method is still assocd. with some uncertainties, its applicability for the detection of BC produced during **vegetation** fires was examd. by analyzing fire-affected and unaffected soil org. matter, including fresh and charred **plant** residues and a charcoal briquette. Comparably to the org. matter in a fire-unaffected soil sampled under pasture, grass and beech sawdust remains were completely oxidized after 4 to 6 h, whereas approx. 12% of the org. carbon (Corg) in pine needles resisted the chem. oxidn. Based on solid-state ^{13}C **NMR** spectroscopy, this Corg was assigned to **plant** waxes. In the fire-unaffected control soils located under pine and oak forests such acid-resistant paraffinic structures accounted for 6 to 22% of Corg of the untreated samples. Approx. half of them were removable by a subsequent Soxhlet extn., clearly demonstrating that their survival is rather explainable by their hydrophobic nature than caused to their chem. recalcitrance. Chem. oxidn. of charcoal briquette for 6 h resulted in a survival of 82% of its Corg. Beech sawdust BC and grass BC showed lower recalcitrance and only 66% and 40% were recovered. Dipolar dephasing **NMR** techniques used to elucidate the av. protonation degree of the arom. C of BC demonstrated that the variable reaction to chem. treatment cannot be explained by differences in the condensation degree. Further, after oxidn., the residual arom. C of the ref. chars shows no major decrease of the protonation degree, which contradicts a possible preferential preservation of polycondensed arom. structures from the oxidative attack. Increasing the treatment time to 24 h, considerably lowered the amt. of chem. oxidn. resistant elemental carbon (COREC) to 18% for the grass BC and 60% for the charcoal briquette. This confirms that the amt. of detd. BC varies not only with source material but also relies strongly on the applied oxidn. time. Considering further a contribution of non-BC derived paraffinic structures of up to 19 mg g⁻¹ soil in the fire-unaffected soils, the reliability of BC data of soil org. matter obtained solely by chem. oxidn. methods is questionable. Therefore, addnl. characterization of extn. residue is obligatory. Using solid-state ^{13}C **NMR** spectroscopy, on the other hand, allowed the identification of BC by signal intensity assignable to arom. C. However, using this signal as a means for BC-**quantification**, one has to encounter that chem. oxidn. even attacks charcoal BC, which is most tentatively a major reason for BC underestimations in soils investigated by this method.

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26. $^{13}\text{CO}_2$ as a universal metabolic tracer in isotopologue perturbation experiments

ByRoemisch-Margl, Werner; Schramek, Nicholas; Radykewicz, Tanja; Ettenhuber, Christian; Eylert, Eva; Huber, Claudia; Roemisch-Margl, Lilla; Schwarz, Christine; Dobner, Maria; Demmel, Norbert; et al

From Phytochemistry (Elsevier) (2007), 68(16-18), 2273-2289. Language: English, Database: CAPLUS, DOI: 10.1016/j.phytochem.2007.03.034

A tobacco **plant** was illuminated for 5 h in an atm. contg. $^{13}\text{CO}_2$ and then maintained for 10 days under std. greenhouse conditions. Nicotine, glucose, and amino acids from proteins were isolated chromatog. Isotopolog abundances of isolated metabolites were detd. **quant.** by **NMR** spectroscopy and mass spectrometry. The obsd. nonstochastic isotopolog patterns indicate (i) formation of multiply labeled photosynthetic carbohydrates during the $^{13}\text{CO}_2$ pulse phase followed by (ii) partial catabolism of the

primary photosynthetic products, and (iii) recombination of the ^{13}C -labeled fragments with unlabeled intermediary metabolites during the chase period. The detected and simulated isotopolog profiles of glucose and amino acids reflect carbon partitioning that is dominated by the Calvin cycle and glycolysis/glucogenesis. Retrobiosynthetic anal. of the nicotine pattern is in line with its known formation from nicotinic acid and putrescine via aspartate, glyceraldehyde phosphate and α -ketoglutarate as basic building blocks. The study demonstrates that pulse/chase labeling with $^{13}\text{CO}_2$ as precursor is a powerful tool for the anal. of **quant.** aspects of **plant** metab. in completely unperturbed whole **plants**.

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27. Flux quantification in central carbon metabolism of *Catharanthus roseus* hairy roots by ^{13}C labeling and comprehensive bondomer balancing

BySriram, Ganesh; Fulton, D. Bruce; Shanks, Jacqueline V.

From Phytochemistry (Elsevier) (2007), 68(16-18), 2243-2257.Language:English, Database: CAPLUS, DOI: 10.1016/j.phytochem.2007.04.009

Methods for accurate and efficient **quantification** of metabolic fluxes are desirable in **plant** metabolic engineering and systems biol. Toward this objective, the authors introduce the application of "bondomers", a computationally efficient and intuitively appealing alternative to the commonly used isotopomer concept, to flux evaluation in **plants**, by using *Catharanthus roseus* hairy roots as a model system. The authors cultured the hairy roots on (5% wt./wt. U- ^{13}C , 95% wt./wt. naturally abundant) sucrose, and acquired two-dimensional [^{13}C , ^1H] and [^1H , ^1H]**NMR** spectra of hydrolyzed aq. ext. from the hairy roots. Anal. of these spectra yielded a data set of 116 bondomers of β -glucans and proteinogenic amino acids from the hairy roots. Fluxes were evaluated from the bondomer data by using comprehensive bondomer balancing. The authors identified most fluxes in a three-compartmental model of central carbon metab. with good precision. The authors obsd. parallel pentose phosphate pathways in the cytosol and the plastid with significantly different fluxes. The anaplerotic fluxes between phosphoenolpyruvate and oxaloacetate in the cytosol and between malate and pyruvate in the mitochondrion were relatively high (60.1 \pm 2.5 mol per 100 mol sucrose uptake, or 22.5 \pm 0.5 mol per 100 mol mitochondrial pyruvate dehydrogenase flux). The development of a comprehensive flux anal. tool for this **plant** hairy root system is expected to be valuable in assessing the metabolic impact of genetic or environmental changes, and this methodol. can be extended to other **plant** systems.

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28. Substrate cycles in the central metabolism of maize root tips under hypoxia

ByAlonso, Ana Paula; Raymond, Philippe; Rolin, Dominique; Dieuaide-Noubhani, Martine

From Phytochemistry (Elsevier) (2007), 68(16-18), 2222-2231.Language:English, Database: CAPLUS, DOI: 10.1016/j.phytochem.2007.04.022

Substrate cycles, also called "futile" cycles, are ubiquitous and lead to a net consumption of ATP which, in the normoxic maize root, have been estd. at about 50% of the total ATP produced. To evaluate their role, the authors studied the substrate cycles of maize root tips under an oxygen limitation of respiration (3% O_2). Short-time labeling expts. with [U- ^{14}C]-Glc were performed to **quantify** the fluxes through sucrose and starch cycles of synthesis and degrdn. Steady-state labeling with [1- ^{13}C]-Glc followed by ^1H **NMR** and ^{13}C **NMR** anal. of sugars and free alanine was used to **quantify** fluxes in the central metabolic pathways, including the Glc-P/Glc cycle and the fructose-P/triose-P cycle of glycolysis. Comparison with results previously obtained in normoxia [Alonso et al., as mentioned above] showed that 3% O_2 induced fermn. and reduced respiration, which led to a lesser amt. of ATP produced. The rates of Glc consumption, glycolytic flux and all substrate cycles were lower, but the proportion of ATP consumed in the substrate cycles remained unchanged. These findings suggest that substrate cycles are not a luxury but an integral part of the organization of the **plant** central metab.

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29. Biosynthetic origins of the isoprene units of gaudichaudianic acid in *Piper gaudichaudianum* (Piperaceae)

ByLopes, Adriana A.; Baldoqui, Debora C.; Lopez, Silvia N.; Kato, Massuo J.; Bolzani, Vanderlan da S.; Furlan, Maysa

From *Phytochemistry* (Elsevier) (2007), 68(15), 2053-2058. Language: English, Database: CAPLUS, DOI: 10.1016/j.phytochem.2007.04.025

The biosynthesis of (2S)-2-methyl-2-(4'-methyl-3'-pentenyl)-8-(3"-methyl-2-butenyl)-2H-1-benzopyran-6-carboxylic acid (gaudichaudianic acid), the major metabolite in leaves and roots of *Piper gaudichaudianum* Kunth (Piperaceae), has been investigated employing [1-¹³C]-D-glucose as precursor. The labeling pattern in the isolated gaudichaudianic acid was detd. by **quant.** ¹³C **NMR** spectroscopy anal. and was consistent with involvement of both mevalonic acid and 2-C-methyl-D-erythritol-4-phosphate pathways in the formation of the dimethylallyl- and geranyl-derived moieties. The results confirmed that both plastidic and cytoplasmic pathways are able to provide isopentenyl diphosphate units for prenylation of p-hydroxybenzoic acid.

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30. Structural ripening-related changes of the arabinan-rich pectic polysaccharides from olive pulp cell walls

ByCardoso, Susana M.; Ferreira, Jose A.; Mafra, Isabel; Silva, Artur M. S.; Coimbra, Manuel A.

From *Journal of Agricultural and Food Chemistry* (2007), 55(17), 7124-7130. Language: English, Database: CAPLUS, DOI: 10.1021/jf070769w

In this study, the structural features and ripening-related changes that occur in the arabinan-rich pectic polysaccharides highly enmeshed in the cellulosic matrix of the olive pulp fruit were evaluated. These pectic polysaccharides, obtained from two consecutive harvests at green, cherry, and black ripening stages, account for 11-19% of the total pectic polysaccharides found in the olive pulp cell walls and were previously shown to occur as calcium chelating dimers. On the basis of the ¹³C **NMR**, (1H, ¹³C) gHSQC, 2D COSYPR, and (1H, ¹³C) gHMBC carbon and proton **resonances** of the variously linked arabinosyl residues, we propose a tentative structure. This structure is particularly characterized by T-β-Araf (1→5)-linked to (1→3,5)-Araf residues and by the occurrence of branched and linear blocks in the arabinan backbone. Methylation anal. showed that these pectic polysaccharides of black olives have more arabinan side chains, which were shorter (less (1→5)-Araf), highly branched (more (1→3,5)-Araf), and with shorter side chains (fewer (1→3)-Araf) than those of green and cherry olives. **Quant.** ¹³C **NMR** data indicated that these modifications involved the disappearance of the characteristic terminally linked β-Araf residue of the arabinans. This odd feature can be used as a diagnostic tool in the evaluation of the stage of ripening of this fruit, as well as a marker for the presence of olive pulp in matrixes contg. pectic polysaccharides samples.

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31. Changes of low molecular weight organic acids, soil organic matter, nitrogen transformation and microbial populations in rhizosphere and bulk soils in a temperate rain forest

ByWang, Ming Kuang; Chiang, Po Neng; Zhuang, Shun Yao; King, Hen Biao

Edited byLivingston, James V

From *Agriculture and Soil Pollution* (2005), 137-161. Language: English, Database: CAPLUS

The ecosystem research in a temperate rain forest was not fully understood. Thus, the aims of this chapter are illustrated the changes of low mol. wt. org. acids (LMWOAs), stable isotope ratios of soil org. matter, forest fire influenced the changes of **vegetation** communities, nitrogen transformation and microbial populations study in rhizosphere and bulk soils, selecting Ta-Ta-Chia long-term ecol. research (LTER) site,

Taiwan in a temperate rain forest as an example. Low mol. wt. org. acids and the nature of org. matter were detd. by gas chromatograph (GC) and CPMAS ^{13}C **NMR** anal. Changes in the meadow-forest boundary at this LTER site detected by stable isotope ratios of soil org. matter of $\delta^{13}\text{C}$ anal. of **plants** and soils. The buried bag incubation method was used to study temporal pattern of net **N** mineralization and nitrification in soils. Several types of microorganisms were counted for their spatial and temporal variations. The recovery percentage of LMWOAs detn. by GC shows a high correlation of $r^2 = 0.99$. All recovery of LMWOAs was above 83.6%. The proportion of org. functional groups in the rhizosphere and bulk soils **quantified** by ^{13}C **NMR** anal. followed the general order: alkyl-C > **O**-alkyl-C > **N**-alkyl-C > acetal-C > arom.-C > carboxylic-C > phenolic-C. $\delta^{13}\text{C}$ PDB values in pedons 1 and 2 tended to decrease with increasing with soil depth. The values of EB, **E** and Bw horizons were close to $\delta^{13}\text{C}$ PDB values of C3 **plants**. The data indicated that SOM was a mixt. of transmorrissonensis (C4), nittakeyamensis (C3) and Tsuga (C3) **plant** residues. $\delta^{13}\text{C}$ PDB values obtained from deeper meadow pedons 1 and 2 of soil layers indicated that the **vegetation** community has changed **over** the years. **M.** transmorrissonensis (C4) **plants** replaced C3 **plants** (e.g., Tsuga). Extractable NO_3^- concns. ranged from 0.2 to 2.1 mg **N** kg^{-1} soil in the meadow zone and from 0.2 to 13.0 mg **N** kg^{-1} soil in the forest zone. No seasonal changes in soil nitrate concn. were present. Extractable NH_4^+ concns. ranged from 1.0 to 12.4 mg **N** kg^{-1} soil in the meadow zone and from 2.8 to 25.0 mg **N** kg^{-1} soil. The NH_4^+ concns. showed highly temporal variations. The net of mineralization and nitrification rates showed spatial and temporal variations, depending on microbial activities and populations. Bacteria were most abundant, followed by cellulolytic microbes, phosphate-solubilizing microbes, nitrogen-fixing microbes, fungi and actinomycetes. Microbial populations showed high correlation with microbial biomass carbon and org. acid contents.

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32. **Characterization of low-molecular-weight organic acids and organic carbon of Taiwan red cypress, peacock pine, and moso bamboo in a temperate rain forest**

ByWang, Ya Nan; Wang, Ming Kuang; Zhuang, Shun Yao; Tu, Ta Chi; Chiang, Kai Yin

From Communications in Soil Science and Plant Analysis (2007), 38(1 & 2), 77-91. Language: English, Database: CAPLUS, DOI: 10.1080/00103620601093686

Low-mol.-wt. org. acids (LMWOAs) derived from root exudates and complexed with available metals in the rhizosphere soils of Taiwan red cypress (*Chamaecyparis formosensis*, FRS), peacock pine (*Cryptomeria japonica*, JRS), and moso bamboo (*Phyllostachys pubescens*, PRS) were identified by gas chromatograph (GC). The fresh **plants** (i.e., leaves, stems, roots, and litters) and soil samples of those 3 vegetations were examd. for their org. functional groups. This study focused on (1) assessing methods for processing LMWOAs in the rhizosphere soils and fresh **plants** by GC anal. and (2) detg. the relative proportions of org. carbon (C) functional groups in the 3 vegetations and fresh **plant** materials with ^{13}C **NMR** anal. The proportion of LMWOAs contents followed the order of PRS > FRS > JRS > bulk soils. The recovery and spiking tests analyzed by GC showed good recovery (> 83.6%) and reproducibility of LMWOAs. The proportion of org. functional groups in the rhizosphere and bulk soil **quantified** by ^{13}C **NMR** anal. follow the general order alkyl-C > arom.-C > **O**-alkyl-C > **N**-alkyl-C > phenolic-C > acetal-C > carboxyl-C. The carbohydrates, hemicellulose, lignin, and cellulose contents obtained by ^{13}C **NMR** anal. suggested that *Phyllostachys pubescens* (PB) cannot easily be decompd. under the mountain forest soil environments.

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33. **Sequestration of a fluorinated analog of 2,4-dichlorophenol and metabolic products by L. minor as evidenced by ^{19}F NMR**

ByTront, Jacqueline M.; Saunders, F. Michael

From Environmental Pollution (Amsterdam, Netherlands) (2007), 145(3), 708-714. Language: English, Database: CAPLUS, DOI: 10.1016/j.envpol.2006.05.039

Fate of halogenated phenols in **plants** was investigated using **NMR** to identify and **quantify** contaminants and their metabolites. Metabolites of 4-chloro-2-fluorophenol (4-Cl-2-FP), as well as the parent compd., were detected in acetonitrile exts. using ¹⁹F **NMR** after various exposure periods. Several fluorinated metabolites

with chem. shifts ~3.5 ppm from the parent compd. were present in **plant** exts. Metabolites isolated in exts.

were tentatively identified as fluorinated-chlorophenol conjugates through examn. of signal-splitting patterns and relative chem. shifts. Signal intensity was used to **quantify** contaminant and metabolite accumulation within **plant** tissues. The **quantity** of 4-Cl-2-F metabolites increased with time and mass balance closures of 90-110% were achieved. In addn., solid phase ¹⁹F **NMR** was used to identify 4-Cl-2-FP which was chem. bound to **plant** material. This work used ¹⁹F **NMR** for developing a time series description of contaminant accumulation and transformation in aquatic **plant** systems. The aquatic **plant** *L. minor* accumulates, sequesters and binds 4-chloro-2-fluorophenol and its metabolites, as was demonstrated using ¹⁹F-**NMR**.

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34. Soil organic matter changes in a spruce ecosystem 25 years after disturbance

BySpielvogel, Sandra; Prietzel, Joerg; Koegel-Knabner, Ingrid

From Soil Science Society of America Journal (2006), 70(6), 2130-2145.Language:English, Database: CAPLUS, DOI: 10.2136/sssaj2005.0027

Long-term effects of forest dieback on soil org. matter (SOM) pools in an unmanaged high-elevation Norway spruce forest were investigated by comparing three dieback sites with three adjacent sites with healthy spruce. The aim was to assess the long-term biogeochem. impact of a major disturbance in unmanaged forest ecosystems due to potential modification of their soil org. carbon (OC) pool. The spruces at the dieback sites had been killed by a bark beetle (*Ips typographus*) infestation 25 yr ago. Total OC stocks in the topsoil of all sites were detd.; different OC pools were **quantified** by d./particle-size fractionation and ¹³C cross polarization magic angle spinning **NMR** (CPMAS **NMR**) spectroscopy. Addnl., the aboveground and belowground **plant**-derived OC input was **quantified** and the OC species were analyzed. The forest floor at the dieback sites showed significantly lower OC stocks, storing <70% of the resp. amt. at the sites with healthy forest. In the forest floor and the light fraction of the Ah horizons at the dieback sites, the C/N ratio and the concn. of O-alkyl C in the OM were significantly lower, whereas the OM of the other fractions and of the bulk SOM in Ah horizons showed no changes. The obsd. SOM changes were caused primarily by an accelerated SOM turnover and only secondarily caused by changed litter input. Particularly the OC pool with a low degree of humification was reduced in its amt. and increased in its decompn. status while the more stable C fractions showed no significant changes.

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35. Quantification of deuterium isotopomers of tree-ring cellulose using nuclear magnetic resonance

ByBetson, Tatiana R.; Augusti, Angela; Schleucher, Juergen

From Analytical Chemistry (2006), 78(24), 8406-8411.Language:English, Database: CAPLUS, DOI: 10.1021/ac061050a

Measurements of the D/H ratio of tree-ring cellulose have proven difficult to interpret, presumably because the D/H ratio of the whole mol. blends the abundances of the seven D isotopomers of cellulose. A method is presented to det. the abundance of the D isotopomers of tree-ring cellulose by **NMR** spectroscopy. The method transforms tree-ring cellulose into a glucose deriv. that gives highly resolved, **quantifiable** deuterium **NMR** spectra. General guidelines for measurement of D isotopomers by **NMR** are described. The transformation was optimized for yield and did not alter the original D isotopomer abundances, thus, conserving the original signals recorded in wood cellulose. In the tree-ring samples tested, the abundances

of D isotopomers varied by approx. $\pm 10\%$ (2% std. error). This large variability can only be caused by biochem. processes and shows that more information is present in D isotopomer abundances, compared to the D/H ratio. Therefore, measurements of the D isotopomer distribution of tree rings may be used to obtain information on long-term adaptations to environmental changes and past climate change.

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36. NMR investigations of natural organic matter in forest ecosystems

ByJohnson, Chris E.

From Abstracts, 34th Northeast Regional Meeting of the American Chemical Society, Binghamton, NY, United States, October 5-7 (2006), NRM-270.Language:English, Database: CAPLUS

Understanding the mechanisms underlying key carbon cycling processes such as decompn. and humification, and how they respond to disturbances such as forestry and conversion to or from agriculture, has become a major focus of research in ecosystem ecol. ^{13}C **NMR** spectroscopy offers direct insight into these processes because it provides information on the chem. structure of natural org. matter, including tissues, **plant** litter, and soil org. matter. Solid-state **NMR** has the added advantage of being non-destructive. By comparing samples from controlled or repeated-measures expts., one can gain insight into structural changes that occur during decompn. or as a result of ecol. disturbance. However, ^{13}C **NMR** spectra of natural org. matter contain broad, overlapping peaks due to the complexity of the material. Soil spectra often have low signal-to-noise ratios, necessitating long anal. times. Therefore, the cross polarization with magic-angle spinning (CPMAS) method is often the only way to analyze large nos. of samples in a reasonable time. Unfortunately, ^{13}C CPMAS **NMR** is not generally **quant.** **NMR** analyses have been conducted on fresh and decompng. **plant** tissues, soil org. matter, org. matter extd. from soils, and org. matter isolated from stream water and soil water from the Hubbard Brook Exptl. Forest, in New Hampshire. Together these samples provide insight into transformations that occur during decompn. and mobilization.

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37. Effect of method of extraction and purification of arabinogalactan from the wood of Siberian larch on its structure and properties

ByMedvedeva, E. N.; Fedorova, T. E.; Vanina, A. S.; Rokhin, A. V.; Es'kova, L. A.; Babkin, V. A.

From Khimiya Rastitel'nogo Syr'ya (2006), (1), 25-32.Language:Russian, Database: CAPLUS

Arabinogalactan (AG) from larch wood possesses a wide spectrum of physiol. activity and due to that it can be applied as a medical product and biol. active food additive. Samples of AG were isolated from water exts. obtained from Siberian larch wood in a pilot **plant** at temp. 80-90°C; these samples were purified by various methods. IR spectroscopy, electrophoresis, amino acid anal. and anal. with Amido Black showed that the investigated samples did not contain glycoproteins. Monosaccharide compn. AG was detd. by the **quant.** ^{13}C **NMR** method. It is shown, that the molar ratio of galactose and arabinose units in the AG samples, as well as the branching degree of AG macromols. depended on the isolation and purifn. of AG samples. Macromols. of AG samples isolated from industrial exts. contain in the compn. almost 2-times of less galactose units than a sample obtained under mild conditions (extn. and drying at room temp.). AG samples of high purity (99%) have Gal:Ara molar ratio of 8.8: 1. Gas-chromatog. data (Sephadex G 150, eluent - 1M NaCl) showed that these products have narrow mol.-wt. distribution ($M_w/M_n = 1.19-1.27$); their av. mol. wt.

is $\sim 20,000$; $[\alpha]_{\text{D}20} = +11^\circ$ (in water), which corresponds to literature data for AG from wood of Siberian and

western larch wood.

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38. Characteristic alterations of quantity and quality of soil organic matter caused by forest fires in continental Mediterranean ecosystems: a solid-state ¹³C NMR study

ByKnicker, H.; Almendros, G.; Gonzalez-Vila, F. J.; Gonzalez-Perez, J. A.; Polvillo, O.

