Sensitivity of Proton NMR Relaxation and Proton NMR Diffusion Measurements to Olive Oil Adulterations with Vegetable Oils

Donatella Ancora[1§], Jerneja Milavec[2#], Anton Gradišek[2], Mario Cifelli[1],*

Ana Sepe[2], Tomaž Apih[2], Boštjan Zalar[2] and Valentina Domenici[1]*

1. Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi, 3 – 56124 Pisa (Italy);

2. Department of Condensed Matter Physics, Jožef Stefan Institute, 39 Jamova Cesta, SI-1000, Ljubljana (Slovenia).

§ former student at Dipartimento di Chimica e Chimica Industriale.

former Ph.D. student at Jozef Stefan Institute.

* Corresponding authors.

E-mail: valentina.domenici@unipi.it & anton.gradisek@ijs.si

SUPPORTING INFORMATION

Table S1: List of oil samples investigated in this work. Producer, Geographical area, Cultivar, harvesting year and additional information are indicated for each sample, with the label and number used in the data analysis.

Sample	Producer	Area	Cultivar	Year	Further information	Label for Figures
at_1	Agriturismo Pane&Vino	Gabbro (LI)	Blend	2012	biologic oil	1
at_2	Agriturismo Cappellese	Castelnuovo della Misericordia (LI)	Frantoio, Leccino, Moraiolo	2012	biologic oil	2
at_3	Azienda Agrituristica Casolar de No' altri	Larciano (PT)	Blend	2010	biologic oil	3
at_4	Azienda Orzalesi	Rosignano Marittimo (LI)	Frantoio, Leccino, Moraiolo	2012		4
at_5	Azienda Agricola "Le Ceppite"	Rosignano Marittimo (LI)	Frantoio, Leccino, Moraiolo	2012		5
at_6	Azienda Agricola "Antica Fonte"	Rosignano Marittimo (LI)	Frantoio, Leccino, Moraiolo	2012		6
at_7	Azienda Agricola "Esposito Susanna et Atria"	Bibbona (LI)	Frantoio, Leccino, Moraiolo	2012		7

at_8	Franci Frantoio IGP	Montenero D'orcia	Frantoio, Leccino, Moraiolo	2012		8
at_9	Oliveto Fonte di Foiano	Castagneto Carducci	Frantoio, Leccino, Moraiolo	2012		9
at_10	Azienda Agricola Giovani	San Lorenzo, Suvereto	Frantoio, Leccino, Moraiolo	2012		10
at_11b	Tenuta "La Pineta"	Catiglion Fibocchi (AR)	Frantoio, Leccino, Moraiolo	2012	Filtered oil	11
at_12	Tenuta "S.Jacopo"	Cavriglia (AR)	Frantoio, Leccino, Moraiolo	2012		12
at_13	Azienda Agricola Cristiana Ruschi	Calci (PI)	Frantoio, Leccino, Moraiolo	2012		13
at_14	Azienda Mannucci Doandri DOP	Ceppeto (AR)	Blend	2011		14
at_15	Azienda "La Salceta"	Lorociuffenna (AR)	Frantoio, Leccino, Moraiolo	2012		15
at_16c	Tenuta "Montefoscoli "	Palaia (PI)	Frantoio, Leccino, Moraiolo	2012	Biologic oil	16
at_18	Azienda Terzi di Monte Oliveto	Asciano (SI)	Blend		Biologic oil	17
at_19	Frantoio Loziro	Murlo (SI)	Frantoio, Leccino, Moraiolo			18

at_20	Azienda Agricola Carraia	Podere Carraia, Petroio (SI)	Blend	2012		19
at_21	Tenuta Montalto	San Miniato (PI)	Frantoio, Leccino, Moraiolo	2012		20
at_22	Cosimo Maria Masina	San Miniato (PI)	Mignola	2012	Monocultivar	21
at_23	Tenuta San Quintino	San Miniato (PI)	Frantoio, Leccino, Moraiolo	2012		22
at_24	Azienda Olearea Chianti	Greve (FI)	Frantoio, Leccino, Moraiolo	2011		23
at_25	Azienda Agricola Donati	Casale Marittimo (PI)	Frantoio, Leccino, Moraiolo	2012		24
at_26	Piacenza Lucia Giole	Castagneto Carducci (LI)	Frantoio, Leccino, Moraiolo	2012		25
at_27	Villa Magra	Santa Luce (PI)	Frantoio, Leccino, Moraiolo	2012		26
at_28	Sopra Le Vigne	Calci (PI)	Frantoio, Leccino, Moraiolo	2012		27
at_29	Azienda Regionale Alberese	Alberese (GR)	Blend	2012	Biologic oil	28
---	---	---	---	---	---	
ap_1a	Azienda Agricola Buondioli	Carpino (FG)	Frantoio	2012	Monocultivar	1

