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# Thermal stability of the linoleic acid/ $\alpha$ - and $\beta$ -cyclodextrin complexes

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#### Abstract

This paper presents a thermal stability study of the linoleic  $\operatorname{acid}/\alpha$ - and  $\beta$ -cyclodextrin ( $\alpha$ - and  $\beta$ CD) complexes. Bionanoparticles were obtained by a solution method and were characterized by differential scanning calorimetry and transmission electron microscopy. The pure linoleic acid, the corresponding thermally (50–150 °C) degraded raw linoleic acid samples or those recovered from the complexes were analyzed by gas chromatography-mass spectrometry, after conversion to the methyl esters. Nanoparticles were obtained with good yields of 88% and 74% for  $\alpha$ - and  $\beta$ CD complexes, respectively. The main degradation products (for the thermally degraded raw samples) were aldehydes, epoxy, dihydroxy derivatives, homologues, and isomers of linoleic acid. A good thermal stability of nanoparticles can be observed, especially for the linoleic acid/ $\alpha$ CD complex, which contains a relative concentration above 98% fatty acid in the case of temperature degradations of 50 and 100 °C. A lower concentration of 92% can be observed in the case of the linoleic acid/ $\beta$ CD complex but, for the temperature degradation of 150 °C, the linoleic acid was partially converted to more stable geometrical isomers.

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Keywords: Nanoparticles; Thermal stability; Linoleic acid; Cyclodextrins; DSC analysis; TEM analysis; GC-MS analysis

#### 1. Introduction

The application of oligo- and polysaccharides in the drug, cosmetic, and food industries represents a very large field. Some of the most used systems for protecting and controlled release of biomolecules are liposomes (Grabielle-Madelmont, Lesieur, & Ollivon, 2003; Kim & Baianu, 1991; Loukas & Gregoriadis, 1997; Saarinen-Savolainen, Järvinen, Taipale, & Urtti, 1997), especially in the pharmaceutical industry and in medical practice. In recent last years, liposomes have been extensively obtained and used as biological membranes and as transporters for various biocompounds (Puglisi, Fresta, Mazzone, Furneri, & Tem-

pera, 1995; Saravolac, Kournikakis, Gorton, & Wong, 1996). Some studies were performed in the immunoisolated cell transplantation field (Li, 1998; Rihova, 2000) and for the encapsulation of proteins, enzymes and antigens (Bollag, Rozycki, & Edelstein, 1996; Gombotz & Wee, 1998).

A very interesting field of supramolecular chemistry is the complexation of organic molecules (guest) in organic structures which contain cavities (host), the process being known as host–guest chemistry, molecular encapsulation, or nanoencapsulation (Szejtli, 1988; Venema, 1996). Most used as host molecules are the cyclodextrins (CDs), which are natural cyclic oligosaccharides, containing 6 ( $\alpha$ CD), 7 ( $\beta$ CD), 8 ( $\gamma$ CD) or more glucopyranose moieties; they all have the structure of a truncated cone with a hydrophobic inner cavity, which can interact with a hydrophobic organic molecule (geometrically compatible) and form a more

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stable, protective (to air, temperature, light), and controlled releasing supramolecular system (Nepogodiev & Stoddart, 1998; Szeitli, 1988). These matrices were especially used for the encapsulation of drugs (Bocanegra, Seijas, & Yibirín, 2003; Diakur, Zuo, & Wiebe, 1999; Kinnarinen, Jarho, Järvinen, & Järvinen, 2003; Veiga & Merino, 2002), odorant and flavouring compounds (Eckert, 1996; Goubert et al., 2001; Liu, Furuta, Yoshii, Linko, & Coumans, 2000; Szejtli, 1982), food additives (Crittenden & Playne, 1996; O'Boyle, Aladin-Kassam, Rubin, & Diosady, 1992), and biomacromolecules (Miertus et al., 1998). Very interesting applications of cyclodextrins are for the microencapsulation, in liposomes, of the complexes with various drugs (Kim & Baianu, 1991) and in the biosensor field (transducers) (Culha, Lavrik, Schell, Tipple, & Sepaniak, 2003).

In our previous work (Hădărugă, Hădărugă, Bandur, & Lupea, 2003, 2004a, 2004b), we have studied the nanoencapsulation of the oleic acid and different volatile oils and odorant compounds in CDs in order to establish the capacity of encapsulation of oligosaccharides and evaluate the stability of complexes. In this study, we have investigated the thermal stability of linoleic acid encapsulated in  $\alpha$ - and  $\beta$ CD, using differential scanning calorimetry (DSC) and gas chromatography-mass spectrometry (GC-MS) analyses. Some linoleic acid degradation products, which appear in the presence of air and humidity, at different temperatures, play an important role in human health and could be responsible for various diseases, e.g., neoplasia. In order to establish the type and the concentration of these degradation products, and to evaluate the protective capacity of CDs, a thermal stability study of the linoleic acid/CDs complexes was carried out.

# 2. Materials and methods

## 2.1. Materials

*Linoleic acid* (>99%, standard for GC) and  $C_8-C_{20}$  *alkane standard solution* were purchased from Fluka Chemie AG (Switzerland),  $\alpha$ - and  $\beta$ -*cyclodextrin* ( $\alpha$ CD and  $\beta$ CD, respectively; >99%, reagent grade), were purchased from Merck Co., Inc., New Jersey, as well as the *methanol* · *BF*<sub>3</sub> reagent used for deriving the fatty acids esters.

