Review Article
Food Science and Technology

ISSN 0101-2061 (Print)
ISSN 1678-457X (Online)

DOI: https://doi.org/10.1590/fst.43622

Application of nuclear magnetic resonance in food analysis

Qian QU[1], Lan JIN[1*]

Abstract

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful techniques to analyze sample components, determine the structures of compounds and study chemical reaction processes. NMR is a rapid and noninvasive analytical method that was initially used to study moisture in food. The structural composition of food can be determined by analyzing the components of oil, protein and carbohydrates. The combination of NMR and multivariate statistical data has become increasingly popular in the field of food science. However, due to its low sensitivity and imperfect technical knowledge, NMR still has great development potential in the field of food science and very bright prospects. This review focuses on the application of NMR in food analysis, including oil, red wine, honey, milk, fruits and vegetables. NMR can quickly identify various compounds, distinguish the geographical origin of species, assess food quality, reveal various fraud behaviors, and predict the shelf life of food.

Keywords: NMR; food science; multivariate statistical analysis; food quality.

Practical Application: Focus on NMR in oil, red wine, the application of the honey, milk, fruit and vegetables.

1 Introduction

Food science is a discipline covering a wide range of fields. It integrates basic subject theories, including applied biology, chemistry, physics, medicine, and engineering, to study the nature of food, the cause of deterioration, the principles of processing, and the transformation of food. Foods are particularly complex matrices containing thousands of ingredients, which is the result of metabolic processes during plant growth and food processing. To make matters more complicated, the composition of food is also related to genetic and geographical sources, environmental and climatic conditions, and differences in farming types, feeding and processing methods (Consonni & Cagliani, 2019). The main components include water, lipids, proteins, carbohydrates, phenols, amino acids and minerals (Hatzakis, 2019). These ingredients determine the nutrition, taste, color and quality of food, while chemical reactions may also occur during storage, transportation, and processing, as well as the addition of flavoring agents to change the composition of food (Kim et al., 2016). As the basic physiological and biochemical energy source of human beings, in recent years, the nutrition and quality of food have received more attention, including flavor and taste, shelf life, type, origin, year and so on. Therefore, it is becoming increasingly important in the food industry to choose appropriate methods to analyze the composition of food, monitor changes in the internal composition of food after multiple processing and transportation steps, and predict the shelf life of food.

Nuclear magnetic resonance (NMR) is a spectroscopic method used to determine the molecular structure and physical properties of substances. NMR was initially applied in the field of physical science and then widely used in chemistry, biology, medicine and other fields. NMR was employed in food science as early as 1957, when low-field NMR was used to measure water in food (Alberti et al., 2002). Due to immature technical theory, low sensitivity and high equipment expenses, NMR was not widely used in food analysis before the 1980s. With the application of Fourier transform spectroscopy, the appearance of superconducting magnets, the progress of probe technology and the continuous development of high-throughput technology, NMR has achieved good results in the evaluation and analysis of various foods, including oil, vegetables, wine and dairy products (Dais & Hatzakis, 2013).

High-resolution NMR is mainly used to obtain frequency domain spectra to record the structural information of compounds. Low-resolution NMR, also known as low-field NMR (LF-NMR), mainly reflects the motion properties of specific protons in the sample by measuring relaxation time T_1/T_2 and diffusion coefficient D and provides information about the physical and chemical environment of the sample. MRI is based on changes in relaxation time and water distribution and mobility in food (Hills et al., 2005; Bertocchi & Paci, 2008; Li et al., 2014; Ebrahimnejad et al., 2018).

In addition, the development of multivariate statistical analysis methods provides an irreplaceable role for the application of NMR in food, and stoichiometry has made NMR a very powerful tool for comprehensive and impartial assessment. Principal component analysis (PCA) in unsupervised pattern recognition technology uses a small number of variables to explain most of the variation. Partial least squares discriminant analysis (PLS-DA) is used to purposefully investigate the established categories of specific variables in the discrimination calibration set. Linear discriminant analysis (LDA), artificial neural networks (ANNs) and independent component analysis (ICA) also have great

---

Received 28 Mar., 2022
Accepted 13 May, 2022

[1] *Shandong Key Laboratory of Carbohydrate Chemistry and Glycobiology, National Glycoengineering Research Center, Shandong University, Qingdao, Shandong, P. R. China*
*Corresponding author: lanjin@sdu.edu.cn

development potential in food assessment (Trygg et al., 2007; Rohman & Windarsih, 2020).

In this review, we present the progress of the application of NMR in food science, mainly focusing on research utilizing some specific foods in the past decade, such as wine, olive oil, honey, etc., including the origin, variety and year identification of food, as well as the quality.

2 Edible oil

Fats and oils are widely found in nature and play a very important role in daily life. The main nutritional components of edible oil are fatty acids, mainly composed of unsaturated oleic acid, linoleic acid, linolenic acid, saturated palmitic acid and stearic acid (Yang et al., 2013). The different compositions of edible oil lead to variations in health benefits, aroma and taste, which also easily cause adulteration (Buckland & Gonzalez, 2015). NMR has been widely used in the analysis of edible oil, playing an important role in identifying the origin of fats, monitoring the oxidation process, determining the oil content of foods or oils, monitoring the quality of frying oil, and identifying adulteration of edible fats (Gómez-Alonso et al., 2007; Girelli et al., 2016; Ferreiro-González et al., 2017).

3 Geographic and plant origin

In the past few years, studies have explored the sources of olive oil through multivariate analysis based on NMR data. ^{13}C NMR provides valuable insights into the location distribution of fatty acids in glycerol and the stereochemistry of unsaturation. ^{1}H NMR provides useful information about fatty acid composition, degree of unsaturation, lipid category and various minor compounds (sterols, squalene, terpenes, VCs, etc.) (Figure 1) (Lioupi et al., 2020).

In Domenico Rongai's research, ^{1}H NMR spectroscopy was used to analyze a collection of extra virgin olive oil from different geographical areas. PCA and OPLS-DA revealed the main differences between Italian and Tunisian virgin olive oil samples. Tunisian oil can be characterized by a relatively high content of polyunsaturated fatty acids (such as linolenic acid) (Rongai et al., 2017). The results indicated that the metabolic map based on NMR may be used to predict the geographic origin of olive oil and evaluate the possible correlation with climate data.

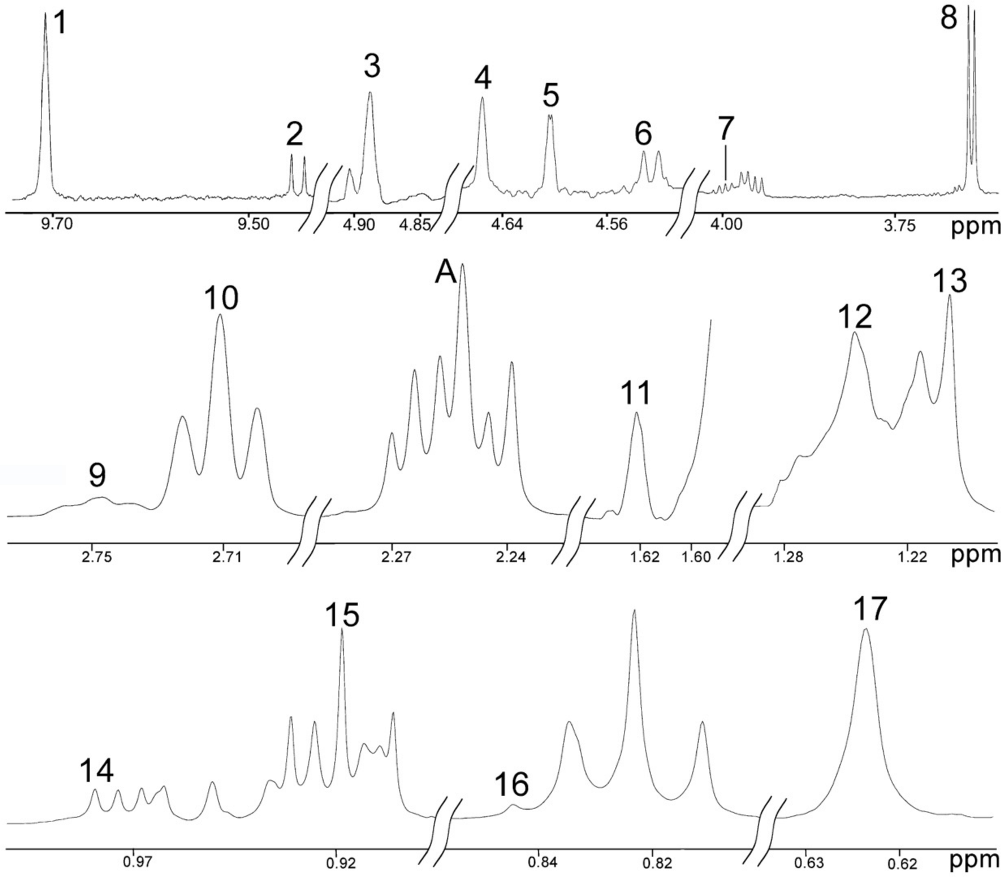

Figure 1. 600.13 MHz 1H NMR spectra assignment of extra virgin olive oil. Peaks: 1, hexanal; 2, trans-2-hexenal; 3-6, terpene; 7, methylenic protons inR-glycerol moiety ofsn-1,3-diglycerides (3.988 ppm); 8, methylenic protons in R-glycerol moiety of sn-1,2-diglycerides; 9, 15, protons of linolenic fatty chains; 10, 16, protons of linoleic fatty chain; 11, squalene; 12, methylenic protons of all unsaturated fatty chains; 13, methylenic protons of palmitic and stearic fatty chains; 14, wax; 17, methyl-18 of β-sitosterol; A, reference peak due to methylenic protons bound to C2 normalized to 1000 (D'Imperio et al., 2010) with reprint permission from American Chemical Society.

Euroun and OK et al. used ANOVA to analyze the ^{1}H MRI signal intensity of olive oil. Different percentage compositions of linoleoyl groups were found in olive oil samples from five distinct geographical regions in Turkey (Ok, 2014). The fatty acyl content of olive oil samples from three regions of Turkey (Marmara, Aegean, and Mediterranean) was also screened. Analysis of variance showed that the three samples could be clearly distinguished, and the best discriminant parameter was the ^{1}H signal of oleoyl content. These results indicated that some compounds may distinguish oil based on geographic origin on a regional level (Ün & Ok, 2018).

The fatty acids in olive oil contribute to the features of olive oil sources, while NMR spectra of phenolic extracts can provide very interesting information about the geographical origin of the samples (Laincer et al., 2016). Alexia et al. used ^{1}H and ^{31}P NMR to chemically analyze olive oil samples from four districts in Greece. The results showed that the distribution of phenolic compounds in olive oils from different varieties and production areas was quite different. Nine phenolic compounds and 2 fatty acids (linolenic acid and linoleic acid) were the most important predictors (Agiomyrgianaki et al., 2012).

