

Supporting information for

Analysis of glycerol bound ω -oxo-fatty acids as ω -dioxane-FAME-derivatives¹

Anne Zartmann^{a,b}, Jean-Marie Galano^c, Simon Hammann^{a,b*}

^a Department of Food Chemistry and Analytical Chemistry, University of Hohenheim, Garbenstraße 28, 70599 Stuttgart, Germany

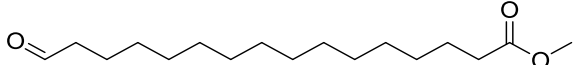
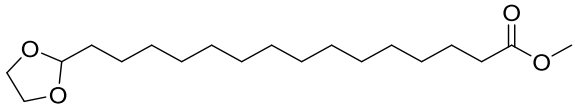
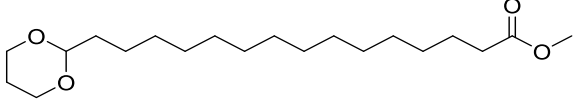
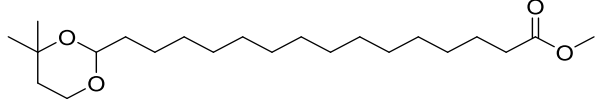
^b Food Chemistry, Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Nikolaus- Fiebiger- Straße 10, 91058 Erlangen, Germany

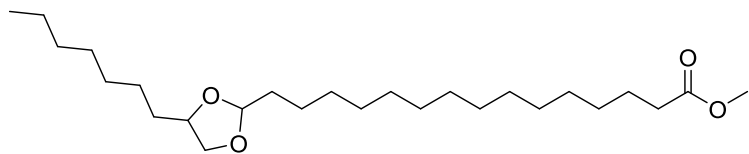
^c Institut des Biomolécules Max Mousseron, IBMM, Université de Montpellier, CNRS, ENSCM. 1919 route de Mende, 34293 Montpellier, France

*Corresponding author at: Department of Food Chemistry and Analytical Chemistry, University of Hohenheim, Garbenstraße 28, 70599 Stuttgart, Germany. E-Mail: simon.hammann@uni-hohenheim.de, telephone: +49711-459-23978

¹ This article is a contribution to the EpiLipidNET Virtual Special Issue on Analysis and Biological Importance of Lipids and Modified Lipids coordinated by Corinne M. Spickett
Corresponding author email: simon.hammann@uni-hohenheim.de

Table 1: Retention times [min] of non-oxidized saturated FAMES and 16-oxo-16:0-ME and its acetal derivatives are shown. Using the retention time and chain length of the non-oxidized FAMES a linear regression ($R^2 > 0.998$) was performed and corresponding retention index of FAME (RI_{FAME}) was calculated for 16-oxo-16:0 ME and the derivatives. ^aThe mean value of the retention times of two diastereomers was used for calculations. ^bThe RI_{FAME} for this derivative was extrapolated.

FAME	Retention time [min]	RI_{FAME} (rounded)	Increase of RI_{FAME} compared to the reactant
18:0-ME	20.83	-	-
20:0-ME	22.59	-	-
21:0-ME	23.42	-	-
22:0-ME	24.21	-	-
23:0-ME	24.98	-	-
24:0-ME	25.70	-	-
 16-oxo-16:0-ME (molecule 0)	21.06	18.18 (18)	-
 15-(1,3-dioxolan-2-yl)-15:0-ME (product 1)	23.34	20.99 (21)	2.81
 15-(1,3-dioxan-2-yl)-15:0-ME (product 2)	24.14	21.97 (22)	3.79
 15-(4,4-dimethyl-1,3-dioxan-2-yl)-15:0-ME (product 3)	24.55	22.48 (22)	4.30



27.02
(26.96 & 27.08)^a

25.52 (26)^b

7.34

15-(4-heptyl-1,3-dioxolan-2-yl)15:0-ME (product 4)

Table 2: Contents of ω -oxo-FAs in sunflower oil without (SO) and with derivatization to the respective dioxanes (SOD) equally rapeseed oil with derivatization (ROD) after 20 h heating at 180°C. ^amean \pm standard deviation (n=3)

	Content of ω -oxo-FAs [mg/g]		
	SO	SOD	ROD
5-A	< LOD	0.0011 \pm 0.002	0.0097 \pm 0.0011
6-A	< LOD	0.028 \pm 0.004	0.031 \pm 0.006
7-A	0.047 \pm 0.009 ^a	0.082 \pm 0.011	0.10 \pm 0.01
8-A	0.29 \pm 0.02	0.39 \pm 0.04	0.35 \pm 0.03
9-A	1.8 \pm 0.1	1.7 \pm 0.1	1.4 \pm 0.1
10-A	0.24 \pm 0.01	0.22 \pm 0.02	0.19 \pm 0.02
Σ	2.3 \pm 0.1	2.5 \pm 0.2	2.1 \pm 0.2

Table 3: NMR-Data of synthesized substances. ¹H-NMR-Data was acquired in CDCl₃ at 400MHz and ¹³C-NMR-Data was in CDCl₃ at 101MHz.