#### 2.2. Complexation

The complexation of the linoleic acid with  $\alpha$ - or  $\beta$ CD was performed by dissolving  $\alpha$ - or  $\beta$ CD in distilled water at 50 ± 1 °C in a thermocontrolled minireactor, equipped with a reflux condenser, and by adding an ethanolic linoleic acid solution (the weight corresponding to the linoleic acid:CDs ratio of 1:1, Table 1). After 15 min of stirring, the complex suspension was slowly cooled to 20 °C in about 4 h; the complex crystallization was completed in the refrigerator at 4 °C for 24 h. The complex was then filtered, washed with ethanol and dried.

Table 1	
Linoleic acid and CD quantities used for complexation	

No	Complex	m <sub>linoleic acid</sub> (mg)	$m_{lpha/eta  ext{CD}}$ (mg)	$m_{\text{complex}}$ (mg)	Yield (%)
1	Linoleic acid/aCD	140.2 140.2	540 671	598.2	87.94 73.95
2	Lilloleic acid/pCD	140.2	0/1	399.9	13.95

#### 2.3. Fatty acid ester derivatives

In order to establish the linoleic acid content (in the raw sample and in the degraded or complex recovered ones) by GC–MS analysis, samples were esterified to the corresponding more volatile methyl esters using the methanol  $\cdot$  BF<sub>3</sub> method: the raw sample, or the hexane solution containing fatty acids, was treated with MeOH  $\cdot$  BF<sub>3</sub> solution, refluxed 2 min on a water bath, and the more hydrophobic esters were extracted in hexane using a saturated NaCl solution for a good separation. The organic layer was separated and dried over anhydrous CaCl<sub>2</sub>.

# 2.4. Fatty acid extraction from the complex

The linoleic acid/ $\alpha$ - or  $\beta$ CD complex was dissolved in distilled water in a minireactor equipped with a reflux condenser and a magnetic stirrer, a small volume of hexane was added to the solution, and the emulsion was stirred for 20 min at 69 °C. After cooling, the organic layer was separated and the aqueous layer was extracted another three times with the same volume of hexane. All organic layers were dried over anhydrous CaCl<sub>2</sub> and analyzed by GC–MS.

## 2.5. Free and complexed linoleic acid degradation

Free and complexed linoleic acid thermal degradations were achieved on glass plates, in a thin film for liquid samples and as fine powder for solid complexes, in a thermocontrolled oven, at a temperature in the range of 50–150 °C, in the presence of air (70% relative humidity) at normal pressure, for 2 h (Table 2).

#### 2.6. DSC analysis

Differential scanning calorimetry (DSC) was carried out on a DSC 204 Netzsch apparatus, with a temperature

Table 2	
Degradation conditions for free and complexed linoleic ac	id

No	Sample name	m <sub>sample</sub> (mg)	Temperature (°C)	Time (min)
1	Linoleic acid	100	50	120
2	Linoleic acid	100	100	120
3	Linoleic acid	100	150	120
4	Linoleic acid/aCD	100	50	120
5	Linoleic acid/aCD	100	100	120
6	Linoleic acid/aCD	100	150	120
7	Linoleic acid/BCD	100	50	120
8	Linoleic acid/BCD	100	100	120
9	Linoleic acid/BCD	100	150	120



Fig. 1. DSC analysis of the linoleic acid/ $\alpha$ - and  $\beta$ CD complexes comparatively with those of the pure linoleic acid,  $\alpha$ CD, and  $\beta$ CD.



Fig. 2. Gas chromatogram for the linoleic acid (raw) for the KI in the range 2000-2600.

Table 3									
MS identification,	quantification,	and Kovats	indices of t	he main	compounds	from the	methyl ester	derived lin	noleic acid sample

No	MS identification	Concentration (%)	Kovats index (KI)
1	Nonanoic acid, 9-oxo-, methyl ester	0.02	1436
2	Octanoic acid, 6,6-dimethoxy-, methyl ester <sup>a</sup>	0.06	1601
3	Linoleic acid, methyl ester	97.3	2121
4	7,10-Octadecadienoic acid, methyl ester	0.03	2152
5	8,11-Octadecadienoic acid, methyl ester	0.08	2196
6	9,12-Octadecadienoic acid, methyl ester (isomer) <sup>a</sup>	0.01	2233
7	6,9,12-Octadecatrienoic acid, methyl ester (isomer 1)	0.09	2253
8	6,9,12-Octadecatrienoic acid, methyl ester (isomer 2)	0.10	2267
9	Linolenic acid, methyl ester	0.15	2299
10	6,9,12-Octadecatrienoic acid, methyl ester (isomer 3)	0.24	2303
11	Oxiraneundecanoic acid, 3-pentyl-, methyl ester, cis- <sup>a</sup>	0.21	2437
12	Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoate <sup>a</sup>	0.17	2525
13	9,12-Octadecadienal, dimethyl acetal <sup>a</sup>	0.33	2579
14	(E)-8-methyl-9-tetradecen-1-ol acetate <sup>a</sup>	0.02	2609

<sup>a</sup> Identified with lower probability matching by NIST MS Search algorithm (see supporting information).

programme of -50 to 200 °C, the heating rate being 4 °C/min. Data acquisition was performed with the DSC Netzsch 204-Acquisition Soft, and the analysis of the data was performed with the Netzsch-Proteus Analysis ver. 4.0 programme (see supporting information for full range DSC analyses).