Different plant sources of edible oil have similar compositions but unique characteristics. The combination of NMR and multivariate statistical analysis provides good feasibility for identifying the source of vegetable oil. The ultrahigh-speed 2D NMR method applied by Gouilleux on a 43 MHz low-field NMR spectrometer was used for the identification of edible oils. PCA highlighted the obvious differences among olive oil, hazelnut oil, sesame oil, rapeseed oil, corn oil and sunflower oil. The experiment compared the effectiveness of 2D and 1D spectra in the classification of vegetable oils. It was obvious that the 2D spectrum avoids the overlap of peaks, the peak intensity of unsaturated fatty acids was enhanced, and it could even be distinguished by visual comparison (Gouilleux et al., 2018).

Ting Shi et al. established a method for the simultaneous determination of squalene and various sterols in different vegetable oils (including camellia oil, corn oil, soybean oil, rapeseed oil, extra virgin olive oil and sunflower oil) based on ^{1}H NMR spectroscopy combined with the PLS method. The signal intensity of the secondary components (diglycerides, squalene and sterols) in the ^{1}H NMR spectrum was different in various vegetable oils. The high accuracy of the PLS model of phasostanol and stigmasterol was similar to that of GC-MS analysis (Shi et al., 2019).

^{1}H and ^{13}C NMR have been successfully applied to analyze refined edible oils from seven plant sources, including sunflower seeds, rapeseed, sesame, soybeans, peanuts, corn and olive oil. Various fatty acids, such as oleic acid, linoleic acid and linolenic acid, in edible oil and their iodine values could be accurately quantified, and their plant sources were identified by PCA (Zhang et al., 2018).

4 Monitoring oil oxidation

The fats in vegetable oils, especially unsaturated fatty acids, can decompose into different oxidation byproducts over time, thereby affecting the safety, nutritional value and sensory properties of the oil (Alberdi-Cedeño et al., 2019). NMR has been used to identify these oxidation products, including primary oxidation products such as hydrogen peroxide and conjugated dienes and secondary products such as aldehydes, ketones, epoxides, alcohols, dimers, polymers and their derivatives (Hwang, 2017). The process of storage, packaging and transportation of edible oil is usually carried out at storage temperatures, and the rates of oxidative degradation and yield are very low. In general, only primary oxidation occurs, and the concentration of the primary oxidation product can be used to measure the oxidation of grease (Gray, 1978).

Zhu used ^{1}H NMR to assess the oxidation process of cold-pressed tea oil, commercial refined tea oil, and extra virgin olive oil (EVOO) stored at room temperature for a one-year period. As the storage time increases, the signal intensity of the conjugated diene ion increases, while the signal of the unsaturated acyl group decreases, indicating that the oxidation effect gradually increases. The order of the degree of oxidation of the three oils is refined camellia oil > cold pressed camellia oil > EVOO. A characteristic aldehyde signal was not detected in all samples, which indicated that no secondary oxidation process occurred after storage at room temperature and natural light for more than 12 months (Zhu et al., 2020). Rosa also studied the stability of virgin olive oil (VOO). During 3 years and 7 months, the ^{1}H NMR signal only slightly changed, indicating that VOO began to undergo certain oxidation and hydrolysis degradation after one year, but no secondary degradation occurred (Alonso-Salces et al., 2011). These results confirm that VOO has high oxidation stability at room temperature, and ^{1}H NMR spectroscopy can accurately predict the shelf life index of vegetable oils (Tanno et al., 2020). For refined vegetable oils, antioxidants such as tocopherols, phytosterols, and polyphenols are removed or degraded through several steps of degumming, neutralization, bleaching and deodorization, and the antioxidant capacity is reduced (Fine et al., 2016).

Fried food tastes good and is popular, but high-temperature frying more easily destroys the nutritional value and forms harmful substances than other cooking methods. The peroxide formed by the oxidation of unsaturated fatty acids is easier to decompose into other secondary oxidation products at high temperatures, especially carbonyl compounds, which can cause rancidity.

Jiang et al. used NMR to quickly determine the degree of deterioration of soybean oil during frying. After 28 h of frying, ^{1}H NMR results showed that the content of linolenic acid and linoleic acid decreased, while the unsaturated fatty acids were easily oxidized during frying (Aladedunye & Przybylski, 2014). The content of hydrogen peroxide first increases and then decreases, forming secondary oxidation products such as aldehydes and ketones. There is a high correlation between the formation of aldehydes (normal alkanes, (E)-2-olefins, (E, E)-2,4-olefins) and total polar compounds; therefore, ^{1}H NMR can be used to monitor soybean oil for deterioration in the bombing process (Jiang et al., 2018).

In another study, Hwang et al. analyzed various signal changes during heating and frying at 180 °C. The content of linoleic acid and linolenic acid decreased greatly, and no signal of hydroperoxides was detected, while the signal corresponding to various aldehydes was observed. The signal changes of protons of alkene (RAO), diallyl acid (RAB = RAD) and allyl group (RAA) relative to those of fat have been determined. These results are highly correlated with conventional analytical methods, indicating that the NMR method can be used as an effective tool for evaluating lipid oxidation (Hwang et al., 2017).

5 Adulteration

Unqualified edible oil will inevitably introduce various harmful substances in the process of recycling and refining. When this oil is mixed into qualified oil or illegal additives are added, it will seriously affect the health of consumers. Quality indicators such as water content, hydroxyl value and acid value can be used to identify unqualified edible oils. Another method of adulteration is to mix pure edible oil with lower-cost alternatives or vegetable oils from different origins; for example, sesame oil is mixed with rapeseed oil, and olive oil is mixed with hazelnut oil (Agiomyrgianaki et al., 2010).

Recently, a MATLAB script expert system was established based on the NMR characteristic peak data of various pure edible oils. The available quality parameters include the contents of linolenic acid, linoleic acid, oleic acid, saturated fatty acid (SFA) and iodine values, acid values, hydroxyl values and carbonyl values. According to the relevant quality parameters, the accuracy rates of the origin identification of the pure and mixed edible oil are 95.83% and 89.58%, and the recovered edible oil and frying oil have been correctly screened and identified. Therefore, the expert system based on ^{1}H NMR is a faster, more accurate and convenient tool, which has great potential for identifying the adulteration of edible oil (Cai et al., 2019).

LF-NMR and support vector machines (SVMs) can be used as new methods for the rapid screening of pure and mixed olive oil. LF-NMR detects the difference in edible oil based on the T_2 distribution, and the oleic acid content and viscosity will affect the decay behavior. According to the variation of the decay curve with the mixing ratio, the SVM is used to establish the identification and classification model. The results show that pure EVOOs and mixed EVOOs can be distinguished well. When the doping rate is above 10%, the classification accuracy rate reaches 84.92%. This method is also applied to the prediction of seed oil grade and type (Wang et al., 2020).

Daniel studied the effectiveness of high-field and low-field NMR techniques in the identification of binary adulteration in cold pressed rapeseed oil (CPRO). The region of a specific fatty acid group can be clearly identified in the 400 MHz spectrum, while in the 60 MHz spectrum, it is less obvious. PLS showed that the classification accuracy of 400 MHz NMR was 100% and 93% in the case of single and multiple dopants, respectively. 60 MHz NMR has a low classification rate, but it can still classify CPRO that may be adulterated (McDowell et al., 2019).

6 Wine

Wine is a very popular fermented alcoholic beverage that is mainly composed of water, ethanol, glycerin, sugar, amino acids, organic acids and bases and inorganic ions (Table 1) (Nilsson et al., 2004; Du et al., 2007). The above chemical components directly affect the quality and flavor of wine. According to a metabolomics research report, wine metabolites are mainly affected by climate, soil, viticulture methods, grape varieties and winemaking processes (Amargianitaki & Spyros, 2017). The chemical analysis of complex mixtures such as wine and other beverages is becoming very important. NMR is used qualitatively and quantitatively to characterize these chemical components, distinguishing wine based on grape variety, geographic origin and year of production.

7 Variety and origin

The minor components of wine play an important role in identification, but the signals of water and ethanol in the ^{1}H NMR spectrum must be eliminated, which can be achieved by freeze-drying or preconcentration with inert gas flow or by various multiple suppression NMR techniques (Esslinger et al., 2015). Therefore, enhancing the detection of NMR signals of minor compounds present in wine promotes their identification.

Samples of Cabernet Sauvignon and Shiraz red wine brewed in 2016 in Shanxi were studied by NMR. The metabolites of the two varieties were significantly different for the components proline, tartaric acid, glycerin, lactic acid, choline, succinic acid and gallate acid. Combining PLS-DA could successfully distinguish these two kinds of wines, with more accurate prediction (Zhu et al., 2018). PLS-DA was also used together with ^{1}H NMR spectroscopy to analyze several protected design of origin (PDO) lamblucco wines. The results showed that Sobala wine was different from other types of wine, and the key discriminators were 2,3-butanediol, lactic acid, succinic acid, threonine and malic acid (Papotti et al., 2013).

Recently, a study conducted NMR analysis on Czech wines. In the chemical shift range from 0.8 to 4.0 ppm, peaks of alcohols, aliphatic organic acids and amino acids could be observed. The region 4.0-6.0 ppm is considered to be the signal of carbohydrate protons, and 6.0-8.5 ppm is the aromatic signal. The combination of proton spectrum and multivariate statistics can simultaneously classify each wine type and wine grape

Table 1. ^{1}H NMR of main components in wines (Son et al., 2008).

	Compound	^{1}H Chemical shift (ppm)
Organic acid and Diol	2,3-butanediol	1.13, 3.61
	Acetic acid	2.08
	Citric acid	2.79, 2.91
	Glycerol	3.56, 3.76, 3.78
	Gallic acid	7.15
	Lactic acid	1.38, 4.29
	Malic acid	2.73, 2.86, 4.46
	Succinic acid	2.64
	Tartaric acid	4.51
Amino acid	Alanine	1.48, 3.80
	Proline	2.0, 2.07, 2.35, 3.33, 3.41, 4.12
	valine	0.87, 0.93
Sugar	α-Glucose	4.64
	β-Glucose	5.23

variety with high accuracy (Mascellani et al., 2021). Dana et al. developed a method in which buffer was added to wine samples to perform similar pH adjustments to preserve the ^{1}H NMR spectrum of individual wines as much as possible. It was found that the spectral region of 5.1-9.8 ppm had the highest potential for geographical and variety resolution and was also the most effective indicator (Magdas et al., 2019).

^{1}H NMR spectrum analysis combined with multiple steps of multivariate statistical analysis was used to distinguish the highly predictable grape varieties in five wine-producing regions of Germany. The accuracy of the classification prediction for the year was 97% in 2008 and 96% in 2009. The quality of wine was also strongly affected by the geographical area where the grapes were grown. Multivariate statistical analysis could reach an accuracy of 89% for the prediction of wines from different regions (Godelmann et al., 2013). Gougeon et al. established an NMR-based metabolomics method that can quantify 33 metabolites, including sugars, amino acids, organic acids, alcohols, and phenolic compounds. The contents of proline, phenylethyl alcohol, gallic acid or succinic acid may be related to the variety. Soil and cultivation measures also play an important role. For wines from different production areas, the classification rate ranged from 71% to 100%. The results showed that NMR-based metabolomics combined with multivariate statistical analysis could distinguish wines according to terrain, variety and year (Gougeon et al., 2019a; Xu et al., 2021).