From European Journal of Soil Science (2006), 57(4), 558-569. Language: English, Database: CAPLUS, DOI: 10.1111/j.1365-2389.2006.00814.x

The variable effect of different types of forest fires on the **quantity** and quality of soil org. matter (SOM) was analyzed by comparing burnt and unburnt soils from six forest ecosystems in central Spain by org. elemental anal. and solid-state ¹³C **NMR** spectroscopy. Whole soil samples were collected 1 to 2 years after the fires and included one site affected by two fires within 2 years. The fire-affected soils showed no common pattern with respect to the amt. of addnl. carbon (C_{add}) but at all sites, the fire enhanced the arom.-C content. The weakest fire intensity resulted in the greatest arom.-C enrichment factor, EFI(aromatic C) indicating the greatest local accumulation of char. The resp. C_{add} disclosed an EFI(aromatic C) to EFI(alkyl C) ratio, B_{char}, of c. 1, which supports a small degree of charring. Extensive combustion and volatilization at stronger fire intensities yielded a decrease of EFI(aromatic C) and an increase in B_{char}. These trends are in good agreement with fire intensity and forest fuel combustibility in the various sites and therefore these indexes could be used to elucidate the quality and **quantity** of char input that occurs during and after forest fires. No ¹³C **NMR** evidence for substantial inputs from non-charred **plant** necromass was found for any of the single-burn soils. The large carboxyl-C content of C_{add} is evidence of the occurrence of oxidn. reactions very shortly after the fire. In comparing the single and double-burn sites, no addnl. char input was obsd. for the double-burn site, possibly because of complete combustion of young shrubs and char remains during the second fire. The large O-alkyl-C portion found in C_{add} of the double-burn soil is best explained by decreased litter degrdn.

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39. Robustness of central carbohydrate metabolism in developing maize kernels

BySpielbauer, Gertraud; Margl, Lilla; Hannah, L. Curtis; Roemisch, Werner; Ettenhuber, Christian; Bacher, Adelbert; Gierl, Alfons; Eisenreich, Wolfgang; Genschel, Ulrich

From Phytochemistry (Elsevier) (2006), 67(14), 1460-1475. Language: English, Database: CAPLUS, DOI: 10.1016/j.phytochem.2006.05.035

The central carbohydrate metab. provides the precursors for the syntheses of various storage products in seeds. While the underlying biochem. map is well established, little is known about the organization and flexibility of carbohydrate metabolic fluxes in the face of changing biosynthetic demands or other perturbations. This question was addressed in developing kernels of maize (*Zea mays* L.), a model system for the study of starch and sugar metab. ¹³C-labeling expts. were carried out with inbred lines, heterotic hybrids, and starch-deficient mutants that were selected to cover a wide range of performances and kernel phenotypes. In total, 46 labeling expts. were carried out using either [U-¹³C₆]glucose or [U-¹³C₁₂]sucrose and up to three stages of kernel development. Carbohydrate flux distributions were estd. based on glucose isotopologue abundances, which were detd. in hydrolyzates of starch by using **quant.** ¹³C-**NMR** and GC-MS. Similar labeling patterns in all samples indicated robustness of carbohydrate fluxes in maize endosperm, and fluxes were rather stable in **response** to glucose or sucrose feeding and during development. A lack of ADP-glucose pyrophosphorylase in the bt2 and sh2 mutants triggered significantly increased hexose cycling. In contrast, other mutations with similar kernel phenotypes had no effect. Thus, the distribution of carbohydrate fluxes is stable and not detd. by sink strength in maize kernels.

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40. The prediction of isotopic patterns in phenylpropanoids from their precursors and the mechanism of the NIH-shift: Basis of the isotopic characteristics of natural aromatic compounds

By Schmidt, Hanns-Ludwig; Werner, Roland A.; Eisenreich, Wolfgang; Fuganti, Claudio; Fronza, Giovanni; Remaud, Gerald; Robins, Richard J.

From *Phytochemistry* (Elsevier) (2006), 67(11), 1094-1103. Language: English, Database: CAPLUS, DOI: 10.1016/j.phytochem.2006.03.014

The theor. 2H-distribution in the arom. ring of phenylpropanoids can be predicted from that of their precursors - erythrose-4-phosphate, phosphoenolpyruvate and NADPH - and by invoking the mechanism of the NIH-shift and implied deuterium isotope effects. For each position in the non-oxygenated ring, the predicted natural 2H-abundance is in excellent agreement with exptl. data obtained from **quant.** 2H **NMR**-measurements on natural compds., esp. concerning the relative 2H-abundances $p > o \geq m$. For the p-hydroxylated derivs., the exptl. detd. 2H-abundance sequence order $m > o$ can also be deduced, assuming an anisotropic migration (intramol. isotope effect) of the p-hydrogen atom to the two differently 2H-substituted **m**-positions during the NIH-shift (intramol. hydrogen transfer) and an in vivo deuterium kinetic

isotope effect of ~ 1.20 on the final hydrogen elimination from the proposed ketodiene intermediate. The

predicted 2H-distribution pattern of Me salicylate 10, a representative of an **o**-hydroxylated natural compd., is in excellent agreement with that reported from 2H **NMR** analyses. However, for salicyl alc., minor differences between the theor. and exptl. detd. pattern are found that cannot yet be satisfactorily explained. On the other hand, a very good agreement is found between the theor. and exptl. pattern of coumarin,

provided a deuterium kinetic isotope effect of ~ 1.30 is assumed for the elimination of the H-atoms from the

ketodiene intermediate. The secondary **m**-hydroxylation of p-coumaric acid in the biosynthesis of vanillin seems to proceed without large isotope effects. Parallel differences are also obsd. for the 18O-kinetic isotope effects on the corresponding monooxygenase-catalyzed reactions. The results demonstrate convincingly that the mechanisms of these general reactions of the phenylpropanoid biosynthetic pathway are identical and follow general principles. Small obsd. differences between the 2H-patterns of individual natural arom. compds. originating from the same hydroxylation type can therefore be assigned to differences of the patterns of the precursors, the extent and the orientation of the hydrogen migration, and the kinetic isotope effect on the final hydrogen elimination. The evidence for the existence of general systematic rules governing isotopic patterns in the shikimic acid pathway and its subsequent reactions is further supported by the recently reported 13C-distribution pattern of vanillin, which is also in agreement with that predicted from the precursors. Hence, it is apparent that the systematics of the isotope patterns of phenylpropanoids are in line with the generally accepted biosynthetic reactions in the shikimic acid pathway and that this knowledge can strengthen their value as an essential support for the distinction of natural and synthetic arom. compds.

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41. 13C NMR analysis of polyphenol biosynthesis in grape cells: Impact of various inducing factors

By Saigne-Soulard, Cassandrine; Richard, Tristan; Merillon, Jean-Michel; Monti, Jean-Pierre

From *Analytica Chimica Acta* (2006), 563(1-2), 137-144. Language: English, Database: CAPLUS, DOI: 10.1016/j.aca.2005.09.073

13C **NMR** spectroscopy was used as a complement to high performance liq. chromatog. (HPLC) or spectrophotometry to analyze stilbene and anthocyanin metab. in grape cell cultures. Stilbene and anthocyanin biosynthesis are closely related. Anthocyanins are major components of grape quality whereas stilbenes play a crucial role in defense mechanisms and are strongly correlated to natural grapevine resistance. Stimulation of stilbene prodn. by natural inducers offers an interesting alternative to the use of pesticides in **plant** protection strategies. **NMR** allowed us to analyze both stilbene and anthocyanin pathways by following step by step the incorporation of the labeled precursor [1-13C]L-phenylalanine along

the entire biosynthetic routes. However, several intermediates of the anthocyanin biosynthetic pathways remained unobservable, providing evidence for metabolic channeling. The effect of various elicitors on stilbene and anthocyanin biosynthesis was also investigated. In complement to **quantification** of the end-products by HPLC and spectrophotometry, ¹³C **NMR** studies provided information at the biosynthetic level. Sucrose addn. stimulated the biosynthesis of anthocyanins without influencing stilbenes. Me jasmonate and fungal elicitor strongly increased stilbene prodn. through the activation of enzymes from phenylalanine ammonia-lyase to stilbene synthase. However, Me jasmonate showed an inhibitory effect on anthocyanin biosynthesis, suggesting the existence of a competition between the two pathways. ¹³C **NMR** spectroscopy, combined with anal. techniques such as HPLC and spectrophotometry, provides a very interesting tool to better understand the mechanisms underlying the prodn. of secondary metabolites and the metabolic processes of **plant** resistance induction by elicitation.

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42. **Quantitative 2H NMR spectroscopy 2. "H/D-Isotope portraits" of cyclic monoterpenes and discrimination of their biosynthetic pathways**

ByGerdov, S. M.; Grishin, Yu. K.; Roznyatovsky, V. A.; Ustynyuk, Yu. A.; Kuchin, A. V.; Alekseev, I. N.; Frolova, L. L.

From Russian Chemical Bulletin (2005), 54(5), 1258-1265. Language: English, Database: CAPLUS, DOI: 10.1007/s11172-005-0391-4

Site-specific deuterium distribution in mols. of the representative series of natural monoterpenes was studied by **quant.** 2H **NMR** spectroscopy. H/D-isotope portraits of these compds. have general characteristic features reflecting biosynthetic pathways. The data obtained suggest that monoterpenes in **plants** are formed through 1-deoxy-D-xylulose-5-phosphate (DXP pathway) rather than by the classical mevalonate scheme.

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43. **Phosphorus cycling in wetland soils: The importance of phosphate diesters**

ByTurner, Benjamin L.; Newman, Susan

From Journal of Environmental Quality (2005), 34(5), 1921-1929. Language: English, Database: CAPLUS, DOI: 10.2134/jeq2005.0060

Productivity in P limited peatlands is regulated in part by the turnover of org. phosphates, which is influenced by the chem. nature of the compds. involved. ³¹P **NMR** spectroscopy was used to **quantify** org. and inorg. phosphates in benthic floc (a mixt. of **plant** detritus and algae) and underlying soil from sites along P gradients in hard water and soft water areas of the northern Florida Everglades, USA. Phosphorus-enriched sites were dominated by cattail (*Typha* spp.), while unenriched sites included sawgrass (*Cladium jamaicense* Crantz) ridges and open-water sloughs. Phosphorus extd. in a soln. contg. 0.25 **M** NaOH and 50 mM EDTA included phosphate, phosphate monoesters, DNA, and pyrophosphate. Signals from phosphate monoesters were consistent with those from alk. hydrolysis products of RNA and phospholipids formed during extn. and anal., whereas phytic acid (myo-inositol hexakisphosphate), the most abundant org. phosphate in most soils, was not detected. Phosphorus compn. was similar among sites, although neither DNA nor pyrophosphate were detected in exts. of benthic floc from a calcareous slough. DNA was a greater proportion of the P extd. from soil compared to benthic floc, while the opposite was true for pyrophosphate. Research on the cycling of org. phosphates in wetlands focuses conventionally on the turnover of phosphate monoesters, but our results suggest strongly that greater emphasis should be given to understanding the role of phosphate diesters and phosphodiesterase activity.

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44. **Monitoring defensive responses in macroalgae - limitations and perspectives**

ByLa Barre, S. L.; Weinberger, F.; Kervarec, N.; Potin, P.

From *Phytochemistry Reviews* (2005), Volume Date 2004, 3(3), 371-379. Language: English, Database: CAPLUS

A review. As part of an ongoing research program aiming at monitoring mol. changes in the tissues and metabolite trafficking in the hydrosphere of algae subjected to chem. stresses, the authors are discussing the various anal. techniques that were employed to characterize, and sometimes to **quantity** these metabolites. High-field multinuclear and solid-state **NMR** spectroscopies are powerful tools for metabolite characterization from exts. and in vivo, but **quantification** and kinetic aspects show some limitations. Modern MS (mass spectrometry) is extremely useful for fingerprinting samples against databases and when dealing with very low concns. of metabolites, the limitations being set by the type of chromatog. sepn. and mode of detection coupled with the mass spectrometer. Regarding chem. communication, optimization in terms of resolu. and efficiency of hydrosphere chem. anal. can theor. be achieved in a system which integrates (i) a multiparametric incubation chamber, (ii) a gas phase or a liq.-phase sepn. system and (iii) mass spectrometer(s) equipped with 1 or 2 detectors responding to the anal. and **quant.** needs. This text reviews some of the techniques that have been employed in various types of **plant** metabolic studies, which may serve as a basis towards an integrative anal. strategy directly applicable to the metabolomics of selected marine macrophytes.

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45. **Stable isotope analysis. Source and authenticity of foods**

BySchmidt, Hanns-Ludwig; Rossmann, Andreas; Stoeckigt, Detlef; Christoph, Norbert

From *Chemie in Unserer Zeit* (2005), 39(2), 90-99. Language: German, Database: CAPLUS, DOI: 10.1002/ciuz.200400335

A review. The correlations between isotope ratios in water, org. mass, and trace elements of food and beverages, and the circumstances and sites of their origin and prodn. are outlined, and the methods of mass spectrometric isotope ratio detn. and the positional 2H anal. by **quant. NMR** measurement are explained. In context with the application of these methods for origin and authenticity investigations of food, examples are given for the proof of watering or sugar addn. to wine and fruit juices and methods for the identification of nondeclared addns. of L-malic and L-ascorbic acids are described. The possibilities of multielement isotope ratio anal. for the identification of origin of animal products (eggs, milk products, meat) and methods for the discriminations between natural and nature identical aroma compds. are outlined. Finally, the possibilities of isotope ratio measurements for the discrimination between **plant** and animal food from conventional and org. prodn. are discussed.

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46. **Toward a quantitative understanding of reactive surface hydroxyl density in feldspar minerals**

ByWashton, N. M.; Fry, R.; Mueller, K. T.; Brantley, S. L.

Edited byWanty, Richard B.; Seal, Robert R., II

From *Water-Rock Interaction, Proceedings of the International Symposium on Water-Rock Interaction*, 11th, Saratoga Springs, NY, United States, June 27-July 2, 2004 (2004), 2, 1665-1669. Language: English, Database: CAPLUS

Of particular importance in geochem. is the surface reactivity of feldspar minerals, an important component of global silicon cycling. The adsorption and dissolu. of feldspars also impacts **plant** nutrient uptake, groundwater chem. compn., and climate control, and these phenomena are controlled by the interfacial region between the bulk mineral and the surrounding soln./environment. Therefore, a crit. element for understanding the mechanisms and kinetics of adsorption and dissolu. is the surface chem. and reactivity of feldspar minerals. In order to clarify the role of surface hydroxyl species in adsorption and dissolu., a **quant.** knowledge of the reactivities of surficial hydroxyl groups must be obtained. **Quantification** of the hydroxyl functionalities of albite (Amelia), anorthite (Miyake-Jima), bytownite (Duluth), oligoclase (Madawaska), and an alkali feldspar (sample 43738) was accomplished using a novel solid-state ¹⁹F magic angle spinning (MAS) **NMR** technique.

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47. **Magnetic Imaging of Pyrolysis Feedstocks to model olefin product yields**

ByVirk, P. S.

From Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2005), 50(1), 234-238. Language: English, Database: CAPLUS

A system for the **Magnetic** Imaging of Pyrolysis Feedstocks, acronym MIPF (pronounced with P silent) has been devised comprising three facets. First, sample prepn. incorporates internal stds. into the feedstock oils, to enable precise anal. of the **NMR** expts. Second, **NMR** expts. are performed to provide **quant.** C13 and H1 spectra, with spectral features elaborated by 1-D and 2-D procedures such as DEPT, COSY and HETCOR. Third, data anal. employs (1) an Integral Regions train, which provides coarse but complete information about all the carbon and hydrogen atoms in a feedstock, particularly the arom. C and H atoms, and (2) a

Canonical Groups train, which provides high-level information about chem. moieties, but detects only ~1/3

of all the atoms in the feedstock, particularly those in n- and methylalkane chains. An example illustrates how the MIPF parameters of an AGO feedstock might presage its performance in an ethylene **plant**.

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48. **The rapid determination of fat and moisture in foods by microwave drying and NMR analysis**

ByMcManus, Bobbie; Horn, Michelle

Edited byLuthria, Devanand L

From Oil Extraction and Analysis: Critical Issues and Comparative Studies, [Papers presented at a Symposium entitled "Critical Issues, Current and Emerging Technologies for Determination of Crude Fat Content in Food, Feed and Seeds"] held at the 94th AOCS Annual Meeting & Expo, Kansas City, MO, United States, May 4-7, 2003 (2004), 137-151. Language: English, Database: CAPLUS

Fat and moisture anal. by microwave drying and **NMR** is a direct method that yields accurate results in minutes without solvents or the frequent calibration required by indirect methods such as near-IR or Fourier transform IR (FTIR). In the past, **NMR** was unreliable for detg. fat content in foods because the signal from moisture present in the sample interfered with the fat reading. There is now a peer-verified, microwave drying and **NMR** anal. (AOAC PVM 1:2003) for **quantification** of the percentage of moisture and fat in meat products. The procedure involves detg. the moisture value of meat samples by microwave drying and using the dried sample to det. the fat value by **NMR** anal. Five meat products were analyzed using a CEM SMART System (Moisture) and the SMART Trac System (Fat). The samples, representing a range of products that meat processors commonly analyze in daily **plant** operations, included the following: (i) fresh ground beef, high fat; (ii) deboned chicken with skins; (iii) fresh pork, low fat; (iv) all beef hot dogs, and (v) NIST std. ref. material samples. The results were compared with moisture and fat values derived from AOAC-approved methods, 950.46 Forced Air Oven Drying and 960.39 Soxhlet Ether Extn. The chapter also discusses the anal. of dairy samples by microwave moisture anal. and **NMR** fat anal. These samples include cream, ice cream, and milk with various levels of fat. Results are compared with the Mojonnier and Gerber techniques.

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49. **Quantification of compartmented metabolic fluxes in developing soybean embryos by employing biosynthetically directed fractional ¹³C labeling, two-dimensional [¹³C, ¹H] nuclear magnetic**

resonance, and comprehensive isotopomer balancing

BySriram, Ganesh; Fulton, D. Bruce; Iyer, Vidya V.; Peterson, Joan Marie; Zhou, Ruilian; Westgate, Mark E.; Spalding, Martin H.; Shanks, Jacqueline V.

From Plant Physiology (2004), 136(2), 3043-3057. Language: English, Database: CAPLUS, DOI: 10.1104/pp.104.050625

Metabolic flux quantification in plants is instrumental in the detailed understanding of metab. but is difficult to perform on a systemic level. Toward this aim, we report the development and application of a computer-aided metabolic flux anal. tool that enables the concurrent evaluation of fluxes in several primary metabolic pathways. Labeling expts. were performed by feeding a mixt. of U-13C Suc, naturally abundant Suc, and Gln to developing soybean (*Glycine max*) embryos. Two-dimensional [13C, 1H]NMR spectra of seed storage protein and starch hydrolyzates were acquired and yielded a labeling data set consisting of 155 13C isotopomer abundances. We developed a computer program to automatically calc. fluxes from this data. This program accepts a user-defined metabolic network model and incorporates recent math. advances toward accurate and efficient flux evaluation. Fluxes were calcd. and statistical anal. was performed to obtain SDS. A high flux was found through the oxidative pentose phosphate pathway (19.99±4.39 $\mu\text{mol d}^{-1}$ cotyledon-1, or 104.2 carbon mol. \pm 23.0 carbon mol. per 100 carbon mol. of Suc uptake). Sep. transketolase and transaldolase fluxes could be distinguished in the plastid and the cytosol, and those in the plastid were found to be at least 6-fold higher. The backflux from triose to hexose phosphate was also found to be substantial in the plastid (21.72±5.00 $\mu\text{mol d}^{-1}$ cotyledon-1, or 113.2 carbon mol. \pm 26.0 carbon mol. per 100 carbon mol. of Suc uptake). Forward and backward directions of anaplerotic fluxes could be distinguished. The glyoxylate shunt flux was found to be negligible. Such a generic flux anal. tool can serve as a **quant.** tool for metabolic studies and phenotype comparisons and can be extended to other **plant** systems.

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50. 23Na NMR microimaging: a tool for non-invasive monitoring of sodium distribution in living plants

ByRokitta, Markus; Medek, Danielle; Pope, James M.; Critchley, Christa

From Functional Plant Biology (2004), 31(9), 879-887. Language: English, Database: CAPLUS, DOI: 10.1071/FP04063

Detailed knowledge of the sodium (Na) distribution within the tissues of highly salt-tolerant Australian native species could help in understanding the physiol. adaptations of salt-tolerance or salt-sensitive **plants**. **23Na NMR** microimaging is presented as a tool to achieve this goal. Maps of the Na distribution in stem tissue were obtained with an in-plane resoln. of approx. 125 μm and a slice thickness of 4 mm. Simultaneously recorded high resoln. 1H **NMR** images showing water distribution in the same slice with 31 μm in-plane resoln. and 1 mm slice thickness, were used as an anatomical ref. together with optical micrographs that were taken immediately after the **NMR** expts. were completed. To **quantify** the Na concn., ref. capillaries with known NaCl concns. were located in the **NMR** probe together with the **plant** sample. Av. concn. values calcd. from signal intensities in the tissue and the capillaries were compared with concn. values obtained from at. emission photometry and optical microscopy performed on digested stem sections harvested immediately after **NMR** expts. Results showed that **23Na NMR** microimaging has great potential for physiol. studies of salt stress at the macroscopic level, and may become a unique tool for diagnosing salt tolerance and sensitivity.

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51. Quantitative high-resolution online NMR spectroscopy in reaction and process monitoring

ByMaiwald, Michael; Fischer, Holger H.; Hasse, Hans

From Chemie Ingenieur Technik (2004), 76(7), 965-969. Language: German, Database: CAPLUS

A review. The application of high-resoln. **NMR** spectroscopy for the process control of **plants** is discussed. In contrast to anal. **NMR** applications, no deuterated solvents are used. The requirements on **NMR** spectroscopy for reaction and process monitoring are described, and the **quant.** evaluation of the **NMR**

spectra is outlined. Two application examples are given. The 1st one deals with the reaction kinetics of a heterogeneously catalyzed ester formation, namely a mixt. of *n*-butanol, HOAc, *n*-butylacetate, and H₂O. The 2nd example describes the reactive adsorption of acidic gases, like CO₂, from aq. amine solns. This method can be used for the removal of CO₂ from waste gases of power stations.

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52. Nitrogen-bonded aromatics in soil organic matter and their implications for a yield decline in intensive rice cropping

BySchmidt-Rohr, K.; Mao, J.-D.; Olk, D. C.

From Proceedings of the National Academy of Sciences of the United States of America (2004), 101(17), 6351-6354. Language: English, Database: CAPLUS, DOI: 10.1073/pnas.0401349101

Long-term intensive cropping of irrigated lowland rice has led to significant grain-yield declines in field trials. The yield decline was attributed to decreased availability of soil nitrogen, which is held mostly in the soil org. matter. By advanced solid-state **NMR** spectroscopy, significant amts. were detected of amide nitrogen directly bonded to arom. rings in a humic acid fraction extd. from a continually submerged, triple-cropped rice soil. Because nitrogen bonded to aroms. is not readily **plant**-available, this observation can explain the yield decline. **Quant.** ¹³C **NMR** combined with advanced spectral editing showed that this humic acid is rich in lignin derivs. (>45% of all carbon), whereas the corresponding humic acid fraction extd. from an aerobic, single-cropped rice soil contains less lignin and less nitrogen bonded to aroms.

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53. Improvements in metabolic flux analysis using carbon bond labeling experiments: bondomer balancing and Boolean function mapping

BySriram, Ganesh; Shanks, Jacqueline V.