# 2.7. TEM analysis

Transmission electron microscopy (TEM) was performed on a Tesla BS-613 apparatus, with an acceleration voltage of 80 kV. One hundred particles were take into account in order to establish the mean particle size and the

Table 4

MS identification, quantification, and Kovats indices of the compounds from the methyl ester derived linoleic acid sample degraded at 50, 100 and 150 °C

	No	MS identification	KI	$c_1^{\rm a}$ (%)	$c_2^{b}$ (%)	$c_3^{c}$ (%)
2       Methyl caproate <sup>2</sup> 0.01       0.24       1.         3       2Heptend, (Z)-       980       0.15       1.58       10,         4       Hexanal dimethyl acetal       980       0.15       1.58       10,         5       Methyl cnanthate       1026       0.044       0.         6       2-Octenal, (Z)-       1059       0.007       0.07         7       Heptans, 1,1-dimethoxys*       1126       0.02       0.55       1.         9       2-Nonenal, (E)-       1136       0.02       0.01       0.02         12       2,4-Hexadiene, 1,6-dimethoxy-, (E,E)-4       1334       0.02       0.         12       2,4-Hexadiene, 1,6-dimethoxy-, (E,E)-4       134       0.02       0.         13       Methyl caproate? (isomer f')       1344       0.02       0.01       0.01         14       Heptane, 1, -dimethoxy-, (E,E)-4       1360       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.02       0.       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.02	1	Malonaldehyde, bis(dimethyl acetal) <sup>d</sup>	883		0.12	0.87
	2	Methyl caproate <sup>e</sup>	925	0.01	0.24	1.83
4       Hex_nal dimethyl acetal       980       0.15       1.58       10.0         6       2-Octenal, (E)-       1059       0.07         7       Heptane, 1,1-dimethoxy- <sup>5</sup> 1080       0.00       0.04       0.0         8       Capylic acid methyl ester       1126       0.02       0.05       1.         9       2-Nonenal, (E)-       1160       0.02       0.05       1.         10       2-Octeadienal       1317       0.01       0.02       0.01         12       2-H-readiena, 1dimethoxy- (E,E)- <sup>d</sup> 1334       0.02       0.0         13       Methyl esproate? (isomer)"       1349       0.02       0.         14       Heptane, 1dimethoxy- ? (aldehyde, dimethyl acetal)"       1440       0.02       0.         15       Nonanoci acid, 9-0-0, methyl ester       1500       0.01       0.15       0.         15       Nonanoci acid, 6-0, methyl ester       1515       0.0       0.55       8.         2       Octanelioic acid, dimethyl ester       155       0.0       0.55       8.         2       Octanelioic acid, dimethyl ester       1660       0.0       0.0       1.0         10       Nonanocicacid, 3.       Me	3	2-Heptenal, (Z)-	958		0.01	
5       Methyl enanthale       1026       0.04       0.0         6       2-Octenal, $(E)$ -       1059       0.07       0         7       Heptane, 1,1-dimethoxy- <sup>5</sup> 1060       0.00       0.04       0.         8       Caprylie acid methyl ester       1126       0.02       0.55       1.         9       2-Nonenal, $(E)$ -       1106       0.02       0.01       0.02       0.01         10       2-4-Decadienal       1317       0.01       0.02       0.01       0.02       0.01         12       2-4-Hexadiene, 1.6-dimethoxy-, $(E,E)^{-d}$ 1354       0.01       0.02       0.01         13       Methyl esoroctanoate       1354       0.02       1.00       0.01       0.15       0.0	4	Hexanal dimethyl acetal	980	0.15	1.58	10.6
6       2-Orienal, (E)-       1059       007         7       Heptane, 1,1-dimethoxy= <sup>6</sup> 1080       0.00       0.04       0.         8       Caprylic add methyl ester       1126       0.02       0.55       1.         9       2-Nonenal, (D)-       1160       0.02       0.55       1.         10       Adbreadine, 1,6-dimethoxy, (E,D)- <sup>di</sup> 1334       0.01       0.01         12       2.4-Hexadines, 1,6-dimethoxy, (E,D)- <sup>di</sup> 1334       0.02       0.0         13       Methyl caproate? (isomer) <sup>6</sup> 1344       0.01       0.01       0.1         14       Heptane, 1,1-dimethoxy-, nethyl ester       1436       0.02       1.09       6.         16       Octanedioic acid, (indimethyl ester       1515       0.0       0.55       8.         10       Octanedioic acid, (indimethyl ester       1550       0.0       0.55       8.         2       2-Octanel, 8,8-dimethoxy-, methyl ester       1500       0.01       0.55       8.         10       Nonanceico acid, (indimethyl ester       1660       0.21       2.51       10.         12       Dimethoxy-docanoica       1660       0.01       0.55       8.         12	5	Methyl enanthate	1026		0.04	0.25