ap_1b	Azienda Agricola Buondioli	Carpino (FG)	Leccino	2012	Monocultivar	2
ap_2c	Azienda Agricola "D.Carbone"	Toritto (BA)	Blend	2012		3
ap_3	Antica Azienda Agricola Ricucci	Rodi Garganco (FG)	Blend	2012		4
ap_4a	Azienda Agricola "Cuonzo Franco"	Palombaio (BA)	Ogliarola	2012	Monocultivar	5
ap_4b	Azienda Agricola "Cuonzo Franco"	Palombaio (BA)	Coratina	2012	Monocultivar	6
ap_5	Masseria Chicco Rizzo	Martignano (LE)	Cellina di Nardò, Ogliarola	2012		7
ap_6	Cooperativa Agricola Olearia Sannicolese	Sannicola (LE)	Cellina di Nardò, Ogliarola	2012		8
ap_7	Tenuta Agricola "Serra Cicora"	Nardò (LE)	Blend	2012		9
ap_8b	Agrié di Nicola Santoro	Cursi (LE)	Cellina di Nardò, Ogliarola	2012		10
ap_9a	Conte	Sternatia (LE)	Coratina	2012	Monocultivar	11

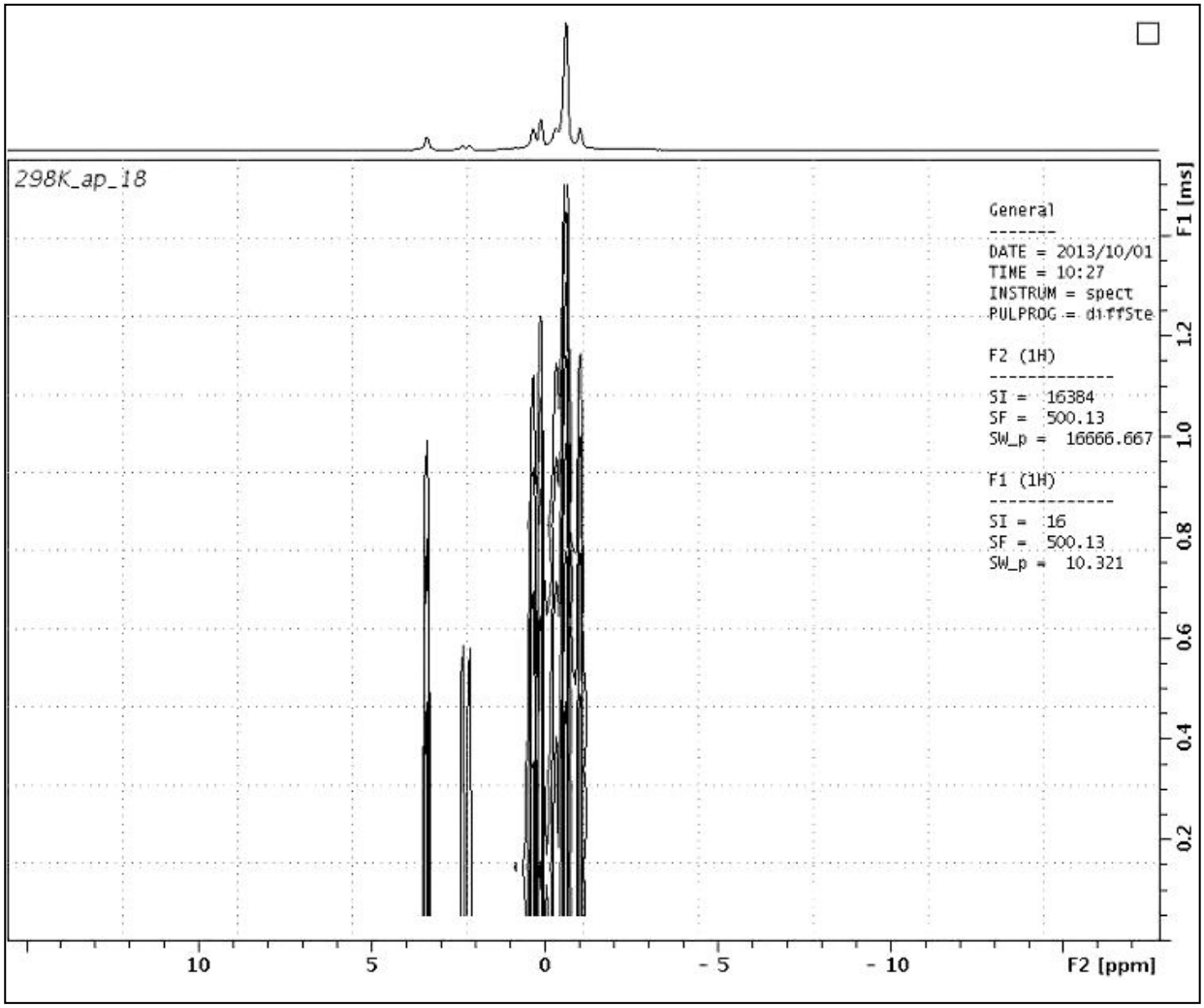
ap_9b	Conte	Sternatia (LE)	Frantoio	2012	Monocultivar	12
ap_9c	Conte	Sternatia (LE)	Picholine	2012	Monocultivar	13
ap_10	Agrosì	Supersano (LE)	Blend	2012		14
ap_11	Terra del Sole	Rignano Garganico (FG)	Blend	2012		15
ap_12a	Adamo	Alliste (LE)	Cellina di Nardò, Ogliarola	2012		16
ap_12b	Adamo	Alliste (LE)	Cellina di Nardò, Ogliarola	2012		17
ap_13a	Agricola Nuova Generazione	Martano (LE)	Blend	2012	Mix green-ripe olives	18
ap_13b	Agricola Nuova Generazione	Martano (LE)	Blend	2012	Green olives	19
ap_13c	Agricola NuovaGenerazione	Martano (LE)	Blend	2012	mature	20
ap_14a3	Agrinn	San Severo (FG)	Blend	2012	silos III	21
ap_14b1	Agrinn	San Severo (FG)	Blend	2012	Biologic oil,silos 1	22
ap_15	FrantoioSciroppo	San Severo (FG)	Peranzana	2012	Monocultivar	23
ap_16a	Macchia del Barone	Melendugno (LE)	Blend	2012		24
ap_16b	Macchia del Barone	Melendugno (LE)	Blend	2012		25
ap_16c	Macchia del Barone	Melendugno (LE)	Blend	2012		26