From Metabolic Engineering (2004), 6(2), 116-132. Language: English, Database: CAPLUS, DOI: 10.1016/j.ymben.2004.02.003

The biosynthetically directed fractional ¹³C labeling method for metabolic flux evaluation relies on performing a 2-D [¹³C, ¹H]**NMR** expt. on exts. from organisms cultured on a uniformly labeled carbon substrate. This article focuses on improvements in the interpretation of data obtained from such an expt. by employing the concept of bondomers. Bondomers take into account the natural abundance of ¹³C; therefore many bondomers in a real network are zero, and can be precluded a priori—thus resulting in fewer balances. Using this method, the authors obtained a set of linear equations which can be solved to obtain anal. formulas for **NMR**-measurable **quantities** in terms of fluxes in glycolysis and the pentose phosphate pathways. For a specific case of this network with four degrees of freedom, a priori identifiability of the fluxes was shown possible for any set of fluxes. For a more general case with five degrees of freedom, the fluxes were shown identifiable for a representative set of fluxes. Minimal sets of measurements which best identify the fluxes are listed. Furthermore, the authors have delineated Boolean function mapping, a new method to iteratively simulate bondomer abundances or efficiently convert carbon skeleton rearrangement information to mapping matrixes. The efficiency of this method is expected to be valuable while analyzing metabolic networks which are not completely known (such as in **plant** metab.) or while implementing iterative bondomer balancing methods.

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54. Deuterium NMR Used To Indicate a Common Mechanism for the Biosynthesis of Ricinoleic Acid by *Ricinus communis* and *Claviceps purpurea*

ByBillault, Isabelle; Mantle, Peter G.; Robins, Richard J.

From Journal of the American Chemical Society (2004), 126(10), 3250-3256. Language: English, Database: CAPLUS, DOI: 10.1021/ja038814d

Previous studies have shown that ricinoleic acid from castor bean oil of *Ricinus communis* is synthesized by the direct hydroxyl substitution of oleate, while it has been proposed that ricinoleate is formed by hydration of linoleate in the ergot fungus *Claviceps purpurea*. The mechanism of the enzymes specific to ricinoleate synthesis has not yet been established, but hydroxylation and desatn. of fatty acids in **plants** apparently involve closely related mechanisms. As mechanistic differences in the enzymes involved in the biosynthesis of natural products can lead to different isotopic distributions in the product, we could expect ricinoleate isolated from castor or ergot oil to show distinct 2H distribution patterns. To obtain information concerning the substrate and isotope effects that occur during the biosynthesis of ricinoleate, the site-specific natural deuterium distributions in Me ricinoleate isolated from castor oil and in Me ricinoleate and Me linoleate isolated from ergot oils have been measured by **quant.** 2H **NMR**. First, the deuterium profiles for Me ricinoleate from the **plant** and fungus are equiv. Second, the deuterium profile for Me linoleate from ergot is incompatible with this chem. species being the precursor of Me ricinoleate. Hence, it is apparent that 12-hydroxylation in *C. purpurea* is consistent with the biosynthetic mechanisms proposed for *R. communis* and is compatible with the general fundamental mechanistic similarities between hydroxylation and desatn. previously proposed for **plant** fatty acid biosynthesis.

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55. Quantitative approaches for analysing fluxes through plant metabolic networks using NMR and stable isotope labelling

By Kruger, N. J.; Ratcliffe, R. G.; Roscher, A.

From Phytochemistry Reviews (2003), 2(1-2), 17-30. Language: English, Database: CAPLUS, DOI: 10.1023/B:PHYT.0000004255.59062.88

A review. The **quant.** anal. of metabolic networks is a prerequisite for understanding the integration and regulation of **plant** metab. and for devising rational approaches for manipulating resource allocation in **plants**. The anal. of steady state stable isotope labeling expts. using **NMR** spectroscopy has developed into a powerful method for detg. these fluxes in micro-organisms and its application to heterotrophic **plant** metab. is increasing. After an introductory discussion of the well known role of stable isotopes in pathway delineation, the review considers their application to metabolic flux anal. in **plants**. These applications are divided into two groups - small scale analyses of fluxes through particular pathways and large scale analyses of multiple fluxes through metabolic networks - and the problems caused by the complexity of intermediary metab. in **plants** are discussed. It is concluded that metabolic flux anal. provides a powerful method for defining the metabolic phenotype of wild type, mutant and transgenic **plants** and that its development should be pursued.

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56. Quantitative assessment of crosstalk between the two isoprenoid biosynthesis pathways in plants by NMR spectroscopy

By Schuhr, Christoph A.; Radykewicz, Tanja; Sagner, Silvia; Latzel, Christoph; Zenk, Meinhard H.; Arigoni, Duilio; Bacher, Adelbert; Rohdich, Felix; Eisenreich, Wolfgang

From Phytochemistry Reviews (2003), 2(1-2), 3-16. Language: English, Database: CAPLUS, DOI: 10.1023/B:PHYT.0000004180.25066.62

Plants have been shown to use the mevalonate pathway for the biosynthesis of sterols and triterpenes in the cytoplasm and the recently discovered deoxyxylulose phosphate pathway for the biosynthesis of a variety of hemiterpenes, monoterpenes, diterpenes, as well as for the biosynthesis of carotenoids and the phytol side chain of chlorophyll in plastids. Despite the compartmental sepn., at least one terpene precursor can be exchanged between the two pathways. In order to assess **quant.** the crosstalk between the two isoprenoid pathways, [2-13C1]mevalonolactone or [U-13C6]glucose were supplied to cell cultures of *Catharanthus roseus* grown under illumination or in darkness. Sitosterol, lutein and phytol were isolated and

analyzed by **NMR** spectroscopy. The incorporations of exogenous [2-¹³C]mevalonolactone were 48% and 7% into the dimethylallyl diphosphate and isopentenyl pyrophosphate precursors of sitosterol and lutein, resp. With [U-¹³C]glucose as precursor, at least 95% of sitosterol precursors were obtained via the mevalonate pathway, whereas phytol appeared to be biosynthesized via the deoxyxylulose phosphate pathway (approx. 60%) as well via the mevalonate pathway (approx. 40%). The apparent ratios for the contribution of the two pathways depend on the nature of the precursor supplied as well as the nature of the target compd. Thus, crosstalk between the two terpenoid pathways cannot be explained in detail by a simple two compartment model and requires an addnl. in depth study of complex regulatory mechanisms.

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57. Cell differentiation, secondary cell-wall formation and transformation of callus tissue of *Pinus radiata* D. Don

ByMoeller, Ralf; McDonald, Armando G.; Walter, Christian; Harris, Philip J.

From *Planta* (2003), 217(5), 736-747. Language: English, Database: CAPLUS, DOI: 10.1007/s00425-003-1053-0

Tracheid and sclereid differentiation was induced in callus cultures of *Pinus radiata* D. Don by culturing on a basal medium contg. activated charcoal but no phytohormones; sclereids differentiated in callus derived from xylem strips, but not in callus derived from hypocotyl segments. The tracheids differentiated in hypocotyl-derived callus had helical, scalariform, reticulated or pitted secondary cell-wall patterns, but those differentiated in xylem-derived callus had a reticulate or pitted pattern. The thickened tracheid and sclereid walls contained lignin as indicated by the red color reaction given with phloroglucinol-HCl. The presence of lignin in the cell walls of differentiated callus was confirmed using pyrolysis gas chromatog.-mass spectrometry by the detection of phenylpropanoid components derived from lignin. Lignin was also detected using solid-state ¹³C cross-polarization/magic-angle spinning **NMR** spectroscopy and **quantified** as thioglycolic acid lignin. Monosaccharide analyses of the cell walls isolated from differentiated and undifferentiated calli showed that the cell walls of the differentiated calli contained higher proportions of glucose and mannose, consistent with the presence of greater proportions of gluco- and/or galactogluco-mannans in the secondary cell walls of the differentiated cells. A protocol for the stable transformation of undifferentiated, xylem-derived cultures was successfully developed. Transgenic cell lines were established following Biolistic particle bombardment with a plasmid contg. the coding region of the nptII gene and the coding region of the cad gene from *P. radiata*. Expression of the nptII gene in transgenic lines was confirmed by an NPTII-ELISA. The overexpression of cad in the transgenic lines resulted in a down-regulation of cinnamyl alc. dehydrogenase (E.C. 1.1.1.195) expression.

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58. Quantitative ²H NMR analysis of deuterium distribution in petroselinic acid isolated from parsley seed

ByGuet, Sebastien; Robins, Richard J.; Lees, Michele; Billault, Isabelle

From *Phytochemistry* (Elsevier) (2003), 64(1), 227-233. Language: English, Database: CAPLUS, DOI: 10.1016/S0031-9422(03)00278-4

We have previously demonstrated that ²H distribution in fatty acids is non-statistical and can be related to isotopic discrimination during chain extension and desatn. Petroselinic acid (C18:1Δ6), a fatty acid characteristic of the seeds of the Apiaceae, has been shown to be biosynthesised from palmitoyl-ACP (C16:0) by two steps, catalyzed by a dedicated Δ4-desaturase and an elongase. We have now demonstrated that the isotopic profile resulting from this pathway is similar to that of the classical **plant** fatty acid pathway but that the isotopic fingerprint from both the desaturase and elongase steps show important differences relative to oleic and linoleic acid biosynthesis.

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59. **Phenylalanine-independent biosynthesis of 1,3,5,8-tetrahydroxyxanthone. A retrobiosynthetic NMR study with root cultures of *Swertia chirata***

ByWang, Chang-Zeng; Maier, Ulrich H.; Keil, Michael; Zenk, Meinhard H.; Bacher, Adelbert; Rohdich, Felix; Eisenreich, Wolfgang
From European Journal of Biochemistry (2003), 270(14), 2950-2958. Language: English, Database: CAPLUS, DOI: 10.1046/j.1432-1033.2003.03669.x

Root cultures of *Swertia chirata* (Gentianaceae) were grown with supplements of [1-¹³C]glucose, [U-¹³C₆]glucose or [carboxy-¹³C]shikimic acid. 1,3,5,8-Tetrahydroxyxanthone was isolated and analyzed by **quant. NMR** anal. The obsd. isotopomer distribution shows that 1,3,5,8-tetrahydroxyxanthone is biosynthesized via a polyketide-type pathway. The starter unit, 3-hydroxybenzoyl-CoA, is obtained from an early shikimate pathway intermediate. Phenylalanine, cinnamic acid and benzoic acid were ruled out as intermediates.

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60. **Characterization of sewage sludge organic matter using solid-state carbon-13 nuclear magnetic resonance spectroscopy**

BySmernik, Ronald J.; Oliver, Ian W.; Merrington, Graham
From Journal of Environmental Quality (2003), 32(4), 1516-1522. Language: English, Database: CAPLUS, DOI: 10.2134/jeq2003.1516

Six sewage sludges from 5 sewage treatment **plants** in Australia were characterized using solid-state ¹³C **NMR** spectroscopy. Spectra were acquired both before and after removal of mineral components through treatment with HF. Carbon mass balance indicated that little org. matter was lost on HF treatment, which significantly improved **NMR** sensitivity and spectral resoln., and decreased acquisition time and hence cost of **NMR** anal. Two **NMR** techniques were used, the std. cross polarization (CP) technique and Bloch decay (BD). The BD technique had not been applied previously to the anal. of sewage sludge. For each sludge sample, both before and after HF treatment, the BD spectrum contained significantly more alkyl carbon. Spin counting, another technique applied to sewage sludge here for the first time, showed that the BD spectra of

the HF-treated sludges were **quant.**, while ~30% of the CP **NMR** signal went undetected. The discrepancy

between CP and BD spectra was attributed to the presence of alkyl carbon with such high mol. mobility that the efficiency of cross polarization is affected. Sewage sludge org. matter is significantly different in chem. to soil org. matter and has implications for the application of sewage sludge to agricultural land.

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61. **Lignification in relation to the biennial growth habit in brassicas**

ByEvans, B. W.; Snape, C. E.; Jarvis, M. C.
From Phytochemistry (Elsevier) (2003), 63(7), 765-769. Language: English, Database: CAPLUS, DOI: 10.1016/S0031-9422(03)00327-3

The forage brassicas are a useful model system for the study of wood formation because the thickened cell walls of their vascular tissue can vary widely in lignin content. Solid-state ¹³C **NMR** spectroscopy was used to **quantify** lignin, and det. features of its structure, in the vascular cell walls of forage rape (*Brassica napus* L.), and Thousandhead and marrowstem cultivars of kale (*Brassica oleracea* L. var. *acephala*). During the first season of vegetative growth, lignin levels in these cell walls remained low in the upper part of the stems despite the phys. resemblance of this tissue to wood. The extended flowering stems produced in the following year were thinner and their vascular tissue contained much more strongly lignified cell walls. The structure of the lignin was typical of angiosperm wood. It showed only small variations in syringyl/guaiacyl

ratio, but this ratio increased with lignin content and thus with the proportion of the lignin that was assoc. with secondary cell-wall layers.

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62. Quantification of myo-inositol hexakisphosphate in alkaline soil extracts by solution ³¹P NMR spectroscopy and spectral deconvolution

ByTurner, Benjamin L.; Mahieu, Nathalie; Condron, Leo M.

From Soil Science (2003), 168(7), 469-478.Language:English, Database: CAPLUS

A relatively simple technique is described using soln. ³¹P **NMR** spectroscopy and spectral deconvolution for the **quantification** of myo-inositol hexakisphosphate (phytic acid), the most abundant soil inositol phosphate, in alk. soil exts. An authentic myo-inositol hexakisphosphate std. added to a re-dissolved soil ext. gave signals at 5.85, 4.92, 4.55, and 4.43 ppm in the ratio 1:2:2:1. Spectral deconvolution **quantified** these signals accurately (102 ± 4%) in solns. contg. a mixt. of model P compds. by resolving the envelope of signals in the orthophosphate monoester region. In NaOH-EDTA exts. from a range of lowland permanent pasture soils in England and Wales, concns. of myo-inositol hexakisphosphate detd. by spectral deconvolution ranged between 26 and 189 mg P kg⁻¹ soil, equiv. to between 11 and 35% of the extd. org. P. Concns. were pos. correlated with oxalate-extractable aluminum and iron but were not correlated with total carbon, total nitrogen, clay, or the microbial biomass. This suggests that myo-inositol hexakisphosphate accumulates in soils by mechanisms at least partially independent of those controlling org. matter stabilization and dynamics. Furthermore, myo-inositol hexakisphosphate concns. were pos. correlated with **plant**-available inorg. P and neg. correlated with the carbon-to-org. P ratio, suggesting that biol. P availability may, in part, regulate myo-inositol hexakisphosphate concns. in soils, perhaps because organisms capable of degrading this compd. are favored in more P-limited environments. Soln. ³¹P **NMR** spectroscopy and spectral deconvolution offers a relatively simple method of **quantifying** myo-inositol hexakisphosphate in soil exts.

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63. Nanofiltration membrane autopsy of a full scale unit : characterization of the organic and inorganic constituents of the foulants

ByCroue, Jean-Philippe; Grasset, Laurent; Bacle, Sylvain; Jacquemet, Valerie

From Maximizing the Resources: Solutions for Pure and Plentiful Water, Membrane Technology Conference Proceedings, Atlanta, GA, United States, Mar. 2-5, 2003 (2003), 671-679.Language:English, Database: CAPLUS

The objective was to conduct the autopsy of nanofiltration membranes from a full-scale filtration. Membrane sheets were obtained from spiral-wound modules taken at different stages of the train of a membrane filtration unit of a drinking water treatment **plant**. The foulant layer was phys. removed from the membrane, sonicated in MilliQ water and centrifuged. The foulant material was sepd. into 2 sub-fractions, sol. and insol. The 2 fractions were **quantified** by wt. and characterized by elemental, FTIR, ¹³C-**NMR** and pyrolysis GC/MS analyses. The low ash content of the isolates indicated that the org. phase was the major constituent of the foulant material. Ca, Fe and Al were the major inorg. species. Elemental anal. of all isolates were quite similar to the one reported for membrane cell residues (i.e. peptidoglycan) isolated from surface waters (higher in H and N as compared to humic substances type material). The structural characterization confirmed the microbial origin of the org. matrix (biofouling). For all selected membranes, the insol. foulant material was more enriched in nitrogenous structures as compared to the sol. material. The sol. fraction incorporated a larger proportion of carbohydrates (i.e. exopolysaccharides).

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64. NMR based determination of minute acid functionality: end-groups in PET

ByMa, Y.; Agarwal, U. S.; Vekemans, J. A. J. M.; Sikkema, D. J.

From Polymer (2003), 44(16), 4429-4434. Language: English, Database: CAPLUS, DOI: 10.1016/S0032-3861(03)00402-6

Conditions are detd. for the carbodiimide-mediated room temp. esterification of the carboxylic acid end-groups of poly(ethylene terephthalate) with hexafluoroisopropanol. The hexafluoroisopropyl ester is **quantified** with ¹⁹F **NMR**, using α,α,α -trifluorotoluene as a secondary std. This provides a technique for accurate detn. of minute amts. of carboxylic acid functionality in small samples of polymers, and potentially in animal- and **plant**-based foods.

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65. Relation of the fragmental composition of humic acids and their physiological activity

ByByambagar, B.; Kushnarev, D. F.; Fedorova, T. I.; Novikova, L. N.; Yakovleva, Yu. N.; Ostrovskaya, P. M.; Proidakov, A. G.; Kalabin, G. A.

From Khimiya Tverdogo Topliva (Moscow, Russian Federation) (2003), (1), 83-90. Language: Russian, Database: CAPLUS

Quant. anal. of humic acids from brown coals of Irkutsk region (Russia) and Mongolia was performed using ¹³C **NMR**. Effect of mech. activation of coals on humic acid structure and biol. activity was studied. Stimulatory (or inhibitory) activity of humic acids on seed germination and growth of seedlings was studied with corn, wheat, barley, and pea in lab. and field expts.

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66. Characterization of soil organic matter in tropical rice soils by advanced solid-state NMR

BySchmidt-Rohr, Klaus; Mao, Jingdong; Olk, Dan C.

From Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003 (2003), GE0C-058. Language: English, Database: CAPLUS

The structures of soil org. matter from a continually submerged, triple-cropped lowland rice soil and that from an aerobic dryland rice soil were investigated and compared using advanced solid-state **NMR (NMR)** techniques. **Quant.** ¹³C **NMR** shows that the humic acid (HA) from the submerged triple-cropped rice soil with large amts. of rice-straw input is rich in lignin derivs. (ca. 45% of carbon) but almost free of charcoal. Significant amts. (>35%) of nitrogen bonded to arom. rings were detected by ¹⁴N-¹³C **NMR**. The ¹³C and ¹⁵N chem. shift and relatively high NCO:NCH ratio indicate NCO bonded to arom. rings. In contrast, the corresponding HA fraction extd. from the dryland soil with lower lignin input shows predominantly NCO and NCH signals of easily degradable peptides, as well as some heterocyclic **N**. Nitrogen species bonded to aroms. are considered as not readily **plant**-available and their accumulation coincides with a substantial long-term grain-yield decline.

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67. Use of fluorinated analogs to explore pollutant fate in plant systems

ByTront, Jacqueline M.; Saunders, F. Michael

From Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003 (2003), BIOT-017. Language: English, Database: CAPLUS

Fate of environmental pollutants was investigated using **NMR (NMR)** to identify and **quantify** metabolites of xenobiotics in aquatic **plant** systems. Liq. extrn. results of **plant** exposed to fluorinated chlorophenols (4-chloro-2-fluorophenol) have shown that metabolites of xenobiotics, as well as parent compds., are detectable using ¹⁹F **NMR**. 4-Chloro-2-fluorophenol was present in **plant** exts. through various exposure periods as demonstrated by chem. shift comparison with unexposed **plant** exts. spiked with parent material.

Several fluorinated metabolites were also present, as was demonstrated by the chem. shift of -3.5 ppm from the parent compd. The metabolites isolated in exts. were fluorinated chlorophenol conjugates, as evidenced by identical signal splitting pattern between parent and metabolites and relatively small chem. shift. This work uses ^{19}F **NMR** for developing a kinetic model that describes xenobiotic accumulation and transformation in aquatic **plants** systems.

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68. Nature of soil organic phosphorus: an assessment of peak assignments in the diester region of ^{31}P NMR spectra

ByMakarov, M. I.; Haumaier, L.; Zech, W.

From Soil Biology & Biochemistry (2002), 34(10), 1467-1477. Language: English, Database: CAPLUS, DOI: 10.1016/S0038-0717(02)00091-3

This study involved a crit. assessment of peak assignments in ^{31}P **NMR** spectra of alk. soil exts. and included ^{31}P **NMR** spectroscopy of (1) 500 mM NaOH solns. of RNA, DNA, and lecithin; (2) 50 mM H_2SO_4 , 500 mM NaHCO_3 (pH 8.5), and 100 mM NaOH exts. from *Pseudomonas putida* (Gram-neg. bacterium), *Bacillus subtilis* (Gram-pos. bacterium), *Penicillium citrinum* (a fungus), *Aspergillus niger* (a fungus), and leaves of *Betula pubescens*, *Picea abies*, and *Pinus cembra*; (3) 100 mM NaOH solns. of evapd. methanol-chloroform exts. from *B. subtilis*, *P. putida*, *B. pubescens* leaves, and from org. and mineral soil horizons; (4) 100 mM NaOH and 50 mM H_2SO_4 exts. from delipidized bacterial cells, and 100 mM NaOH exts. from delipidized birch leaves and soil samples. Results showed that the **resonance** at 0 ppm, previously assigned to phospholipids and **nucleic** acids, was caused by DNA-P. **Resonances** of phospholipids of **plant** and microbial origin were obsd. at about 1.5-1.7 and 0.6-0.7 ppm, in regions previously assigned to teichoic acid-P by various authors. Nonlipidic compds. extd. from *B. subtilis* and **resonating** at 1.9 ppm probably were represented by teichoic acids. ^{31}P **NMR** spectroscopy cannot differentiate signals derived from P of phospholipids and nonlipidic compds. in the low field of the diester region of spectra of alk. exts. from soils, while **quant.** differentiation of DNA-P and the other diesters seems to be quite a simple task. An unknown **resonance** at -1.5 ppm remained unidentified. The real concns. of diester-P in soils can be considerably underestimated and those of monoester-P overestimated, when analyzed in alk. exts., because of almost complete hydrolysis of RNA and partial hydrolysis of phospholipids to monoesters.

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69. Quantification of substructures of refractory organic substances by means of nuclear magnetic resonance

ByHaiber, S.; Herzog, H.; Buddrus, J.; Burba, P.; Lambert, J.

Edited byFrimmel, Fritz H

From Refractory Organic Substances in the Environment (2002), 115-128. Language: English, Database: CAPLUS

Soln.-state **NMR** has been used to identify and **quantify** structural fragments in refractory org. substances (ROS). A variety of substructures, e.g. fatty acids, amino acids, lignin substructures, and carbohydrates can be assigned. The portions of the lignin substructures coumaryl, guaiacyl, and syringyl can be obtained non-destructively by combination of 1-dimensional (1D) and 2-dimensional (2D) **NMR** techniques. For the

samples studied, ROS HO13 FA and HO13 HA, lignin and lignin-derived structural units account for ~20%

of the total carbon or 50% of the total arom. C. Guaiacyl-type structures are more abundant (15 % of the total C) than coumaryl (1%) and syringyl (4%). The total carbohydrate content of ROS can be reliably estd. by **NMR**. **Plant** derived carbohydrates account for 10% of the total C of HO13 FA and HO13 HA. The results suggest that the major contribution to the ROS studied is from lignocelluloses. Two-dimensional

heteronuclear multiple quantum-coherence (HMQC) ^1H NMR was used for structural studies of ROS fractions of HO13 XAD8 obtained from multistage ultrafiltration (MSTUF). The results of the combined procedure indicate that structural units in isolated ROS can be enriched in different mass fractions, for instance fatty acids in the fraction <1 kDa, amino acids in the 10-50 kDa fraction, and Me groups attached to quaternary carbon atoms in the high-mol. mass fraction >50 kDa. A structural model of ROS is promoted in which aggregates of different mol. size also have different primary structures.

