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## **SUPPLEMENTARY MATERIAL**

### **Individual and Joint Effect of Alpha-Tocopherol and Hydroxytyrosol Acetate on the Oxidation of Sunflower Oil Submitted to Oxidative Conditions: A Study by Proton Nuclear Magnetic Resonance**

Sofía del Caño-Ochoa, Ainhoa Ruiz-Aracama, María D Guillén \*

Food Technology. Faculty of Pharmacy. Lascaray Research Center. University of the  
Basque Country (UPV/EHU). Paseo de la Universidad nº 7, 01006 Vitoria, Spain, Telf:

34-945-013081. E-mail: [mariadolores.guillen@ehu.eus](mailto:mariadolores.guillen@ehu.eus)

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Table S1. Standard compounds used for identification purposes.

2 <i>E</i> -hexenal <sup>a</sup>	2 <i>E</i> -heptenal <sup>a</sup>
2 <i>E</i> -decenal <sup>a</sup>	2 <i>E</i> ,4 <i>E</i> -hexadienal <sup>a</sup>
2 <i>E</i> ,4 <i>E</i> -heptadienal <sup>a</sup>	2 <i>E</i> ,4 <i>E</i> -decadienal <sup>a</sup>
4,5-epoxy-2 <i>E</i> -decenal <sup>a</sup>	12,13-epoxy-9 <i>Z</i> -octadecenoic acid methyl ester (isoleukotoxin methyl ester) <sup>a</sup>
2-pentylfuran <sup>a</sup>	2-ethylfuran <sup>a</sup>
amylformate <sup>a</sup>	octylfor-mate <sup>a</sup>
<i>alpha</i> -tocopherol <sup>a</sup>	9,10-epoxy-12 <i>Z</i> -octadecenoic acid (leukotoxin) <sup>b</sup>
12,13- <i>E</i> -epoxy-9 <i>Z</i> -octadecenoic acid <sup>b</sup>	4-hydroxy-2 <i>E</i> -nonenal <sup>b</sup>
4-hydroperoxy-2 <i>E</i> -nonenal <sup>b</sup>	4-oxo-2 <i>E</i> -nonenal <sup>b</sup>
9,10-dihydroxy-12 <i>Z</i> -octadecenoic acid (leukotoxin diol) <sup>b</sup>	12,13-dihydroxy-9 <i>Z</i> -octadecenoic acid (isoleukotoxin diol) <sup>b</sup>
9-keto-12,13- <i>E</i> -epoxy-10 <i>E</i> -octadecenoic acid <sup>b</sup>	9-keto-10 <i>E</i> ,12 <i>E</i> -octadecadienoic acid <sup>b</sup>
9-keto-10 <i>E</i> ,12 <i>Z</i> -octadecadienoic acid <sup>b</sup>	13-keto-9 <i>Z</i> ,11 <i>E</i> -octadecadienoic acid <sup>b</sup>
12 <i>R</i> -hydroxy-9 <i>Z</i> -octadecenoic acid methyl ester (ricinoleic acid methyl ester) <sup>b</sup>	9 <i>S</i> -hydroxy-10 <i>E</i> ,12 <i>E</i> -octadecadienoic acid (Dimorphecolic acid) <sup>c</sup>
methyl 13 <i>S</i> -hydroxy-9 <i>S</i> ,10 <i>R</i> -epoxy-11 <i>E</i> -octadecenoate <sup>c</sup>	11 <i>S</i> -hydroxy-9 <i>S</i> ,10 <i>S</i> -epoxy-12 <i>Z</i> -octadecenoic acid methyl ester <sup>c</sup>
13 <i>S</i> -hydroxy-11 <i>S</i> ,12 <i>S</i> -epoxy-9 <i>Z</i> -octadecenoic acid methyl ester <sup>c</sup>	9-hydroxy-10-keto-12 <i>Z</i> -octadecenoic acid <sup>c</sup>
9,10- <i>Z</i> -12,13- <i>Z</i> -diepoxyoctadecanoic acid <sup>c</sup>	13-hydroxy-12-keto-9 <i>Z</i> -octadecenoic acid <sup>c</sup>
hydroxytyrosol acetate <sup>d</sup>	

Acquired from: <sup>a</sup> Sigma-Aldrich (St. Louis, MO, USA); <sup>b</sup> Cayman Chemical (Ann Arbor, MI, USA); <sup>c</sup> Larodan (Malmö, Sweeden); <sup>d</sup> Seprox Biotech (Madrid, Spain).

Table S2.  $^1\text{H}$  NMR signals, obtained in  $\text{CDCl}_3$ , of protons of main sunflower oil components, their chemical shifts, multiplicities and assignments to protons of different functional groups present in edible oils.