7       Heptane, 1,1-dimethoxy-a       1080       0.00       0.04       0.         8       Caprylic acid methyl ester       1126       0.02       0.55       1.         9       2-Nonenal, (b)       0.01       0.02       0.01       0.02         10       2.4-Decadienal       1317       0.01       0.02       0.01         11       Methyl 8-oxootanoate       1334       0.01       0.02       0.01         12       2.4-Hexadiene, 1,6-dimethoxy-, ( <i>E</i> , <i>D</i> , <sup>d</sup> 1334       0.02       0.0         13       Methyl eaproat2 (isomer) <sup>6</sup> 1394       0.02       0.0         14       Heptane, 1,1-dimethoxy-? (aldehyde, dimethyl acetal) <sup>6</sup> 1400       0.01       0.01       0.02       0.0         15       Mothyl eaproat2 (isomer) <sup>6</sup> 1436       0.02       0.0       0.55       8.         16       Octanoicia acid, dimethyl ester       1550       0.00       0.55       8.         17       Nonanocia acid, dimethyl ester       1550       0.00       0.55       8.         10       Methyl 8(2-furyllocanoate       1660       0.21       2.51       10.         11       Methyl 1(-xo.0undecenoate       1698       0.04       <	6	2-Octenal. (E)-	1059		0.07	
8       Caprylic add methyl ester       1126       0.02       0.55       1.         9       2-Nonenal, $(E)$ -       1160       0.02       0.02         11       Methyl 8-oxoctanoate       1334       0.01         12       2-Hexadinen, 1, 6-dimethoxy-, $(E, E)^{-d}$ 1334       0.02       0.02         13       Methyl caproate? (isomethys, $(E, E)^{-d}$ 1334       0.02       0.01         14       Heptane, 1, 1-dimethoxy-? (aldehyde, dimethyl acetal) <sup>6</sup> 1440       0.02       0.0         15       Nonanoic acid, 9-oxo, methyl ester       1440       0.02       0.0         16       Octancolic acid, 6.6-diretnamethoxy-       1515       0.00       0.55       8.         0       2-Octanol, 8,8-dimethoxy-s       1515       0.00       0.55       8.         0       2-Octanol, 8,8-dimethoxy-d       1600       0.21       2.51       10.         11       Methyl 8-(2-furyl)octanoate       1630       0.04       0.         12       Decanceloic acid, dimethyl ester       1550       0.00       0.08         2       Methyl 11-cox-9docecnoate       1698       0.04       0.         2       Methyl 12-cox-9doceconoate       1690       0.04	7	Heptane, 1,1-dimethoxy- <sup>e</sup>	1080	0.00	0.04	0.27
9 $2 \cdot Nonenal, (E)$ .       1160       0.02         10 $2.4 \cdot Decadenal       1317       0.01         11       Methyl 8-oxooctanoate       1334       0.01         12       2.4 \cdot Hexadiene, 1, 6-dimethoxy, (E, E)^{-d}       1334       0.01         13       Methyl aprotate? (isomer)*       1394       0.02       0.         14       Heptane, 1, 1-dimethoxy-? (aldehyde, dimethyl acetal)°       1400       0.01       0.02       0.         15       Nonanoic acid, 6-d-dimethyl ster       1436       0.02       1.09       6.         0.01       Octanoic acid, 6, 6-dimethoxy-, methyl ester       1500       0.01       0.15       0.         18       3-Hexanone, 1, 5, 6, 6-tetramethoxy-       1515       0.       0.00       0.55       8.         2-Octanol, 8, 8-dimethoxy-       1600       0.21       2.51       10.         19       Nonanedicic acid, dimethyl ester       1600       0.21       2.51       10.         20       Decanedicic acid, dimethyl ester       1600       0.21       2.51       10.         21       I-12-Dimethoxydoceanoite       1624       0.00       0.18       0.01       0.         21       Methyl 12-xoo-9-dodceenoate $	8	Caprylic acid methyl ester	1126	0.02	0.55	1.39
10       2.4-Decadienal       1317       0.01         11       Methyl 8-oxoctanoate       1334       0.0         12       2.4-Hexadinen, 1,6-dimethoxy, $(E,E)^{c1}$ 1334       0.02       0.         13       Methyl caproate? (isomer)*       1394       0.02       0.         14       Heptane, 1,1-dimethoxy, ? (aldehyde, dimethyl acetal)c       1400       0.01       0.01       0.01         15       Nonanoic acid, 6-dimethoxy, methyl ester       1436       0.02       1.09       6.         16       Octanedioic acid, dimethyl ester       1500       0.01       0.15       0.         18       3-Hexanone, 1,5,6,6-tetramethoxy-       1515       0.       0.         19       Nonanecioic acid, dimethyl ester       1600       0.21       2.51       10.         10       Methyl 8-(2-furyl)octanoate       1660       0.01       0.         20       Decaredioic acid, dimethyl ester       1698       0.04       0.         21       Decaredioic acid, dimethyl ester       1690       0.01       0.         22       Methyl 11-oxo-9-undecenoate       1690       0.04       0.         23       Methyl 12-oxo-9-dodecenoate       1690       0.02       0. <td>9</td> <td>2-Nonenal, (E)-</td> <td>1160</td> <td></td> <td>0.02</td> <td></td>	9	2-Nonenal, (E)-	1160		0.02	
11       Methyl 8-xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx	10	2,4-Decadienal	1317		0.01	