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70. Natural deuterium distribution in branched-chain medium-length fatty acids is nonstatistical: A site-specific study by quantitative ^2H NMR spectroscopy of the fatty acids of capsaicinoids

ByMarkai, Sandrine; Marchand, Patrice A.; Mabon, Françoise; Baguet, Evelyne; Billault, Isabelle; Robins, Richard J.

From ChemBioChem (2002), 3(2-3), 212-218. Language: English, Database: CAPLUS, DOI: 10.1002/1439-7633(20020301)3:2/3<212::AID-CBIC212>3.0.CO;2-R

Quant. ^2H NMR spectroscopy has been used to det. the natural abundance site-specific ^2H isotopic content of 6,7-dihydro-capsaicin (1) and capsaicin (2). Prior to anal., the fatty acyl moieties were released as Me 8-methylnonanoate (3) and Me E-8-methylnon-6-enoate (4), resp. A marked and similar nonstatistical isotopic distribution of ^2H is obsd. for both fatty acids. Notably, it can be seen that: (1) the iso-Bu portion of 3 is more impoverished in ^2H than the methylenic portion; (2) the iso-Bu portion of 4 is more impoverished than that of 3; (3) an alternating pattern occurs in the $(^2\text{H}/^1\text{H})_i$ between the C3 to C7 positions; and (4) the ethylenic hydrogens at C6 and C7 of 4 are, resp., impoverished and unchanged relative to these positions in 3. These observations are compatible with the proposed biosynthetic origins of the different parts of 1 and 2, and with the view that 1 is a proximal precursor of 2. Furthermore, it can be suggested that, firstly, the hydrogen atoms at C3 to C7 originate alternatively from the substrate and from the environment and, secondly, that the $\delta^6\text{-E}$ desatn. is introduced by a mechanism closely mimicking that of the Z desatn. of higher plants.

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71. Incorporation of [^{13}C]1-deoxy-d-xylulose into isoprenoids of the liverwort *Conocephalum conicum*

ByThiel, Rolf; Adam, Klaus Peter

From Phytochemistry (2002), 59(3), 269-274. Language: English, Database: CAPLUS

The incorporation of ^{13}C labeled 1-deoxy-d-xylulose into the monoterpene bornyl acetate, the sesquiterpene cubebanol, and the diterpene phytol has been studied in axenic cultures of the liverwort *Conocephalum conicum*. **Quant.** ^{13}C NMR spectroscopic anal. of the labeling patterns of the sesquiterpene indicated a possible degrdn. of 1-deoxy-d-xylulose to acetate and subsequent incorporation via the mevalonic acid pathway. In bornyl acetate, the labeling occurred only in the acetate moiety whereas the isoprene units remained unlabeled. The isoprene units of the diterpene phytol showed incorporation of intact deoxy-d-xylulose. These results indicate the involvement of both IPP biosynthetic pathways and two independently operating compartments/cell types with MEP pathway machinery. One MEP compartment is presumably the plastid where phytol is formed; the second, involved in the build-up of the isoprene part of bornyl acetate, might be located in the oil cells. The acetylation of borneol to bornyl acetate in turn occurs in a cellular compartment that is not involved in the build-up of the isoprene units of borneol.

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72. Biosynthesis of a hopane triterpene and three diterpenes in the liverwort *Fossombronina alaskana*

ByHertewich, Ursula; Zapp, Josef; Becker, Hans; Adam, Klaus Peter

From Phytochemistry (2001), 58(7), 1049-1054. Language: English, Database: CAPLUS, DOI: 10.1016/S0031-9422(01)00359-4

The biosynthesis of the triterpene 22-(30)-hopene-29-acid and the diterpenes 7,17-sacculatadiene-11,12-dial (sacculatal), trans-phytol and a new neoverrucosane-type diterpenoid (5-oxo-neoverrucos-(13)-ene) was studied by incorporation of [1-¹³C]-labeled glucose into axenic cultures of the arctic liverwort *Fossombronia alaskana*. **Quant.** ¹³C NMR spectroscopic anal. of the resulting labeling patterns showed that the isoprene units of the triterpene are derived from the mevalonic acid pathway, whereas the isoprene units of the diterpenes are built up via the methylerythritol phosphate pathway.

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73. Biosynthesis of thiophenes in *Tagetes patula*

By Margl, Lilla; Eisenreich, Wolfgang; Adam, Petra; Bacher, Adelbert; Zenk, Meinhard H.

From Phytochemistry (2001), 58(6), 875-881. Language: English, Database: CAPLUS, DOI: 10.1016/S0031-9422(01)00360-0

The biosynthesis of 5-(3-buten-1-ynyl)-2,2'-bithiophene was studied in root cultures of *Tagetes patula*. Organ cultures were grown with [U-¹³C₆]glucose or [1-¹³C]glucose. The bithiophene and amino acids from cell protein were isolated and analyzed by **quant. NMR** spectroscopy. Retrobiosynthetic anal. establish acetyl-CoA or a closely related compd. (e.g. malonyl-CoA) as building blocks and their orientations in the bithiophene. The data confirm a previously suggested biosynthetic route via long-chain fatty acids and polyacetylenes. However, a polyketide-like biosynthesis via a carbocyclic intermediate cannot be excluded.

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74. Stress metabolism. IX. Effect of salt stress on trigonelline accumulation in tomato

By Rajasekaran, Lada R.; Aspinall, D.; Jones, G. P.; Paleg, L. G.

From Canadian Journal of Plant Science (2001), 81(3), 487-498. Language: English, Database: CAPLUS

The presence of quaternary ammonium compds. (QAC) and their accumulation in tomato (*Lycopersicon esculentum* Mill.) cv. Duke in **response** to different modes for causing NaCl stress were studied. Pre-germinated tomato seeds were grown in sand culture and 25-d-old seedlings were subjected to abrupt, progressive or prolonged salt stress using NaCl at various osmotic potentials. **Plant** water status was measured using psychrometry and quaternary ammonium compds. were visualized using thin-layer chromatog. and then confirmed and **quantified** using **NMR** spectrometry. Leaf water potential and osmotic potential declined depending on the osmotic potential of the rooting medium and the mode of stress imposition. A greater decline in osmotic potential compared with the total water potential led to turgor maintenance in **plants** under progressive or prolonged NaCl stress. The QAC, trigonelline and choline were identified in tomato. Trigonelline, but not choline, accumulated rapidly in **response** to abrupt, progressive or prolonged NaCl stress. The threshold external water potential (ψ_{ext}) for trigonelline accumulation was -0.565 MPa. Trigonelline accumulation correlated with changes in ψ_L ($r = -0.92^{***}$), ψ_S ($r = -0.94^{***}$) and ψ_P ($r = 0.85^{***}$). Trigonelline contributed only -0.035 MPa to the osmotic adjustment, suggesting that its role may also lie in areas other than osmoregulation.

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75. Detection of added beet or cane sugar in maple syrup by the site-specific deuterium nuclear magnetic resonance (SNIF-NMR) method: collaborative study

By Martin, Yves-Loic; Christoph, N.; Blanch-Cortes, A.-I.; Dennis, J.; Giraudon, S.; Guillon, C.; Hermann, A.; Le Leuch, A.; Mazac, J.; Naulet, N.; et al

From Journal of AOAC International (2001), 84(5), 1509-1521. Language: English, Database: CAPLUS

Results of a collaborative study are reported for the detection of added beet or cane sugar in maple syrup by

the site-specific natural isotope fractionation-**NMR** (SNIF-**NMR**) method. The method is based on the fact that the deuterium content at specific positions of the sugar mols. is different in maple syrup from that in beet or cane sugar. The syrup is dild. with pure water and fermented; the alc. is distd. with a **quant.** yield and analyzed with a high-field **NMR** spectrometer fitted with a deuterium probe and fluorine lock. The proportion of ethanol mols. monodeuterated at the Me site is recorded. This parameter (D/H)I is decreased when beet sugar is added and increased when cane sugar is added to the maple syrup. The precision of the method for measuring (D/H)I was found to be in good agreement with the values already published for the application of this method to fruit juice concs. (AOAC Official Method 995.17). An excellent correlation was found between the percentage of added beet sugar and the (D/H)I isotopic ratio measured in this collaborative study. Consequently, all samples in which exogenous sugars were added were found to have a (D/H)I isotopic ratio significantly different from the normal value for an authentic maple syrup. By extension of what is known about **plants** having the C4 cycle, the method can be applied to corn sweeteners as well as to cane sugar. One limitation of the method is its reduced sensitivity when applied to specific blends of beet and cane sugars or corn sweeteners. In such case, the C13 ratio measurement (see AOAC Official Method 984.23, Corn Syrup and Cane Sugar in Maple Syrup) may be used in conjunction.

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76. **Natural deuterium distribution in long-chain fatty acids is nonstatistical: a site-specific study by quantitative 2H NMR spectroscopy**

ByBillault, Isabelle; Guet, Sebastien; Mabon, Francoise; Robins, Richard

From ChemBioChem (2001), 2(6), 425-431.Language:English, Database: CAPLUS, DOI: 10.1002/1439-7633(20010601)2:6<425::AID-CBIC425>3.0.CO;2-Z

Quant. 2H **NMR** spectroscopy has been used to study the site-specific natural occurrence of 2H in common unsatd. fatty acids. A marked nonstatistical isotopic distribution of 2H is obsd. in both Me oleate and Me linoleate. By chem. modification, the internal isotopic 2H signatures of these products have been partially accessed. Notably, it can be seen that (1) the sites of desatn. show a strong impoverishment at only one ethylenic position of each desatn.; (2) the level of impoverishment reflects the source of the hydrogen atoms present; and (3) a gradient of 2H content occurs along the chain. These effects can in part be related to the mechanisms proposed for the enzymes responsible for the various steps of biosynthesis of unsatd. fatty acids in **plants**.

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77. **Determination of low molecular weight dicarboxylic acids and organic functional groups in rhizosphere and bulk soils of Tsuga and Yushania in a temperate rain forest**

ByChen, Meng-Chun; Wang, Ming-Kuang; Chiu, Chih-Yu; Huang, Pan-Ming; King, Hen-Biau

From Plant and Soil (2001), 231(1), 37-44.Language:English, Database: CAPLUS

Low-mol.-wt. org. acids (LMWOAs) derived from root exudates, decomp. org. matter, and other sources are important ligands. The species of these LMWOAs in the Tsuga rhizosphere soil (TRS), and Yushania rhizosphere soil (YRS), and bulk soil (BS) from an alpine forest region were identified. LMWOA and org. functional groups were compared to those fresh twigs and leaves, litter, and roots. The objectives of this study were to (1) develop a method that could be used to det. LMWOAs in soil soln. by gas chromatog. (GC), (2) assess methods for processing LMWOAs in soil samples, and (3) det. the relative proportions of org. carbon functional groups in the TRS, YRS and BS, and fresh **plant** materials with 13C-**NMR** anal. The gas chromatograph was equipped with a flame ionization detector; an AJ & W scientific GC column (30 m x 0.5 mm i.d.) coated with DB-FFAP was used, with He as carrier gas. The proportion of org. acid contents followed the order of YRS > TRS > BS, and also showed significant differences (P < 0.05) from GC anal. The amts. of malonic, fumaric and succinic acids in the YRS samples were greater than in the TRS and BS.

Samples analyzed after 1 mo of deep freeze storage (-24°) showed no signs of decompn. The proportion of org. functional groups in the rhizosphere and bulk soils **quantified** by ¹³C **NMR** analyses followed the general order: alkyl-C >O-alkyl-C >N-alkyl-C > acetal-C > arom.-C > carboxylic-C > phenolic-C.

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78. Biosynthesis of the hemi- and monoterpene moieties of isoprenyl phenyl ethers from the liverwort *Trichocolea tomentella*

ByBarlow, A. J.; Becker, H.; Adam, K. P.

From *Phytochemistry* (2001), 57(1), 7-14. Language: English, Database: CAPLUS, DOI: 10.1016/S0031-9422(01)00002-4

The incorporation of ¹³C labeled glucose into trichocolein, deoxytomentellin, trans-phytol and stigmasterol has been studied in axenic cultures of the liverwort *Trichocolea tomentella*. **Quant.** ¹³C **NMR** spectroscopic anal. of the resulting labeling patterns showed that the isoprene units of the hemi- and monoterpene moieties and the diterpene phytol are derived from the methylerythritol phosphate pathway, whereas the isoprene units of stigmasterol are built up via the mevalonic acid pathway. These results indicate the involvement of both IPP biosynthetic pathways in different cellular compartments. A new, hydroperoxy geranyl Ph ether deriv. is also described.

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79. Comparative analysis of black carbon in soils

BySchmidt, Michael W. I.; Skjemstad, Jan O.; Czimczik, Claudia I.; Glaser, Bruno; Prentice, Ken M.; Gelinas, Yves; Kuhlbusch, Thomas A. J.

From *Global Biogeochemical Cycles* (2001), 15(1), 163-167. Language: English, Database: CAPLUS, DOI: 10.1029/2000GB001284

Black carbon (BC), produced by incomplete combustion of fossil fuels and **vegetation**, occurs ubiquitously in soils and sediments. BC exists as a continuum from partly charred material to highly graphitized soot particles, with no general agreement on clear-cut boundaries of definition or anal. In a comparative anal., we measured BC forms in eight soil samples by six established methods. All methods involved removal of the non-BC components from the sample by thermal or chem. means or a combination of both. The remaining carbon, operationally defined as BC, was **quantified** via mass balance, by elemental compn., by exploiting benzenecarboxylic acids as mol. markers, or by applying ¹³C MAS **NMR** (magic angle spinning **NMR**) spectroscopy. BC concns. measured for individual samples vary **over 2** orders of magnitude (up to a factor of 571). One possible explanation for this wide range of results is that the individual BC methods rely on operational definitions with clearcut but different boundaries, which were developed for specific scientific questions, whereas BC represents a continuum of materials with widely contrasting physicochem. properties. Thus, the methods are inherently designed to anal. det. different parts of the continuum, and it is crucial to know how measurements made by different techniques relate to each other. It is clear from this preliminary comparative anal. that a collection of BC ref. materials should be established as soon as possible (1) to ensure long-term intra-lab. and interlab. data quality and (2) to facilitate comparative analyses between different anal. techniques and scientific approaches.

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80. ¹³C-NMR of forest soil lipids

ByAlmendros, Gonzalo; Tinoco, Pilar; Gonzalez-Vila, Francisco Javier; Ludemann, Hans-Dietrich; Sanz, Jesus; Velasco, Francisco

From *Soil Science* (2001), 166(3), 186-196. Language: English, Database: CAPLUS

Mol. characterization of soil lipids often provides valuable biogeochem. information about the impact of **vegetation**, microorganisms, and abiotic factors on the soil C sequestration process. The total lipid extd.

with petroleum ether from nine soils developed under three types of Mediterranean forest (stone pine (*Pinus pinea* L.), evergreen oak (*Quercus rotundifolia* L.), and Spanish juniper (*Juniperus thurifera* L)) has been analyzed by high-resoln. ^{13}C **NMR** under **quant.** acquisition conditions. Tentative assignments of the spectral peaks are presented, and the spectra of soil lipids are compared with those from the lipids extd. directly from leaves of the corresponding trees. This comparison evidenced that soil lipids behaved as biomarker soil fractions when analyzed by ^{13}C -**NMR** as a whole. Anal. by gas chromatog.-mass spectrometry (GC/MS) reveals that the volatile fraction of the lipid ext. (46%, on av., as estd. by internal ref.) consisted mainly of free alkanes, alkanolic acids (<C30), and diterpene resin acids. Some differences were obsd. between the chem. structures suggested by ^{13}C -**NMR** and GC/MS. This was interpreted as a portion of soil and **plant** lipids consisting of extractable material that cannot be detected by std. GC methods. The complex signal pattern in the 0 to 30 ppm chem. shift range showed typical signals for carbons in acyl polymethylene chains, which overlapped with a pattern suggesting isoprenoid-like branching in long-chain

structures (major signals at ~22, 26, and 32 ppm). In addn., periodic unsaturations suggested by signals at

~124 and 135 ppm are also compatible with polyprenoid-type backbones. The alkyl region coincided with

those of mono- to triacylglycerol fatty esters. It seems evident that ^{13}C -**NMR** allows us to characterize structures present in nonvolatile complex material.

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81. **Retrobiosynthetic nuclear magnetic resonance analysis of amino acid biosynthesis and intermediary metabolism. Metabolic flux in developing maize kernels**

ByGlawischnig, Erich; Gierl, Alfons; Tomas, Adriana; Bacher, Adelbert; Eisenreich, Wolfgang

From *Plant Physiology* (2001), 125(3), 1178-1186. Language: English, Database: CAPLUS, DOI: 10.1104/pp.125.3.1178

Information on metabolic networks could provide the basis for the design of targets for metabolic engineering. To study metabolic flux in cereals, developing maize (*Zea mays*) kernels were grown in sterile culture on medium contg. [^{13}C]glucose or [^{13}C]acetate. After growth, amino acids, lipids, and sitosterol were isolated from kernels as well as from the cobs, and their ^{13}C isotopomer compns. were detd. by **quant. NMR** spectroscopy. The highly specific labeling patterns were used to analyze the metabolic pathways leading to amino acids and the triterpene on a **quant.** basis. The data show that serine is generated from phosphoglycerate, as well as from glycine. Lysine is formed entirely via the diaminopimelate pathway and sitosterol is synthesized entirely via the mevalonate route. The labeling data of amino acids and sitosterol were used to reconstruct the labeling patterns of key metabolic intermediates (e.g., acetyl-CoA, pyruvate, phosphoenolpyruvate, erythrose 4-phosphate, and Rib 5-phosphate) that revealed **quant.** information about carbon flux in the intermediary metab. of developing maize kernels. Exogenous acetate served as an efficient precursor of sitosterol, as well as of amino acids of the aspartate and glutamate family; in comparison, metabolites formed in the plastidic compartments showed low acetate incorporation.

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82. **Chemical and spectroscopic study of the biodegradation of lignin in forest soils affected by nitrogen deposition**

ByDignac, Marie-France; Matzner, Egbert; Michel, Kerstin; Knicker, Heike; Kogel-Knabner, Ingrid

From *Abstracts of Papers*, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), GEOC-

024.Language:English, Database: CAPLUS

Lignin is generally the most recalcitrant component in **plant** litter, and its decompn. regulates that of the total org. matter (OM) in forest soils. Its biodegrdn. is controlled by the concn. of **N** available for the soil biomass, a parameter affected by **N** deposition caused by anthropogenic emissions. The chem. and structural features of forest soil OM were followed according to **N** content of soil. The OM was characterized in the humus layer and mineral soil of 15 spruce sites using specific analyses for lignin and polysaccharides, hydrolyzable-**Nquantification** and solid-state ¹³C and ¹⁵N **NMR (NMR)**. The effect of **N** content on lignin degrdn. was neg. in the mineral soil layer and pos. in the humus layer. Some differences in the quality of OM from the different sites were underlined with **NMR** spectroscopy.

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83. **Molecular spectroscopic investigations into microbial degradation of plants**

ByCody, George D.; Goodell, Barry; Jellisson, Jody; Filley, Timothy

From Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), GEOC-015.Language:English, Database: CAPLUS

Solid State **NMR (NMR)** spectroscopy (¹³C) and Carbon X-ray Absorption Near Edge Spectroscopy (C-XANES) are powerful anal. tools for investigations into the **quant.** chem. and phys. changes that occur in wood vascular tissue upon degrdn. by fungal micro-organisms. As a demonstration, we present the results of a study of samples degraded by the brown rot fungi, *P. placenta* and *G.* These organisms preferentially metabolize structural polysaccharides. Solid state ¹³C **NMR** spectroscopy provides **quantification** of the loss cellulose and hemicellulose that occurs with progressive degrdn. Detailed anal. of spectral intensity in the lignin regions reveals the systematic loss of the Me group from methoxy groups. The solid state **NMR** data suggest similar chem. operating in the case of both organisms, albeit with different apparent degrdn. rates. C-XANES and soft X-ray microscopy [utilizing contrast derived from variation in intensity of absorption assocd. with the lignin derived arom. carbon's 1s- π^* transition ($E=285$ eV)] point to strikingly different modes of attack. In addn. to fungal microorganisms we will discuss data derived from studies of other organisms and other types of wood.

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84. **Deuterium nuclear magnetic resonance spectroscopy and stable carbon isotope ratio analysis/mass spectrometry of certain monofloral honeys**

ByGiraudon, Sylvie; Danzart, Marc; Merle, Marc H.

From Journal of AOAC International (2000), 83(6), 1401-1409.Language:English, Database: CAPLUS

Quant. deuterium **NMR** spectroscopy (**NMR**) has been used in conjunction with stable carbon isotope ratioanal./mass spectrometry to refine the detection of sugars that have been added to monofloral honeys. The ¹³C content of sugars indicates the type of photosynthetic metab. of the **plant** that synthesized them; the deuterium content is more characteristic of secondary metab. and of environmental factors. Consequently, detn. of the ¹³C content of honeys and of proteins extd. from the honeys can be used to detect the addn. of C4 **plant** sugars (cane or corn), but it does not reveal the addn. of C3 **plant** sugars such as beet sugar. Deuterium **NMR** gives useful information for some monofloral honeys. **NMR** measurement is performed on ethanol obtained from fermn. of the honey and extd. by distn. The isotopic compn. of the ethanol indicates the nature of the sugars from which it was derived. Various types of monofloral honeys were studied, and the results obtained with com. available honeys demonstrate the usefulness of isotopic anal. and the need to compile a database of authentic honeys to validate or affirm certain results.

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85. **Quantitation of aliphatic suberin in *Quercus suber* L. cork by FTIR spectroscopy and solid-state ¹³C-NMR spectroscopy**

ByLopes, M. H.; Pascoal Neto, C.; Barros, A. S.; Rutledge, D.; Delgadillo, I.; Gil, A. M.

From Biopolymers (2000), 57(6), 344-351. Language: English, Database: CAPLUS, DOI: 10.1002/1097-0282(2000)57:6<344::AID-BIP40>3.0.CO;2-#

This work detd. that the percentage of suberin in cork may be found by solid-state ¹³C cross polarization/magic angle spinning (CP/MAS) **NMR** spectroscopy and by FTIR with photoacoustic detection (FTIR-PAS) spectroscopy. A linear relationship is found between the suberin content measured through CP/MAS spectral areas and that measured gravimetrically. Furthermore, application of a partial least squares (PLS1) regression model to the **NMR** and gravimetric data sets clearly correlates the two sets, enabling suberin **quantification** with 90% precision. Suberin **quantitation** by FTIR-PAS spectroscopy is also achieved by a PLS1 regression model, giving 90% accurate ests. of the percentage of suberin in cork. Therefore, ¹³C-CP/MAS **NMR** and FTIR-PAS proved to be useful and accurate noninvasive techniques to **quantify** suberin in cork, thus avoiding the traditional time consuming and destructive chem. methods.