Chemical shift (ppm) <sup>a, **</sup>	Multiplicity	Functional group	
		Type of protons <sup>*</sup>	Compound
0.83-0.93	t	$-\text{CH}_3$	Saturated, oleic and linoleic acyl group
1.19-1.42	m	$-(\text{CH}_2)_n-$	Acyl groups
1.52-1.70	m	$-\text{OCO}-\text{CH}_2-\text{CH}_2-$	Acyl groups
1.94-2.14	m	$-\text{CH}_2-\text{CH}=\text{CH}-$	Acyl groups
2.23-2.36	dt	$-\text{OCO}-\text{CH}_2-$	Acyl groups
2.70-2.84	t	$=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$	Acyl groups
3.73	$m^b$	$\text{ROCH}_2-\text{CH}(\text{OR}')-\text{CH}_2\text{OH}$	1,2-DG
4.10-4.32	dd,dd	$-\text{CH}_2\text{OCOR}$	Glycerol groups
5.20-5.29	m	$-\text{CHOCOR}$	Glycerol groups
5.29-5.46	m	$-\text{CH}=\text{CH}-$	Acyl groups

Abbreviations: dd: double doublet; t: triplet; dt: double triplet; m: multiplet.

<sup>\*</sup> Area of the signals due to the protons in bold were used for the quantification of each compound.

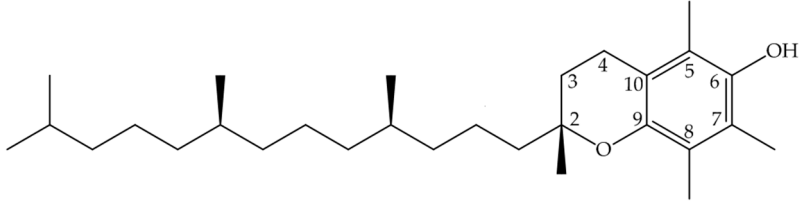
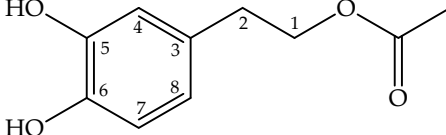
<sup>\*\*</sup> The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of main components was made with the data taken from the literature:

<sup>a</sup> Guillén, M.D.; Ruiz, A. (2003). *Eur. J. Lipid Sci. Tech.* 105(11), 688-696.

<sup>b</sup> This signal shows different multiplicity if the spectrum is acquired from the pure compound or taking part in the mixture.

Table S3. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of *alpha*-tocopherol and hydroxytyrosol acetate.

<i>Alpha</i> -tocopherol			
			
Chemical shift (ppm) <sup>a, **</sup>	Multiplicity	Functional group	Type of protons <sup>*</sup>
4.18	s	Hydroxy group bonded to C6	-OH
<b>2.60</b>	t	Methylene group in position 4	-CH <sub>2</sub> -
2.15	s	Methyl group bonded to C7	-CH <sub>3</sub>
2.11	s	Methyl group bonded to C5 and C8	-CH <sub>3</sub>
1.8	m	Methylene group in position 3	-CH <sub>2</sub> -
1.22	s	Methyl group bonded to C2	-CH <sub>3</sub>
1.1-1.5	m	Chain methylene groups	-CH <sub>2</sub> -
		Chain methine groups	-CH-
0.83-0.88	m	Chain methyl groups	-CH <sub>3</sub>
Hydroxytyrosol acetate			
			
Chemical shift (ppm) <sup>b, **</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>	
<b>6.71</b>	d	-CH=CH- (H-7 of the dihydroxyphenyl group)	
6.67	d	=CH- (H-4 of the dihydroxyphenyl group)	
6.54	dd	-CH=CH- (H-8 of the dihydroxyphenyl group)	
4.12	t	-CH <sub>2</sub> -OCO-	
2.73	t	-CH <sub>2</sub> -CH <sub>2</sub> -OCO-	
2.00	s	-OCO-CH <sub>3</sub>	

Abbreviations: s: singlet; d: doublet; dd: double doublet; t: triplet; m: multiplet.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

<sup>\*\*</sup> The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of *alpha*-tocopherol and hydroxytyrosol acetate was made with the data taken from the literature:

<sup>a</sup> Baker, J.K.; Myers, C.W. (1991). *Pharm. Res.* 8(6), 763-770.

<sup>b</sup> Bouallagui, Z.; Bouaziz, M.; Lassoued, S.; Engasser, J.M.; Ghoul, M.; Sayadi, S. (2011). *Appl. Biochem. Biotechnol.* 163(5), 592-599.

<sup>b</sup> Ammendola, S.; Giusti, A. M.; Masci, A.; Mosca, L.; Saso, L.; Bovicelli, P. (2011). *J. Sci. Ind. Res.* 70(11), 929-937.