12 $2,4$ -Hexadiene, $1,6$ -dimethoxy-, $(E,E)^{-d}$ 1354       0.01         13       Methyl caproate? (isomer) <sup>2</sup> 1400       0.02       0.02         14       Heptane, $1,1$ -dimethoxy-? (aldehyde, dimethyl acetal) <sup>e</sup> 1436       0.02       1.09       6.         16       Octanoic acid, 6-odimethoxy- methyl ester       1500       0.01       0.15       0.02       0.0         17       Octanoic acid, 6-odimethoxy-, methyl ester       1500       0.01       0.15       0.0         18       3-Hexanone, 1,5,6,6-terramethoxy-       1515       0.00       0.55       8.         2-Octanoic acid, dimethyl ester       1600       0.21       2.31       10.         19       Nonanedioic acid, dimethyl ester       1600       0.21       2.31       10.         10       Methyl 8-(2-furyl)octanoate       1624       0.0       0.02         20       Decanedioic acid, dimethyl ester       1600       0.01       0.         21       Methyl 12-oxo-9-docecnoate       1800       0.01       0.02       0.         21       Octanoic acid, 6, 6-dimethoxy-, methyl ester       1817       0.04       0.02       0.         23       Methyl 12-oxo-9-docecenoate       1800       0.01	11	Methyl 8-oxooctanoate	1334			0.53
13       Methyl caproate? (isomer) <sup>6</sup> 1394       0.02       0.         14       Heptane, 1, 1-dimethoxy-? (ialdehyde, dimethyl acetal) <sup>6</sup> 1400       0.01         15       Nonanoic acid, 9-oxo, methyl ester       1436       0.02       1.09         16       Octanedioic acid, 6, 6-dimethoxy-, methyl ester       1500       0.01       0.15       0.         3       Hexanone, 1, 5, 66-terramethoxy-       1515       0.0       0.55       8.         0       2-Octanoic acid, dimethyl ester       1550       0.00       0.55       8.         0.2       Decanedioic acid, dimethyl ester       1660       0.21       2.51       10.         21       Methyl 1-xox-9-undecenoate       1698       0.044       0.         22       Octanoic acid, 6-dimethoxy-       1800       0.10       0.08         23       Methyl 1-xox-9-undecenoate       1800       0.01       0.04         24       12,12-Dimethoxydodecanoic acid, methyl ester       1817       0.04         25       Methyl 12-oxo-9-dodecenoate       1800       0.01       0.02         26       Nonaneal, 3.7-dimethoxy-       184       0.03       0.18         27       Tetradecanoic acid, 6-dimethoxy-       1954       <	12	2,4-Hexadiene, 1,6-dimethoxy-, (E,E)- <sup>d</sup>	1354	0.01		
14       Heptane, 1, 1-dimethoxy- $\frac{9}{2}$ (aldehyde, dimethyl acetal) <sup>e</sup> 1400       0.01         15       Nonanoic acid, 0-oxo-, methyl ester       1436       0.02       1.09       6.6         15       Octanoic acid, 6,6-dimethoxy-, methyl ester       1500       0.01       0.15       0.         16       Octanoic acid, 6,6-dimethoxy-, methyl ester       1500       0.01       0.15       0.         17       Octanoic acid, 6,6-dimethoxy-, methyl ester       1550       0.00       0.55       8.         18       3-Hexanone, 1,5,6-fetramethoxy-       1515       0.0       0.55       8.         19       Nonancioic acid, dimethyl ester       1600       0.21       2.51       10.         2       Octanoic, 8.8-dimethoxy-d <sup>4</sup> 1600       0.21       2.51       10.         2       Decancito acid, dimethyl ester       1650       0.0       0.55       8.         0       Decancito acid, dimethyl ester       1600       0.01       0.08       0.04       0.0         2       Dectanoic acid, 6,6-dimethoxy-, methyl ester <sup>4</sup> 1700       0.08       0.08       0.03       0.18         2       Methyl 12-oxo-9-undecenoate       1800       0.01       0.07       0.04       0.02<	13	Methyl caproate? (isomer) <sup>e</sup>	1394		0.02	0.27
15       Nonanoic acid, 9-oxo-, methyl ester       1436       0.02       1.09       64         16       Octanedioic acid, 6-dimethoxy-, methyl ester       1500       0.01       0.15       0.01         18       3-Hexanone, 1,5,6,6-tetramethoxy-       1515       0.01       0.25       8.         19       Nonanedioic acid, 6-dimethoxy-       1600       0.21       2.51       10.         20       Cotanol, 8.8-dimethoxy-4       1600       0.21       2.51       10.         21       Methyl 8-(2-furyl)octanoate       1624       0.         22       Decanedioic acid, dimethyl ester       1669       0.04       0.         24       12,12-Dimethoxydodecanoic acid, methyl ester <sup>4</sup> 1700       0.08       0.04         25       Methyl 12-oxo-9-undecenoate       1800       0.10       0.04         27       Heptanal, 7.7-dimethoxy-4       1884       0.03       0.18         28       6-Nonenal, 3.7-dimethyl-1, methyl ester <sup>4</sup> 1905       0.04         29       Tetradecanoic acid, 6-dimethoxy-4       1954       0.02       0.         20       Tetradecanoic acid, 0-dimethyl-1, methyl ester <sup>4</sup> 1925       0.00       0.02       0.         20       PLoctadecacan	14	Heptane, 1,1-dimethoxy-? (aldehyde, dimethyl acetal) <sup>e</sup>	1400	0.01		