ap_17	Bosco delleVergini	Bitonto (BA)	Cima di Bitonto	2012	Monocultivar	27
ap_18	Olio Colella	Corato (BA)	Coratina	2012	Monocultivar	28
ap_19a	Alea	Martano (LE)	Ogliarola	2012	Monocultivar	29
ap_19b	Alea	Martano (LE)	Cellina di Nardò, Ogliarola	2012		30
ap_19c	Alea	Martano (LE)	Cellina di Nardò	2012	Monocultivar	31

^{1}H NMR DOSY EXPERIMENTAL DETAILS:

2D cross-peaks are displayed, where the centres of the cross-peaks correspond to the calculated diffusion constant. An example of 2D DOSY experiment is shown in **Figure S1**.

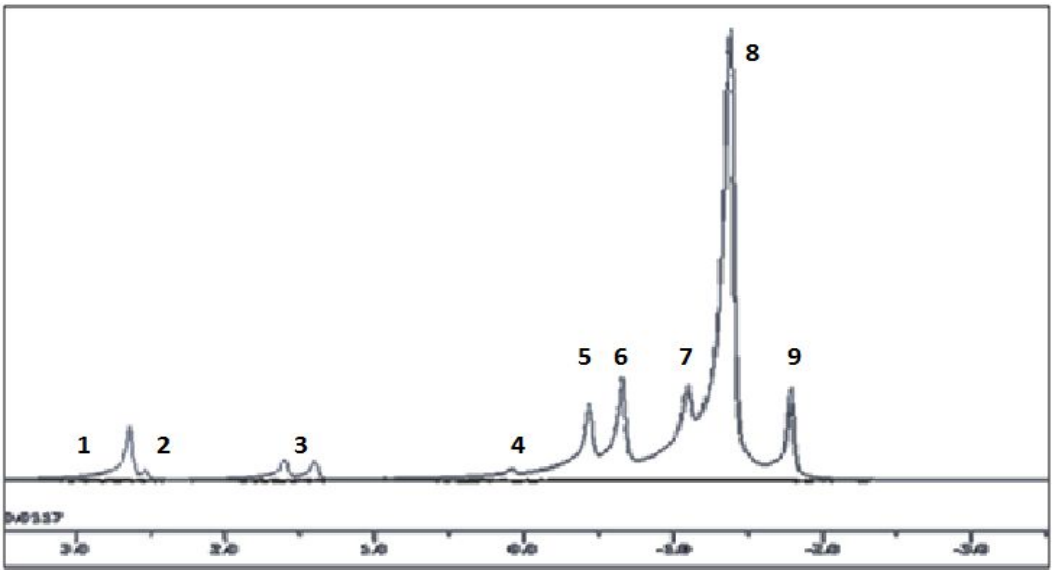
Figure S1: Example of a 2D DOSY ^{1}H NMR plot resulting from the experiment on the EVOO sample (*ap_18*) acquired at T=298K.