Table S4. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of monohydroperoxy conjugated octadecadienes (mHPO-c-dEs) coming from linoleic groups.

<b>mHPO-c(Z,E)-dEs</b>		
(9-hydroperoxy-10 <i>E</i> ,12 <i>Z</i> -octadecadienoate; 13-hydroperoxy-9 <i>Z</i> ,11 <i>E</i> -octadecadienoate)		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) *
<b>6.58</b>	dddd	- <b><u>CH</u></b> =CH-CHOOH-
6.00	ddtd	-CH= <b><u>CH</u></b> -CH=CH-CHOOH-
5.56	ddm	-CH= <b><u>CH</u></b> -CHOOH-
5.51	dtm	- <b><u>CH</u></b> =CH-CH=CH-CHOOH-
4.37	dtd	- <b><u>CH</u></b> OOH-
2.30	t	-OCO- <b><u>CH</u></b> <sub>2</sub> -
2.19	dtd	- <b><u>CH</u></b> <sub>2</sub> -CH=CH-
1.55-1.71	m	-CHOOH- <b><u>CH</u></b> <sub>2</sub> - -OCO-CH <sub>2</sub> - <b><u>CH</u></b> <sub>2</sub> -
1.24-1.43	m	- <b><u>CH</u></b> <sub>2</sub> -
0.89	t	- <b><u>CH</u></b> <sub>3</sub>
<b>mHPO-c(E,E)-dEs</b>		
(9-hydroperoxy-10 <i>E</i> ,12 <i>E</i> -octadecadienoate; 13-hydroperoxy-9 <i>E</i> ,11 <i>E</i> -octadecadienoate)		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) *
<b>6.27</b>	ddm	- <b><u>CH</u></b> =CH-CHOOH-
6.06	ddtd	-CH= <b><u>CH</u></b> -CH=CH-CHOOH-
5.76	dtm	- <b><u>CH</u></b> =CH-CH=CH-CHOOH-
5.47	ddm	-CH= <b><u>CH</u></b> -CHOOH-
4.32	dtd	- <b><u>CH</u></b> OOH-
2.30	t	-OCO- <b><u>CH</u></b> <sub>2</sub> -
2.09	dtd	- <b><u>CH</u></b> <sub>2</sub> -CH=CH-
1.42-1.66	m	-CHOOH- <b><u>CH</u></b> <sub>2</sub> - -OCO-CH <sub>2</sub> - <b><u>CH</u></b> <sub>2</sub> -
1.25-1.43	m	- <b><u>CH</u></b> <sub>2</sub> -
0.89	t	- <b><u>CH</u></b> <sub>3</sub>

Abbreviations: dddd: double of double of double doublet; ddtd: double of double of triple doublet; dtd: double of triple doublet; t: triplet; m: multiplet; ddm: double of double multiplet; dtm: double of triple multiplet.

\*Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

\*\*The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of mHPO-c-dEs derived from linoleic acyl groups was made with the data taken from the literature:

<sup>a</sup> Goicoechea, E.; Guillén, M.D. (2010). *J. Agric. Food Chem.* 58, 6234-6245.

<sup>a</sup> Pajunen, T.I.; Koskela, H.; Hase, T.; Hopia, A. (2008). *Chem. Phys. Lipids.* 154, 105-114.

Table S5. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of dihydroperoxy non conjugated *E,E*-octadecadienes (dHPO-nc(*E,E*)-dEs).

<b>dHPO-nc(<i>E,E</i>)-dEs</b>		
(9,12-dihydroperoxy-10 <i>E</i> ,13 <i>E</i> -octadecadienoate; 10,13-dihydroperoxy-8 <i>E</i> ,11 <i>E</i> -octadecadienoate)		
Chemical shift (ppm) <sup>a</sup>	Multiplicity	Functional group (Type of protons) *
5.56-5.87	m	-CHOOH- <u>CH</u> = <u>CH</u> -CHOOH- -CHOOH- <u>CH</u> =CH-CH <sub>2</sub> -
5.36-5.50	m	-CHOOH-CH= <u>CH</u> -CH <sub>2</sub> -
<b>4.81</b>	dd	- <u>CH</u> OOH-
4.30-4.39	m	-CH <u>OOH</u> -
2.33	t	-OCO-CH <sub>2</sub> -
2.02-2.11	m	-CH=CH-CH <sub>2</sub> -
1.54-1.69	m	-OCO-CH <sub>2</sub> -CH <sub>2</sub> -
1.16-1.43	m	-CH <sub>2</sub> -
0.81-0.91	t	-CH <sub>3</sub>

Abbreviations: dd: double doublet; t: triplet; m: multiplet.

\* Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

The assignment of the  $^1\text{H}$  NMR signals of the protons of dHPO-nc(*E,E*)-dEs was made with the data taken from the literature:

<sup>a</sup> Zhang, W. (2008). Synthesis and Fragmentation Reactions of Linoleic Acid-Derived Hydroperoxides (Doctoral dissertation, Case Western Reserve University).