16       Octanedioic acid, dimethyl ester       1449       0.02       0,         17       Octanoic acid, 6,6-dimethoxy-, methyl ester       1500       0.01       0.15       0,         13       Hexanore, 1,5,6-tetramethoxy-       1515       0.00       0.55       8.         19       Nonanedioic acid, dimethyl ester       1600       0.21       2.51       10.         14       Methyl 8(-2-furyl)octanoate       1624       0.02       0.02         20       Decanedioic acid, dimethyl ester       1650       0.04       0.         21       Decanedioic acid, dimethyl ester       1650       0.0       0.02         22       Decanedioic acid, dimethyl ester <sup>d</sup> 1700       0.08       0.10       0.10         23       Methyl 12-oxo-9-dodecenoate       1800       0.10       0.02       0.04       0.10         24       Heptanal, 7,7-dimethoxy-4       1884       0.03       0.18       0.03       0.03       0.02       0.0         25       Methyl 12-oxo-9-dodecenoate       1905       0.04       0.02       0.02       0.0       0.02       0.0         26       Oxonoic acid, 6-d-imethoxy-4       1905       0.04       0.02       0.0       0.02       0.	15	Nonanoic acid. 9-oxo-, methyl ester	1436	0.02	1.09	6.07
	16	Octanedioic acid, dimethyl ester	1449		0.02	0.85
18       3-Hexanone, 1,5,6,6-tetramethoxy-       1515       0.0         19       Nonanedioic acid, dimethyl ester       1550       0.00       0.55       8.         20       2-Octanol, 8,8-dimethoxy- <sup>d</sup> 1600       0.21       2.51       10.         10       Methyl 8(2-furyl)octanoate       1624       0.         20       Decanedioic acid, dimethyl ester       1650       0.         21       Decanedioic acid, dimethyl ester       1650       0.         22       Decanedioic acid, dimethyl ester <sup>d</sup> 1700       0.08         23       Methyl 11-oxo-9-undecenoate       1800       0.10         24       Octanoic acid, 6.6-dimethoxy-, methyl ester <sup>d</sup> 1800       0.10         25       Methyl 12-oxo-9-dodecenoate       1800       0.10       0.04         26       Octanoic acid, 6.6-dimethoxy-, methyl ester <sup>d</sup> 1905       0.04       0.02         27       Hydraal, 7.7-dimethyl-, methyl ester <sup>d</sup> 1926       0.00       0.02       0.         20       Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 1954       0.02       0.2         21       Hydroxyhexadecyl butanoate <sup>d</sup> 1963       0.03       0.12         3       Hesanone, 1, 5,6-6-tetramethoxy- <sup>d</sup> <	17	Octanoic acid, 6.6-dimethoxy-, methyl ester	1500	0.01	0.15	0.56
19       Nonanedioic acid, dimethyl ester       1550       0.00       0.55       8.         20       2-Octanol, 8,8-dimethoxy-d       1600       0.21       2.51       10.         21       Methyl 8-(2-furyl)octanoate       1624       0.         22       Decanedioic acid, dimethyl ester       1650       0.         23       Methyl 11-oxo-9-undecenoate       1698       0.04       0.         24       12,12-Dimethoxydodecanoic acid, methyl ester <sup>d</sup> 1700       0.08         25       Methyl 11-oxo-9-dodecenoate       1800       0.10         26       Octanoic acid, 6,6-dimethoxy-, methyl ester       1817       0.04         27       Heptanal, 7,7-dimethoy. <sup>d</sup> 1884       0.03       0.18         28       6-Nonenal, 3,7-dimethyl-, methyl ester <sup>d</sup> 1926       0.00       0.02       0.         29       Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 1954       0.02       0.         29       Tetradecadecialenal, dimethyl acetal <sup>d</sup> 1963       0.03         29       12-Hydroxyhexadecyl butanota <sup>d</sup> 1963       0.02         30       Butanoic acid, methyl ester       2017       0.01       0.07         31       2-Hydroxyhexadecyl butanota <sup>d</sup>	18	3-Hexanone, 1.5.6.6-tetramethoxy-	1515			0.31
202-Octanol, 8,8-dimethoxy-d16000.212.5110.21Methyl 8,2-furyl)octanoate16240.22Decanedioic acid, dimethyl ester16500.23Methyl 11-oxo-9-undecenoate16980.040.2412,12-Dimethoxydodecanoic acid, methyl ester <sup>d</sup> 17000.080.1025Methyl 11-oxo-9-undecenoate18000.100.1026Octanoic acid, 6,6-dimethoxy-, methyl ester18170.040.27Heptanal, 7,7-dimethoxy-d18840.030.180.8286-Nonenal, 3,7-dimethyl-d19050.040.29Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 19050.040.0220Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19540.020.312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.030.12312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.030.1233Methyl (Z)-11-teradecenoate20010.070.12343-Hexanone, 1,5,6,6-terramethoxy- <sup>d</sup> 21170.010.1235Linoleic acid, methyl ester (isomer 1)21470.010.220.399,12-Octadecadienoic acid, methyl ester (isomer 2)21920.040.220.38406,9,12-Octadecatrienoic acid, methyl ester (isomer 2)21920.040.220.38416,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22940.220.38 <tr <td="">0ealdehyde, dimethyl</tr>	19	Nonanedioic acid, dimethyl ester	1550	0.00	0.55	8.41