Substance		Signals
Methyl 16-oxohexadecanoate	¹ H	δ [ppm] 9.76 (t, J = 1.9 Hz, 1H), 3.66 (s, 3H), 2.42 (td, J = 7.4, 1.9 Hz, 2H), 2.30 (t, J = 7.6 Hz, 2H), 1.61 (m, 4H), 1.40 – 1.20 (m, 20H).
	¹³ C	δ [ppm] 203.40, 174.73, 51.81, 44.28, 34.47, 29.95, 29.92, 29.79, 29.77, 29.70, 29.60, 29.51, 29.50, 25.30, 22.43.
Ethyl 3-((1R*,2S*)-2-(3-oxopropyl)cyclopropyl) Propanoate (IS-EE)	¹ H	δ [ppm] 9.80 (t, J = 1.8 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.55 (td, J = 7.3, 1.8 Hz, 2H), 2.40 (t, J = 7.6 Hz, 2H), 1.84 – 1.69 (m, 2H), 1.59 – 1.43 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 0.84 – 0.70 (m, 2H), 0.65 (m, 1H), -0.21 (m, 1H).
	¹³ C	δ [ppm] 202.67, 173.61, 60.31, 44.38, 34.76, 24.19, 21.42, 15.56, 15.37, 14.27, 10.86.
15-(1,3-dioxan-2-yl)-15:0-ME	¹ H	δ [ppm] 4.50 (t, J = 5.2 Hz, 1H), 4.10 (m, 2H), 3.81 – 3.71 (m, 2H), 3.66 (s, 3H), 2.30 (t, J = 7.6 Hz, 2H), 2.15 – 2.00 (m, 2H), 1.66 – 1.50 (m, 4H), 1.41 – 1.17 (m, 22H).
	¹³ C	δ [ppm] 174.74, 102.82, 67.26, 51.81, 35.61, 34.48, 29.98, 29.94, 29.90, 29.88, 29.85, 29.80, 29.61, 29.50, 26.21, 25.31, 24.33.