In ***Figure S2*** it is possible to see the ^{1}H NMR spectrum of the olive oil sample that shows the presence of nine peaks. Diffusion coefficients were calculated on four peaks indicated as 1, 3, 8 and 9.

Diffusion constant for the other peaks were not measured because their relatively low intensity under the optimised conditions for the applied NMR spin-echo sequence. In the main part of this research, for each oil sample, a single average value of diffusion coefficient, *D*, has been calculated as the average over the entire spectrum and these average values of the diffusion coefficient are reported and discussed in the Results and Discussion.

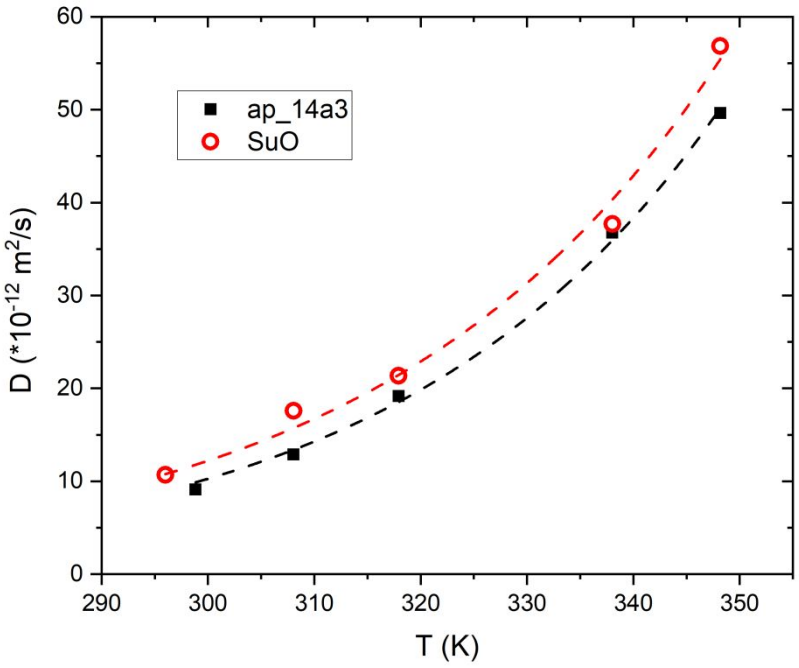
Figure S2: ^{1}H NMR spectrum of the olive oil (*ap_18*) acquired at T=298K at 500 MHz without any sample preparation.



Temperature dependence of Diffusion coefficients in Olive oil and Sunflower oil.

The self-diffusion constant in oils is temperature-dependent. **Figure S3** shows the temperature dependence for two oils, EVOO ***ap_14a3*** and sunflower oil. As seen from the figure, both oils show similar temperature trends.

Figure S3: Temperature dependence of self-diffusion constant D for EVOO ***ap14_a3*** (see Table S1) and sunflower oil (SuO), measured by means of ^{1}H NMR DOSY technique. Dashed lines are data fits to an exponential function and serve as guides to an eye.



The self-diffusion constant is strictly connected with the viscosity parameter through the Stokes-Einstein equation. Assuming an Arrhenius-type relationship for viscosity, the temperature dependence of diffusion constant can be expressed as:

$$D = D_0 \cdot e^{-\frac{E_a}{RT}} \qquad \text{(S1)}$$

The values of activation energy of the self-diffusion process in the analysed oils could be estimated from **Figure S3** (E_a~30.3 kJ/mol for EVOO and E_a~26.4 kJ/mol for SuO). These values are in agreement with data found in the literature (A. Rachocki & J. Tritt-Goc, 2014).