8 Fermentation and aging

Although grapes provide the basic chemical components of wine, most chemicals found in wine are produced by the metabolic activities of yeast and lactic acid bacteria during the winemaking process (Hong., 2011). The transformation of histidine and malic acid fermentation during wine alcohol fermentation were monitored by NMR. Histidine was transformed into histamine alcohol during alcohol fermentation, and histamine was converted into histamine during malic acid lactic acid fermentation. However, histamine production can be avoided by using lactic acid bacteria in the malic acid lactic acid fermentation process (López-Rituerto et al., 2013).

Mazzei et al. used ^{1}H NMR spectroscopy to analyze the differences in wine metabolites caused by commercially available yeast starters and selected self-produced Saccharomyces cerevisiae starters, which can accurately and effectively distinguish wines fermented with different yeast starters (Mazzei et al., 2013). Nardi et al. studied the effects of nonyeast bacteria and different malolactic fermentation management methods on the quality of Barbera red wine in alcohol fermentation. ^{1}H NMR spectroscopy combined with multivariate statistical analysis determined the main changes in metabolites in the AF and MLF processes. The combined use of nonyeast bacteria will not interfere with the fermentation of alcohol and malolactic acid and can produce wines with richer flavor and richness (Nardi et al., 2019).

Another study used ^{1}H NMR and metabonomics studies to identify organic and biodynamic wines. The chemical shift region at 0.8-4.0 ppm was related to amino acids and organic acids, and phenols were in the special spectral region of 5.5-8.5 ppm. The organic brewing scheme had a high concentration of tyrosine and resveratrol and a low content of trans-caffeic acid. The results showed that the production year and winemaking plan have a greater impact on the metabolic characteristics of wine (Laghi et al., 2014).

Wine aging refers to the beginning of winemaking, after bottling, and continuing until drinking. In addition to the color change, this process also improves the sensory (smell and taste) characteristics of the wine. The polyphenols in wine cause their different tastes and colors. During the aging process of wine, slow condensation and oxidation reactions will occur, leading to the conversion and precipitation of polyphenols, forming oligomeric and polymeric derivatives (Saucier et al., 1998).

Solid-state NMR was used to quantitatively evaluate the precipitates obtained in Bordeaux wine from 2012 and 2013 at - 4 °C or 4 °C for 2-6 days, and the change in the sediment within one year was monitored. At low temperatures, vintage 2012 produced much more precipitation than 2013. The sediment mainly contained potassium tartrate, polyphenols, a small amount of polysaccharides, organic acids and free amino acids, and tartaric acid plays an important role in the stability of wine. This might indicate that the amount of precipitation obtained depends on the year, temperature and grape variety and has little to do with the degree of aging (Prakash et al., 2016).

Analysis of 10 different wines after being bottled for 3 months and stored at 12 °C for 48 months showed that ^{1}H NMR spectrum combined with statistical analysis can distinguish the samples in the two aging stages. Wine aging could also cause subtle changes in metabolites. Organic acids such as lactic acid, succinic acid and tartaric acid were observed to decrease during the aging process, while ethyl acetate and ethyl lactate increased. The content of catechin and epicatechin in polyphenols was reduced, while gallic acid was increased in almost all red wines, which might be due to the hydrolysis of tannins (Cassino et al., 2019). Although the sensitivity of NMR metabolic analysis is lower than that of other analytical methods, it is helpful to comprehensively describe the evolution of wine.

9 Adulteration

Adulteration refers to all kinds of fraudulent behaviors, such as diluting wine with water, adding alcohol, pigment and seasoning, mixing or replacing wine with low-quality wine, and mislabeling, that is, fraudulently distorting varieties and geographical sources (Versari et al., 2014).

In a real case of wine certification, a multitechnical method and q-NMR method were used to compare authentic wine and suspicious wine. The contents of succinic acid, acetaldehyde, inositol and isoamyl alcohol were different in sample B, while methanol, gallic acid, glucose and threonine were different in sample C. Fake wine and genuine wine did not seem to come from the same grape variety (Gougeon et al., 2019b).

NMR was used to characterize single binary mixed wine. LDA gave a good separation effect for several kinds of mixed wine. On the other hand, a single-layer artificial neural network was used to predict the relative content of liquor in the mixture, and the accuracy was approximately 10% (Imparato et al., 2011).

Kubala and his team analyzed suspected liquor samples from Russia and Kenya by ^{1}H NMR and compared them with authentic liquor samples. The results showed that the counterfeit products in Russia were added with some flavorings and colorants on the basis of diluted alcohol. In fake vogat, the content of methanol was 16 times higher than that of genuine vogat. In the Kenyan sample analysis, the counterfeit product added sweetener glycerin and a small amount of higher alcohol (Kuballa et al., 2018).

The structures of various compounds in Scotch whisky were characterized by 1D and 2D NMR, and the Scotch whisky was classified by PCA and OPLS-DA. Blend and malt whisky were classified correctly, and 3-methylbutanol was the key to classification. In the test of the genuine and fake whisky, the fake whisky contained glycerol and sugar, and the content of vanillin was too high. These substances are used as discriminant quantities to successfully distinguish genuine and fake whisky samples (Kew et al., 2019).

As the world's leading provider of analytical technology, Bruker launched the FoodScreener™ innovation platform based on NMR technology. The Wine-Profiling™ module database on the NMR FoodScreener™ platform contains nearly 26,000 samples, including 22 grape varieties from countries such as France, Italy and Spain. By comparing the spectral fingerprints of each sample with those of a large database of authentic wine samples, questions about composition, geographic origin, grape variety and vintage can be answered. In addition, the platform can quickly and accurately determine the authenticity of products such as honey, wine and fruit juice, and other related solutions such as olive oil are being developed (Bruker, 2020).

10 Honey

Honey, derived from various plant secretions, is a highly praised natural product produced by bees that possesses very high nutritional value and rich bioactive compounds (Consonni et al., 2019). Sugar is the main component of honey, accounting for approximately 95% of the dry weight of honey. The composition of sugar determines the physical and chemical properties of honey. A large amount of fructose and glucose results in sweetness similar to granular sugar (Cavia et al., 2002; Ball, 2007). However, there are also some minor components, such as proteins and enzymes, amino acids, minerals, vitamins and polyphenols, that contribute to the sensory and biological properties of honey (Zheng et al., 2016; Consonni et al., 2019). The taste, aroma and nutritional value of honey are also closely related to their plant and geographic origin. Honey is a food that is often adulterated. Therefore, the control and characterization of honey quality and source is of great significance in beekeeping.

11 Plant source

The composition of honey is diverse and closely related to its plant origin. Sugar accounts for approximately 60-80% of the total honey quality, and there are no significant differences among different varieties of honey. However, the content of secondary components in honey varies greatly from one flower source to another. Ren et al. distinguished the botanical sources of single-flower honey based on the nonsugar components (NSCs) present in honey. The NSCs in 50 honey samples were determined and compared. Among them, jujube honey has the highest NSC content, followed by acacia honey, and the lowest is pure honey (Ren et al., 2019).

The ^{1}H NMR fingerprint can accurately distinguish three different single-flower honey samples. In addition, this method has been proven to identify other typical botanical origins in China. The application of chemometrics to ^{1}H NMR spectroscopy can distinguish eucalyptus, citrus and wildflower honey produced in Sao Paulo and characterize specific identification signals. Eucalyptus honey contained more lactic acid, wild flower honey had higher phenylalanine and tyrosine contents, and citrus honey contained more sucrose. KNN, SIMCA and PLS-DA pattern recognition models were used to correctly classify all samples (Boffo et al., 2012).

In addition, the main source of phenolic compounds in honey is plants, and phenolic compounds have been proven to be an effective method for studying honey flowers. Salgueiro and his partners used XAD-4 resin to prepare 53 kinds of honey extracts rich in polyphenols. ^{1}H NMR spectra and multivariate analysis were used to detect possible flower sources. Samples of eucalyptus honey, citrus honey and campal honey were successfully identified (Salgueiro et al., 2016). Myricetin, cephalotaxine, luteolin, quercetin, kaempferol and other benzoic acid derivatives were considered flower markers of eucalyptus honey, while quercetin, hesperidin and chrysin were described as potential markers for citrus honey (Kaškonienė & Venskutonis, 2010).

Schievano and his team established an OPLS-DA classification model based on the NMR spectra of chloroform extracts from different plant samples. Due to the special characteristics of the chloroform spectrum, these characteristics showed the diagnostic resonance of almost every botanical source (Schievano et al., 2016). The markers of Acacia honey were chrysin and pineal membrane protein. The six resonances of the orange honey model were all derived from caffeine and 8-hydroxylinalool. The signal for identifying eucalyptus honey comes from dehydroemetic leaf alcohol, and all seven signals of chestnut honey fall in the region of 7.90-8.50 ppm (Schievano et al., 2012). This technique successfully predicted the primary and secondary flower origins in honey samples and verified the authenticity of single flower honey.

12 Geographical origin

The composition of honey varies naturally depending on different climate and environmental conditions. Several compounds have been found and used to determine their geographical and botanical sources. A new method for the simultaneous quantification of 13 metabolites in honey, including acids, amino acids, sugars, ethanol and hydroxymethylfurfural, has been proposed (Campo et al., 2016).

The organic extract of honey contains specific markers of each plant origin, which can usually be identified by simple visual inspection of NMR spectroscopy. Schievano's research proposed a method based on the NMR metabolic analysis of organic extracts to identify Acacia honey geographically. The NMR spectrum of this extract successfully achieved a geographical distinction between Italian and Eastern European Acacia honey, with an overall correct classification rate of 100% (Schievano et al., 2019).

Based on NMR and HPLC, the geographical identification of honey from pine and fir trees produced in Greece was carried out. The sugar, free amino acid and organic acid contents, as well as the water and sugar ratios or sugar/water ratios in honey, provided useful information about geographical origin. The two discriminant functions could distinguish honey from different regions in Greece, and the prediction accuracy was 76.9% and 80.6%, respectively (Karabagias et al., 2018).

Consonni et al. applied OPLS-DA to selected spectral regions in the ^{1}H NMR spectrum to geographically identify honey from three different flower sources based on the sugar content. The results showed that honey from China, Hungary, Italy and South America demonstrated surprising variance (Consonni et al., 2013).

13 Adulteration

Due to its health and unique flavor characteristics, the increased demand for honey has led to the adulteration of different syrups. Various cheaper sweeteners, such as refined sucrose, beet sugar, HFCS (high fructose corn syrup) and maltose syrup, were added. It has become very common to adulterate honey by feeding bees sugar or syrup. Mistaken labeling of honey of botanical or geographical origin also occurred (Guler et al., 2014).

Pure honey and honey with different proportions of corn syrup with high fructose were studied by low-field NMR and physicochemical analysis. There were obvious differences between adulterated and pure nectar in water, pH, water activity, ash content and color. The concentration of dopant in pure honey significantly affected the relaxation time. The higher the fructose syrup concentration was, the shorter the relaxation time was. Therefore, LF-^{1}H-NMR can distinguish different proportions of adulteration (Ribeiro et al., 2014).

