Triacylglycerol analysis of argan oil by proton magnetic resonance

Julio A. Seijas,* Xesús Feás, M. Pilar Vázquez-Tato*

Departamento de Química Orgánica. Facultad de Ciencias. Universidad de Santiago de Compostela. Campus Lugo. 27080-Lugo. Spain

Introduction

Argan oil (AO) is produced from the kernels of the tree *Argania spinosa (Sapotaceae)* and is one of the most expensive oils in the world. The therapeutic benefits of AO consumption have been claimed for more than eight centuries and appear to be very promising leads for possible pharmaceutical exploitation since modern science has made it possible to specify their potential medical significance with cardioprotective properties and in the treatment of skin infections [1,2].

In recent years, both industry and consumers have shown an increased interest in oil compositions. ^{1}H-NMR has become one of the most promising methods to determine organic structures in complex matrices since do not depend on the efficiency of the sample treatment processes [3]. In ^{1}H-NMR methodology, data is collected without sample pretreatment, thus rendering a simpler and faster analysis than the conventional methods. Moreover, it avoids several problems, such as lipid oxidation, involved in the traditional GC analysis and it does not require calibration with standards [4]. Furthermore, ^{1}H-NMR offers advantages over HPLC or GC methodology because it allows the simultaneous, noninvasive, and nondestructive study of oil composition, and also provides information about the acyl position and distribution of triacylglycerides (TAGs) [5-9].

Continuing with our studies on vegetable oils composition [10,11] we draw our attention to AO. The aim of this work was to study the triglyceride composition of this oil by ^{1}H-NMR analysis.

Results

The structure of the major TAGs present in argan oil is highlighted by the characteristic hydrogen signals from the NMR spectrum [11]. Thus, vinylic hydrogens have a characteristic chemical shift, and could be used to determine the ratio of saturated to unsaturated esters; bisallylic hydrogens could be used to differentiate the nature of the polyunsaturated components and the tertiary hydrogen in

the glycerin moiety could be used to quantify the ratio of saturated to unsaturated esters since there is only one hydrogen for each TAG molecule. The proton resonances of the TAG acyl chains were assigned according to the literature data [12] and are shown in Table 1.

Table 1. Assignment of the signals of argan oil ^{1}H-NMR spectra (750 MHz for ^{1}H)

Signal	Functional group	Multiplicity	Chemical shift (ppm)
1	$–CH_3$	t	0.89 - 0.86
2	$–CH_2$-	m	1.35 -1.23
3	$–CH_2$-C-CO_2-	m	1.64 -1.57
4	–C–CH_2-C=C-oleic	m	2.02 - 1.98
5	–C–CH_2-C=C-linoleic and linolenic	m	2.06 - 2.02
6	-–CH_2-CO_2-	dt	2.31- 2.29
7	–C=C–CH_2-C=C-	t	2.77 - 2.75
8	–C=C–CH_2-C=C- CH_2-C=C	m	2.81 - 2.78
9	–C- CH_2-O-CO-C	dd	4.15 - 4.12
10	–C- CH_2-O-CO-C	dd	4.29 - 4.27
11	CH(-C-O-CO-C-)$_2$	m	5.27 - 5.24
12	C-HC=CH-C	m	5.39 - 5.30

Signal multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet; dt, doublet of triplets; dd, doublet of doublets.

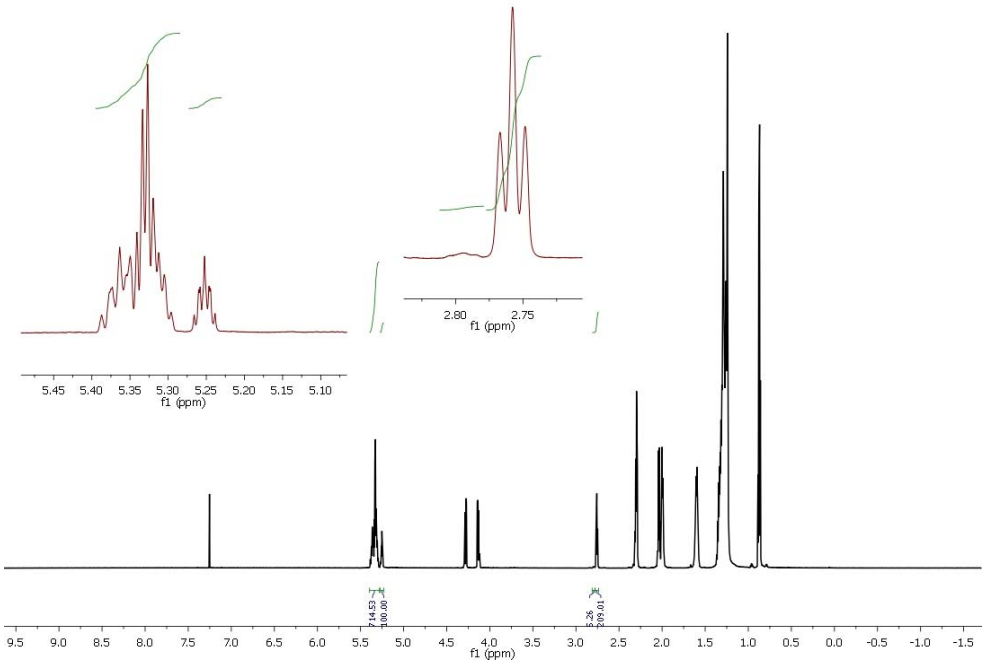

Figure 1. 750MHz ^{1}H-NMR of oil from *Argania Spinosa.*

The ^{1}H-NMR spectrum of the analyzed AO is showed in figure 1 where the peak of the tertiary hydrogen of the glycerin moiety (δ 5.27 - 5.24 ppm) was normalized to 100, leading to an integral value for vinyl hydrogens (δ 5.39 - 5.30 ppm) of 714.53 and for the bisallylic hydrogens (δ 2.81 - 2.78 ppm) of 209.01 and 5.260, corresponding to linoleic and linolenic acids, respectively.

Defining A, B, C and D as the proportion of each kind of fatty acid involved in the triglyceride structure of oil (oleic, linoleic, linolenic and aliphatic respectively), the following equations were defined: [vinylic H = 7.1453 = 2A+4B+6C]; [bisallylic H = 4C=0.0526] and [bisallylic H = 2B=2.0901].

Therefore the values of each kind of acid in oil from AO are: A 48.1%, B 34.8%, C 0.5%, and D 16.6%, for oleic, linoleic, linolenic and saturated fatty acids, respectively. These values agree with those obtained from other techniques of analysis like HPLC or GC [13].

In conclusion, a direct and simple method to evaluate the fatty acid composition oils using 750 MHz ^{1}H-NMR spectroscopy was stablished showing that argan oil is particularly rich in diinsaturated linoleic acid when compared to olive oil.

Material and Methods

Argan oil was purchased from authorized local producers in Moroco (May 2013) [14]. ^{1}H-NMR analyses were performed on Varian Inova 750 (750 MHz for ^{1}H) instruments (Agilent Technologies®, Palo Alto, CA, USA), equipped with a 5 mm probe. Each oil sample, weighing 0.2 g, was dissolved in 400 μL of $CDCl_3$, shaken in a vortex mixer, and the resulting mixture was placed into a 5-mm diameter ultra-precision NMR sample tubes. The temperature of the sample in the probe was 30 °C. The chemical shifts are reported in ppm, using the solvent proton signal as standard.

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