Table S6. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of *non vicinal* monohydroperoxy monoepoxy *E*-octadecamonoenes (mHPO-mEPO-*E*-mEs).

<b>mHPO-<i>E</i>-mEPO-<i>E</i>-mEs</b>		
(9-hydroperoxy-12,13- <i>E</i> -epoxy-10 <i>E</i> -octadecenoate)		
Chemical shift (ppm) <sup>a</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>5.85</b>	dd	-CHOCH-CH=CH-CHOOH-
5.47	dd	-CHOCH-CH=CH-CHOOH-
4.33	m	-CHOOH-
3.11	dd	-CHOCH-CH=CH-
2.84	m	-CHOCH-CH=CH-
2.30	t	-OCO-CH <sub>2</sub> -
1.51	m	-OCO-CH <sub>2</sub> -CH <sub>2</sub> -
1.31	m	-CH <sub>2</sub> -
0.89	t	-CH <sub>3</sub>
<b>mHPO-<i>Z</i>-mEPO-<i>E</i>-mEs</b>		
(13-hydroperoxy-9,10- <i>Z</i> -epoxy-11 <i>E</i> -octadecenoate)		
Chemical shift (ppm) <sup>b</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>5.84</b>	dd	-CHOCH-CH=CH-CHOOH-
5.5-5.7	m	-CHOCH-CH=CH-CHOOH-
4.2-4.4	m	-CHOOH-
3.42	dd	-CHOCH-CH=CH-
3.0-3.2	m	-CHOCH-CH=CH-
2.32	t	-OCO-CH <sub>2</sub> -
1.1-1.8	m	-CH <sub>2</sub> -
0.85	t	-CH <sub>3</sub>

Abbreviations: dd: double doublet; t: triplet; m: multiplet.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

The assignment of the  $^1\text{H}$  NMR signals of the protons of mHPO-mEPO-*E*-mEs was made with the data taken from the literature:

<sup>a</sup> Gardner, H.W.; Weisleder, D.; Kleiman, R. (1978). *Lipids*, 13(4), 246-252.

<sup>b</sup> Gu, X.; Salomon, R. (2012). *Free Radical Biol. Med.* 52, 601-606.

Table S7. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of monohydroxy conjugated *Z,E*-octadecadienes (mHO-c(*Z,E*)-dEs).

<b>mHO-c(<i>Z,E</i>)-dEs</b> (13-hydroxy-9 <i>Z</i> ,11 <i>E</i> -octadecadienoate; 9-hydroxy-10 <i>E</i> ,12 <i>Z</i> -octadecadienoate)		
Chemical shift (ppm) <sup>a, **</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>6.46</b>	ddd	- <b><math>\text{CH}</math></b> =CH-CHOOH-
5.94	dd	-CH= <b><math>\text{CH}</math></b> -CH=CH-CHOOH-
5.64	dd	-CH= <b><math>\text{CH}</math></b> -CHOOH-
5.42	ddt	- <b><math>\text{CH}</math></b> =CH-CH=CH-CHOOH-
4.13	m	- <b><math>\text{CH}</math></b> OH-
2.27	t	-OCO- <b><math>\text{CH}_2</math></b> -
2.15	m	-CH=CH- <b><math>\text{CH}_2</math></b> -
1.2-1.7	m	- <b><math>\text{CH}_2</math></b> -
0.86	t	- <b><math>\text{CH}_3</math></b>

Abbreviations: dd: double doublet; ddd: double of double doublet; t: triplet; ddt: double of double triplet; m: multiplet.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

<sup>\*\*</sup> The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of mHO-c(*Z,E*)-dEs was made with the data taken from the literature:

<sup>a</sup> Kuklev, D. V.; Christie, W. W.; Durand, T.; Rossi, J. C.; Vidal, J. P.; Kasyanov, S. P.;... Bezuglov, V. V. (1997). *Chem. Phys. Lipids*, 85(2), 125-134.



Table S8. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of monohydroxy monoepoxy *E*-octadecamonoenes (mHO-mEPO-*E*-mEs).