Recently, due to the similar appearance and taste of rice syrup and honey, adulteration in the honey market has increased rapidly. The ^{1}H NMR spectra of honey and brown rice syrup (BRS) were studied by PCA. It was found that there was a characteristic peak at 5.39 ppm to identify BRS. The quantitative determination of BRS in two commercial honey samples was successfully carried out by using ^{1}H q-NMR. The detection accuracy was 22.3% and 37.3%, and the precision was 0.1-1%. This method has sufficient accuracy and precision within the estimated concentration range and is faster and simpler (Musharraf et al., 2016).

Spiteri et al. used proton NMR analysis to solve the problem of adulteration and quality deviation in honey. Combined with appropriate quantitative procedures and statistical models, when the labeled peak was present in the adulterants, the results showed that the lowest detection limit was approximately 10% (Spiteri et al., 2015). According to the spectrum, Manuka honey could be distinguished from other flower types according to methylglyoxal and dihydroxyacetone, and "pure manuka" and mixture could also be distinguished (Spiteri et al., 2017).

In another study, high-resolution NMR technology was used to identify and quantitatively analyze 65 components in honey. Combined with multivariate statistical analysis methods, the accuracy of the identification of adulterated honey and genuine honey was 97.6%. Proline, xylobiose, uridine, β-glucose, maltose, furanose and lysine have a significant contribution to the identification of adulterated honey (He et al., 2020).

Recently, a new NMR method based on CSSF-TOCSY experiments was proposed. The method, without pretreatment, quantifies 22 common sugars in water-soluble raw honey samples. In the detection of chestnut honey, there was a large difference between normal honey (black trace) and honey supplemented with raffinose (red trace) (Figure 2). Unlike ^{1}H NMR, the CSSF-TOCSY spectra could clearly observe the additional signal of raffinose, making it easier to identify honey adulteration (Schievano et al., 2017).

Bruker introduced the latest version of the NMR Honey-Profiling™ module for advanced detection of changing honey adulteration patterns. The new module expands the growing database to 28,000 honey reference samples, covering more than 50 countries, 100 single-flower species and many multiflower species. Based on Honey NMR fingerprints obtained by Bruker NMR Honey-Profiling™, the Worker Bee Honey Co project is working to generate a Honey NMR database for all parts of British Columbia, Canada. By comparing the NMR spectrum of the honey sample with the database, the matching of the real honey pattern can be confirmed (Bruker, 2021a).

14 Milk

Milk is popular among consumers because of its sensory quality and high nutritional value. The main components of milk are polysaccharides, proteins, phospholipids and minerals,

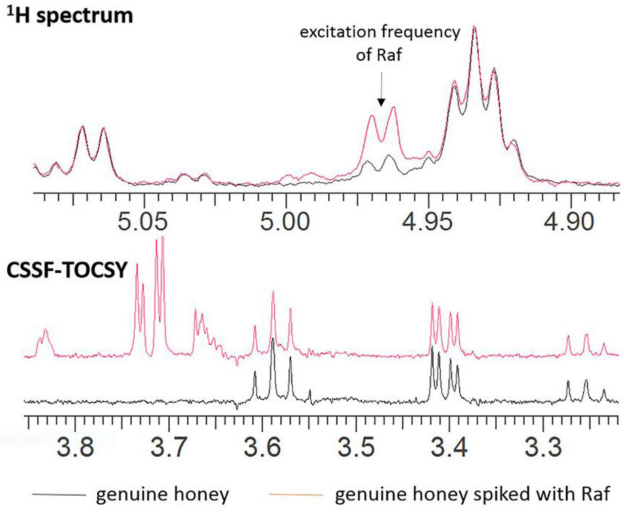

Figure 2. Top: conventional ^{1}H spectra of chestnut honey. Bottom: CSSF-TOCSY spectra of chestnut honey resulting from excitation at the frequency indicated. The black and the red traces refer to the genuine and the raffinose-spiked samples, respectively (Schievano et al., 2017) with reprint permission from American Chemical Society.

which contain a large number of fat particles, resulting in the emulsion of the sample, affecting the magnetic field uniformity and reducing the resolution of the spectrum. As early as 1999, a review described the application of NMR in dairy products, including the physical and chemical properties of milk and other dairy products, and analyzed the properties and conformation of specific milk proteins (Belloque & Ramos, 1999; Markoska et al., 2020). In recent years, NMR has been widely used to study the metabolite spectra of milk and various dairy products, including animal health, milk quality, geographical origin and other aspects (Harnly et al., 2018; Cui et al., 2019; Scano et al., 2019; Markoska et al., 2020; Balthazar et al., 2021).

15 Feeding mode

NMR was used to compare the metabolites in the fat composition of organic milk from Cyprus and ordinary milk. Compared with conventional samples, the contents of conjugated (9-cis, 11-trans) 18:2 linoleic acid (CLA), α-linolenic acid, linoleic acid, allyl protons and total unsaturated fatty acids (UFAs) in organic samples increased significantly. Organic milk can improve the nutritional quality of milk by increasing the composition of fatty acids, which is closely related to the forage and feeding methods (Tsiafoulis et al., 2019).

Refinement of multinuclear NMR results through PCA can determine the metabolome of buffalo milk and distinguish buffalo milk from conventional feed milk or biological feed milk (CFM and BFM, respectively) at the same time. The T_2-edited spectra showed that the BFM sample contained more lactose than the CFM sample, and the BFM milk showed more monounsaturated and polyunsaturated fat in the ^1H diffusion-edited spectra and ^{13}C spectra. Biological feeding patterns affect the composition and sensory and nutritional properties of buffalo milk (Mazzei & Piccolo, 2018). TD-NMR, a low-cost alternative to high-field NMR, has been used to study the molecular mobility of water in solidified and heat-treated whole milk and goat milk during rennet and dehydration, with significant relaxation differences, possibly due to protein-modification interactions associated with heat treatment (Curti et al., 2019).

NMR can also be used to evaluate the metabolic state and nutritional value of milk cows. ^1H NMR was used to analyze dichloromethane-extracted samples to obtain better spectra of two important metabolites, β-hydroxybutyric acid and creatine. This provides important information for the diagnosis of bovine ketosis and various neurological symptoms (Tenori et al., 2018). In addition, the ^1H NMR spectrum of metabolites can distinguish between healthy cows and mastitis cows. Mayuree identified alanine, pentanoic acid and N-acetyl glucosamine and 46 other metabolites in milk, in addition to the published biomarkers for the diagnosis of mastitis (Luangwilai et al., 2021).

Tomassin et al. used the ^1H NMR method to detect changes in the metabolic spectrum of milk during lactation. Combined with PLS-DA analysis, it can distinguish between Friesian milk and native milk secreted for 200-300 days. From 200 to 300 days of milk lactation sampling, N-acetyl-X2 P, galactose, and glucose-1-1-P decreased significantly, while N-acetyl-X4 increased. The results showed that the difference in milk composition in different RACES was closely related to the late lactation period (Tomassini et al., 2019).

16 Dairy

The chemical components of milk powder products are lactose, protein, minerals and fats, as well as vitamins A, B and D. TD-NMR and stoichiometry were used to determine the fat content of several milk powder samples without solvent (Nascimento et al., 2017). Based on the multivariate model of T_2 decay, the fat percentage (g/100 g) in solid milk powder was measured to be 0.75%~26%, and the moisture content was measured to be 1.9%~3.9%. Sanchez et al. conducted a comprehensive characterization of whole fat goat milk powder (GMP), identifying 44 metabolites from fat, sugar, and aromatic regions based on NMR. The main signals of aliphatic (0.5-3.5 ppm) and aromatic (6.0-9.5 ppm) groups correspond to metabolites such as creatine, carnitine, lactose, galactose, lecithin and sucrose. The metabolites corresponding to weak signals, such as lactic acid and equuric acid, were strongly associated with breast infection. These metabolites are very important in identifying GMP quality and characteristics (Sanchez et al., 2021).

Segato et al. used ^1H NMR to identify the water-soluble metabolomics of Alpine Asiago cheese at three maturation times. Lactic acids contributed to the main signals in the ^1H NMR spectra, in addition to some other strong signals, including acetic acid, glycerol, hydrophobic amino acids, ethanol and citric acid. 2,3-Butanediol is one of the hallmarks of ranch cheese because its content disappears with maturity. Lysine was associated with a medium to short ripening period of cheese, and phenylalanine was one of the main indicators of long mature cheese. The results showed that ^1H NMR was an effective method to identify cheese samples with the shortest ripening period (Segato et al., 2019).

17 Adulteration

NMR is a powerful tool to detect the adulteration of dairy products (Mafra et al., 2022). Li et al. used NMR to distinguish cow milk, goat milk and soy milk and to detect the addition of soy milk to the milk samples. Eleven metabolites were identified according to 1D and 2D NMR spectra. Ten metabolites (carnitine, N-acetyl carbohydrate, acetic acid, choline, ethanolamine, citric acid, creatine, lecithin, D-sucrose and D-lactose) were selected as characteristic variables and could be used for PCA classification. In addition, adulteration can meet the needs of daily testing; the LOQ value of adulteration in milk is 2% (v/v), the relative standard deviation of adulteration in soy milk is 2% (v/v), and the adulteration concentration in goat milk is 5% (v/v) (Li et al., 2017).

Santos et al. innovated a method for evaluating milk quality using ^1H TD-NMR. Whey, urea, hydrogen peroxide, synthetic urine and synthetic milk were added to milk at 5%, 15%, 25%, 35% and 50% (v/v), respectively. The analysis of the dispersion index of ^1H TD-NMR relaxation attenuation showed that the milk sample contained only water, and the T_2 relaxation time was significantly different with the change in doping amount (Santos et al., 2016).

High-field ^{1}H NMR spectroscopy and conformance index analysis can clearly distinguish genuine and adulterated skimmed milk powder. For samples containing nitrogen-rich small molecules (melamine and dicyandiamide), the detection threshold was ≥ 0.005-0.05% (w/w). The lowest concentration of milk metabolites for the detection of urea, sucrose and maltodextrin was ≥ 0.5% (w/w). At 5% w/w, the matrix effect of milk metabolites could indirectly indicate adulteration (Bergana et al., 2019). The above results were consistent with the analysis of adulterated milk powder by Harnly and colleagues using proton NMR, which also illustrated the potential of NMR technology in detecting adulterated milk powder.

18 Fruits and vegetables

NMR spectroscopy has been widely used in the characterization of fruits and vegetables (Table 2). All fruits and vegetables have specific components that are closely related to their nutritional value, aroma, taste and biological activity.

18.1 Composition and metabolic changes

^{1}H NMR and 2D NMR spectroscopy were used to study pomegranates in different regions of Iran to improve the ecotype of pomegranates. In the spectrum of pomegranate juice, glucose, sucrose and glucoside were the main components. The main organic acids, citric acid and malic acid, could be used to identify different habitats, which may be related to climate and topography. The amino acid and sugar spectra of pomegranate juice from Pakistan, Fordoss and Kashma are similar, but the total phenol content is obviously different. Phenolic compounds can be used to distinguish the three producing areas (Hasanpour et al., 2020).

Amino acids are the main metabolites involved in cell functions and provide valuable information for distinguishing the plant origin of fruits. Botoran's team identified ten types of amino acids that showed significant differences in different varieties of juice, except for glutamic acid. Based on the amino acid profile, stoichiometric methods (PCA, LDA) can correctly classify juices from different plant sources (Botoran et al., 2019).

