Study on the application of NMR spectroscopies for the evaluation of food quality

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（食品品質評価のための NMR 法の応用に関する研究）

区　　分　：　甲

論　文　内　容　の　要　旨

NMR spectroscopy is often used for the determination of the content, purity, and molecular structure of analyte. It is accurate and nondestructive, but it has some disadvantages for the analysis of mixtures, like foods. In this work, advanced NMR spectroscopies were extensively applied to evaluate food quality in both quantitative and qualitative aspects.

In quantitative NMR (qNMR) analysis, 1D qNMR may involve serious difficulties due to extensive signal overlap. Diffusion ordered NMR spectroscopy (DOSY-NMR), a two dimensional NMR technique, is useful to overcome this problem. It enables to separate spectra of mixtures into each component by their individual diffusion coefficient (*D*) values at an appropriate pulsed-field gradient strength, and was proposed as a quantitative method (DOSY-qNMR) in this study. DOSY-qNMR was firstly applied to quantify D-(+)-glucose in fruit juices. The 90º pulse-width and spin-lattice relaxation delay (T_1) value in DOSY acquisition conditions for D-(+)-glucose were optimized to be 10.1 μs and 3.0 s, respectively. The *D* value of D-(+)-glucose in deuterium oxide at 30ºC was 5.6×10^{-10} m^2/s at field gradient pulse between 5.0×10^{-2} and 3.0×10^{-1} T/m. By the aid of β-C1 proton (5.25 ppm) in D-glucuronic acid (50.0 g/L) as internal standard, the target proton, namely α-C1 proton (5.21 ppm) in D-(+)-glucose was normalized for quantitation (r^2 = 0.9998). DOSY-qNMR successfully quantified D-(+)-glucose in orange juice (18.3 ± 1.0 g/L), apple juice (26.3 ± 0.4 g/L) and grape juice (45.6 ± 0.6 g/L), in accordance with those by enzymatic method (F-kit glucose assay). The proposed DOSY-qNMR method provided adequate quantitation of D-(+)-glucose, with good recovery of > 94%, repeatability (RSD < 6%), and limits of detection of > *ca.* 0.3 g/L. The proposed DOSY-qNMR was also applied to quantify sucrose (*D* value: 4.9×10^{-10} m^2/s) in orange juice, pineapple juice, and a sports drink. Results of sucrose quantitation were well validated and consistent with those by F-kit sucrose assay. The proposed DOSY-qNMR was, thus, illustrated to be applicable for sugar determination in commercially available beverages.

By using some NMR spectroscopies including DOSY-NMR, the interaction of water-insoluble food compound (*e.g.*, hesperidin) with polyphenols was investigated. Among polyphenols *i.e.*, caffeine, (−)-epigallocatechin-3-*O*-gallate, theasinensin A and B (TSA and TSB), TSA was the most significant to improve hesperidin solubility ($P < 0.05$), by approximately 3-fold at Hesp-TSA (hesperidin and TSA) of mole ratio 1:10 in 10% DMSO. The combination of hesperidin with TSA caused changes for chemical shift ($\Delta\delta$: 0.01 - 0.27 ppm) and D value (ΔD: 0.66 - 1.32×10-^{10} m^2/s) of hesperidin at Hesp-TSA of mole ratio 1:1 to 1:10 in 10% DMSO-d_6. The rotating frame nuclear Overhauser effect (ROE) correlation signals between hesperidin and TSA, as well as the quantum mechanical calculation characterized the proximity of B ring in hesperidin to the space between B, G rings in TSA. Structure of two hesperidin molecules stably complexed with one TSA (2:1 complex) with the ΔG of -23.5 kJ/mol in water, involving in enhanced solubility of hesperidin by TSA.

In conclusion, the NMR spectroscopy was applied to a wider range in food analysis. In the quantitative way, DOSY-qNMR was successfully used to determine D-(+)-glucose and sucrose respectively in commercially available beverages. In the qualitative way, NMR techniques, combined with theoretical analysis, comprehensively clarified the mechanism of solubilization of hesperidin through interaction with TSA. The present study increases the perspective of NMR techniques for the evaluation of food quality.