<b>mHO-<i>E</i>-mEPO-<i>E</i>-mEs</b>		
(9-hydroxy-12,13- <i>E</i> -epoxi-10 <i>E</i> -octadecenoate; 13-hydroxy-9,10- <i>E</i> -epoxy-11 <i>E</i> -octadecenoate <sup>**</sup> )		
Chemical shift (ppm) <sup>a</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>5.93</b>	dd	-CH=CH- <b>CH</b> -CHOH-
5.41	ddd	-CH=CH-CHOH-
4.14	m	-CH-CHOH-
3.09	dd	-CHOCH-CH=CH-
2.81	dt	-CH-CHOCH-CH=CH-
2.30	t	-OCO-CH <sub>2</sub> -
1.49	m	-OCO-CH <sub>2</sub> -CH <sub>2</sub> -
1.31	m	-CH <sub>2</sub> -
0.89	t	-CH <sub>3</sub>
<b>mHO-<i>Z</i>-mEPO-<i>E</i>-mEs</b>		
(13-hydroxy-9,10- <i>Z</i> -epoxy-11 <i>E</i> -octadecenoate)		
Chemical shift (ppm) <sup>b</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>5.95</b>	dd	-CH=CH- <b>CH</b> -CHOH-
5.54	ddd	-CH=CH-CHOH-
3.41	dd	-CHOCH-CH=CH-
3.07	dt	-CH-CHOCH-CH=CH-
2.30	t	-OCO-CH <sub>2</sub> -
2.10	br	-CHOH-
1.2-1.6	m	-CH <sub>2</sub> -
0.89	t	-CH <sub>3</sub>

Abbreviations: dd: double doublet; ddd: double of double doublet; t: triplet; dt: double triplet; m: multiplet; br: broad signal.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

<sup>\*\*</sup> The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of mHO-mEPO-*E*-mEs was made with the data taken from the literature:

<sup>a</sup> Gardner, H.W.; Weisleder, D.; Kleiman, R. (1978). *Lipids*, 13(4), 246-252.

<sup>a</sup> Schieberle, P.; Trebert, Y.; Firl, J.; Grosch, W. (1988). *Chem. Phys. Lipids*, 48(3-4), 281-288.

<sup>a</sup> Ramsden, C.E.; Domenichiello, A.F.; Yuan, Z.X.; Sapio, M.R.; Keyes, G.S.; Mishra, S. K.; ... Davis, J.M. (2017). *Sci. Sign.* 10(493), eaa15241.

<sup>b</sup> Hidalgo, F.J.; Zamora, R.; Vioque, E. (1992). *Chem. Phys. Lipids*, 60(3), 225-233.

Table S9. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of monoketo conjugated octadecadienes (mKO-c-dEs).

<b>mKO-c(Z,E)-dEs</b>		
(13-keto-9Z,11E-octadecadienoate; 9-keto-10E,12Z-octadecadienoate)		
Chemical shift (ppm) <sup>a, **</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>7.49</b>	ddd	-CO-CH=CH-
6.16	d	-CO-CH=CH-
6.12	dd	-CO-CH=CH-CH=CH-
5.91	dt	-CO-CH=CH-CH=CH-
2.55	t	-CH <sub>2</sub> -CO-
2.34	t	-OCO-CH <sub>2</sub> -
2.30	m	-CH=CH-CH <sub>2</sub> -
1.32-1.63	m	-CH <sub>2</sub> -
0.88	t	-CH <sub>3</sub>
<b>mKO-c(E,E)-dEs</b>		
(13-keto-9E,11E-octadecadienoate; 9-keto-10E,12E-octadecadienoate)		
Chemical shift (ppm) <sup>a, **</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>7.13</b>	dm	-CO-CH=CH-
6.14-6.19	m	-CO-CH=CH-CH=CH-
6.07	d	-CO-CH=CH-
2.53	t	-CH <sub>2</sub> -CO-
2.35	t	-OCO-CH <sub>2</sub> -
2.17	m	-CH=CH-CH <sub>2</sub> -
1.32-1.63	m	-CH <sub>2</sub> -
0.88	t	-CH <sub>3</sub>

Abbreviations: d: doublet; dd: double doublet; ddd; double of double doublet; t: triplet; dt: double triplet; m: multiplet; dm: double multiplet.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

<sup>\*\*</sup> The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of mKO-c-dEs was made with the data taken from the literature:

<sup>a</sup> Dufour, C.; Loonis, M. (2005). *Chem. Phys. Lipids*. 138(1), 60-68.

Table S10. Chemical shift assignments and multiplicities of <sup>1</sup>H NMR signals in CDCl<sub>3</sub> of protons of monoketo monoepoxy *E*-octadecamonoenes (mKO-mEPO-*E*-mEs).