The metabolite spectrum of Piemonte Apple was studied by NMR. Fructose seems to be the most abundant among all apple varieties, and the relative contents of glucose and sucrose are highly variable. Piemonte varieties are usually characterized by high content of chlorogenic acid. Di unsaturated fatty acids are the main fatty acids, followed by saturated fatty acids. The contents of phloridin/phloridin, rhamnol and citric acid have great advantages in identifying apple varieties (Matteo et al., 2021).

NMR is also used to detect the changes in metabolites during fruit ripening. It was used to characterize and explain the changes in major metabolites at the four different stages of fruit ripening. During the maturation process, most organic acids used as respiratory substrates to produce ATP were reduced, amino acids were consumed, and starch or sucrose might degrade to fructose and glucose. Phenolic compounds such as vanillin and epicatechin are closely related to the biological activity of black raspberry. NMR provides a very important reference for the medicinal value of black raspberry (Kim et al., 2011).

The 1D and 2D NMR spectra combined with PCA showed the changes in metabolites at five different maturation stages of banana. Sugar, amino acids, organic acids and fatty acids were the main metabolites. The metabolism of carbohydrates and amino acids occurred in five aging stages and affected the quality of bananas. Obviously, the third and fourth stages had better quality. In the fifth stage, dopamine converted to salbutamol, which was also a sign of banana aging (Yuan et al., 2017). NMR spectral data provide objective standards for fruit ripening and senescence.

18.2 Water activity

The water activity of food determines its stability, and the measurement of water activity is crucial in food, especially during the drying process. Fruits and vegetables contain a large amount of water, which affects metabolism and growth. Measuring the dynamic changes in water helps to elucidate the growth, storage and deterioration of fruits and vegetables from a microscopic perspective. Recently, Lv innovated a microwave vacuum drying (MVD)-low field nuclear magnetic resonance (NMR) device to evaluate the moisture status of vegetables. Signal amplitude T_2 was used to reflect the state of water. Each vegetable had a different water distribution, among which free water was the main water type lost during MVD. Although the signal amplitudes of bonded water, fixed water, free water and whole water (A2) in different drying stages are greatly correlated with the water content, only A2 can be used to determine the end time of drying by a linear fitting model (Lv et al., 2017).

LF-NMR spectroscopy was used to monitor the changes in the water state during the drying process of several fruits and vegetables. Drying led to a decrease in water activity and a shift

Table 2. Key applications of NMR in analysis and structural characterization of fruits and vegetables.

Food	Research objective	NMR method	Multivariate analysis	Reference
Apple	antioxidant capacity of dehydrated apple	^{1}H NMR	ANOVA, PCA	Francini et al., 2017
Banana	changes of metabolites during banana senescence after harvest	^{1}H NMR, COSY, JRES, HSQC,	PCA	Yuan et al., 2017
Mango	analyze the authenticity of Alphonso mango	^{1}H NMR	local outlier factor	Strecker & Ara, 2022
Tomatoes	distinguish Organic Tomato from conventional tomato	^{1}H NMR	PCA, LDA	Hohmann et al., 2014
Celery	biomarkers of celery metabolites and geographical sources	^{1}H NMR	PCA, PLS-DA	Lau et al., 2020
Sweet orange	identify the components and geographical indications of Chinese sweet orange	^{1}H NMR	PCA, PLS-DA, CV-ANOVA	Lin et al., 2021

of the T_2 peak to the left. The T_2 values of simple dried samples and sugar-treated samples were similar, showing a downward trend, which may be due to the change in sugar state in the drying process to reduce shrinkage. However, salt-treated samples lead to tissue damage, and the T_2 relaxation time becomes longer. The water activity of the samples treated with sugar and salt both decreased, but the effect on T_2 relaxation time was completely different (Chitrakar et al., 2019).

Francini studied the antioxidant capacity and polyphenol content of dried and fresh apples. The contents of total polyphenols in the six kinds of fresh apples were different. The oxygen radical absorbance capacity decreased after dehydration but still had high antioxidant activity. The results showed that antioxidant activity was highly dependent on the content of phenol, and the correlation coefficient was 0.842 ($P < 0.001$) (Francini et al., 2017).

Spin-generated fingerprint profiling (SGF-Profile) is a fruit juice analysis method developed jointly by Bruker and SGF International. The database currently collects spectra of more than 3,000 reference juices, including more than 30 different types of fruit from more than 50 countries. Based on the automatic execution data analysis and report of the SGF-PROFILE system, the main sugars, amino acids, organic acids, acetyl groups, arbutin, benzaldehyde, hydroxymethyl furfural, acetaldehyde, methanol, ethanol and 29 other compounds in apple juice were quantitatively analyzed. In addition, depending on the model used, it can predict the differentiation of fruit and product type, adulteration of added sugar or acid, origin and fruit mixture (Bruker, 2021b).

19 Conclusions

NMR spectroscopy is an important analytical method for the characterization of chemical composition, molecular structure and change of compounds. It is promoting a deeper understanding of food. Its application covers the origin, quality, safety and authenticity of food. NMR is a fast and simple analytical method that has the advantages of accurate measurement and high repeatability and can be applied to all kinds of food. The analysis of NMR data is specialized and complex. Compared with other technologies, the sensitivity of NMR is low, which limits the application of NMR in food detection. Sensitivity depends on the instrument, and the type of probe, magnetic field strength, type of experiment and sample properties all affect the spectral resolution. NMR spectrum databases of certain kinds of food can be very important for data analysis and application. With the further improvement of NMR technology, it will have broader prospects in the field of food science.

References

Agiomyrgianaki, A., Petrakis, P. V., & Dais, P. (2010). Detection of refined olive oil adulteration with refined hazelnut oil by employing NMR spectroscopy and multivariate statistical analysis. *Talanta*, 80(5), 2165-2171. http://dx.doi.org/10.1016/j.talanta.2009.11.024. PMid:20152467.

Agiomyrgianaki, A., Petrakis, P. V., & Dais, P. (2012). Influence of harvest year, cultivar and geographical origin on Greek extra virgin olive oils composition: a study by NMR spectroscopy and biometric analysis. *Food Chemistry*, 135(4), 2561-2568. http://dx.doi.org/10.1016/j.foodchem.2012.07.050. PMid:22980843.

Aladedunye, F., & Przybylski, R. (2014). Performance of palm olein and modified rapeseed, sunflower, and soybean oils in intermittent deep-frying. *European Journal of Lipid Science and Technology*, 116(2), 144-152. http://dx.doi.org/10.1002/ejlt.201300284.

Alberdi-Cedeño, J., Ibargoitia, M. L., & Guillén, M. D. (2019). Monitoring of minor compounds in corn oil oxidation by direct immersion-solid phase microextraction-gas chromatography/mass spectrometry. *Food Chemistry*, 290, 286-294. http://dx.doi.org/10.1016/j.foodchem.2019.04.001. PMid:31000049.

Alberti, E., Belton, P., & Gil, A. (2002). Applications of NMR to food science. *Annual Reports on NMR Spectroscopy*, 47, 109-148. http://dx.doi.org/10.1016/S0066-4103(02)47039-1.

Alonso-Salces, R. M., Holland, M. V., & Guillou, C. (2011). ^{1}H-NMR fingerprinting to evaluate the stability of olive oil. *Food Control*, 22(12), 2041-2046. http://dx.doi.org/10.1016/j.foodcont.2011.05.026.

Amargianitaki, M., & Spyros, A. (2017). NMR-based metabolomics in wine quality control and authentication. *Chemical and Biological Technologies in Agriculture*, 4(1), 9. http://dx.doi.org/10.1186/s40538-017-0092-x.

Ball, D. W. (2007). The chemical composition of honey. *Journal of Chemical Education*, 84(10), 1643. http://dx.doi.org/10.1021/ed084p1643.

Balthazar, C. F., Guimarães, J. T., Rocha, R. S., Pimentel, T. C., Cucineli, R. P. No., Tavares, M. I. B., Graça, J. S., Alves, E. G. Fo., Freitas, M. Q., Esmerino, E. A., Granato, D., Rodrigues, S., Raices, R. S. L., Silva, M. C., Sant'Ana, A. S., & Cruz, A. G. (2021). Nuclear magnetic resonance as an analytical tool for monitoring the quality and authenticity of dairy foods. *Trends in Food Science & Technology*, 108, 84-91. http://dx.doi.org/10.1016/j.tifs.2020.12.011.

Belloque, J., & Ramos, M. (1999). Application of NMR spectroscopy to milk and dairy products. *Trends in Food Science & Technology*, 10(10), 313-320. http://dx.doi.org/10.1016/S0924-2244(00)00012-1.

Bergana, M. M., Adams, K. M., Harnly, J., Moore, J. C., & Xie, Z. (2019). Non-targeted detection of milk powder adulteration by ^{1}H NMR spectroscopy and conformity index analysis. *Journal of Food Composition and Analysis*, 78, 49-58. http://dx.doi.org/10.1016/j.jfca.2019.01.016.

Bertocchi, F., & Paci, M. (2008). Applications of high-resolution solid-state NMR spectroscopy in food science. *Journal of Agricultural and Food Chemistry*, 56(20), 9317-9327. http://dx.doi.org/10.1021/jf8019776. PMid:18821771.

Boffo, E. F., Tavares, L. A., Tobias, A. C. T., Ferreira, M. M. C., & Ferreira, A. G. (2012). Identification of components of Brazilian honey by ^{1}H NMR and classification of its botanical origin by chemometric methods. *LWT*, 49(1), 55-63. http://dx.doi.org/10.1016/j.lwt.2012.04.024.

Botoran, O. R., Ionete, R. E., Miricioiu, M. G., Costinel, D., Radu, G. L., & Popescu, R. (2019). Amino acid profile of fruits as ptential fingerprints of varietal origin. *Molecules*, 24(24), 4500. http://dx.doi.org/10.3390/molecules24244500. PMid:31818015.

Bruker. (2020). *Wine analysis module: wine profiling*. Retrieved from https://www.bruker.com/zh/products-and-solutions/mr/nmr-food-solutions/wine-profiling.html

Bruker. (2021a). *Honey analysis module: honey-profing*. Retrieved from https://www.bruker.com/zh/products-and-solutions/mr/nmr-food-solutions/honey-profiling.html

Bruker. (2021b). *Juice analysis module: juice profiling*. Retrieved from https://www.bruker.com/zh/products-and-solutions/mr/nmr-food-solutions/juice-profiling.html

Buckland, G., & Gonzalez, C. A. (2015). The role of olive oil in disease prevention: a focus on the recent epidemiological evidence from cohort studies and dietary intervention trials. *British Journal of Nutrition*, 113(Suppl. 2), S94-S101. http://dx.doi.org/10.1017/S0007114514003936. PMid:26148926.

Cai, S., Zhang, Y., Xia, F., Shen, G., & Feng, J. (2019). An expert system based on ^{1}H NMR spectroscopy for quality evaluation and adulteration identification of edible oils. *Journal of Food Composition and Analysis*, 84(2), 103316. http://dx.doi.org/10.1016/j.jfca.2019.103316.