11Methyl 8-(2-furyl)octanoate1624162412Decanedioic acid, dimethyl ester16500.13Methyl 11-oxo-9-undecenoate16980.040.1412,12-Dimethoxydodecanoic acid, methyl ester <sup>d</sup> 17000.0815Methyl 12-oxo-9-dodecenoate18000.1016Octanoic acid, 6,6-dimethoxy-, methyl ester18170.0417Heptanal, 7,7-dimethyl-d19050.04186-Nonenal, 3,7-dimethyl-d19050.0419Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 19260.000.0210Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19540.020.20Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19630.030.12312-Hydroxyhexadecyl butanoate <sup>d</sup> 19700.120.1233Methyl (Z)-11-tetradecenoate20010.070.12343-Hexanone, 1,5,6,6-tetramethoxy-d21079,7.586.254.3511-Octadecadienoic acid, methyl ester (isomer 1)21470.010.12346,9,12-Octadecadienoic acid, methyl ester (isomer 2)22990.380.38416,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22990.380.34420.12-Octadecatrienoic acid, acthyl ester (isomer 3) <sup>d</sup> 23500.010.02436,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.310.220.446,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> <td>20</td> <td>2-Octanol. 8.8-dimethoxy-<sup>d</sup></td> <td>1600</td> <td>0.21</td> <td>2.51</td> <td>10.5</td>	20	2-Octanol. 8.8-dimethoxy- <sup>d</sup>	1600	0.21	2.51	10.5
22Decanedioic acid, dimethyl ester16500.33Methyl 11-oxo-9-undecenoate16980.040.2412,12-Dimethoxydodecanoic acid, methyl ester <sup>d</sup> 17000.0825Methyl 12-oxo-9-dodecenoate18000.1026Octanoic acid, 6,6-dimethoxy-, methyl ester18170.0427Heptanal, 7,7-dimethoxy- <sup>d</sup> 18840.030.18286-Nonenal, 3,7-dimethoxy- <sup>d</sup> 19050.0429Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 19260.000.0230Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19540.02312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.03329,12-Octadecadienal, dimethyl acetal <sup>d</sup> 19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy- <sup>d</sup> 20170.0135Linoleic acid, methyl ester21079.7.586.254.368,11-Octadecadienoic acid, methyl ester (isomer 1)21470.01379,12-Octadecadienoic acid, methyl ester (isomer 2)22990.38416,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22990.3842Cyclopropaneoctanoic acid, act, 4_r[2-r[2-(2-ethylcyclopropyl]methyl]cyclopropyl]methyl, methyl ester23740.020.3543Olealdehyde, dimethyl acetal <sup>d</sup> 23740.020.350.449,12-Octadecadienal, adimethyl acetal23740.020.350.4	21	Methyl 8-(2-furyl)octanoate	1624			0.67
23Methyl 11-oxo-9-undecenoate16980.040.2412,12-Dimethoxydodecanoic acid, methyl ester17000.0825Methyl 12-oxo-9-dodecenoate18000.1026Octanoic acid, 6,6-dimethoxy-, methyl ester18170.0427Heptanal, 7,7-dimethoxy-d18840.030.18286-Nonenal, 3,7-dimethyl-419050.0429Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 19260.000.020.30Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19540.020.33312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.033329,12-Octadecadienal, dimethyl acetal <sup>d</sup> 19700.12333Methyl (Z)-11-tetradecenoate20010.073343-Hexanone, 1,5,6,6-tetramethoxy- <sup>d</sup> 210797.586.254.358,11-Octadecadienoic acid, methyl ester (isomer 1)21470.013349,12-Octadecadienoic acid, methyl ester (isomer 2)21920.043359,12-Octadecatienoic acid, methyl ester (isomer 2)21920.043366,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22990.383416,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22990.383420,22-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.313430.12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.31344<	22	Decanedioic acid, dimethyl ester	1650			0.30
2412,12-Dimethoxydodecanoic acid, methyl ester17000.0825Methyl 12-oxo-9-dodecenoate18000.1026Octanoic acid, 6,6-dimethoxy-, methyl ester18170.0427Heptanal, 7,7-dimethyl-418840.030.18286-Nonenal, 3,7-dimethyl-419050.0429Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 19260.000.0230Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19540.02312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.03329,12-Octadecadienal, dimethyl acetal <sup>d</sup> 19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy- <sup>d</sup> 20170.0135Linoleic acid, methyl ester210797.586.254.368,11-Octadecadienoic acid, methyl ester (isomer 1)21470.0114399,12-Octadecadienoic acid, methyl ester (isomer 2)21920.0414396,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22990.3814406,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.311441Cyclopropaneoctanoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.3114420.1823740.020.350.436,9,12-Octadecatienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.3114449,12-Octadecatienoic acid, methyl ester (isomer 3) <sup>d</sup> 23500.0114	23	Methyl 11-oxo-9-undecenoate	1698		0.04	0.27