<b><i>non vicinal-mKO-Z-mEPO-E-mEs</i></b>		
(13-keto-9,10- <i>Z</i> -epoxy-11 <i>E</i> -octadecenoate; 9-keto-12,13- <i>Z</i> -epoxy-10 <i>E</i> -octadecenoate)		
Chemical shift (ppm) <sup>a</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>6.66</b>	dd	-CO-CH=CH-
6.40	d	-CO-CH=CH-
3.52	dd	-CH=CH-CH <sub>2</sub> OH-
3.20	dd	-CH=CH-CH <sub>2</sub> OH-
2.55	t	-CH <sub>2</sub> -CO-
2.30	t	-OCO-CH <sub>2</sub> -
1.2-1.7	m	-CH <sub>2</sub> -
0.89	t	-CH <sub>3</sub>
<b><i>non vicinal-mKO-E-mEPO-E-mEs</i></b>		
(13-keto-9,10- <i>E</i> -epoxy-11 <i>E</i> -octadecenoate; 9-keto-12,13- <i>E</i> -epoxy-10 <i>E</i> -octadecenoate)		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
6.52	dd	-CO-CH=CH-
6.38	d	-CO-CH=CH-
<b>3.21</b>	dd	-CH=CH-CH <sub>2</sub> OH-
2.89	td	-CH=CH-CH <sub>2</sub> OH-
2.53	t	-CH <sub>2</sub> -CO-
2.30	t	-OCO-CH <sub>2</sub> -
1.2-1.6	m	-CH <sub>2</sub> -
0.86	t	-CH <sub>3</sub>
<b><i>vicinal-mKO-E-mEPO-E-mEs</i></b>		
(11-keto-12,13- <i>E</i> -epoxy-9 <i>E</i> -octadecenoate; 11-keto-9,10- <i>E</i> -epoxy-12 <i>E</i> -octadecenoate)		
Chemical shift (ppm) <sup>b</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>7.02</b>	dt	-CO-CH=CH-
6.16-6.23	dt	-CO-CH=CH-
3.28-3.34	d	-CHOCH <sub>2</sub> -CO-
2.98-3.04	ddd	-CHOCH <sub>2</sub> -CO-
2.29-2.34	t	-OCO-CH <sub>2</sub> -
2.16-2.22	dtd	-CH=CH-CH <sub>2</sub> -
1.25-1.70	m	-CH <sub>2</sub> -
0.82-0.89	t	-CH <sub>3</sub>

Abbreviations: d: doublet; dd: double doublet; td: triple doublet; ddd: double of double doublet; dtd: double of triple doublet; t: triplet; dt: double triplet; m: multiplet.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

<sup>\*\*</sup> The assignment of the <sup>1</sup>H NMR signals of the protons was made with the aid of standard compounds.

The assignment of the <sup>1</sup>H NMR signals of the protons of mKO-mEPO-*E*-mEs was made with the data taken from the literature:

<sup>a</sup> Hidalgo, F.J.; Zamora, R.; Vioque, E. (1992). *Chem. Phys. Lipids*. 60(3), 225-233.

<sup>a,b</sup> Lin, D.; Zhang, J.; Sayre, L.M. (2007). *J. Org. Chem.* 72(25), 9471-9480.

<sup>a</sup> Ramsden, C.E.; Domenichiello, A.F.; Yuan, Z.X.; Sapio, M.R.; Keyes, G.S.; Mishra, S.K.; Gross, J.R.; Majchrzak-Hong, S.; Zamora, D.; Horowitz, M. S.; et al. (2017). *Sci. Sign.*, 10(493), eaal5241.

<sup>a</sup> Gardner, H.W.; Kleiman, R.; Weisleder, D. (1974). *Lipids*, 9 (9), 696-706.

Table S11. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of different types of aldehydes.

<b><i>n</i>-alkanals</b>		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) *
<b>9.75</b>	t	- <b><u>C</u>H</b> O
2.40	dt	CHO-CH- <b><u>C</u>H</b> -
1.61	m	CHO-CH <sub>2</sub> - <b><u>C</u>H</b> -
1.27-1.32	br	- <b><u>C</u>H</b> -
0.88	t	- <b><u>C</u>H</b> <sub>3</sub>
<b><i>2E</i>-alkenals</b>		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) *
<b>9.49</b>	d	- <b><u>C</u>H</b> O
6.85	tt	CHO-CH=CH-
6.11	dd	CHO-CH=CH-
2.32	q	-CH=CH- <b><u>C</u>H</b> -
1.69-1.19	br	- <b><u>C</u>H</b> -
0.89	t	- <b><u>C</u>H</b> <sub>3</sub>
<b><i>2E,4E</i>-alkadienals</b>		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) *
<b>9.53</b>	d	- <b><u>C</u>H</b> O
7.09	m	CHO-CH=CH-
6.30	m	-CH=CH-
6.08	dd	CHO-CH=CH-
2.22	m	-CH=CH- <b><u>C</u>H</b> -
1.30-1.47	m	- <b><u>C</u>H</b> -
0.90	t	- <b><u>C</u>H</b> <sub>3</sub>
<b><i>4,5</i>-epoxy-<i>2E</i>-alkenals</b>		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) *
<b>9.54</b>	d	- <b><u>C</u>H</b> O
6.56	dd	CHO-CH=CH-
6.40	dd	CHO-CH=CH-
3.33	dd	- <b><u>C</u>H</b> OCH-
2.96	td	- <b><u>C</u>H</b> OCH-
1.33-1.65	m	- <b><u>C</u>H</b> -
0.91	t	- <b><u>C</u>H</b> <sub>3</sub>
<b><i>4</i>-hydroperoxy-<i>2E</i>-alkenals</b>		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) *