Campo, G., Zuriarrain, J., Zuriarrain, A., & Berregi, I. (2016). Quantitative determination of carboxylic acids, amino acids, carbohydrates, ethanol and hydroxymethylfurfural in honey by ^{1}H NMR. *Food Chemistry*, 196, 1031-1039. http://dx.doi.org/10.1016/j.foodchem.2015.10.036. PMid:26593586.

Cassino, C., Tsolakis, C., Bonello, F., Gianotti, V., & Osella, D. (2019). Wine evolution during bottle aging, studied by ^{1}H NMR spectroscopy and multivariate statistical analysis. *Food Research International*, 116, 566-577. http://dx.doi.org/10.1016/j.foodres.2018.08.075. PMid:30716981.

Cavia, M. M., Fernández-Muiño, M. A., Gömez-Alonso, E., Montes-Pérez, M. J., Huidobro, J. F., & Sancho, M. T. (2002). Evolution of fructose and glucose in honey over one year: influence of induced granulation. *Food Chemistry*, 78(2), 157-161. http://dx.doi.org/10.1016/S0308-8146(01)00393-4.

Chitrakar, B., Zhang, M., & Bhandari, B. (2019). Novel intelligent detection of safer water activity by LF-NMR spectra for selected fruits and vegetables during drying. *Food and Bioprocess Technology*, 12(7), 1093-1101. http://dx.doi.org/10.1007/s11947-019-02278-y.

Consonni, R., & Cagliani, L. R. (2019). The potentiality of NMR-based metabolomics in food science and food authentication assessment. *Magnetic Resonance in Chemistry*, 57(9), 558-578. http://dx.doi.org/10.1002/mrc.4807. PMid:30447115.

Consonni, R., Bernareggi, F., & Cagliani, L. R. (2019). NMR-based metabolomic approach to differentiate organic and conventional Italian honey. *Food Control*, 98, 133-140. http://dx.doi.org/10.1016/j.foodcont.2018.11.007.

Consonni, R., Cagliani, L. R., & Cogliati, C. (2013). Geographical discrimination of honeys by saccharides analysis. *Food Control*, 32(2), 543-548. http://dx.doi.org/10.1016/j.foodcont.2013.01.038.

Cui, J., Zhu, D., Su, M., Tan, D., Zhang, X., Jia, M., & Chen, G. (2019). The combined use of ^{1}H and 2D NMR-based metabolomics and chemometrics for non-targeted screening of biomarkers and identification of reconstituted milk. *Journal of the Science of Food and Agriculture*, 99(14), 6455-6461. http://dx.doi.org/10.1002/jsfa.9924. PMid:31294826.

Curti, E., Pardu, A., Vigo, S., Sanna, R., & Anedda, R. (2019). Non-invasive monitoring of curd syneresis upon renneting of raw and heat-treated cow's and goat's milk. *International Dairy Journal*, 90, 95-97. http://dx.doi.org/10.1016/j.idairyj.2018.11.003.

D'Imperio, M., Gobbino, M., Picanza, A., Costanzo, S., Corte, A. D., & Mannina, L. (2010). Influence of harvest method and period on olive oil composition: an NMR and statistical study. *Journal of Agricultural and Food Chemistry*, 58(20), 11043-11051. http://dx.doi.org/10.1021/jf1026982. PMid:20923192.

Dais, P., & Hatzakis, E. (2013). Quality assessment and authentication of virgin olive oil by NMR spectroscopy: a critical review. *Analytica Chimica Acta*, 765, 1-27. http://dx.doi.org/10.1016/j.aca.2012.12.003. PMid:23410622.

Du, Y., Bai, G., Zhang, X., & Liu, M. (2007). Classification of wines based on combination of ^{1}H NMR spectroscopy and principal component analysis. *Chinese Journal of Chemistry*, 25(7), 930-936. http://dx.doi.org/10.1002/cjoc.200790181.

Ebrahimnejad, H., Ebrahimnejad, H., Salajegheh, A., & Barghi, H. (2018). Use of magnetic resonance imaging in food quality control: a review. *Journal of Biomedical Physics & Engineering*, 8(1), 127-132. PMid:29732347.

Esslinger, S., Fauhl-Hassek, C., & Wittkowski, R. (2015). Authentication of wine by ^{1}H-NMR spectroscopy: opportunities and challenges. In S. B. Ebeler, G. Sacks, S. Vidal & P. Winterhalter (Eds.), *Advances in wine research* (ACS Symposium Series, Vol. 1203, pp. 85-108). Washington, DC: American Chemical Society. http://dx.doi.org/10.1021/bk-2015-1203.ch006.

Ferreiro-González, M., Barbero, G. F., Álvarez, J. A., Ruiz, A., Palma, M., & Ayuso, J. (2017). Authentication of virgin olive oil by a novel curve resolution approach combined with visible spectroscopy. *Food Chemistry*, 220, 331-336. http://dx.doi.org/10.1016/j.foodchem.2016.10.015. PMid:27855908.

Fine, F., Brochet, C., Gaud, M., Carre, P., Simon, N., Ramli, F., & Joffre, F. (2016). Micronutrients in vegetable oils: the impact of crushing and refining processes on vitamins and antioxidants in sunflower, rapeseed, and soybean oils. *European Journal of Lipid Science and Technology*, 118(5), 680-697. http://dx.doi.org/10.1002/ejlt.201400400.

Francini, A., Romeo, S., Cifelli, M., Gori, D., Domenici, V., & Sebastiani, L. (2017). ^{1}H NMR and PCA-based analysis revealed variety dependent changes in phenolic contents of apple fruit after drying. *Food Chemistry*, 221(Pt 2), 1206-1213. http://dx.doi.org/10.1016/j.foodchem.2016.11.038. PMid:27979079.

Girelli, C. R., Coco, L., & Fanizzi, F. P. (2016). ^{1}H NMR spectroscopy and multivariate analysis as possible tool to assess cultivars, from specific geographical areas, in EVOOs. *European Journal of Lipid Science and Technology*, 118(9), 1380-1388. http://dx.doi.org/10.1002/ejlt.201500401.

Godelmann, R., Fang, F., Humpfer, E., Schütz, B., Bansbach, M., Schäfer, H., & Spraul, M. (2013). Targeted and nontargeted wine analysis by ^{1}H NMR spectroscopy combined with multivariate statistical analysis. Differentiation of important parameters: grape variety, geographical origin, year of vintage. *Journal of Agricultural and Food Chemistry*, 61(23), 5610-5619. http://dx.doi.org/10.1021/jf400800d. PMid:23682581.

Gómez-Alonso, S., Mancebo-Campos, V., Salvador, M. D., & Fregapane, G. (2007). Evolution of major and minor components and oxidation indices of virgin olive oil during 21 months storage at room temperature. *Food Chemistry*, 100(1), 36-42. http://dx.doi.org/10.1016/j.foodchem.2005.09.006.

Gougeon, L., Costa, G., Guyon, F., & Richard, T. (2019a). ^{1}H NMR metabolomics applied to Bordeaux red wines. *Food Chemistry*, 301, 125257. http://dx.doi.org/10.1016/j.foodchem.2019.125257. PMid:31357002.

Gougeon, L., Costa, G., Richard, T., & Guyon, F. (2019b). Wine authenticity by quantitative ^{1}H NMR versus multitechnique analysis: a case study. *Food Analytical Methods*, 12(4), 956-965. http://dx.doi.org/10.1007/s12161-018-01425-z.

Gouilleux, B., Marchand, J., Charrier, B., Remaud, G. S., & Giraudeau, P. (2018). High-throughput authentication of edible oils with benchtop Ultrafast 2D NMR. *Food Chemistry*, 244, 153-158. http://dx.doi.org/10.1016/j.foodchem.2017.10.016. PMid:29120763.

Gray, J. I. (1978). Measurement of lipid oxidation: a review. *Journal of the American Oil Chemists' Society*, 55(6), 539-546. http://dx.doi.org/10.1007/BF02668066.

Guler, A., Kocaokutgen, H., Garipoglu, A. V., Onder, H., Ekinci, D., & Biyik, S. (2014). Detection of adulterated honey produced by honeybee (Apis mellifera L.) colonies fed with different levels of commercial industrial sugar (C3 and C4 plants) syrups by the carbon isotope ratio analysis. *Food Chemistry*, 155, 155-160. http://dx.doi.org/10.1016/j.foodchem.2014.01.033. PMid:24594168.

Harnly, J., Bergana, M. M., Adams, K. M., Xie, Z., & Moore, J. C. (2018). Variance of commercial powdered milks analyzed by proton nuclear magnetic resonance and impact on detection of adulterants. *Journal of Agricultural and Food Chemistry*, 66(32), 8478-8488. http://dx.doi.org/10.1021/acs.jafc.8b00432. PMid:29697263.

Hasanpour, M., Saberi, S., & Iranshahi, M. (2020). Metabolic profiling and untargeted ^{1}H-NMR-based metabolomics study of different Iranian pomegranate (punica granatum) ecotypes. *Planta Medica*, 86(3), 212-219. http://dx.doi.org/10.1055/a-1038-6592. PMid:31853912.

Hatzakis, E. (2019). Nuclear magnetic resonance (NMR) spectroscopy in food science: a comprehensive review. *Comprehensive Reviews in Food Science and Food Safety*, 18(1), 189-220. http://dx.doi.org/10.1111/1541-4337.12408. PMid:33337022.

He, C., Liu, Y., Liu, H., Zheng, X., Shen, G., & Feng, J. (2020). Compositional identification and authentication of Chinese honeys by ^{1}H NMR combined with multivariate analysis. *Food Research International*, 130, 108936. http://dx.doi.org/10.1016/j.foodres.2019.108936. PMid:32156383.

Hills, B. P., Wright, K. M., & Gillies, D. G. (2005). A low-field, low-cost Halbach magnet array for open-access NMR. *Journal of Magnetic Resonance*, 175(2), 336-339. http://dx.doi.org/10.1016/j.jmr.2005.04.015. PMid:15935715.

Hohmann, M., Christoph, N., Wachter, H., & Holzgrabe, U. (2014). ^{1}H NMR profiling as an approach to differentiate conventionally and organically grown tomatoes. *Journal of Agricultural and Food Chemistry*, 62(33), 8530-8540. http://dx.doi.org/10.1021/jf502113r. PMid:25066078.

Hong, Y.-S. (2011). NMR-based metabolomics in wine science. *Magnetic Resonance in Chemistry*, 49(Suppl. 1), S13-S21. http://dx.doi.org/10.1002/mrc.2832. PMid:22290704.

Hwang, H., Winkler-Moser, J. K., & Liu, S. X. (2017). Reliability of ^{1}H NMR analysis for assessment of lipid oxidation at frying temperatures. *Journal of the American Oil Chemists' Society*, 94(2), 257-270. http://dx.doi.org/10.1007/s11746-016-2945-z.

Hwang, H.-S. (2017). *Advances in NMR spectroscopy for lipid oxidation assessment*. Cham: Springer. http://dx.doi.org/10.1007/978-3-319-54196-9.

Imparato, G., Paolo, E., Braca, A., & Lamanna, R. (2011). Nuclear magnetic resonance profiling of wine blends. *Journal of Agricultural and Food Chemistry*, 59(9), 4429-4434. http://dx.doi.org/10.1021/jf200587n. PMid:21425876.