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86. **Advances in determination of aluminum in environmental and biological materials by ²⁷Al nuclear magnetic resonance spectroscopy**

ByWang, Xian-Long; Zou, Gong-Wei; Bi, Shu-Ping

From Wujia Huaxue Xuebao (2000), 16(4), 548-560. Language: Chinese, Database: CAPLUS

A review, with 77 refs., is given. ²⁷Al **NMR** spectroscopy, as a rapid, direct and nondestructive anal. tool, was used to study the hydrolysis process of aluminum(III) in the presence and absence of other org. and inorg. ligands, to study the structure and reactivity of aluminum(III) complexes with environmentally and biol. important ligands, to **quant.** determinate different aluminum(III) species present in environmental and biol. samples and to monitor the transport process of aluminum in **plants**, animals, yeast and other organisms during the last twenty years. It can deal with not only the high aluminum content solns. but also the natural dil. (10⁻⁶ mol L⁻¹) aluminum(III) samples from the environment and biol. materials. ²⁷Al MASNMR can characterize and determinate aluminum in the solid samples. The advances of these applications were reviewed and a lot of ²⁷Al chem. shift data of species present in aq. soln. were collected.

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87. **Quantitative characterization of humic substances by solid-state Carbon-13 nuclear magnetic resonance**

ByMao, J-D.; Hu, W-G.; Schmidt-Rohr, K.; Davies, G.; Ghabbour, E. A.; Xing, B.

From Soil Science Society of America Journal (2000), 64(3), 873-884. Language: English, Database: CAPLUS, DOI: 10.2136/sssaj2000.643873x

The compns. of humic acids (HAs) from various Histosols in North America and Europe, of similarly treated **plant-extd.** materials (PEMs), of coal-extd. humic acids, and of International Humic Substances Society (IHSS) Florida peat were **quantified** by solid-state ¹³C **NMR**. In order to obtain **quant.** intensities, the peak areas in direct-polarization 13-kHz magic-angle spinning (DPMAS) ¹³C **NMR** spectra were cor. for incomplete relaxation by factors measured in cross-polarization spin-lattice relaxation time (CP/T1) expts. with total sideband suppression (TOSS). The elemental compns. (%C, %H, %O + N) of a peat sample, 8 HAs and 2 PEMs were estd. from the **NMR** results and compared with chem. analyses, as well as soln. **NMR** for two of the HAs. The results are in good agreement, which shows that DPMAS cor. by CP/T1-TOSS permits **quant.** characterization of HAs and PEMs. The compns. of the PEMs deviate significantly from those of the Histosol HAs. The compns. in terms of nine types of chem. groups were computed. The investigated HAs consist of more than 60% of arom. and CO carbons (including both carbonyl and carboxyl

groups). Previous cross-polarization magic-angle spinning (CPMAS) **NMR** expts. have significantly underestimated the ratio of sp²- to sp³-carbons; in particular, the true COO carbon fraction is a factor of two larger than estd. by CPMAS **NMR**. In spite of their wide range of geog. origins, the compns. of the Histosol HAs appear to be relatively uniform, suggesting that the search for a general model of Histosol HA structure is worthwhile. Eight models proposed in the literature do not reproduce the exptl. detd. compns., but a few models show promising partial agreement.

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88. Comparative NMR analysis of stable isotope labeling patterns. Biosynthesis of gallic acid

By Eisenreich, Wolfgang; Werner, Ingo; Bacher, Adelbert

Edited by Barbotin, Jean-Noel; Portais, Jean-Charles

From *NMR in Microbiology* (2000), 381-409. Language: English, Database: CAPLUS

The biosynthesis of gallic acid was studied in cultures of the fungus *Phycomyces blakesleeanus* and in leaves of the tree *Rhus typhina* by labeling expts. using [1-¹³C]glucose and a mixt. of [U-¹³C₆]glucose and unlabeled glucose (1:25, wt./wt.). A detailed **quant. NMR** anal. of gallic acid and amino acids isolated from the cells showed that the bulk amt. of gallic acid is formed directly via 5-dehydroshikimate and not via phenylalanine. The retro-biosynthetic approach used in this study is described in detail and compared with classical approaches of in vivo incorporation expts.

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89. The NMR Microscope: a Unique and Promising Tool for Plant Science

By Ishida, Nobuaki; Koizumi, Mika; Kano, Hiromi

From *Annals of Botany (London)* (2000), 86(2), 259-278. Language: English, Database: CAPLUS, DOI: 10.1006/anbo.2000.1181

A review with many refs. An outline is given of **NMR** microscopy and its application to **plant** science. An **NMR** microscope non-destructively detects free water in tissues and creates anatomical images of the tissues. Since the **quantity** and mobility of cell-assocd. water is closely related to the condition of the cells, ¹H-**NMR** images represent physiol. maps of the tissue. In addn., the technique locates sol. org. compds. accumulated in the tissues, such as sugars in vacuoles or fatty acids stored as oil droplets in vesicles. ²³Na-**NMR** imaging is suitable for studying the physiol. of salt-tolerant **plants**. Diffusion measurements provide information about the transport of substances and ions accompanied by water movement. The recently developed techniques of three-dimensional imaging, flow-encoded imaging and spectroscopic imaging open up new opportunities for **plant** biologists. The **NMR** microscope is thus a unique and promising tool for the study of living **plant** systems in relation to morphol., the true features of which are often lost during prepn. for more conventional tissue anal. (c) 2000 Annals of Botany Company.

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90. Quantification of muconic acid-type structures in high molecular weight material from bleach plant effluents

By Vilen, E. J.; McKague, A. B.; Reeve, D. W.

From *Holzforschung* (2000), 54(3), 273-278. Language: English, Database: CAPLUS, DOI: 10.1515/HF.2000.046

Effluent from ClO₂ bleaching of chem. pulps were characterized with respect to high and low mol. wt. material, COD, total org. C, elemental compn., and carboxylic acid and Me ester content. A method was developed to **quant.** est. muconic acid-type structures as moieties of the high mol. wt. material. This method is based on the use of **quant. ¹³C NMR** and pH-dependent cyclization of muconic acids in aq. soln. A total of 20-40% of carboxylic acids in the high mol. wt. material isolated from bleach **plant** effluents from 3 soft-wood kraft mills exhibited muconic acid-type behavior.

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91. Application of nuclear magnetic resonance in agriculture

ByGambhir, Prem N.; Nagarajan, Shantha

From PINSA-A: Proceedings of the Indian National Science Academy, Part A: Physical Sciences (1999), 65(6), 731-765.Language:English, Database: CAPLUS

A review, with 35 refs. In agricultural research, the major emphasis is given to anal. of large no. of samples for various chem. constituents and phys. properties. The method should be rapid and non-invasive esp. in germplasm evaluation and **plant** breeding programs. **NMR** technique which has the potential to meet both these demands has been extensively used in studies related to agricultural **plants** and their products. The principle of free induction decay (FID) of low field **NMR** is used for rapid and non-destructive detn. of oil and moisture in oil seeds. Both spin-spin and spin-lattice relaxation times (T1 & T2) are exploited to obtain degree of satn. of oil in oil seeds and dry rubber content in natural rubber latex. They are extensively used to study water status and their cellular compartmentation in **plant** tissues and to develop a screening technique for drought tolerance in wheat. The application of high resolu. **NMR** esp. with ³¹P and ¹³C **nuclei** are also quite substantial. The fatty acid compn. of oil in a single intact seed is obtained using ¹³C **NMR**. Phosphorus **NMR** is extensively used to elucidate the mechanism of phosphate uptake and compartmentation in roots, anoxia in developing seeds and adaptation of roots to osmotic stress. The application of proton **NMR** imaging in studying the in vivo changes in water status in stems is also explored. Thus the review covers in detail the work carried out by our group using **NMR** techniques in characterizing and **quantifyingplant** traits of agriculturally important crops.

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92. Supramolecular structure of cellulose II: Is there a memory-effect of the native cellulose structure?.

ByLennholm, Helena; Fransson, Johan; Larsson, Per Tomas

From Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 (2000), CELL-030.Language:English, Database: CAPLUS

Despite the fact that cellulose is historically one of the most studied org. compds. little is known about the supramol. arrangement of cellulose from different **plants** and organisms and the influence of the supramol. arrangement on the chem. and mech. properties of the cell wall. A unique method, based on CP/MAS ¹³C-**NMR** (Cross-Polarisation Magic Angle Spinning Carbon-13 **NMR**) spectroscopy in combination with spectral fitting, for **quantifying** cellulose in different forms of order has recently been developed and confirmed at STFI. Using the method, spectra of cellulose can be interpreted and based on the interpretation ests. for e.g. the crystallinity, lateral fibril dimensions and lateral fibril aggregate dimensions can be made. In the present work we have studied which factors det. the formation of cellulose II from native cellulose samples. We choose the starting cellulose materials to represent variations in the proportion of cellulose Ia and Ib, microfibril size and state of order. We used algal cellulose, bacterial cellulose, cotton linters and birch kraft pulp. Further, we varied the state of order of the starting materials by ball milling. The starting materials and ball-milled starting materials were all mercerised and regenerated, to enable formation of cellulose II. We recorded CP/MAS ¹³C-**NMR** spectra on all samples and evaluated the spectra with chemometrics. The results indicate that the native cellulose structure affects the formation of cellulose II, i.e. there is a memory-effect of the cellulose I-structure.

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93. Introduction of polyphosphate as a novel phosphate pool in the chloroplast of transgenic potato plants modifies carbohydrate partitioning

ByVan Voorthuysen, Tijmen; Regierer, Babette; Springer, Franziska; Dijkema, Cor; Vreugdenhil, Dick; Kossmann, Jens

From Journal of Biotechnology (2000), 77(1), 65-80.Language:English, Database: CAPLUS, DOI: 10.1016/S0168-1656(99)00208-4

Potato **plants** (*Solanum tuberosum* L., cv. Desiree) were transformed with the polyphosphate kinase gene from *Escherichia coli* fused to the leader sequence of the ferredoxin oxidoreductase gene (FNR) from *Spinacea oleracea* under the control of the leaf specific St-LS1 promoter to introduce a novel phosphate pool in the chloroplasts of green tissues. Transgenic **plants** (cpPPK) in tissue culture developed necrotic lesions in older leaves and showed earlier leaf senescence while greenhouse **plants** showed no noticeable phenotype. Leaves of cpPPK **plants** contained less starch but higher concns. of sol. sugars. The presence of polyphosphate in cpPPK leaves was demonstrated by toluidine blue staining and unambiguously verified and **quantified** by in vitro ³¹P-NMR of exts. Polyphosphate accumulated during leaf development from 0.06 in juvenile leaves to 0.83 mg P g⁻¹ DW in old leaves and had an av. chain length of 18 residues in mature leaves. In situ ³¹P-NMR on small leaf pieces perfused with well-oxygenated medium showed only 0.036 mg P g⁻¹ DW polyphosphate that was, however, greatly increased upon treatment with 50 mM ammonium sulfate at pH 7.3. This phenomenon along with a yield of 0.47 mg P g⁻¹ DW polyphosphate from an ext. of the same leaf material suggests that 93% of the polyphosphate pool is immobile. This conclusion is substantiated by the observation that no differences in polyphosphate pool sizes could be discerned between darkened and illuminated leaves, leaves treated with methylviologen or anaerobic and control leaves, treatments causing a change in the pool of ATP available for polyPi synthesis. Results are discussed in the context of the chelating properties of polyphosphates for cations and its consequences for the partitioning of photoassimilate between starch and sol. sugars.

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94. Nondestructive NMR determination of oil composition in transformed canola seeds

ByHutton, William C.; Garbow, Joel R.; Hayes, Thomas R.

From Lipids (1999), 34(12), 1339-1346.Language:English, Database: CAPLUS, DOI: 10.1007/s11745-999-0487-0

Magic-angle spinning (MAS) ¹³C NMR spectroscopy is a convenient method for nondestructive, **quant.** characterization of seed oil compn. The authors describe results for intact hybrid and transformed canola seeds. The MAS ¹³C NMR technique complements and agrees with gas chromatog. results. The spectral resolu. approaches that of neat, liq. oils. MAS ¹³C NMR data allow **quant.** anal. of major oil components, including sats. and oleic, linoleic, and linolenic acyl chains. ¹³C NMR directly and **quant.** elucidates, triglyceride regiochem. and acyl chain cis-trans isomers that cannot be quickly detected by other methods. MAS ¹³C NMR can serve as the primary method for development of near-IR seed oil calibrations. These **NMR** methods are nondestructive and attractive for **plant**-breeding programs or other studies (e.g., functional genomics) where loss of seed viability is inconvenient.

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95. Incorporation of 1-[1-¹³C]Deoxy-D-xylulose in Chamomile Sesquiterpenes

ByAdam, Klaus-Peter; Thiel, Rolf; Zapp, Josef

From Archives of Biochemistry and Biophysics (1999), 369(1), 127-132.Language:English, Database: CAPLUS

Incorporation of synthetically prepd. 1-[1-¹³C]deoxy-D-xylulose into chamomile sesquiterpenes has been achieved by injecting an aq. soln. into the antheridia of the **plant**. The anal. of labeling patterns and abs. ¹³C abundances of the isolated sesquiterpenes bisabololoxide A, bisabololoxide B, and chamazulene using **quant.** ¹³C NMR spectroscopy showed that 1-[1-¹³C]deoxy-D-xylulose was efficiently incorporated in all three isoprene building blocks of the sesquiterpenes. A significantly lower ¹³C abundance of the labeled carbon atom in the biogenetically terminal isoprene unit confirms the mixed biosynthesis of this unit, involving both the mevalonic acid pathway and the methylerythritol phosphate pathway. (c) 1999 Academic

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96. **Quantitative Assessment of Metabolic Flux by ¹³C NMR Analysis. Biosynthesis of Anthraquinones in *Rubia tinctorum***

ByEichinger, Dietmar; Bacher, Adelbert; Zenk, Meinhard H.; Eisenreich, Wolfgang

From Journal of the American Chemical Society (1999), 121(33), 7469-7475.Language:English, Database: CAPLUS, DOI: 10.1021/ja990622o

Cell cultures of the **plant***Rubia tinctorum* were grown with supplements of [¹⁻¹³C]- or [U-¹³C₆]glucose. Amino acids were obtained by hydrolysis of biomass, and their ¹³C labeling patterns were used to reconstruct the labeling patterns of acetyl CoA, pyruvate, phosphoenol pyruvate, erythrose 4-phosphate, and α-ketoglutarate by retrobiosynthetic anal. These patterns were used to construct hypothetical labeling patterns for the anthraquinone, lucidin primveroside, via different hypothetical pathways. The predicted labeling pattern based on the precursors **o**-succinylbenzoate and dimethylallyl pyrophosphate derived via the deoxyxylulose pathway was in excellent agreement with the obsd. labeling pattern of the anthraquinone deriv. The data show that the retrobiosynthetic concept can be used to **quant.** est. the flux of metabolites via different metabolic pathways.

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97. **Quantification and identification of forms on silicon in rice plant using solid-state nuclear magnetic resonance spectroscopy**

ByHori, Kazuyuki; Murakami, Shou

From Nippon Dojo Hiriyogaku Zasshi (1999), 70(3), 271-276.Language:Japanese, Database: CAPLUS

We attempted to research the **quantification** and identification of forms on silicon in rice by using solid-state **NMR** spectroscopy and the nitric acid/perchloric acid digestion method. The silicon in the rice **plant** mainly existed as a regular tetrahedron structure and each of the four coordination sites of silicon were occupied by four (**O**-Si) units (Q₄), showing that the silicon signal shifted around -110 ppm for each ²⁹Si-**NMR** spectra of rice sample. A good relationship was found between digestion and ²⁹Si-**NMR** anal., indicating the capability of ²⁹Si-**NMR** anal. for the **quant.** detn. of silicon.

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98. **Analysis of metabolic pathways via quantitative prediction of isotope labeling patterns: a retrobiosynthetic ¹³C NMR study on the monoterpene loganin**

ByEichinger, Dietmar; Bacher, Adelbert; Zenk, Meinhard H.; Eisenreich, Wolfgang

From Phytochemistry (1999), 51(2), 223-236.Language:English, Database: CAPLUS, DOI: 10.1016/S0031-9422(98)00733-X

The monoterpene loganin serves as a precursor in the biosynthetic pathways of numerous indole alkaloids. The authors present evidence that the biosynthesis of loganin in *Rauwolfia serpentina* cells proceeds mainly via the deoxyxylulose pathway and not by the mevalonate pathway. This conclusion is based on expts. using a **R.** *serpentina* cell culture supplied with ¹³C-labeled samples of glucose, ribose/ribulose, pyruvate or glycerol. Loganin was isolated from biomass, and the hydrolysis of cellular protein afforded amino acids. The isolated metabolites were analyzed by **NMR** spectroscopy. The ¹³C-labeling patterns of isolated amino acids were then used to reconstruct the labeling patterns of phosphoenol pyruvate, pyruvate and acetyl CoA. These labeling patterns were subsequently used to predict labeling patterns for dimethylallyl pyrophosphate and isopentenyl pyrophosphate via the mevalonate and deoxyxylulose pathway, resp. The obsd. labeling patterns of the terpenoid moieties in loganin were in excellent agreement with the

deoxyxylulose prediction. The minor incorporation of mevalonate into loganin obsd. in earlier studies can be attributed to metabolite exchange between the two terpenoid pathways. The possibility of crosstalk between the two pathways in **plants** and **plant** cell cultures stresses the need for a **quant.** anal. of general carbon metab. in order to det. the partitioning between the mevalonate and deoxyxylulose pathway. The present study shows that a wide variety of general metabolic precursors can fulfill this task in conjunction with the retrobiosynthetic concept.

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99. **Recombinant Production of the p10CKS1At Protein from Arabidopsis thaliana and 13C and 15N Double-Isotopic Enrichment for NMR Studies**

ByLandrieu, Isabelle; Casteels, Peter; Odaert, Benoit; De Veylder, Lieven; Portetelle, Daniel; Lippens, Guy; Van Montagu, Marc; Inze, Dirk
From Protein Expression and Purification (1999), 16(1), 144-151.Language:English, Database: CAPLUS

The CKS1At gene product, p10CKS1At from *Arabidopsis thaliana*, is a member of the cyclin-dependent kinase subunit (CKS) family of small proteins. These proteins bind the cyclin-dependent kinase (CDK)/cyclin complexes and play an essential, but still not precisely known role in cell cycle progression. To solve the structure of p10CKS1At, a protocol was needed to produce the **quantity** of protein large enough for **NMR (NMR)** spectroscopy. The first attempt to express CKS1At in *Escherichia coli* under the control of the T7 promoter was not successful. *E. coli* BL21(DE3) cotransformed with the CKS1At gene and the *E. coli* argU gene that encoded the arginine acceptor tRNA^{UCU} produced a sufficient amt. of p10CKS1At to start the structural study by **NMR**. Replacement of four rare codons in the CKS1At gene sequence, including a tandem arginine, by highly used codons in *E. coli*, restored also a high expression of the recombinant protein. Double-isotopic enrichment by 13C and 15N is reported that will facilitate the **NMR** study. Isotopically labeled p10CKS1At was purified to yield as much as 55 mg from 1 L of minimal media by a two-step chromatog. procedure. Preliminary results of **NMR** spectroscopy demonstrate that a full structural anal. using triple-**resonance** spectra is feasible for the labeled p10CKS1At protein. (c) 1999 Academic Press.

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100. **Carbon metabolism in the subantarctic Kerguelen cabbage *Pringlea antiscorbutica*R. Br.: environmental controls over carbohydrates and proline contents and relation to phenology**

ByAubert, S.; Assard, N.; Boutin, J.-P.; Frenot, Y.; Dorne, A.-J.

From Plant, Cell and Environment (1999), 22(3), 243-254.Language:English, Database: CAPLUS, DOI: 10.1046/j.1365-3040.1999.00417.x

The subantarctic Brassicaceae *P. antiscorbutica* (Kerguelen cabbage) was used as a model to study the physiol. adaptations of higher **plants** to the subantarctic environment. 13C-**NMR** permitted, in combination with biochem. methods, the identification and **quantification** of the major solutes in leaves, stem and roots. As characterized in many Brassicaceae, proline was a major solute in all organs of the **plants**, and its accumulation was mainly controlled by salt stress rather than temp. Glucose was the major sol. sugar in the leaves, while sucrose and starch accumulated in stems and roots. **Over** 1 yr, we found strong correlations between (i) glucose content in leaves and irradiance, and (ii) starch content in nonphotosynthetic organs and air temp. The pattern of carbohydrate accumulation indirectly indicated that photosynthesis was sustained throughout the year, even during cold days when the temp. remained near 0°. This is consistent with the direct gas exchange measurements, showing that photosynthetic capacity is mainly influenced by irradiance and weakly by temp. These characteristics demonstrated that the growth and development cycle occurs without a period of dormancy.

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101. **Consistency of NMR and mass spectrometry determinations of natural-abundance site-**

specific carbon isotope ratios. The case of glycerol

ByZhang, Ben-Li; Trierweiler, Michel; Jouitteau, Catherine; Martin, Gerard J.

From Analytical Chemistry (1999), 71(13), 2301-2306. Language: English, Database: CAPLUS, DOI: 10.1021/AC9812375

Quant. detns. of natural-abundance carbon isotope ratios by **NMR** (SNIF-**NMR**) were optimized by appropriate selection of the exptl. conditions and by signal anal. based on a dedicated algorithm. To check the consistency of the isotopic values obtained by **NMR** and mass spectrometry (IRMS) the same glycerol samples were studied by both techniques. To have access to site-specific isotope ratios by IRMS, the products were degraded and transformed into two derivs., one of which contains carbons 1 and 3 and the other carbon 2 of glycerol. The sensitivity of the isotopic parameters detd. by IRMS to fractionation effects possibly occurring in the chem. transformations was studied, and the repeatability and reproducibility of both anal. chains were estd. The good agreement obsd. between the two series of isotopic results supports the reliability of the two different approaches. SNIF-**NMR** is therefore a very attractive tool for routine detn., in a single nondestructive expt., of the carbon isotope distribution in glycerol, and the method can be applied to other compds. Using this method, the isotopic distributions were compared for glycerol samples, obtained from **plant** or animal oils, extd. from fermented media, or prepd. by chem. synthesis. Typical behaviors were characterized.

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102. NMR in flavor chemistry

ByMartin, G. J.

From Book of Abstracts, 216th ACS National Meeting, Boston, August 23-27 (1998), AGFD-049. Language: English, Database: CAPLUS

During the last three decades flavor chem. has greatly benefited from the spectacular tech. and conceptual developments of **NMR** spectroscopy. The structure and stereochem. of most of the aroma components have been unambiguously characterized by mono- and multi-dimensional **NMR**, and sub-milligram **quantities** can now be investigated. The knowledge of biosynthetic pathways and the identification of flavor precursors have been significantly improved by a no. of in-vitro and even in-vivo studies involving isotopic labeling. Recently, chemometrics techniques allied to high field ¹H- and ¹³C-spectroscopies have provided new tools for the study of complex mixts. of arom. mols. Finally, the field of product authentication was considerably extended by the **NMR** study of Site-specific Natural Isotope Fractionation (SNIF-**NMR**). Thus, the hydrogen isotopic fingerprint detd. by natural abundance ²H-**NMR** is a powerful source of information on the natural or synthetic origin of the products, on the botanical species of the **plant** precursor and on the metabolic pathway.