<b>9.58</b>	d	- <b>CHO</b>
8.20	d	-OOH
6.80	dd	CHO-CH=CH-
6.33	m	CHO-CH=CH-
4.66	dd	-CHOH-
1.21-1.73	m	-CH <sub>2</sub> -
0.89	t	-CH <sub>3</sub>

#### 4-hydroxy-2E-alkenals

Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>9.57</b>	d	- <b>CHO</b>
6.84	dd	CHO-CH=CH-
6.33	dddd	CHO-CH=CH-
4.43	m	-CHOH-
1.30-1.70	m	-CH <sub>2</sub> -
0.90	t	-CH <sub>3</sub>

#### 2Z-alkenals

Chemical shift (ppm) <sup>b</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
<b>10.06</b>	d	- <b>CHO</b>

Abbreviations: d: doublet; dd: double doublet; td: triple doublet; t: triplet; tt: triple triplet; q: quadruplet; m: multiplet; br: broad signal.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

<sup>\*\*</sup> The assignment of the <sup>1</sup>H NMR signals of the protons was made with the aid of standard compounds.

The assignment of the <sup>1</sup>H NMR signals of the protons of aldehydes was made with the data taken from the literature:

<sup>a</sup> Guillén, M.D.; Ruiz, A. (2004). *Eur. J. Lipid Sci. Tech.* 106(10), 680-687.

<sup>a</sup> Guillén, M.D.; Ruiz, A. (2005a). *Eur. J. Lipid Sci. Tech.* 107(1), 36-47.

<sup>a</sup> Guillén, M.D. ; Ruiz, A. (2005b). *J. Sci. Food Agric.* 85(14), 2413-2420.

<sup>a</sup> Goicoechea, E.; Guillen, M.D. (2010). *J. Agric. Food Chem.* 58(10), 6234-6245.

<sup>b</sup> Moumtaz, S.; Percival, B.C.; Parmar, D.; Grootveld, K.L.; Jansson, P.; Grootveld, M. (2019). *Sci. Rep.* 9, 1-21.

Table S12. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of furan groups.

Alkyl-furans		
Chemical shift (ppm) **	Multiplicity	Functional group (Type of protons) *
7.27	dd	$-\text{CH}=\text{CH}-$ (ar. C-4)
6.24	dd	$-\text{CH}=\text{CH}-$ (ar. C-3)
5.94	m	$-\text{CH}-$ (ar. C-5)
Alkyl furanones (5-pentyl-(5H)-furan-2-one)		
Chemical shift (ppm) <sup>a</sup>	Multiplicity	Functional group (Type of protons) *
<b>7.46</b>	dd	$-\text{CH}=\text{CH}-$ (ar. C-4)
6.10	dd	$-\text{CH}=\text{CH}-$ (ar. C-3)
5.04	m	$-\text{CH}-$ (ar. C-5)
1.26-2.80	m	$-\text{CH}_2-$
0.90	t	$-\text{CH}_3$

Abbreviations: dd: double doublet; t: triplet; m: multiplet.

\* Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

\*\* The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of 5-pentyl-(5H)-furan-2-one was made with the data taken from the literature:

<sup>a</sup> Bonete, P.; Najera, C. (1994). *J. Org. Chem.* 59(11), 3202-3209.

<sup>a</sup> Braukmüller, S.; Brückner, R. (2006). *Eur. J. Org. Chem.* 2006(9), 2110-2118.

Table S13. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of epoxy derivatives coming from linoleic acyl groups.

<b>Z epoxides coming from linoleic acyl groups</b> (Mono-epoxides)		
Chemical shift (ppm) <sup>a,b, **</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
5.50-5.60	m	-CHOCH-CH <sub>2</sub> -CH=CH-
5.35-5.50	m	-CHOCH-CH <sub>2</sub> -CH=CH-
<b>2.95</b>	m	- <b>CHOCH</b> -CH <sub>2</sub> -CH=CH-
2.20-2.40	m	-CHOCH-CH <sub>2</sub> -CH=CH-
1.45-1.60	m	-CH <sub>2</sub> -CH <sub>2</sub> -CHOCH-
0.87	t	-CH <sub>3</sub>
<b>Z epoxides coming from linoleic acyl groups</b> (Di-epoxides)		
Chemical shift (ppm) <sup>a, b, **</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
3.09-3.14	m	-CHOCH-CH <sub>2</sub> -CHOCH-
3.00	m	-CHOCH-CH <sub>2</sub> -CHOCH-
1.70-1.85	m	-CHOCH-CH <sub>2</sub> -CHOCH-
1.45-1.60	m	-CH <sub>2</sub> -CH <sub>2</sub> -CHOCH-
0.87	t	-CH <sub>3</sub>
<b>E epoxides coming from linoleic acyl groups</b> (Mono-epoxides)		
Chemical shift (ppm) <sup>a, **</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
5.47-5.56	m	-CHOCH-CH <sub>2</sub> -CH=CH-
5.33-5.42	m	-CHOCH-CH <sub>2</sub> -CH=CH-
<b>2.66-2.71</b>	m	- <b>CHOCH</b> -
2.35-2.44	m	-CHOCH-CH <sub>2</sub> -CH=CH-
1.26-1.66	m	-CH <sub>2</sub> -
0.87	t	-CH <sub>3</sub>