Jiang, X., Huang, R., Wu, S., Wang, Q., & Zhang, Z. (2018). Correlations between ^{1}H NMR and conventional methods for evaluating soybean oil deterioration during deep frying. *Journal of Food Measurement and Characterization*, 12(2), 1420-1426. http://dx.doi.org/10.1007/s11694-018-9757-9.

Karabagias, I. K., Vlasiou, M., Kontakos, S., Drouza, C., Kontominas, M. G., & Keramidas, A. D. (2018). Geographical discrimination of pine and fir honeys using multivariate analyses of major and minor honey components identified by ^{1}H NMR and HPLC along with physicochemical data. *European Food Research and Technology*, 244(7), 1249-1259. http://dx.doi.org/10.1007/s00217-018-3040-5.

Kaškonienė, V., & Venskutonis, P. R. (2010). Floral markers in honey of various botanical and geographic origins: a review. *Comprehensive Reviews in Food Science and Food Safety*, 9(6), 620-634. http://dx.doi.org/10.1111/j.1541-4337.2010.00130.x. PMid:33467823.

Kew, W., Goodall, I., & Uhrín, D. (2019). Analysis of scotch whisky by ^{1}H NMR and chemometrics yields insight into its complex chemistry. *Food Chemistry*, 298, 125052. http://dx.doi.org/10.1016/j.foodchem.2019.125052. PMid:31261003.

Kim, H., Park, S. J., Hyun, S., Yang, S., Lee, J., Auh, J., Kim, J., Cho, S., Marriott, P. J., & Choi, H. (2011). Biochemical monitoring of black raspberry (Rubus coreanus Miquel) fruits according to maturation stage by ^{1}H NMR using multiple solvent systems. *Food Research International*, 44(7), 1977-1987. http://dx.doi.org/10.1016/j.foodres.2011.01.023.

Kim, S., Kim, J., Yun, E. J., & Kim, K. H. (2016). Food metabolomics: from farm to human. *Current Opinion in Biotechnology*, 37, 16-23. http://dx.doi.org/10.1016/j.copbio.2015.09.004. PMid:26426959.

Kuballa, T., Hausler, T., Okaru, A. O., Neufeld, M., Abuga, K. O., Kibwage, I. O., Rehm, J., Luy, B., Walch, S. G., & Lachenmeier, D. W. (2018). Detection of counterfeit brand spirits using ^{1}H NMR fingerprints in comparison to sensory analysis. *Food Chemistry*, 245, 112-118. http://dx.doi.org/10.1016/j.foodchem.2017.10.065. PMid:29287330.

Laghi, L., Versari, A., Marcolini, E., & Parpinello, G. P. (2014). Metabonomic investigation by ^{1}H-NMR to discriminate between red wines from organic and biodynamic grapes. *Food and Nutrition Sciences*, 5(1), 52-59. http://dx.doi.org/10.4236/fns.2014.51007.

Laincer, F., Iaccarino, N., Amato, J., Pagano, B., Pagano, A., Tenore, G., Tamendjari, A., Rovellini, P., Venturini, S., Bellan, G., Ritieni, A., Mannina, L., Novellino, E., & Randazzo, A. (2016). Characterization of monovarietal extra virgin olive oils from the province of Béjaïa (Algeria). *Food Research International*, 89, 1123-1133. http://dx.doi.org/10.1016/j.foodres.2016.04.024.

Lau, H., Laserna, A. K. C., & Li, S. F. Y. (2020). ^{1}H NMR-based metabolomics for the discrimination of celery (Apium graveolens L. var. dulce) from different geographical origins. *Food Chemistry*, 332, 127424. http://dx.doi.org/10.1016/j.foodchem.2020.127424. PMid:32619947.

Li, Q., Yu, Z., Zhu, D., Meng, X., Pang, X., Liu, Y., Frew, R., Chen, H., & Chen, G. (2017). The application of NMR-based milk metabolite analysis in milk authenticity identification. *Journal of the Science of Food and Agriculture*, 97(9), 2875-2882. http://dx.doi.org/10.1002/jsfa.8118. PMid:27790701.

Li, T., Rui, X., Li, W., Chen, X., Jiang, M., & Dong, M. (2014). Water distribution in Tofu and application of T2 relaxation measurements in dtermination of Tofu's water-holding capacity. *Journal of Agricultural and Food Chemistry*, 62(34), 8594-8601. http://dx.doi.org/10.1021/jf503427m. PMid:25094026.

Lin, H., He, C., Liu, H., Shen, G., Xia, F., & Feng, J. (2021). NMR-based quantitative component analysis and geographical origin identification of China's sweet orange. *Food Control*, 130, 108292. http://dx.doi.org/10.1016/j.foodcont.2021.108292.

Lioupi, A., Nenadis, N., & Theodoridis, G. (2020). Virgin olive oil metabolomics: a review. *Journal of Chromatography B*, 1150, 122161. http://dx.doi.org/10.1016/j.jchromb.2020.122161. PMid:32505112.

López-Rituerto, E., Avenoza, A., Busto, J. H., & Peregrina, J. M. (2013). NMR study of histidine metabolism during alcoholic and malolactic fermentations of wine and their influence on histamine production. *Journal of Agricultural and Food Chemistry*, 61(39), 9464-9469. http://dx.doi.org/10.1021/jf402489g. PMid:24053312.

Luangwilai, M., Duangmal, K., Chantaprasarn, N., & Settachaimongkon, S. (2021). Comparative metabolite profiling of raw milk from subclinical and clinical mastitis cows using ^{1}H-NMR combined with chemometric analysis. *International Journal of Food Science & Technology*, 56(1), 493-503. http://dx.doi.org/10.1111/ijfs.14665.

Lv, W., Zhang, M., Bhandari, B., Li, L., & Wang, Y. (2017). Smart NMR method of measurement of moisture content of vegetables during microwave vacuum drying. *Food and Bioprocess Technology*, 10(12), 2251-2260. http://dx.doi.org/10.1007/s11947-017-1991-3.

Mafra, I., Honrado, M., & Amaral, J. S. (2022). Animal species authentication in dairy products. *Foods*, 11(8), 1124. http://dx.doi.org/10.3390/foods11081124. PMid:35454711.

Magdas, D. A., Pirnau, A., Feher, I., Guyon, F., & Cozar, B. I. (2019). Alternative approach of applying ^{1}H NMR in conjunction with chemometrics for wine classification. *LWT*, 109, 422-428. http://dx.doi.org/10.1016/j.lwt.2019.04.054.

Markoska, T., Vasiljevic, T., & Huppertz, T. (2020). Unravelling conformational aspects of milk protein structure-contributions from nuclear magnetic resonance studies. *Foods*, 9(8), 1128. http://dx.doi.org/10.3390/foods9081128. PMid:32824355.

Mascellani, A., Hoca, G., Babisz, M., Krska, P., Kloucek, P., & Havlik, J. (2021). ^{1}H NMR chemometric models for classification of Czech wine type and variety. *Food Chemistry*, 339, 127852. http://dx.doi.org/10.1016/j.foodchem.2020.127852. PMid:32889133.

Matteo, G., Spano, M., Esposito, C., Santarcangelo, C., Baldi, A., Daglia, M., Mannina, L., Ingallina, C., & Sobolev, A. P. (2021). NMR characterization of ten apple cultivars from the piedmont region. *Foods*, 10(2), 289. http://dx.doi.org/10.3390/foods10020289. PMid:33535442.

Mazzei, P., & Piccolo, A. (2018). NMR-based metabolomics of water-buffalo milk after conventional or biological feeding. *Chemical and Biological Technologies in Agriculture*, 5(1), 3. http://dx.doi.org/10.1186/s40538-017-0116-6.

Mazzei, P., Spaccini, R., Francesca, N., Moschetti, G., & Piccolo, A. (2013). Metabolomic by ^{1}H NMR spectroscopy differentiates "Fiano Di Avellino" white wines obtained with different yeast strains. *Journal of Agricultural and Food Chemistry*, 61(45), 10816-10822. http://dx.doi.org/10.1021/jf403567x. PMid:24117410.

McDowell, D., Defernez, M., Kemsley, E. K., Elliott, C. T., & Koidis, A. (2019). Low vs high field ^{1}H NMR spectroscopy for the detection of adulteration of cold pressed rapeseed oil with refined oils. *LWT*, 111, 490-499. http://dx.doi.org/10.1016/j.lwt.2019.05.065.

Musharraf, S. G., Fatima, S. A., Siddiqui, A. J., Choudhary, M. I., & Atta-ur-Rahman, A. (2016). ^{1}H-NMR fingerprinting of brown rice syrup as a common adulterant in honey. *Analytical Methods*, 8(34), 6444-6451. http://dx.doi.org/10.1039/C6AY01082B.

Nardi, T., Panero, L., Petrozziello, M., Guaita, M., Tsolakis, C., Cassino, C., Vagnoli, P., & Bosso, A. (2019). Managing wine quality using Torulaspora delbrueckii and Oenococcus oeni starters in mixed fermentations of a red Barbera wine. *European Food Research and Technology*, 245(2), 293-307. http://dx.doi.org/10.1007/s00217-018-3161-x.

Nascimento, P. A. M., Barsanelli, P. L., Rebellato, A. P., Pallone, J. A. L., Colnago, L. A., & Pereira, F. M. V. (2017). Time-domain nuclear magnetic resonance (TD-NMR) and chemometrics for determination of fat content in commercial products of milk powder. *Journal of AOAC International*, 100(2), 330-334. http://dx.doi.org/10.5740/jaoacint.16-0408. PMid:28055818.

Nilsson, M., Duarte, I. F., Almeida, C., Delgadillo, I., Goodfellow, B. J., Gil, A. M., & Morris, G. A. (2004). High-resolution NMR and diffusion-ordered spectroscopy of port wine. *Journal of Agricultural and Food Chemistry*, 52(12), 3736-3743. http://dx.doi.org/10.1021/jf049797u. PMid:15186090.

Ok, S. (2014). Fast screening of turkish olive oil by NMR spectroscopy for geographical determination and discrimination purposes. *Grasas y Aceites*, 65(2), e024. http://dx.doi.org/10.3989/gya.122413.

Papotti, G., Bertelli, D., Graziosi, R., Silvestri, M., Bertacchini, L., Durante, C., & Plessi, M. (2013). Application of one- and two-dimensional NMR spectroscopy for the characterization of protected designation of origin lambrusco wines of modena. *Journal of Agricultural and Food Chemistry*, 61(8), 1741-1746. http://dx.doi.org/10.1021/jf302728b. PMid:22967082.

Prakash, S., Iturmendi, N., Grelard, A., Moine, V., & Dufourc, E. (2016). Quantitative analysis of bordeaux red wine precipitates by solid-state NMR: role of tartrates and polyphenols. *Food Chemistry*, 199, 229-237. http://dx.doi.org/10.1016/j.foodchem.2015.12.013. PMid:26775965.

Ren, H., Yue, J., Wang, D., Fan, J., & An, L. (2019). HPLC and ^{1}H-NMR combined with chemometrics analysis for rapid discrimination of floral origin of honey. *Journal of Food Measurement and Characterization*, 13(2), 1195-1204. http://dx.doi.org/10.1007/s11694-019-00035-5.