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103. Biosynthesis of the isoprene units of chamomile sesquiterpenes

ByAdam, Klaus-Peter; Zapp, Josef

From Phytochemistry (1998), 48(6), 953-959. Language: English, Database: CAPLUS, DOI: 10.1016/S0031-9422(97)00992-8

Chamomile sesquiterpenes were labeled with ¹³C by injection of an [¹⁻¹³C]glucose soln. into the antheridia of the **plant**. The sesquiterpenes bisabololoxide A and chamazulene were isolated from the hydrodistillate of the labeled flowers. Anal. of the labeling patterns and abs. ¹³C abundances using **quant. 13C NMR** spectroscopy showed that two of the isoprene building blocks were predominantly formed via the new triose/pyruvate pathway, whereas the third unit was of mixed origin, being derived from both the mevalonic acid pathway and the triose/pyruvate pathway.

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104. **Involvement of the mevalonic acid pathway and the glyceraldehyde-pyruvate pathway in terpenoid biosynthesis of the liverworts *Ricciocarpos natans* and *Conocephalum conicum***

By Adam, Klaus-Peter; Thiel, Rolf; Zapp, Josef; Becker, Hans

From Archives of Biochemistry and Biophysics (1998), 354(1), 181-187. Language: English, Database: CAPLUS, DOI: 10.1006/abbi.1998.0666

The incorporation of ¹³C-labeled glucose into borneol, bornyl acetate, the sesquiterpenes cubebanol and ricciocarpin A, phytol, and stigmaterol has been studied in axenic cultures of the liverworts *Ricciocarpos natans* and *Conocephalum conicum*. **Quant.** ¹³C NMR spectroscopic anal. of the resulting labeling patterns showed that the isoprene building blocks of the sesquiterpenes and stigmaterol are built up via the mevalonic acid pathway, whereas the isoprene units of the monoterpenes and the diterpene phytol are exclusively derived from the glyceraldehyde-pyruvate pathway. These results indicate the involvement of both isopentenyl diphosphate biosynthetic pathways in different cellular compartments. (c) 1998 Academic Press.

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105. **Chemical variability of *Lavandula stoechas* L. ssp. *stoechas* from Corsica**

By Baldovini, N.; Muselli, A.; Ristorcelli, D.; Tomi, F.; Casanova, J.

From Rivista Italiana EPPOS (1998), (Spec. Num.), 773-780. Language: French, Database: CAPLUS

The essential oil obtained by hydrodistn. of *Lavandula stoechas* L. ssp. *stoechas*, a wild **plant** from the Mediterranean area, is known for its pharmaceutic properties. Sixty-three samples of the corsican essential oil were studied by a method developed in the authors lab. and based on ¹³C NMR for the identification of the components and CPG-IK for **quantification**. This method is well-suited for chem. polymorphism studies and can also be used for the detn. of the enantiomeric compn. of some compds. Camphor and fenchone are the two major products but the fenchone/camphor ratio ranges greatly and seems to be correlated with geog. criteria. All the samples in which fenchone is the main product were harvested at the northern part of the island; while the camphor-rich ones come from the south.

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106. **Retrobiosynthetic NMR studies with ¹³C-labeled glucose. Formation of gallic acid in plants and fungi**

By Werner, Ingo; Bacher, Adelbert; Eisenreich, Wolfgang

From Journal of Biological Chemistry (1997), 272(41), 25474-25482. Language: English, Database: CAPLUS, DOI: 10.1074/jbc.272.41.25474

The biosynthesis of gallic acid was studied in cultures of the fungus *Phycomyces blakesleeanus* and in leaves of the tree *Rhus typhina*. Fungal cultures were grown with [1-¹³C]glucose or with a mixt. of unlabeled glucose and [U-¹³C₆]glucose. Young leaves of *R. typhina* were kept in an incubation chamber and were supplied with a soln. contg. a mixt. of unlabeled glucose and [U-¹³C₆]glucose via the leaf stem. Isotope distributions in isolated gallic acid and arom. amino acids were analyzed by one-dimensional ¹H and ¹³C NMR spectroscopy. A **quant.** anal. of the complex isotopomer compn. of metabolites was obtained by deconvolution of the ¹³C¹³C coupling multiplets using numerical simulation methods. This approach required the accurate anal. of heavy isotope chem. shift effects in a variety of different isotopomers and the anal. of long range ¹³C¹³C coupling consts. The resulting isotopomer patterns were interpreted using a retrobiosynthetic approach based on a comparison between the isotopomer patterns of gallic acid and tyrosine. The data show that both in the fungus and in the **plant** all carbon atoms of gallic acid are biosynthetically equiv. to carbon atoms of shikimate. Notably, the carboxylic group of gallic acid is derived from the carboxylic group of an early intermediate of the shikimate pathway and not from the side chain of phenylalanine or tyrosine. It follows that the committed precursor of gallic acid is an intermediate of the shikimate pathway prior to prephenate or arogenate, most probably 5-dehydroshikimate. A formation of gallic acid via phenylalanine, the lignin precursor, caffeic acid, or 3,4,5-trihydroxycinnamic acid can be ruled

out as major pathways in the fungus and in young leaves of *R. typhina*. The incorporation of uniformly ^{13}C -labeled glucose followed by **quant. NMR** anal. of isotopomer patterns is suggested as a general method for biosynthetic studies. As shown by the **plant** expt., this approach is also applicable to systems with low incorporation rates.

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107. **Biosynthesis of nornicotine in root cultures of *Nicotiana alata* does not involve oxidation at C-5' of nicotine**

ByBotte, Michele; Mabon, Françoise; Le Mouillour, Marc; Robins, Richard J.

From *Phytochemistry* (1997), 46(1), 117-122. Language: English, Database: CAPLUS, DOI: 10.1016/S0031-9422(97)00271-9

The mechanism of the demethylation of nicotine [3-(1-methyl-2-pyrrolidiny)pyridine] to nornicotine [3-(2-pyrrolidiny)pyridine] has been studied in root cultures of *Nicotiana alata* using nicotine selectively labeled with ^2H . Administered [4',4',5',5'- $^2\text{H}_4$]nicotine was effectively incorporated into [4',4',5',5'- $^2\text{H}_4$]nornicotine without a significant alteration in the molar fractions of ^2H at the four substituted positions, as detd. by **quant. ^2H NMR**. Incorporation into cotinine- d_2 and myosmine- d_4 was also obsd. In contrast, no incorporation into either nornicotine or nicotine was found when [4',4'- $^2\text{H}_2$]cotinine was administered. Taken together, these findings provide direct evidence that neither of the protons on C-5' of nicotine takes part in the demethylation reaction.

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108. **Variations in chemical composition and structure of macromolecular components in different morphological regions and maturity stages of *Arundo donax***

ByPascoal Neto, C.; Seca, A.; Nunes, A.M.; Coimbra, M.A.; Domingues, F.; Evtuguin, D.; Silvestre, A.; Cavaleiro, J.A.S.

From *Industrial Crops and Products* (1997), 6(1), 51-58. Language: English, Database: CAPLUS

Arundo donax plants were manually sepd. into fractions of different morphol. regions (internodes, nodes and foliage) at different stages of maturity and submitted to chem. compn. studies. General chem. compn. was detd. by established methods. The polysaccharides were fractionated by successive extns. of holocellulose with aq. KOH solns. The sugar compn. was detd. by hydrolysis of polysaccharides followed by GC anal. of neutral sugars as alditol acetates and spectrophotometric detn. of uronic acids. In situ lignins, milled wood lignins (MWL) and dioxane lignin were characterized by permanganate oxidn. followed by GC and GC-MS anal. of the methylated oxidn. products and by **quant. ^{13}C NMR** spectroscopy. The results of general chem. anal. evidenced the different relative abundance of holocellulose, lignin, proteins, extractives and ashes in internodes, nodes and foliage, at different stages of maturity. In internodes, nodes and foliage about 70-80% of hemicelluloses (21-30% o.d. material) were easily extd. with 5% KOH aq. solns. The anal. of hemicelluloses indicated that they are constituted mainly by arabinoglucuronoxylans with a xylose:arabinose:uronic acid ratio of 91-93:5-7:2 for internodes. The high content of xylose in *Arundo donax* stem (24-27% o.d. material) and the easy extn. of hemicelluloses opens new perspectives for the use of this reed as a source of pentosans. The results obtained by the permanganate oxidn. method indicated that *Arundo donax* lignins are essentially H-G-type with approx. H:G:S proportions of (32-36):(59-61):(5-8) in internodes. The H units are constituted mainly by esterified p-coumaric acid. These results were confirmed by **quant. ^{13}C NMR** spectroscopy of isolated dioxane lignin. The **quantity** of condensed structures in in situ lignin decreases from the older to the younger parts of the stems and is much higher in nodes than internodes.

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109. **Quantitative evaluation of NMR and MRI methods to measure sucrose concentrations in plants**

ByTse, T. Y.; Spanswick, R. M.; Jelinski, L. W.

From Protoplasma (1996), 194(1-2), 54-62. Language: English, Database: CAPLUS, DOI: 10.1007/BF01273167

Developing pea (*Pisum sativum* L.) seeds were chosen to evaluate the performance of various **NMR** and **magnetic resonance** imaging (MRI) methods of detecting sucrose in **plants**. The methods included chem. shift selective imaging (CHESS), heteronuclear correlation via ¹³C-¹H coupling (HMQC), and homonuclear correlation via ¹H-¹H coupling (DQF). The same expts. were also performed on sucrose phantom samples to evaluate the methods in the absence of the line broadening obsd. in **plant** systems. Using the spin echo technique for multi-slice imaging, we could discern the detailed internal structure of the intact seed with a resolu. of tens of microns. The proton spin-lattice relaxation time and linewidth as a function of the age of the seed were measured to optimize the efficiency of the **NMR** and MR expts. The age-dependent changes in these **NMR** parameters are consistent with the accumulation of insol. starch as age increases. Both the **NMR** and MRI results are in accord with the results of chem. anal., which reveal that the sucrose concn. is higher in the embryo than in the seed coat, and glucose is at low concn. throughout the seed. Of the three methods for proton observation, the enhanced version of the CHESS approach (CD-CHESS) provides the best combination of sucrose detection and water suppression. Direct observation of ¹³C is preferable to indirect detection using HMQC because of water signal bleed-through in samples with large (>200 Hz) linewidths.

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110. **Quantitative method for the survey of starch phosphate derivatives and starch phospholipids by ³¹P nuclear magnetic resonance spectroscopy**

ByKasemsuwan, Tunyawat; Jane, Jay-Lin

From Cereal Chemistry (1996), 73(6), 702-707. Language: English, Database: CAPLUS

Phosphorus of different chem. structures (e.g., phospholipids, starch phosphate monoester, and inorg. phosphate) are found in starch. In contrast to the colorimetric chem. method (Smith and Caruso 1964), which dets. total phosphorus content in starch without differentiating phosphate monoester from phospholipids, ³¹P **NMR** spectroscopy dets. phosphorus chem. structures and their individual contents. The relaxation times (T₁) of starch phosphate monoesters, phospholipids, inorg. phosphate, and phosphate derivs. in NAD (internal ref. std.) ranged from 1.0 to 2.1 s. To ensure full relaxation between pulses for **quant.** results, a relaxation delay of 11 s was programmed between data acquisitions. DMSO soln. (45%, vol./vol.) was used to improve α-limited dextrin soly. ³¹P **NMR** spectroscopy of this soln. provided **quant.** results. ³¹P **NMR** results showed that potato starch contained mainly phosphate monoester (0.086%), wheat starch contained mostly phospholipids (0.058%), mung bean starch contained mainly phosphate monoester (0.083%) and phospholipids (0.0006%), tapioca starch contained mainly phosphate monoester (0.0065%), high-amylose (50% amylose) maize starch contained mainly phospholipids (0.015%) and phosphate monoester (0.0049%), and waxy maize starch contained only a trace of phosphate monoester. The total phosphorus contents in starches obtained by ³¹P **NMR** spectroscopy agreed with those obtained from the colorimetric chem. method. Acid hydrolysis of starch and high-temp. operation were attempted to improve the α-limited dextrin soly., but the amylose-phospholipid complexes remained insol. in the aq. soln., and the structures of phosphate derivs. and phospholipids were altered.

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111. **Detection of added beet sugar in concentrated and single strength fruit juices by deuterium nuclear magnetic resonance (SNIF-NMR1 method): collaborative study**

ByMartin, Gilles G.; Wood, Roger; Martin, Gerard J.

From Journal of AOAC International (1996), 79(4), 917-928. Language: English, Database: CAPLUS

A collaborative study of the site-specific natural isotope fractionation-**NMR** (SNIF-**NMR**) method for detecting added beet sugar in fruit juices is reported. This method is complementary to the stable carbon isotope ratio anal. (SCIRA) (AOAC Official Methods 981.09 and 982.21), which can detect sugars derived from **plants** exhibiting C₄ metab. (corn and sugarcane). It is based on the fact that the deuterium content at specific positions of the sugar mols. is higher in fruit sugars than in beet sugar. The fruit juices are fermented, and the alc. is distd. with a **quant.** yield and analyzed with a highfield **NMR** spectrometer fitted with a deuterium probe and fluorine lock. The proportion of ethanol mols. monodeuterated on the Me site is recorded. This parameter (D/H)_i is lowered when beet sugar is added to a fruit juice or conc. The precision of that method for measuring (D/H)_i was obsd. to be similar to that of other isotope ratio methods: sr values ranged from 0.19 to 0.25 ppm and sR values varied between 0.21 and 0.37 ppm. An excellent correlation was obsd. between the percentage of added beet sugar and the (D/H)_i isotope ratio measured in this collaborative study. Consequently, all samples in which beet sugar was added were found to have a (D/H)_i isotope ratio significantly below the normal value for authentic juice or conc. of that fruit. The SNIF-**NMR** method for detection of added beet sugar in fruit juices has been adopted by AOAC INTERNATIONAL.

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112. **Metabolism of nitrate and ammonium in seedlings of Norway spruce (*Picea abies*) measured by in vivo ¹⁴N and ¹⁵N NMR spectroscopy**

By Aarnes, Halvor; Eriksen, Aud B.; Southon, Timothy E.

From Physiologia Plantarum (1995), 94(3), 384-90. Language: English, Database: CAPLUS

In vivo ¹⁵N and ¹⁴N **NMR** spectroscopy was used to investigate the assimilation of nitrate and ammonium in seedlings of Norway spruce (*Picea abies*). The main objective was to study accumulation of free NH₄⁺ and examine to what extent the nitrogen source affects the compn. of the free amino acid pools in roots, stems, and needles. NH₄⁺ concns. in **plants** growing in the presence of 0.5-50 mM ammonium were **quantified** using ¹⁴N **NMR**. The NH₄⁺ values in tissues ranged from 6 to 46 μmol (g fresh wt.)⁻¹, with highest concns. in roots and needles. The tissue NH₄⁺ peaked at 5.0 mM NH₄⁺ in the medium, and failed to increase when NH₄⁺ in the medium was increased to 50 mM, indicating metabolic control of the concn. of this cation in tissues. The ¹⁴N **NMR** spectra were used to est. pH of the NH₄⁺ storage pools. Based on the pH sensitivity of the quintet of ¹⁴NH₄⁺ **resonance**, we suggest that the pH of the ammonium storage compartments in the roots and stems should be 3.7-3.8, and in needles 3.4-3.5, representing extremely low pH values of the tissue. ¹⁵N from nitrate or ammonium was first incorporated into the amide group of glutamine and then into α-amino groups, confirming that the glutamine synthetase/glutamate synthase cycle is the major route of nitrogen assimilation into amino acids and thus plays a role in lowering the levels of NH₄⁺ in the cytoplasm. NH₄⁺ can also be assimilated in roots in **plants** growing in darkness. The main ¹⁵N-labeled amino acids were glutamine, arginine and alanine. Almost no ¹⁵N signals from needles were obsd. Double labeling (δ¹⁵N + ω,ω¹⁵N) of arginine is consistent with the operation of the ornithine cycle, and enrichment indicates that this cycle is a major sink of newly assimilated nitrogen. Nitrogen assimilation in roots in the presence of added methionine sulfoximine and glutamate indicated the catabolic action of glutamate dehydrogenase. The ¹⁵N **NMR** spectra of **plants** grown on ¹⁵N-urea showed a marked increase in the labeling of ammonium and glutamine, indicating high urease activity. Amino acids were also **quantified** using high pressure liq. chromatog. Arginine was found to be an important transport form of nitrogen in the stem.

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113. **Quantitative ²⁷Al NMR spectroscopic studies of Al(III) complexes with organic acid ligands and their comparison with GEOCHEM predicted values**

By Kerven, G. L.; Larsen, P. L.; Bell, L. C.; Edwards, D. G.

From Plant and Soil (1995), 171(1), 35-9. Language: English, Database: CAPLUS, DOI: 10.1007/BF00009561

The toxic inorg. monomeric forms of aluminum (Al) that limit **plant** growth have been shown to be effectively detoxified by complexation with org. acid ligands released by breakdown of added org. materials. The binding capacity of these acids is dependent on the degree of dissociation of their carboxyl groups and their ability to form bonds with Al. ²⁷Al **NMR** spectroscopy provides a non-invasive technique to study the bonding of Al with potential ligands without disturbing the equilibrium of the system. In single ligand systems containing oxalic acid, three ²⁷Al **resonance** peaks were observed at 6.4, 11.4, and 16.0 ppm downfield from the Al³⁺ reference peak at 0 ppm. These were assigned to AlOx, AlOx₂ and AlOx₃ complexes, respectively, and were observable at pH values down to 3.5. In the presence of the citrate ligand, two ²⁷Al **resonance** peaks at 6.1 and 11.3 ppm, assigned respectively to the Alcit and Alcit₂ complexes, were observed at pH 3.4. At pH 4.3 and an Al: citrate molar ratio of 1:2, a 6.1 ppm peak was not visible, and the second peak further downfield was split into two unresolved peaks at 10.8 and 12.4 ppm indicating the presence of two forms of the Alcit₂ complex. Distribution of Al between the various species, based on integration of the **resonance** peaks and equilibrium calculations carried out using GEOCHEM, is discussed in light of the stability constants present in the database of GEOCHEM version (v.) 1.23 and GEOCHEM-PC v. 2.0. Large discrepancies between the computed values and the **NMR** measured values indicate the need to incorporate more recent literature values in the database for realistic equilibrium calculations in systems containing organic acid ligands. The potential of using **quantitative** ²⁷Al **NMR** measurements to calculate stability constants is discussed.

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114. **Fatty acid distribution by carbon-13 NMR spectroscopy**

By Diehl, B. W. K.; Ockels, W.

From Fett Wissenschaft Technologie (1995), 97(3), 115-18. Language: German, Database: CAPLUS

The possibilities of ¹³C **NMR** spectrometry to get qualitative and **quantitative** values of total and individual fatty acid distribution related to the position at the glycerol backbone of triglycerides and phospholipids without derivatization or use of standards are demonstrated. Signals are assigned for triglycerides from different sources like **plants**, single cells, and fish. The carbonyl signals in the region between $\delta = 171-173$ ppm are well separated for fatty acids of the Δ^4 to Δ^9 type and even for the saturated type. Using the methyl signals, distinction of omega-3 and omega-8 fatty acids is possible. Additionally, the carbonyl signals for fatty acids in sn-1/3 and sn-2 are separated. The distribution of arachidonic and docosahexaenoic acid in egg yolk lecithin is also demonstrated with ¹³C **NMR** spectrometry.

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115. **Carbon-13 CP/MAS solid-state NMR and FT-IR spectroscopy of wood cell wall biodegradation**

By Gilardi, Gianfranco; Abis, Luigi; Cass, Anthony E. G.

From Enzyme and Microbial Technology (1995), 17(3), 268-75. Language: English, Database: CAPLUS, DOI: 10.1016/0141-0229(94)00019-N

The study of the degradation carried out by microorganisms on **plant** cell walls poses several problems in the analysis of the degraded solid materials. In this article this analytical problem has been studied by solid-state, high-resolution, carbon-13 cross-polarization/magic angle spinning **NMR** (CP/MAS **NMR**) and Fourier-transformed IR (FT-IR) spectroscopy. These two nondestructive techniques proved to be able to give insights into the modifications at a molecular level that the cell wall components undergo during attack by Basidiomycetes fungi. Spruce (*Pinus sylvestris*) and beech wood samples (*Fagus sylvatica*) were exposed for 6 weeks to the activity of brown-rot (*Coniophora puteana*) and white-rot (*Coriolus versicolor*) fungi. Brown-rot fungi appeared preferentially to degrade the polysaccharides, leaving a modified lignin network, whereas white-rot fungi were able to degrade extensively both the polysaccharides and the lignin. A **quantitative** approach based on integration of CP/MAS **NMR** spectra showed that spruce lignin was degraded to 77% of its weight by brown-rot,

and to 39% by white-rot fungi.

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116. **Determination of phenolic structures in flax fiber by solid-state ¹³C NMR**

ByLove, G. D.; Snape, C. E.; Jarvis, M. C.; Morrison, I. M.

From *Phytochemistry* (1994), 35(2), 489-91. Language: English, Database: CAPLUS

The content of bound phenolic substances in flax fibers was detd. by ¹³C CP-MAS solid-state **NMR** spectroscopy, a novel method that has not previously been applied to **plant** materials of very low lignin content. Van Soest (modified Klason) lignin and acetyl bromide lignin were also detd. for comparison. The ¹³C **NMR** spectra were obtained at low field (25 MHz) under conditions that had been shown, by comparison with single-pulse excitation, to give **quant. responses** from the arom. carbon atoms of wood lignin. The Van Soest lignin content was 3.2% and the acetyl bromide lignin content was 2.4%. The solid-state ¹³C **NMR** spectra showed that these values were considerably overestimated and that the **quantity** of arom. carbon present corresponded to a lignin content of 0.9%. However, the arom. material present was not lignin but appeared to be predominantly an anthocyanin of the cyanidin type. These results illustrate the deficiencies of the accepted methods of detg. lignin at low levels, and the potential of solid-state ¹³C **NMR** for this purpose.

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117. **Quantitative aspects of the ³¹P-NMR detection of manganese in plant tissues**

ByQuiquampoix, H.; Bacic, G.; Loughman, B. C.; Ratcliffe, R. G.

From *Journal of Experimental Botany* (1993), 44(269), 1809-18. Language: English, Database: CAPLUS

The uptake of manganese by maize roots was monitored *in vivo* by ³¹P **NMR (NMR)** spectroscopy and a **quant. anal.** was developed on the basis of the line broadening of the vacuolar orthophosphate (Pi) signal. The line broadening, which was followed indirectly by measuring changes in the reciprocal peak height of the Pi signal in fully relaxed spectra, was found to depend on pH and Pi concn., as well as on the presence of org. acids, but for Pi concns. in the millimolar range the method was sensitive to Mn²⁺ concns. as low as 0.1-1 μM. A linear relation was established between the reciprocal peak height of the vacuolar Pi signal *obsd. in vivo* and the total manganese content of the tissue detd. subsequently by at. absorption. However, the paramagnetic contribution to the line width *obsd. in vivo* was much smaller than expected from measurements on simple solns. and freeze-thaw exts. and it was concluded that less than 5% of the manganese taken up by the root tissue was present in the vacuoles as sol. Mn²⁺. The ability to detect the free pool of divalent manganese is one of several advantages of the ³¹P-**NMR** method relative to the analogous ¹H-**NMR** method based on the interaction between manganese and water; and the non-invasive nature of the method, coupled with the potential to distinguish the cytoplasmic and vacuolar manganese fractions, allows the **NMR** method to complement the information obtained by at. absorption.

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118. **Quantitative solid-state carbon-13 nuclear magnetic resonance spectrometric analyses of wood xylem: Effect of increasing carbohydrate content**

ByBates, Anne L.; Hatcher, Patrick G.