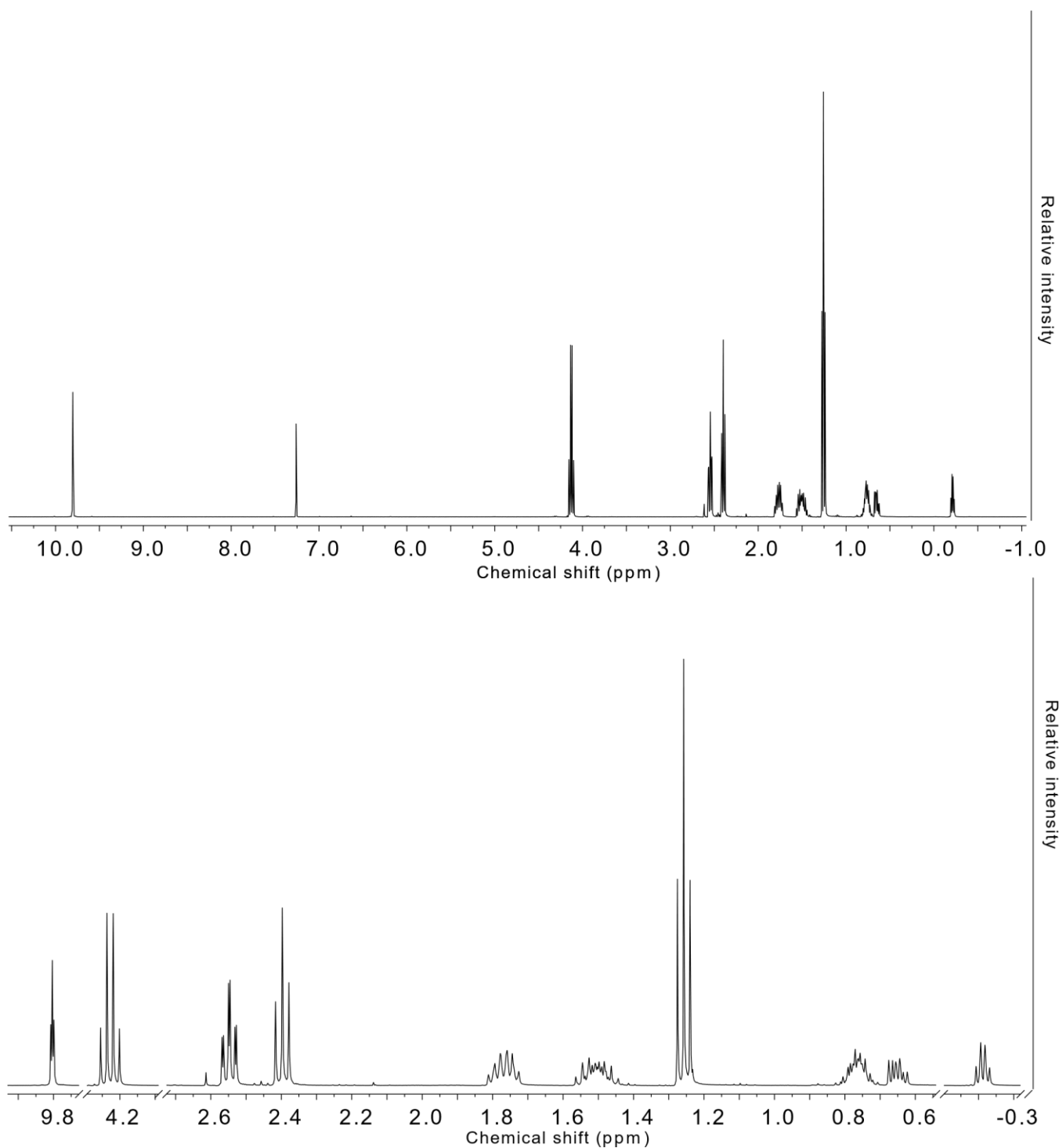


Figure 1: ¹H-NMR-spectra (400 MHz) of ethyl 3-((1R*,2S*)-2-(3-oxopropyl)cyclopropyl)propanoate (IS-EE) in CDCl₃. The top figure shows the entire, the lower sections of the spectrum (please note the truncated x-axis)

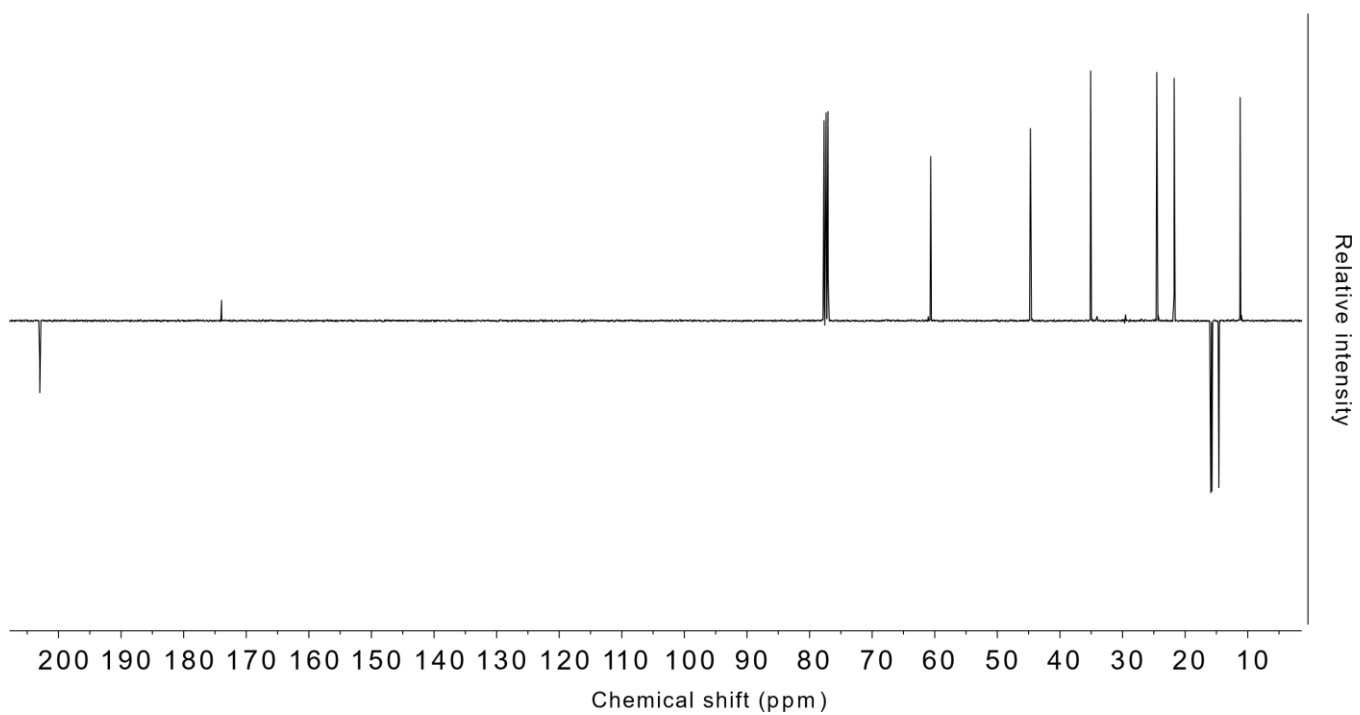


Figure 2: ^{13}C -NMR-spectra (101 MHz) of ethyl 3-((1R*,2S*)-2-(3-oxopropyl)cyclopropyl)propanoate (IS-EE) in CDCl_3 .