Ribeiro, R. O. R., Marsico, E. T., Carneiro, C. S., Monteiro, M. L. G., Conte, C. Jr., & Jesus, E. F. O. (2014). Detection of honey adulteration of high fructose corn syrup by Low Field Nuclear Magnetic Resonance (LF ^{1}H NMR). *Journal of Food Engineering*, 135, 39-43. http://dx.doi.org/10.1016/j.jfoodeng.2014.03.009.

Rohman, A., & Windarsih, A. (2020). The application of molecular spectroscopy in combination with chemometrics for halal authentication analysis: a review. *International Journal of Molecular Sciences*, 21(14), 5155. http://dx.doi.org/10.3390/ijms21145155. PMid:32708254.

Rongai, D., Sabatini, N., Coco, L., Perri, E., Re, P., Simone, N., Marchegiani, D., & Fanizzi, F. (2017). ^{1}H NMR and multivariate analysis for geographic characterization of commercial extra virgin olive oil: a possible correlation with climate data. *Foods*, 6(11), 96. http://dx.doi.org/10.3390/foods6110096. PMid:29112134.

Salgueiro, F. B., Lira, A. F., Rumjanek, V. M., & Castro, R. N. (2016). Botanical characterization of Brazilian honeys by nuclear magnetic resonance spectroscopy and chemometrics. *Revista Virtual de Química*, 8(1), 277-287. http://dx.doi.org/10.5935/1984-6835.20160018.

Sanchez, L. J., Zhu, D., Frew, R., & Kebede, B. (2021). Optimization of nuclear magnetic resonance and gas chromatography-mass spectrometry-based fingerprinting methods to characterize goat milk powder. *Journal of Dairy Science*, 104(1), 102-111. http://dx.doi.org/10.3168/jds.2020-18467. PMid:33189291.

Santos, P. M., Pereira-Filho, E. R., & Colnago, L. A. (2016). Detection and quantification of milk adulteration using time domain nuclear magnetic resonance (TD-NMR). *Microchemical Journal*, 124, 15-19. http://dx.doi.org/10.1016/j.microc.2015.07.013.

Saucier, C., Pianet, I., Laguerre, M., & Glories, Y. (1998). NMR and molecular modeling: application to wine ageing. *Journal de Chimie Physique et de Physico-Chimie Biologique*, 95(2), 357-365. http://dx.doi.org/10.1051/jcp:1998145.

Scano, P., Cusano, E., Caboni, P., & Consonni, R. (2019). NMR metabolite profiles of dairy: a review. *International Dairy Journal*, 90, 56-67. http://dx.doi.org/10.1016/j.idairyj.2018.11.004.

Schievano, E., Finotello, C., Uddin, J., Mammi, S., & Piana, L. (2016). Objective definition of monofloral and polyfloral honeys based on NMR metabolomic profiling. *Journal of Agricultural and Food Chemistry*, 64(18), 3645-3652. http://dx.doi.org/10.1021/acs.jafc.6b00619. PMid:27086991.

Schievano, E., Stocchero, M., Morelato, E., Facchin, C., & Mammi, S. (2012). An NMR-based metabolomic approach to identify the botanical origin of honey. *Metabolomics*, 8(4), 679-690. http://dx.doi.org/10.1007/s11306-011-0362-8.

Schievano, E., Stocchero, M., Zuccato, V., Conti, I., & Piana, L. (2019). NMR assessment of European acacia honey origin and composition of EU-blend based on geographical floral markers. *Food Chemistry*, 288, 96-101. http://dx.doi.org/10.1016/j.foodchem.2019.02.062. PMid:30902320.

Schievano, E., Tonoli, M., & Rastrelli, F. (2017). NMR quantification of carbohydrates in complex mixtures. A challenge on honey. *Analytical*

Chemistry, 89(24), 13405-13414. http://dx.doi.org/10.1021/acs.analchem.7b03656. PMid:29110461.

Segato, S., Caligiani, A., Contiero, B., Galaverna, G., Bisutti, V., & Cozzi, G. (2019). ^{1}H NMR metabolic profile to discriminate pasture based alpine asiago PDO cheeses. *Animals*, 9(10), 722. http://dx.doi.org/10.3390/ani9100722. PMid:31557876.

Shi, T., Zhu, M., Zhou, X., Huo, X., Long, Y., Zeng, X., & Chen, Y. (2019). ^{1}H NMR combined with PLS for the rapid determination of squalene and sterols in vegetable oils. *Food Chemistry*, 287, 46-54. http://dx.doi.org/10.1016/j.foodchem.2019.02.072. PMid:30857717.

Son, H.-S., Kim, K. M., van den Berg, F., Hwang, G.-S., Park, W.-M., Lee, C.-H., & Hong, Y.-S. (2008). ^{1}H nuclear magnetic resonance-based metabolomic characterization of wines by grape varieties and production areas. *Journal of Agricultural and Food Chemistry*, 56(17), 8007-8016. http://dx.doi.org/10.1021/jf801424u. PMid:18707121.

Spiteri, M., Jamin, E., Thomas, F., Rebours, A., Lees, M., Rogers, K. M., & Rutledge, D. N. (2015). Fast and global authenticity screening of honey using ^{1}H-NMR profiling. *Food Chemistry*, 189, 60-66. http://dx.doi.org/10.1016/j.foodchem.2014.11.099. PMid:26190601.

Spiteri, M., Rogers, K. M., Jamin, E., Thomas, F., Guyader, S., Lees, M., & Rutledge, D. N. (2017). Combination of ^{1}H NMR and chemometrics to discriminate manuka honey from other floral honey types from Oceania. *Food Chemistry*, 217, 766-772. http://dx.doi.org/10.1016/j.foodchem.2016.09.027. PMid:27664696.

Strecker, C., & Ara, V. (2022). Detecting Admixture to Mango Purée of the Alphonso Cultivar (Mangifera indica L. cv. Alphonso) by 1H-NMR Spectroscopy. *Food Analytical Methods,* 15, 203-211. https://doi.org/10.1007/s12161-021-02116-y.

Tanno, R., Kato, S., Shimizu, N., Ito, J., Sato, S., Ogura, Y., Sakaino, M., Sano, T., Eitsuka, T., Kuwahara, S., Miyazawa, T., & Nakagawa, K. (2020). Analysis of oxidation products of α-tocopherol in extra virgin olive oil using liquid chromatography-tandem mass spectrometry. *Food Chemistry*, 306, 125582. http://dx.doi.org/10.1016/j.foodchem.2019.125582. PMid:31622834.

Tenori, L., Santucci, C., Meoni, G., Morrocchi, V., Matteucci, G., & Luchinat, C. (2018). NMR metabolomic fingerprinting distinguishes milk from different farms. *Food Research International*, 113, 131-139. http://dx.doi.org/10.1016/j.foodres.2018.06.066. PMid:30195505.

Tomassini, A., Curone, G., Sole, M., Capuani, G., Sciubba, F., Conta, G., Miccheli, A., & Vigo, D. (2019). NMR-based metabolomics to evaluate the milk composition from Friesian and autochthonous cows of northern Italy at different lactation times. *Natural Product Research*, 33(8), 1085-1091. http://dx.doi.org/10.1080/14786419.2018.1462183. PMid:29658316.

Trygg, J., Holmes, E., & Lundstedt, T. (2007). Chemometrics in metabonomics. *Journal of Proteome Research*, 6(2), 469-479. http://dx.doi.org/10.1021/pr060594q. PMid:17269704.

Tsiafoulis, C. G., Papaemmanouil, C., Alivertis, D., Tzamaloukas, O., Miltiadou, D., Balayssac, S., Malet-Martino, M., & Gerothanassis, I. P. (2019). NMR-based metabolomics of the lipid fraction of organic and conventional bovine milk. *Molecules*, 24(6), 1067. http://dx.doi.org/10.3390/molecules24061067. PMid:30889921.

Ün, İ., & Ok, S. (2018). Analysis of olive oil for authentication and shelf life determination. *Journal of Food Science and Technology*, 55(7), 2476-2487. http://dx.doi.org/10.1007/s13197-018-3165-3. PMid:30042563.

Versari, A., Laurie, V. F., Ricci, A., Laghi, L., & Parpinello, G. P. (2014). Progress in authentication, typification and traceability of grapes and wines by chemometric approaches. *Food Research International*, 60, 2-18. http://dx.doi.org/10.1016/j.foodres.2014.02.007.

Wang, X., Wang, G., Hou, X., & Nie, S. (2020). A rapid screening approach for authentication of olive oil and classification of binary blends of olive oils osing low-field nuclear magnetic resonance spectra and support vector machine. *Food Analytical Methods*, 13(10), 1894-1905. http://dx.doi.org/10.1007/s12161-020-01799-z.

Xu, S., Zhu, J., Zhao, Q., Gao, J., Zhang, H., & Hu, B. (2021). Quality evaluation of Cabernet Sauvignon wines in different vintages by ^{1}H nuclear magnetic resonance-based metabolomics. *Open Chemistry*, 19(1), 385-399. http://dx.doi.org/10.1515/chem-2020-0126.

Yang, M., Zheng, C., Zhou, Q., Huang, F., Liu, C., & Wang, H. (2013). Minor components and oxidative stability of cold-pressed oil from rapeseed cultivars in China. *Journal of Food Composition and Analysis*, 29(1), 1-9. http://dx.doi.org/10.1016/j.jfca.2012.08.009.

Yuan, Y., Zhao, Y., Yang, J., Jiang, Y., Lu, F., Jia, Y., & Yang, B. (2017). Metabolomic analyses of banana during postharvest senescence by ^{1}H-high resolution-NMR. *Food Chemistry*, 218, 406-412. http://dx.doi.org/10.1016/j.foodchem.2016.09.080. PMid:27719928.

Zhang, Y., Zhao, Y., Shen, G., Zhong, S., & Feng, J. (2018). NMR spectroscopy in conjugation with multivariate statistical analysis for distinguishing plant origin of edible oils. *Journal of Food Composition and Analysis*, 69, 140-148. http://dx.doi.org/10.1016/j.jfca.2018.03.006.

Zheng, X., Zhao, Y., Wu, H., Dong, J., & Feng, J. (2016). Origin identification and qantitative analysis of honeys by nuclear magnetic resonance and chemometric techniques. *Food Analytical Methods*, 9(6), 1470-1479. http://dx.doi.org/10.1007/s12161-015-0325-1.

Zhu, J., Hu, B., Lu, J., & Xu, S. (2018). Analysis of metabolites in cabernet sauvignon and shiraz dry red wines from Shanxi by ^{1}H NMR spectroscopy combined with pattern recognition analysis. *Open Chemistry*, 16(1), 446-452. http://dx.doi.org/10.1515/chem-2018-0052.

Zhu, M., Shi, T., Guo, Z., Liao, H., & Chen, Y. (2020). Comparative study of the oxidation of cold-pressed and commercial refined camellia oil during storage with ^{1}H and ^{31}P NMR spectroscopy. *Food Chemistry*, 321, 126640. http://dx.doi.org/10.1016/j.foodchem.2020.126640. PMid:32247885.