From *Organic Geochemistry* (1992), 18(4), 407-16. Language: English, Database: CAPLUS

Isolated lignin with a low carbohydrate content was spiked with increasing amts. of α-cellulose, and then analyzed by solid-state ¹³C **NMR** by using CPMAS and dipolar dephasing methods in order to assess the

quant. reliability of CPMAS measurement of carbohydrate content and to det. how increasingly intense **resonances** for carbohydrate carbons affect calcns. of the degree of lignin's arom. ring substitution and methoxyl carbon content. Comparisons were made of the carbohydrate content calcd. by **NMR** with carbohydrate concns. obtained by phenol-sulfuric acid assay and by calcn. from the known amts. of cellulose added. The **NMR** methods used in this study yield overestimates for carbohydrate carbons due to **resonance** area overlap from the aliph. side chain carbons of lignin. When corrections are made for these overlapping **resonance** areas, the **NMR** results agree very well with results obtained by other methods. Neither the calcd. methoxyl carbon content nor the degree of arom. ring substitution in lignin, both calcd. from dipolar dephasing spectra, change with cellulose content. Likewise, lignin methoxyl content does not correlate with cellulose abundance when measured by integration of CPMAS spectra. The study was made in relation to wood degrdn. as a stage in coalification.

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119. **Determination of site-specific carbon isotope ratios at natural abundance by carbon-13 nuclear magnetic resonance spectroscopy**

ByCaer, Valerie; Trierweiler, Michel; Martin, Gerard J.; Martin, Maryvonne L.

From Analytical Chemistry (1991), 63(20), 2306-13. Language: English, Database: CAPLUS, DOI: 10.1021/ac00020a021

Site-specific natural isotope fractionation of H studied by 2H **NMR** (SNIF-**NMR**) spectroscopy is a powerful source of information on H pathways occurring in biosyntheses in natural conditions. The potential of the C counterpart of this method was investigated and compared. Three typical mol. species, EtOH, HOAc, and vanillin, were considered. By taking into account the requirements of **quant.** 13C **NMR**, appropriate exptl. procedures were defined and the repeatability and reproducibility of the isotope ratio detns. were checked under different conditions. The C version of the SNIF-**NMR** method can detect small differences in the 13C content of the Et fragment of EtOH from different botanical or synthetic origins. The results agree with mass spectrometry detns. of the overall C isotope ratios. Deviations with respect to a statistical distribution of 13C were detected in the case of HOAc and vanillin. However, since the method is very sensitive to several kinds of systematic error, only a relative significance can be attached at present to the internal parameters directly accessible. Isotope-diln. expts. were carried out to check the consistency of the results. In the present state of exptl. accuracy, the 13C **NMR** method is of more limited potential than 2H SNIF-**NMR** spectroscopy. However, it may provide complementary information. It is particularly efficient for detecting and **quantifying** adulterations that aim to mimic the overall 13C content of a natural compd. by adding a selectively enriched species to a less expensive substrate from a different origin.

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120. **Quantitative triacylglycerol analysis of whole vegetable seeds by proton and carbon-13 magic angle sample spinning NMR spectroscopy**

ByWollenberg, Kurt

From Journal of the American Oil Chemists' Society (1991), 68(6), 391-400. Language: English, Database: CAPLUS

High-resoln. 13C and 1H magic-angle-sample-spinning **NMR** spectra were obtained and used to define the relative unsatd. acyl distribution of triacylglycerols in whole oilseeds. Inverse gated proton-decoupled 13C and 1H **NMR** spectra permit the **quant.** anal. of seeds contg. simple oils, e.g., sunflower seeds contg. oleyl and linoleyl unsaturates only. More sensitive 13C **NMR** techniques are necessary for the anal. of specific seed classes. One such class is the rapeseed, which is esp. difficult due to its low oil content (≈ 2 mg oil/seed) and complex unsatd. acyl profile of oleyl, linoleyl, linolenyl, erucyl, and eicosenoyl. The Distortionless Enhancement by Polarization Transfer technique significantly improves sensitivity to the extent that single rapeseeds can be examd. within 1 h of acquisition time. Furthermore, some positional (1,3- or 2-glycerol attachment) groups can be identified leading to a partial estn. of the 1,3- and 2-acyl distribution.

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121. **Quantitative determination of aluminum in tea by means of aluminum-27 nuclear magnetic resonance spectroscopy**

ByKoch, Klaus R.

From Analyst (Cambridge, United Kingdom) (1990), 115(6), 823-5. Language: English, Database: CAPLUS

A method for detg. the Al levels in tea leaf digests and tea infusions by means of ^{27}Al **NMR** spectroscopy is described. **Quant.** results down to $2.0 \mu\text{g cm}^{-3}$ of Al in 0.5-cm^{-3} acidified samples are readily obtainable in std. 5-mm **NMR** tubes. An acceptable **quant.** detn. is achieved by using an internal Al std. in a 1-mm capillary in conjunction with europium nitrate as a shift reagent.

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122. **Chemical nature of organic phosphorus in cultivated and uncultivated soils under different environmental conditions**

ByCondron, L. M.; Frossard, E.; Tiessen, H.; Newman, R. H.; Stewart, J. W. B.

From Journal of Soil Science (1990), 41(1), 41-50. Language: English, Database: CAPLUS

A sequential alkali extrn. procedure followed by ultrafiltration and **quant.** ^{31}P **NMR** spectroscopy was used to examine org. P in a Brown Chernozem, an adjacent Gleysol developed under native prairie **vegetation**, and a Gray Luvisol formed under aspen forest in Saskatchewan, Canada. Differences in the nature of org. P in the native soils were related to moisture status and **vegetation**. In the grassland soils, a greater proportion of orthophosphate diester P was found in the bottom-slope Gleysol. This difference was partly attributed to less favorable conditions for mineralization in the bottom slope soil compared with the mid-slope Brown Chernozem. Teichoic acid P occurred only in the native Gray Luvisol (**NMR** δ ppm 0.36-0.95) under boreal forest and not under native grassland. At all 3 sites, soils under long-term cultivation (cereal-fallow crop rotation) were also examd. and while orthophosphate monoester P (83.4-94.6% total Po), orthophosphate diester P (3.9-8.7% total Po) and teichoic acid P (12.7% total Po in forested Gray Luvisol) were detected in native soils, only orthophosphate monoester P was found in the corresponding soils that had been cultivated for 70-80 yr. These findings suggest that orthophosphate diester P and teichoic acid P are more readily mineralized in the soil environment than orthophosphate monoester P forms.

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123. **Solid-state carbon-13 nuclear magnetic resonance studies of coalified gymnosperm xylem tissue from Australian brown coals**

ByHatcher, Patrick G.; Lerch, Harry E., III; Bates, Anne L.; Verheyen, Vincent

From Organic Geochemistry (1989), 14(2), 145-55. Language: English, Database: CAPLUS

Solid-state ^{13}C **NMR** spectroscopy is used to contrast the av. chem. compn. of modern degraded gymnosperm woods with fossil gymnosperm woods from Australian brown coals (Miocene). The **quant.** nature of the **NMR** techniques was established for these samples, so that the conventional solid-state ^{13}C **NMR** spectra and the dipolar dephasing **NMR** spectra could be used with a high degree of reliability to depict av. chem. compns. The **NMR** results provide some valuable insights into the early coalification of xylem tissue from gymnosperms. Though the cellulosic components of wood are degraded to varying degrees during peat formation and ensuing coalification, it is unlikely that they play a major role in the formation of arom. structures in coalified woods. The **NMR** data show that gymnosperm lignin, the primary arom. contribution to the coal, is altered in part by demethylation of guaiacyl-units to catechol-like structures. The dipolar dephasing **NMR** data indicate that the lignin also becomes more cross-linked or condensed.

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124. **Starch biosynthesis in developing wheat grain. Evidence against the direct involvement of triose phosphates in the metabolic pathway**

ByKeeling, Peter L.; Wood, John R.; Tyson, R. Huw; Bridges, Ian G.

From Plant Physiology (1988), 87(2), 311-19. Language:English, Database: CAPLUS, DOI: 10.1104/pp.87.2.311

¹³C-labeled sugars and **NMR** spectrometry were used to study the metabolic pathway of starch biosynthesis in developing wheat grain (*Triticum aestivum* cv Mardler). The aim was to examine the extent of redistribution of ¹³C between carbons atoms 1 and 6 of [1-¹³C] or [6-¹³C]glucose (or fructose) incorporated into starch, and hence provide evidence for or against the involvement of triose phosphates in the metabolic pathway. Starch synthesis in the endosperm tissue was studied in two exptl. systems. First, the ¹³C sugars were supplied to isolated endosperm tissue incubated in vitro, and second, the ¹³C sugars were supplied in vivo to the intact **plant**. The ¹³C starch produced by the endosperm tissue of the grain was isolated and enzymically degraded to glucose using amyloglucosidase, and the distribution of ¹³C in all glycosyl carbons was **quantified** by ¹³C-**NMR** spectrometry. In all of the expts., irresp. of the incubation time or incubation conditions, there was a similar pattern of partial (between 15 and 20%) redistribution of label between carbons 1 and 6 of glucose recovered from starch. There was no detectable increase **over** background ¹³C incidence in carbons 2 to 5. Within each expt., the same pattern of partial redistribution of label was found in the glucosyl and fructosyl moieties of sucrose extd. from the tissue. Since it is unlikely that sucrose is present in the amyloplast, it is suggested that the obsd. redistribution of label occurred in the cytosolic compartment of the endosperm cells and that both sucrose and starch are synthesized from a common pool of intermediates, such as hexose phosphate. It is suggested that redistribution of label occurs via a cytosolic pathway cycle involving conversion of hexose phosphate to triose phosphate, interconversion of triose phosphate by triose phosphate isomerase, and resynthesis of hexose phosphate in the cytosol. A further round of triose phosphate interconversion in the amyloplast could not be detected. These data seriously weaken the argument for the selective uptake of triose phosphates by the amyloplast as part of the pathway of starch biosynthesis from sucrose in **plant** storage tissues. Instead, it is suggested that a hexose phosphate such as glucose 1-phosphate, glucose 6-phosphate, or fructose 6-phosphate is the most likely candidate for entry into the amyloplast. A pathway of starch biosynthesis is presented, which is consistent with present data and with the current information on the intracellular distribution of enzymes in **plant** storage tissues.

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125. **Detection and measurement of fluoroacetate in plant extracts by fluorine-19 NMR**

ByBaron, Margaret L.; Bothroyd, Caroline M.; Rogers, Glenn I.; Staffa, Alfred; Rae, Ian D.

From Phytochemistry (1987), 26(8), 2293-5. Language:English, Database: CAPLUS

Examn. of exts. from seeds and foliage of several species known to contain fluoroacetate, using ¹⁹F **NMR** spectroscopy, showed the presence of the characteristic FCH₂-signal in most of them and enabled **quant.** detn. of their fluoroacetate content. No other F-contg. **plant** metabolites were detected; fluoroacetate was

not detected in the exts. of several nontoxic species. The limit of detection is estd. to be ~4 µg/g.

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126. **Quantitative analysis of pyrrolizidine alkaloid mixtures from *Senecio vulgaris* by carbon-13 nuclear magnetic resonance spectroscopy**

ByPieters, L. A. C.; Vlietinck, A. J.

From Magnetic Resonance in Chemistry (1987), 25(1), 8-10. Language: English, Database: CAPLUS, DOI: 10.1002/mrc.1260250103

A **13C NMR** method has been developed for obtaining simultaneously structural and **quant.** information on mixts. of pyrrolizidine alkaloids from *S. vulgaris* (Compositae). Samples contained seneciphylline, senecionine, retrorsine, and the corresponding **E** geometrical isomers, spartiodine, integerrimine, and usaramine. The spin-lattice relaxation times were measured and, after establishing the instrumental requirements for **quant.** **13C FT NMR**, all the alkaloids of the mixt. could be detd. **Quant.** **1H** and **13C FT NMR** analyses were carried out, and the advantages and limitations of these methods are discussed.

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127. **Deuterium NMR characterization of anetholes. Factorial analysis of specific isotope ratios**

ByMartin, G. J.; Janvier, P.; Mabon, F.

From Analisis (1985), 13(6), 267-74. Language: French, Database: CAPLUS

Fifty samples of anethole [104-46-1] of different origins (mainly from star anise tree and semisynthetic) were studied by **quant.** **2H-NMR** at the natural abundance level. The exptl. conditions for spectrum acquisition were carefully selected and then applied to the detn. of Site-specific Natural Isotope Fractionation factors [SNIF-**NMR** ratios: (D/H)_i, or R_{i/j} where j is a ref. site of the mol.]. The anisotropy of **2H** distribution along 3 specific axes (arom., olefinic and methyl) was considered as 3 variables in a discriminating factorial anal. for which a sufficient no. of observations (50) were available. Anethole samples of a given origin are clustered in a specific region of the factorial space. Identification of unknown samples can be easily performed by factorial anal. in a bidimensional space.

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128. **Carbon-13 nuclear magnetic resonance of herbaceous plants and their components, using cross polarization and magic-angle spinning**

ByMaciel, Gary E.; Haw, James F.; Smith, Danny H.; Gabrielson, Byron C.; Hatfield, Galen R.

From Journal of Agricultural and Food Chemistry (1985), 33(2), 185-91. Language: English, Database: CAPLUS, DOI: 10.1021/jf00062a006

13C NMR spectra, obtained with cross polarization and magic-angle spinning (CP/MAS), were obtained on the following untreated herbage samples: forage sorghum, sorghum × Sudangrass, Jerusalem artichoke, kochia, and Russian thistle. The diversity of compn. of these materials is manifested in the complexity of the **NMR** spectra. Detailed assignments for forage sorghum and Jerusalem artichoke are made via studies of crude cell wall fractions, holocellulose, α-cellulose, and hemicellulose and with the aid of difference spectra and interrupted decoupling. Spectra of representative nonstructural carbohydrates are also presented for comparison. The lignins in forage sorghum and Jerusalem artichoke were found to be very different. This conclusion is based on the detailed appearance of the arom. signals in the **NMR** spectra and on the observation that the lignin of Jerusalem artichoke was substantially retained in the holocellulose fraction, in contrast to the results for forage sorghum. Some features of the ability and limitations of **13C CP/MAS NMR** for **quant.** anal. in **plant** samples of this type are discussed.

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129. **Nutritional evaluation of forages by high-resolution solid state carbon-13 NMR**

ByEflon, R. M.; Ripmeester, J. A.; Cyr, N.; Milligan, L. P.; Mathison, G.

From Canadian Journal of Animal Science (1984), 64(1), 93-102. Language: English, Database: CAPLUS

The **NMR** technique known as ^{13}C cross-polarization-magic angle spinning with proton decoupling (CP/MAS) was examd. as an approach to the direct measurement of the nutritional value of forages. Preliminary results indicate that the relative amts. of protein, lignin [9005-53-2], and carbohydrate can be estd. not only in single species but also on mixts. thereof without special treatment. This technique reveals changes due to maturation which should in turn be related to digestibility of forages. Use of a dipolar dephasing (spectra with delay) technique can be used to enhance **resonance** signals due to protein and lignin and probably distinguish the fructose moiety from the remaining carbohydrate complex. Although detailed **quant.** correlations between **NMR** spectra and nutritional values remain to be established, the scope of the technique and some of the problems to be overcome are discussed.

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130. **Phosphorus nutrition and the intracellular distribution of inorganic phosphate in pea root tips: a quantitative study using phosphorus-31 NMR**

By Lee, R. B.; Ratcliffe, R. G.

From Journal of Experimental Botany (1983), 34(146), 1222-44. Language: English, Database: CAPLUS

Pea plants (*Pisum sativum*) were supplied with external phosphate for differing periods of time, so that their P status varied, and the intracellular distribution of inorg. phosphate (Pi) in the roots was examd. by ^{31}P **NMR**. Over the range of P nutrition investigated, the **quantity** of vacuolar Pi per unit fresh wt. of root tip changed considerably, whereas the **quantity** of cytoplasmic Pi per unit fresh wt. of root tip did not alter. The relative vols. of the cytoplasm and the vacuole in pea root tips seemed to be little affected by differences in P nutrition, and this implied that the concn. of Pi in the cytoplasm was kept almost const., at a level estd. to

be ~18 mM. The rate of absorption of ^{32}P -labeled phosphate was neg. correlated with the vacuolar Pi

concn., but there was no clear correlation with the concn. of Pi in the cytoplasm.

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131. **Identification of the origin of natural alcohols by natural abundance hydrogen-2 nuclear magnetic resonance**

By Martin, Gerard J.; Martin, Maryvonne L.; Mabon, Françoise; Michon, Marie Jo

From Analytical Chemistry (1982), 54(13), 2380-2. Language: English, Database: CAPLUS, DOI: 10.1021/ac00250a057

A new method for the identification of the natural origin of various ethanols was developed by using **quant. D NMR** spectrometry at the natural abundance level. This technique enables the relative deuterium content (D/H) of the various nonequiv. sites of a mol. to be detd. The relative depletion in D of the Me- with the respect to the methylene-group in the ethanol mol. can be measured rapidly (in 3 h) and accurately ($\pm 0.5\%$). It is then possible to identify the nature of the **plant** (or the olefin) from which the ethanol was prepd. by fermn. (or hydration) and to obtain new information on the climatol. factors which contribute to the isotopic fractionation during the photosynthetic cycle.

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132. **A new method for the identification of the origin of natural products. Quantitative deuterium NMR at the natural abundance level applied to the characterization of anetholes**

ByMartin, G. J.; Martin, M. L.; Mabon, F.; Bricout, J.

From Journal of the American Chemical Society (1982), 104(9), 2658-9. Language: English, Database: CAPLUS, DOI: 10.1021/ja00373a064

A new method for the characterization of the origin of natural products is proposed and illustrated in the case of various anethole samples obtained from fennel, Chinese anise, and chem. synthesis. The method is based on the detection of very spectacular differences in the internal distribution of D at the natural abundance level by means of **quant. 2H NMR**. In particular it is capable of distinguishing samples from different origins even when their D/H contents obtained by mass spectroscopy are equal.

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133. **Detection of refined olive oil adulteration with refined hazelnut oil by employing NMR spectroscopy and multivariate statistical analysis**

ByAgiomyrgianaki Alexia; Petrakis Panos V; Dais Photis

From Talanta (2010), 80(5), 2165-71. Language: English, Database: MEDLINE

NMR spectroscopy was employed for the detection of adulteration of refined olive oil with refined hazelnut oil. Fatty acids and iodine number were determined by (1)H **NMR**, whereas (31)P **NMR** was used for the **quantification** of minor compounds including phenolic compounds, diacylglycerols, sterols, and free fatty acids (free acidity). Classification of the refined oils based on their fatty acids content and the concentration of their minor compounds was achieved by using the forward stepwise canonical discriminant analysis (CDA) and the classification binary trees (CBTs). Both methods provided good discrimination between the refined hazelnut and olive oils. Different admixtures of refined olive oils with refined hazelnut oils were prepared and analyzed by (1)H **NMR** and (31)P **NMR** spectroscopy. Subsequent application of CDA to the **NMR** data allowed the detection of the presence of refined hazelnut oils in refined olive oils at percentages higher than 5%. Application of the non-linear classification method of the binary trees offered better possibilities of measuring adulteration of the refined olive oils at a lower limit of detection than that obtained by the CDA method.

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134. **Biomass characterization of *Buddleja davidii*: a potential feedstock for biofuel production**

ByHallac Bassem B; Sannigrahi Poulomi; Pu Yunqiao; Ray Michael; Murphy Richard J; Ragauskas Arthur J

From Journal of agricultural and food chemistry (2009), 57(4), 1275-81. Language: English, Database: MEDLINE

A compositional analysis was performed on *Buddleja davidii* to determine its general biomass characteristics and provide detailed analysis of the chemical structures of its cellulose and lignin using **NMR**. *B. davidii* is a new potential lignocellulosic bioresource for producing bioethanol because it has several attractive agroenergy features. The biomass composition of *B. davidii* is 30% lignin, 35% cellulose, and 34% hemicellulose. Solid-state CP/MAS (13)C **NMR** showed that 33% of the cellulose is para-crystalline and 41% is at inaccessible surfaces. Both **quantitative** (13)C and (31)P **NMR** were used to examine the structure of lignin. The lignin was determined to be guaiacyl and syringyl with an h:g:s ratio of 0:81:19.

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135. **Determination of phospholipids in olive oil by 31P NMR spectroscopy**

ByHatzakis Emmanuel; Koidis Anastasios; Boskou Dimitrios; Dais Photis

From Journal of agricultural and food chemistry (2008), 56(15), 6232-40. Language: English, Database: MEDLINE

A nondestructive analytical method based on **NMR** spectroscopy was developed for the determination of phospholipids in olive oil. The phospholipids extracted from virgin olive oil with a mixture of ethanol/water (2:1 v/v) were identified and **quantified** by high resolution (31)P **NMR** spectroscopy. The main

phospholipids found in olive oil were phosphatidic acid, lyso-phosphatidic acid, and phosphatidylinositol. Validation of the $(31)\text{P}$ **NMR** methodology for **quantitative** analysis of phospholipids in olive oil was performed. Sensitivity was satisfactory with detection limits of 0.25-1.24 $\mu\text{mol}/\text{mL}$. In addition, the composition of fatty acids in phospholipids model compounds and those in olive oil samples was estimated by employing one- and two-dimensional $(1)\text{H}$ **NMR**. The results indicated that the fatty acid composition in phospholipids and triacylglycerols of olive oil was similar.

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136. **Hydrogen exchange during cellulose synthesis distinguishes climatic and biochemical isotope fractionations in tree rings**

ByAugusti Angela; Betson Tatiana R; Schleucher Jurgen

From The New phytologist (2006), 172(3), 490-9.Language:English, Database: MEDLINE

The abundance of the hydrogen isotope deuterium (D) in tree rings is an attractive record of climate; however, use of this record has proved difficult so far, presumably because climatic and physiological influences on D abundance are difficult to distinguish. Using D labelling, we created a D gradient in trees. Leaf soluble sugars of relatively low D abundance entered cellulose synthesis in stems containing strongly D-labelled water. We used **nuclear magnetic resonance (NMR)** spectroscopy to **quantify** D in the C-H groups of leaf glucose and of tree-ring cellulose. Ratios of D abundances of individual C-H groups of leaf glucose depended only weakly on leaf D labelling, indicating that the D abundance pattern was determined by physiological influences. The D abundance pattern of tree-ring cellulose revealed C-H groups that exchanged strongly (C(2)-H) or weakly (C(6)-H₂) with water during cellulose synthesis. We propose that strongly exchanging C-H groups of tree-ring cellulose adopt a climate signal stemming from the D abundance of source water. C-H groups that exchange weakly retain their D abundance established in leaf glucose, which reflects physiological influences. Combining both types of groups may allow simultaneous reconstruction of climate and physiology from tree rings.

