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Enhanced detection of aldehydes in Extra-Virgin Olive Oil by means of band selective NMR spectroscopy

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HIGHLIGHTS

- Several unknown aldehydes are found in some Extra-Virgin Olive Oils.
- Band selective NMR techniques allow direct profiling of aldehydes in crude oils.
- The 2D extension of such techniques enabled deeper molecular insights.
- Four structural classes of aldehydes are identified without any chemical work-up.

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ABSTRACT

High resolution Nuclear Magnetic Resonance (NMR) spectroscopy is a very powerful tool for comprehensive food analyses and especially for Extra-Virgin Olive Oils (EVOOs). We use the NMR technique to study the spectral region of aldehydes (8–10 ppm) for EVOOs coming from the south part of Italy. We perform novel experiments by using mono and bidimensional band selective spin-echo pulse sequences and identify four structural classes of aldehydes in EVOOs. For the first time such species are identified in EVOOs without any chemical treatment; only dilution with CDCl₃ is employed.

This would allow the discrimination of different EVOOs for the aldehydes content increasing the potentiality of the NMR technique in the screening of metabolites for geographical characterization of EVOOs.

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1. Introduction

The Nuclear Magnetic Resonance (NMR) spectroscopy has been used with great success in the field of food science in the last two decades [1]. Indeed, despite its low sensitivity that limits the detection of minor components in complex mixtures, the quick data acquisition, the many pulse sequences developed for different investigations and the no need for sample treatment are the main reasons of NMR success [2–5]. The NMR spectroscopy is a non-destructive technique that allows the identification and quantification of the main metabolites within a complex system such as any foodstuffs. In fact, together with a proper statistical analysis, the NMR spectroscopy is able to distinguish between different products in order to certify the

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quality or to prevent any commercial frauds [6,7]. One of the most important foodstuffs for its nutritional properties [8–10] and for its commercial value is the Extra-Virgin Olive Oil (EVOO) which is essentially the hydrophobic phase obtained by squeezing the *Olea europaea* drupes. Because of its high quality among the vegetable oils and of its main role in the Mediterranean diet, it is probably the most studied product in the South of Europe. Food characterization, and in particular EVOO characterization, is a very challenging topic and there is a large amount of studies aimed to the development of analytical methods for its characterization [7,11–14].

The determination of the main metabolites constituting EVOOs is essential to certify its genuine origin and quality and to unmask possible frauds. ^1H and ^{13}C NMR techniques provide different thorough information which were successfully exploited in the study of EVOOs [11,15]. However, the main signal being due to fatty acids, little is known about aldehydes also because their weak signals are often buried under the noise of a standard ^1H NMR spectrum in the chemical shift region from 8 to 10 ppm [7,11,16–20].

Aldehydes are organic compounds containing a formyl group (R-CHO) in which a carbonyl group is bonded to one hydrogen atom and to one R group. Aldehydes are common in organic chemistry and constitute the main ingredient of many fragrances such as essential oils.

In this paper we exploit a powerful NMR technique that can overcome the low sensitivity, theoretically limited by the “dynamic range” [12,13], by using Double Pulsed Field Gradient Spin Echo (DPFGSE) pulse sequences that involve selective shaped pulses coupled to gradient refocusing spin-echoes [21]. In particular, we were able to detect and assign aldehydic resonances with a greatly enhanced signal to noise ratio. This allows to understand the chemical nature of these species and to characterize a particular EVOO by its aldehydic constitution.

2. Materials and methods

Different monovarietal EVOO cultivars, coming from the south part of Italy (*Arbequina*, *Arbosana*, *Mandanicese*, *Triolo*, *Cerasuola*, *Biancolilla*, *Nocellara del Belice*, *Nocellara Etna*, *Ottobratica Calabrese*, *Uovo di Piccione*, *Ogliarola Messinese*, *UOBNA*) and produced in the last 3 years, were analyzed as fresh samples by NMR.

Samples were prepared by adding 150 μl of EVOO (corresponding at about 130 mg) to 450 μl of CDCl_3 . We have chosen these quantities, after different trials, in order to have an high oil concentration and therefore an intense aldehydic signal without losing spectral resolution because almost all the oil components are completely dissolved. Hence, we can state that our result is not dependent on the concentration of CDCl_3 because we detected the aldehydic signals even at lower oil concentration. However, we have chosen this concentration to increase the proton signal of minor compounds. High purity CDCl_3 was bought from Sigma-Aldrich Co and its use is twofold: it both provides a deuterium lock for the NMR spectrometer (necessary for a fine optimization of the static magnetic field homogeneity) and it is a good solvent without originating any proton signal in the chemical shift region of our interest. The spectra were calibrated by using the residual chloroform resonance at 7.27 ppm and the methyl squalene signal at 1.66 ppm.

The experiments were performed by using a Bruker Avance 500 MHz NMR spectrometer equipped with a Smart-Probe at the “Bruker Biospin AG factory” (Fällanden, CH, Europe). After a quick analysis of the standard proton spectrum on the EVOO samples, we optimized specific gauss-shaped pulses in order to obtain the best selectivity and sensitivity for the ^1H -1D-DPFGSE spectrum (see e.g., Fig. 1). Furthermore, we use the same pulse sequence on the F2 projection of the HSQC, TOCSY and NOESY 2D-versions [22,23]. Note that, albeit it is a customized modification of the excitation sculpting sequence, the here presented 2D experiments are absolutely a novelty for EVOOs. C-H correlations of aldehydic substrates in crude EVOOs, well below the usual limit of detection, were detected by means of the combined sensitivity enhancement of the F2 selection by shaped pulse refocused by gradient spin-echoes and of the F1 ^{13}C band selection [24,25].

Standard ^1H and ^1H -DPFGSE (in the region 7.5–10.5 ppm) spectra were run with 128 number of transients, 2 s of acquisition time and 3 more seconds as relaxation delay for a total time of about 10 min per experiment. For the optimization of the acquisition parameter of 2D experiments, we performed 1D-TOCSY experiments [26,27] for each aldehydic species in about 22 min with 256 number of transients, 2.5 s of acquisition time and 2.5 s of relaxation delay. 2D experiments: F2-DPFGSE band selective HSQC, TOCSY and NOESY with 16 scans for any single experiment on the F2 dimension were performed over night. The temperature of the samples was kept at 300 K by a cold N_2 flow and a heating element. All spectra were processed and analyzed with MestReNova (version 6.0.25475 for PC. Mestrelab for research S.L.).

3. Results and discussions

The standard ^1H NMR spectrum of the EVOO shows mainly the signals coming from triglyceridic compounds however, it is possible to detect other chemicals such as the diglycerides, terpenes, β -sitosterol, squalene and other substances present in about mg over g proportion [16–20,28]. For what concerns the aldehydic region, in order to get a suitable signal to noise ratio, one has usually to perform very long experiments acquiring a large number of transients.

On the contrary, by using the band selective excitation technique few minutes are necessary to obtain a good spectrum. As an example, Fig. 1 shows the ^1H -1D-DPFGSE spectrum of the EVOO sample *Olio di Piccione* in the aldehydic region that we were able to obtain. As it can be observed, the weak signals in the 8.0–10.0 ppm region are clearly detectable in few scans. In Fig. 1 the four different kinds of aldehydes (A, B, C and D) we were able to assign are reported by highlighting the corresponding spectral regions.

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