Abbreviations: t: triplet; m: multiplet.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

<sup>\*\*</sup> The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of epoxides derived from linoleic acyl groups was made with the data taken from the literature:

<sup>a</sup> Nilewski, C.; Chapelain, C.L.; Wolfrum, S.; Carreira, E.M. (2015). *Org. Lett.* 17(22), 5602-5605.

<sup>b</sup> Xia, W.; Budge, S.M.; Lumsden, M.D. (2016). *J. Am. Oil. Chem. Soc.* 93, 467-478.



Table S14. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of different types of dihydroxy groups (dHO).

<b>dHO</b> (9,10-dihydroxy-12Z-octadecanoate)		
Chemical shift (ppm) <sup>a,**</sup>	Multiplicity	Functional group (Type of protons) <sup>*</sup>
5.52	m	-CH=CH-CH <sub>2</sub> -CHOH-CHOH-
5.42	m	-CH=CH-CH <sub>2</sub> -CHOH-CHOH-
<b>3.42</b>	br	-CH <sub>2</sub> OH-CH <sub>2</sub> OH-
2.62	br	-CHOH-CHOH-
2.27	t	-OCO-CH <sub>2</sub> -
2.25	q	-CH=CH-CH <sub>2</sub> -CHOH-CHOH-
2.02	q	-CH <sub>2</sub> -CH=CH-CH <sub>2</sub> -CHOH-CHOH-
1.28-1.60	br	-CH <sub>2</sub> -
0.87	t	-CH <sub>3</sub>

Abbreviations: t: triplet; q:quadruplet; m: multiplet; br: broad signal.

<sup>\*</sup> Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

<sup>\*\*</sup> The assignment of the  $^1\text{H}$  NMR signals of the protons was made with the aid of standard compounds.

The assignment of the  $^1\text{H}$  NMR signals of the protons of dHO was made with the data taken from the literature:

<sup>a</sup> Nilewski, C.; Chapelain, C.L.; Wolfrum, S.; Carreira, E.M. (2015). *Org. Lett.* 17(22), 5602-5605.

<sup>a</sup> Yang, J.; Morton, M.D.; Hill, D.W.; Grant, D.F. (2006). *Chem. Phys. Lipids.* 140 (1-2), 75-87.

Table S15. Chemical shift assignments and multiplicities of  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$  of protons of formic acid and formates.

Formic acid		
Chemical shift (ppm) <sup>a</sup>	Multiplicity	Functional group (Type of protons) *
<b>8.01</b>	s	<b><u>H</u></b> -COOH
Formates or polyformates		
Chemical shift (ppm) <sup>b</sup>	Multiplicity	Functional group (Type of protons) *
<b>8.05-8.20</b>	m	-CH <sub>2</sub> -CH-O <b><u>C</u></b> H=O-
2.3	t	-OCO- <b><u>C</u></b> H <sub>2</sub> -
2.05	s	-CH <sub>2</sub> -CH-OCH=O-
1.3-1.5	m	- <b><u>C</u></b> H <sub>2</sub> -
0.9	t	- <b><u>C</u></b> H <sub>3</sub>

Abbreviations: s: singlet; t: triplet; m: multiplet.

\* Area of the signals due to the protons in bold, together with the area of the *sn*-1 and *sn*-3 signals of TG shown in Table S1, were used for the quantification of each compound, using the equation [eq. 1] showed in the Materials and Methods.

The assignment of the  $^1\text{H}$  NMR signals of the protons of formic acid and formates was made with the data taken from the literature:

<sup>a</sup> Babij, N. R.; McCusker, E. O.; Whiteker, G. T.; Canturk, B.; Choy, N.; Creemer, L. C.; ... Li, F. (2016). *Org. Process Res. Dev.* 20(3), 661-667.

<sup>b</sup> Harry-O'kuru, R.E.; Biresaw, G.; Tisserat, B.; Evangelista, R. (2016). *J. Lipids*, ID 3128604, 12.