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137. **Determination of the 1,3- and 2-positional distribution of fatty acids in olive oil triacylglycerols by ^{13}C nuclear magnetic resonance spectroscopy**

ByVlahov Giovanna

From Journal of AOAC International (2006), 89(4), 1071-6.Language:English, Database: MEDLINE

Linear models were selected from a large data set acquired for Italian olive oil samples by **quantitative ^{13}C nuclear magnetic resonance (NMR)** spectroscopy with distortionless enhancement by polarization transfer (DEPT). The models were used to determine the composition of the 2 fatty acid pools esterifying the 1,3- and 2-positions of triacylglycerols. The linear models selected proved that the 1,3- and 2-distribution of saturated, oleate, and linoleate chains in olive oil triacylglycerols deviated from the random distribution pattern to an extent that depended on the concentration of the fatty acid in the whole triacylglycerol. To calculate the fatty acid composition of the 1,3- and 2-positions of olive oil triacylglycerols, the equations of the selected linear models were applied to the fatty acid percentages determined by gas chromatography. These data were compared with the values predicted by the computer method (used to determine the theoretical amounts of triacylglycerols), which is based on the 1,3-random-2-random theory of the fatty acid distribution in triacylglycerols. The biggest differences were found in the linoleate chain, which is the chain that deviated the most from a random distribution pattern. The results confirmed that the 1,3-random-2-random distribution theory provides an approximate method for determining the structure of triacylglycerols; however, the linear models calculated by the direct method that applies ^{13}C **NMR** spectroscopy represent a more precise measurement of the composition of the 2 fatty acid pools esterifying the 1,3- and 2-positions of triacylglycerols.

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138. **Inhibition of cellulase, xylanase and beta-glucosidase activities by softwood lignin preparations**

ByBerlin Alex; Balakshin Mikhail; Gilkes Neil; Kadla John; Maximenko Vera; Kubo Satoshi; Saddler Jack

From Journal of biotechnology (2006), 125(2), 198-209.Language:English, Database: MEDLINE

The conversion of lignocellulosic biomass to fuel ethanol typically involves a disruptive pretreatment process followed by enzyme-catalyzed hydrolysis of the cellulose and hemicellulose components to fermentable sugars. Attempts to improve process economics include protein engineering of cellulases, xylanases and related hydrolases to improve their specific activity or stability. However, it is recognized that enzyme performance is reduced during lignocellulose hydrolysis by interaction with lignin or lignin-carbohydrate complex (LCC), so the selection or engineering of enzymes with reduced lignin interaction offers an alternative means of enzyme improvement. This study examines the inhibition of seven cellulase preparations, three xylanase preparations and a beta-glucosidase preparation by two purified, particulate lignin preparations derived from softwood using an organosolv pretreatment process followed by enzymatic hydrolysis. The two lignin preparations had similar particle sizes and surface areas but differed significantly in other physical properties and in their chemical compositions determined by a 2D correlation HSQC **NMR** technique and **quantitative** ¹³C **NMR** spectroscopy. The various cellulases differed by up to 3.5-fold in their inhibition by lignin, while the xylanases showed less variability (< or = 1.7-fold). Of all the enzymes tested, beta-glucosidase was least affected by lignin.

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139. **Novel approach to the detection and quantification of phenolic compounds in olive oil based on ³¹P nuclear magnetic resonance spectroscopy**

ByChristophoridou Stella; Dais Photis

From Journal of agricultural and food chemistry (2006), 54(3), 656-64.Language:English, Database: MEDLINE

³¹P **NMR** spectroscopy has been employed to detect and **quantify** phenolic compounds in the polar fraction of virgin olive oil. This novel analytical method is based on the derivatization of the hydroxyl and carboxyl groups of phenolic compounds with 2-chloro-4,4,5,5-tetramethyldioxaphospholane and the identification of the phosphitylated compounds on the basis of the ³¹P chemical shifts. **Quantification** of a large number of phenolic compounds in virgin olive oil can be accomplished by integration of the appropriate signals in the ³¹P **NMR** spectrum and the use of the phosphitylated cyclohexanol as internal standard. Finally, the validity of this technique for **quantitative** measurements was thoroughly examined.

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140. **Identification and quantitative determination of eudesmane-type acids from the essential oil of *Dittrichia viscosa* sp. viscosa using ¹³C-NMR spectroscopy**

ByBlanc Marie-Cecile; Bradesi Pascale; Casanova Joseph

From Phytochemical analysis : PCA (2005), 16(3), 150-4.Language:English, Database: MEDLINE

A procedure that allows the identification and **quantitative** determination of eudesmane-type acids in the acidic part of the essential oil of *Dittrichia viscosa* sp. viscosa is described. The method involves the computer-aided analysis of the ¹³C-**NMR** spectrum of the mixture without the requirement of previous separation or derivatisation. The **quantitative** procedure was verified with costic acid standard and applied to three other acids which possess the same eudesmane framework.

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141. **Direct identification and quantitative determination of costunolide and dehydrocostuslactone in the fixed oil of *Laurus novocanariensis* by ¹³C-NMR spectroscopy**

ByFerrari Bernard; Castilho Paula; Tomi Felix; Rodrigues Ana Isabel; do Ceu Costa Maria; Casanova Joseph

From Phytochemical analysis : PCA (2005), 16(2), 104-7.Language:English, Database: MEDLINE

The fixed oil of *Laurus novocanariensis* (previously *L. azorica*) contains mostly glycerides together with minor non-saponifiable compounds. The direct identification and **quantitative** determination of costunolide and dehydrocostuslactone, two sesquiterpene lactones components of the oil that exhibit biological activities, is described. The analysis was carried out using ¹³C-NMR spectroscopy (signal acquisition with inverse gated decoupling of protons; diglyme as internal standard) without separation, derivatisation or any sample preparation.

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142. **Quantitative deuterium isotopic profiling at natural abundance indicates mechanistic differences for delta 12-epoxidase and delta 12-desaturase in *Vernonia galamensis***

ByBillault Isabelle; Duan Jia-Rong; Guet Sebastien; Robins Richard J

From The Journal of biological chemistry (2005), 280(18), 17645-51.Language:English, Database: MEDLINE

Quantitative (2)H NMR spectroscopy can determine the natural abundance ((2)H/(1)H) ratio at each site of a molecule. In natural products, variation in these values is related to the reaction mechanisms in the pertinent biosynthetic pathway. For the first time, this novel approach has been exploited to probe for mechanistic differences in the introduction of different functionalities into a long-chain fatty acid. Vernolic acid, a major component of the seed oil of *Vernonia galamensis*, contains both an epoxide and a desaturation. The site-specific isotopic distribution ((2)H/(1)H)(i) has been determined for both vernolic acid and linoleic acid isolated from the same *V. galamensis* oil. It is found that the ((2)H/(1)H) ratio of vernolic acid shows a pattern along the entire length of the chain, consistent with linoleic acid being its immediate precursor. Notably, the C13 relates to the C13 of linoleic acid but not to the C13 of oleic acid. Furthermore, the C12 and C13 positions in vernolic acid are less depleted, consistent with a change in hybridization state from sp(2) to sp(3). However, the C11 position shows a marked relative enrichment in the vernolic acid, implying that it plays a role in the epoxidase but not the desaturase mechanism. Thus, although it can be concluded that the catalytic mechanisms for the epoxidase and desaturase activities are similar, marked differences in the residual ((2)H/(1)H) patterns indicate that the reaction mechanisms are not identical.

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143. **Combined analysis of the essential oil of *Chenopodium ambrosioides* by GC, GC-MS and ¹³C-NMR spectroscopy: quantitative determination of ascaridole, a heat-sensitive compound**

ByCavalli Jean-Francois; Tomi Felix; Bernardini Antoine-Francois; Casanova Joseph

From Phytochemical analysis : PCA (2004), 15(5), 275-9.Language:English, Database: MEDLINE

A commercial sample of the essential oil of *Chenopodium ambrosioides* L. from Madagascar was analysed by GC, GC-MS and ¹³C-NMR. By GC analysis, the major constituents were found to be ascaridole (1) (41.8%), isoascaridole (2) (18.1%), p-cymene (16.2%), alpha-terpinene (9.7%) and limonene (3.8%). However, ascaridole undergoes a partial thermal isomerisation to 2 and hence the amount of 1 is underestimated by GC analysis. The actual contents of 1 and 2 (55.3 and 4.6%, respectively) were obtained following combined analysis of the sample by GC and ¹³C-NMR. Several hydroxy- and polyhydroxymenthanes were identified by ¹³C-NMR.

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144. **Kinetics of diglyceride formation and isomerization in virgin olive oils by employing ³¹P NMR spectroscopy. Formulation of a quantitative measure to assess olive oil storage history**

BySpyros Apostolos; Philippidis Angelos; Dais Photis

From Journal of agricultural and food chemistry (2004), 52(2), 157-64.Language:English, Database: MEDLINE

Diacylglycerol isomers and free acidity were determined for five extra virgin olive oils of different initial acidities by employing a facile (³¹P) NMR methodology as a function of storage time and storage conditions. The kinetic treatment of the hydrolysis of triacylglycerols (TGs) and the isomerization of 1,2-diacylglycerols (1,2-DGs) to 1,3-diacylglycerols (1,3-DGs) during storage of 18 months at ambient temperature in the dark and light and at 5 degrees C in the dark showed that the isomerization is strongly dependent on the rate of the TGs hydrolysis, the initial free acidity (H(0)) of the virgin olive oil samples, and storage conditions. Although the time-evolution of the diacylglycerols (DGs) depends on the TGs hydrolysis, the ratio D of the concentration of 1,2-DGs to the total amount of DGs was found to be independent of this factor. From the kinetic expression of the ratio D, a **quantitative** measure was formulated that allows the estimation of the storage time or age of virgin olive oils. Application of this **quantitative** measure to several olive oil samples of known and unknown storage history resulted in a very good agreement with respect to the actual storage time for up to 10-12 months of storage. For a longer storage period, where the isomerization of DGs is close to its equilibrium state, the calculated age index is only indicative.

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145. **Natural deuterium distribution in fatty acids isolated from peanut seed oil: a site-specific study by quantitative ²H NMR spectroscopy**

ByDuan Jia-Rong; Billault Isabelle; Mabon Francoise; Robins Richard

From Chembiochem : a European journal of chemical biology (2002), 3(8), 752-9.Language:English, Database: MEDLINE

Quantitative (²H) NMR spectroscopy has been used to measure the distribution of deuterium at natural abundance in long-chain fatty acids extracted from the same vegetable oil. Peanut seed oil was selected, due to its suitable oleic and linoleic acid content. The methyl esters of the fatty acids were prepared by transesterification and isolated by modified argentation column chromatography on silica. In order to measure the natural isotopic fractionation of deuterium (D) at the maximum number of positions, the purified methyl oleate and methyl linoleate were chemically cleaved and the (D/H)(i) values determined by **quantitative** (²H) NMR spectroscopy. It was thus possible to demonstrate that fractionation in deuterium occurs during the desaturation of oleate to linoleate. Furthermore, the previously observed distribution of deuterium at the sites of desaturation is confirmed, as is the alternating pattern of (D/H)(i), which relates to the origin of the pertinent hydrogen atoms. The data obtained are discussed in terms of the kinetic isotopic effects intrinsic to the enzymes-synthetases and desaturases-involved in the biosynthesis of fatty acids.

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146. **Biosynthesis of the sesquiterpene germacrene D in *Solidago canadensis*: ¹³C and (²H) labeling studies**

BySteliopoulos Panagiotis; Wust Matthias; Adam Klaus-Peter; Mosandl Armin

From Phytochemistry (2002), 60(1), 13-20.Language:English, Database: MEDLINE

The biogenetic origin of the isoprenoid building blocks of the sesquiterpene germacrene D was studied in *Solidago canadensis*. Feeding experiments were carried out with 1-[5,5-D(2)]deoxy-D-xylulose-5-phosphate (D(2)-DOXP), [5-¹³C]mevalonolactone (13C-MVL) and [1-¹³C]-D-glucose. The hydrodistillate of a cut shoot fed with D(2)-DOXP was investigated by enantio-MDGC-MS and the volatile fraction of a shoot supplied with 13C-MVL was examined by GC-C-IRMS. The incorporation of [1-¹³C]-D-glucose was analyzed by

quantitative ^{13}C **NMR** spectroscopy after isolation of germacrene D from the essential oil. Our labeling studies revealed that the biosynthesis of the C-15 skeleton of sesquiterpene germacrene D in *Solidago canadensis* proceeds predominantly via the methylerythritol phosphate pathway.

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147. **Soil and litter phosphorus-31 nuclear magnetic resonance spectroscopy: extractants, metals, and phosphorus relaxation times**

ByCade-Menun B J; Liu C W; Nunlist R; McColl J G

From Journal of environmental quality (2002), 31(2), 457-65.Language:English, Database: MEDLINE

Phosphorus-31 **nuclearmagneticresonance (NMR)** spectroscopy is an excellent tool with which to study soil organic P, allowing **quantitative**, comparative analysis of P forms. However, for ^{31}P **NMR** to be tative, all peaks must be completely visible, and in their correct relative proportions. There must be no line broadening, and adequate delay times must be used to avoid saturation of peaks. The objective of this study was to examine the effects of extractants on delay times and peak saturation. Two samples (a forest litter and a mineral soil sample) and three extractants (0.25 M NaOH, NaOH plus Chelex (Bio-Rad Laboratories, Hercules, CA), and NaOH plus EDTA) were used to determine the differences in the concentration of P and cations solubilized by each extractant, and to measure spin-lattice (T_1) relaxation times of P peaks in each extract. For both soil and litter, NaOH-Chelex extracted the lowest concentrations of P. For the litter sample, T_1 values were short for all extractants due to the high Fe concentration remaining after extraction. For the soil sample, there were noticeable differences among the extractants. The NaOH-Chelex sample had less Fe and Mn remaining in solution after extraction than the other extractants, and the longest delay times used in the study, 6.4 s, were not long enough for **quantitative** analysis. Delay times of 1.5 to 2 s for the NaOH and NaOH-EDTA were adequate. Line broadening was highest in the NaOH extracts, which had the highest concentration of Fe. On the basis of these results, recommendations for future analyses of soil and litter samples by solution ^{31}P **NMR** spectroscopy include: careful selection of an extractant; measurement of paramagnetic ions extracted with P; use of appropriate delay times and the minimum number of scans; and measurement of T_1 values whenever possible.

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148. **Solid-phase synthesis of oligosaccharides and on-resin quantitative monitoring using gated decoupling (^{13}C NMR)**

ByKanemitsu Takuya; Wong Chi-Huey; Kanie Osamu

From Journal of the American Chemical Society (2002), 124(14), 3591-9.Language:English, Database: MEDLINE

A general strategy for solid-phase oligosaccharide synthesis capable of nondestructive **quantitative** monitoring has been developed. The synthesis was carried out on TentaGel using thioglycosides as glycosylating agents and dimethylthiomethylsulfonium triflate as the activator. An acylsulfonamide linker was introduced to cleave the oligosaccharide from the resin. The solid-phase reactions were monitored **quantitatively** by using the inverse gated decoupling technique of (^{13}C **NMR**, where two (^{13}C -enriched markers were used to monitor the reactions: one was (^{13}C -enriched glycine incorporated as a part of the linker and as an internal standard, and the other was a (^{13}C -enriched acetyl group used as a protecting group of the glycosylation reagent. A representative synthesis of sialyl Lewis X branched tetrasaccharide was demonstrated.

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149. **Identification and quantitative determination of furanodiene, a heat-sensitive compound, in**

essential oil by ¹³C-NMR

ByBaldovini N; Tomi F; Casanova J

From Phytochemical analysis : PCA (2001), 12(1), 58-63.Language:English, Database: MEDLINE

A method based on ¹³C-NMR has been used as a tool for the identification and **quantitative** determination of two furanic sesquiterpenes: a heat-sensitive compound, furanodiene, and its rearrangement product, furanoelemene. Following a preliminary study using artificial mixtures which permitted the construction and verification of calibration curves for each compound, the method was used for the qualitative and **quantitative** analysis of furanodiene and furanoelemene in the essential oil of *Smyrniololus*.

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150. Intracellular pH regulation in maize root tips exposed to ammonium at high external pH

ByGerendas J; Ratcliffe R G

From Journal of experimental botany (2000), 51(343), 207-19.Language:English, Database: MEDLINE

Ammonium-induced changes in the cytoplasmic and vacuolar pH values of excised maize (*Zea mays* L.) root tips, measured by in vivo ³¹P **nuclear magnetic resonance (NMR)** spectroscopy, were correlated with the ammonium content of the tissue, determined by ¹⁴N **NMR**. Calculations based on these measurements indicated that the pH changes observed during exposure to 10 mM ammonium for 1 h at pH 9.0, and in the recovery following the removal of the external ammonium supply, were largely determined by the influx and efflux of the weak base NH₃. Carboxylate synthesis, detected by both in vivo ¹³C **NMR** and the incorporation of [¹⁴C]bicarbonate, was stimulated by the ammonium-induced alkalization of the root tips, but the contribution that this proton-generating process made to pH regulation during and after the ammonium treatment was **quantitatively** insignificant. Similarly, ammonium assimilation, which was shown to occur via the proton-generating glutamine synthetase/glutamate synthase pathway using in vivo ¹⁵N **NMR**, was also **quantitatively** insignificant in comparison with the large changes in ammonium content that occurred during the ammonium treatment and subsequent recovery. The results are discussed in relation to several recent studies in which ammonium was used to perturb intracellular pH values, and it is argued (i) that a new method for probing the subcellular compartmentation of amino acids, based on an ammonium-induced alkalization of the cytoplasm may be difficult to implement in dense heterogeneous tissues; and (ii) that observations on the apparently proton-consuming effect of ammonium assimilation in rice root hairs may actually reflect unusually rapid assimilation.

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151. NMR adventures in the metabolic labyrinth within plants

ByRoberts J K

From Trends in plant science (2000), 5(1), 30-4.Language:English, Database: MEDLINE

The era of metabolic engineering has begun, but there is only limited knowledge about metabolic fluxes and how they are regulated in **plants**. Particular challenges are the non-linearities between enzyme abundances, metabolite concentrations and metabolic fluxes, and the existence of metabolic networks that provide multiple routes between many important metabolites. **NMR** offers the means to distinguish and **quantitate** the fluxes along different routes to key metabolites. **NMR** can therefore help us understand and resolve the apparent paradox of, on the one hand, great metabolic flexibility evident in the natural **responses** of **plants** and, on the other hand, the unpredictable changes in metabolism reported in genetically engineered **plants**.

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152. **Application of (31)P NMR spectroscopy in food analysis. 1. Quantitative determination of the mono- and diglyceride composition of olive oils**

BySpyros A; Dais P

From Journal of agricultural and food chemistry (2000), 48(3), 802-5.Language:English, Database: MEDLINE

This paper introduces a facile method to determine the amount of mono- and diglycerides in virgin olive oils. This method is based on the phosphorylation of the free hydroxyls of the mono- and diglycerides with 2-chloro-4,4,5,5-tetramethyldioxaphospholane and the integration of the appropriate peaks in the (31)P **NMR** spectrum. **Quantitative** (31)P **NMR** spectroscopy can be extended to the **quantification** of other constituents of olive oils bearing functional groups with labile protons.

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153. **Recognition and quantitation cis-vaccenic and eicosenoic fatty acids in olive oils by 13C nuclear magnetic resonance spectroscopy**

ByScano P; Casu M; Lai A; Saba G; Dessi M A; Deiana M; Corongiu F P; Bandino G

From Lipids (1999), 34(7), 757-9.Language:English, Database: MEDLINE

The presence of 11-cis monoenoic fatty acids was detected in olive oil samples by means of 13C **nuclearmagneticresonance** spectroscopy, and the positional isomery on the glycerol backbone was derived. The 11-cis vaccenic and eicosenoic fatty acid **resonances** were recognized and the amounts of the fatty acids **quantified**. For comparison purposes, a **quantitative** analysis was also made by gas chromatography.

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154. **In situ measurements of ribulose-1,5-bisphosphate carboxylase activity by nuclear magnetic resonance**

ByWang Z Y; Luo S; Sato K; Kobayashi M; Nozawa T

From Analytical biochemistry (1998), 257(1), 26-32.Language:English, Database: MEDLINE

High-resolution **NMR** spectroscopy is demonstrated to be capable of monitoring in situ the carboxylation reaction catalyzed by ribulose-1,5-bisphosphate carboxylase. Specific activities are determined for three enzymes from different sources containing higher **plant** and photosynthetic bacteria, and they are in agreement with those measured by other methods. Several important features of the reaction have been confirmed at the atomic level. A decrease in activity with time after the reaction started has also been observed for both enzymes with L8S8 and L2 structures from photosynthetic bacteria and higher **plants**, suggesting that the "fallover" of activity may be a more general phenomenon. 1H spectra obtained with H₂O as solvent provide the most efficient **quantitative** measurement of the reaction product, 3-phosphoglycerate. 31P spectra give essentially the same result as 1H **NMR** but have the advantage of showing the degree of reaction at any time during the reaction. The incorporated carbon atom is unequivocally identified as the C-1 carbon of 3-phosphoglycerate from the 13C spectrum.

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155. **Qualitative and quantitative determination of fluoroacetic acid in *Arrabidea bilabiata* and *Palicourea marcgravii* by 19F-NMR spectroscopy**

ByKrebs H C; Kemmerling W; Habermehl G

From Toxicon : official journal of the International Society on Toxinology (1994), 32(8), 909-13.Language:English, Database: MEDLINE

Qualitative and **quantitative** examination of *Arrabidea bilabiata* and *Palicourea marcgravii* by 19F-

NMRspectroscopy has shown the presence of fluoroacetic acid. By acid-base enrichment it is possible to detect amounts of fluoroacetic acid which otherwise are below detection rate. The detection limit (without enrichment) is estimated to be about 4 micrograms/g. Disturbing metal ions of higher oxidation states are also removed by this way. *Arrabidea bilabiata* contains 64.1 micrograms/g (seeds) and 3.0 micrograms/g (leaves), and *Palicourea marcgravii* contains 5.4 micrograms/g (leaves).

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156. **Comparison of capillary gas chromatography with ¹H and ¹³C nuclear magnetic resonance spectroscopy for the quantitation of pyrrolizidine alkaloids from *Senecio vernalis***

By Pieters L A; Hartmann T; Janssens J; Vlietinck A J

From Journal of chromatography (1989), 462, 387-91. Language: English, Database: MEDLINE

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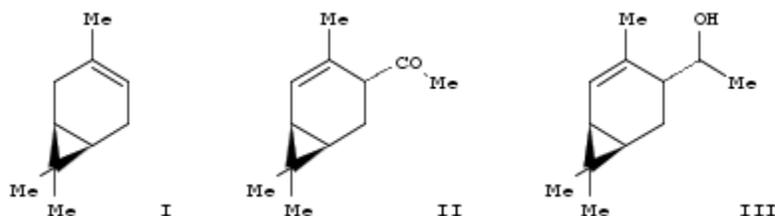
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157. **Quantitative ²H NMR spectroscopy: 3. Stereochemistry and the mechanism of acylation of 3-carene**

By Grishin, Yu. K.; Gloriovov, I. P.; Gerdov, S. M.; Roznyatovsky, V. A.; Frolova, L. L.; Kuchin, A. V.; Ustynyuk, Yu. A.

From Russian Chemical Bulletin (2008), 57(8), 1689-1696. Language: English, Database: CAPLUS, DOI: 10.1007/s11172-008-0223-4

The selectivity of deuterium distribution between the nonequivalent positions in 3-carene (I), 4- α -acetyl-2-carene (II), and 4-(1-hydroxyethyl)-2-carene (III) was measured by ²H-¹H NMR spectroscopy at the natural abundance of deuterium. These "H/D-isotope portraits" were shown to be typical of terpenes and terpenoids produced in **plants** via the biosynthetic DXP pathway. The mechanism of acylation of I was studied by the d. functional theory method (PBE functional, TZ2p basis set). The six-membered ring in I is planar. However, the endo attack of electrophiles on this ring is more favorable both kinetically and thermodynamically. It was shown both exptl. and theor. that the elimination of a hydrogen atom in the second reaction step proceeds stereoselectively at the C(2) atom from the anti position with respect to the three-membered ring and occurs with pronounced nucleophilic assistance from the carbonyl group.



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