25Methyl 12-oxo-9-dodecenoate18000.1026Octanoic acid, 6,6-dimethoxy-, methyl ester18170.0427Heptanal, 7,7-dimethoxy-d18840.030.18286-Nonenal, 3,7-dimethyl-d19050.0429Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 19260.000.020.30Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19540.020.312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.030.12329,12-Octadecadienal, dimethyl acetal <sup>d</sup> 19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy- <sup>d</sup> 20170.0135Linoleic acid, methyl ester210797.586.254.368,11-Octadecadienoic acid, methyl ester (isomer 1)21470.01144735Q.12-Octadecadienoic acid, methyl ester (isomer 2)21920.041447366,9,12-Octadecatrienoic acid, methyl ester (isomer 1)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 2)21920.04144416,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.3114242Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.31143436,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.31144449,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.3114445	24	12.12-Dimethoxydodecanoic acid, methyl ester <sup>d</sup>	1700		0.08	
26Octanoic acid, 6,6-dimethoxy-, methyl ester18170.0427Heptanal, 7,7-dimethoxy-d18840.030.18286-Nonenal, 3,7-dimethyl-d19050.0429Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 19260.000.020.30Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19540.020.312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.03329,12-Octadecadienal, dimethyl acetal <sup>d</sup> 19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy- <sup>d</sup> 210797.586.2368,11-Octadecadienoic acid, methyl ester21120.590.40379,12-Octadecadienoic acid, methyl ester (isomer 1)21470.01389,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatirenoic acid, methyl ester (isomer 2)21920.04306,9,12-Octadecatirenoic acid, methyl ester (isomer 2)22940.220.396,9,12-Octadecatirenoic acid, methyl ester (isomer 2)22990.38406,9,12-Octadecatirenoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.31416,9,12-Octadecatirenoic acid, acid, 12-[[2-[(2-ethylcyclopropyl]methyl]-ymethyl ester23500.01420.220.3123740.020.350.430.12-Octadecadienoic acid, dimethyl acetal (isomer 3) <sup>d</sup> 24220.18449,12-O	25	Methyl 12-oxo-9-dodecenoate	1800		0.10	
27Heptanal, 7,7-dimethoxy-d18840.030.18286-Nonenal, 3,7-dimethyl-d19050.0429Tetradecanoic acid, 10,13-dimethyl-, methyl ester <sup>d</sup> 19260.000.020.30Butanoic acid, 2-ethyl-, methyl ester <sup>d</sup> 19540.020.312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.030.12329,12-Octadecadienal, dimethyl acetal <sup>d</sup> 19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy-d20170.0135Linoleic acid, methyl ester210797.586.2368,11-Octadecadienoic acid, methyl ester (isomer 1)21470.01399,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatirenoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatirenoic acid, methyl ester (isomer 2)22940.220.406,9,12-Octadecatirenoic acid, methyl ester (isomer 2)23200.3123200.3142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl]methyl]-ymethyl ester <sup>d</sup> 23500.0114430.12-Octadecadienoic acid, methyl acetal (isomer 3) <sup>d</sup> 24220.1823740.020.350.449,12-Octadecadienoic acid, 2-[[2-[(2-ethylcyclopropyl]methyl]-ymethyl ester <sup>d</sup> 23500.011545Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecended25210.534.654.65	26	Octanoic acid, 6.6-dimethoxy-, methyl ester	1817		0.04	
286-Nonenal, 3,7-dimethyl.d19050.0429Tetradecanoic acid, 10,13-dimethyl-, methyl esterd19260.000.020.30Butanoic acid, 2-ethyl-, methyl esterd19540.020.312-Hydroxyhexadecyl butanoated19630.03329,12-Octadecadienal, dimethyl acetald19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy-d20170.0135Linoleic acid, methyl ester210797.586.2368,11-Octadecadienoic acid, methyl ester21120.590.40379,12-Octadecadienoic acid, methyl ester (isomer 1)21470.01389,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 3)^d23200.311416,9,12-Octadecatrienoic acid, methyl ester (isomer 3)^d23200.31142Olealdehyde, dimethyl acetald23740.020.350.43Olealdehyde, dimethyl acetal0.020.350.0.449,12-Octadecadienal, dimethyl acetal (isomer 3)^d24220.18145Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoated25210.534.65	27	Heptanal, 7.7-dimethoxy- <sup>d</sup>	1884	0.03	0.18	
29Tetradecanoic acid, 10,13-dimethyl-, methyl ester19260.000.020.0230Butanoic acid, 2-ethyl-, methyl ester19540.02312-Hydroxyhexadecyl butanoated19630.03329,12-Octadecadienal, dimethyl acetald19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy-d20170.0135Linoleic acid, methyl ester210797.586.2368,11-Octadecadienoic acid, methyl ester (isomer 1)21470.01379,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatienoic acid, methyl ester (isomer 1)21470.01396,9,12-Octadecatienoic acid, methyl ester (isomer 2)22940.220.406,9,12-Octadecatienoic acid, methyl ester (isomer 3)23200.31141Olcaldehyde, dimethyl acetal (isomer 3)^d23200.31142Olcaldehyde, dimethyl acetal (isomer 3)^d24220.18143Olcaldehyde, dimethyl acetal (isomer 3)^d24220.181449,12-Octadecadienal, dimethyl acetal (isomer 3)^d24220.18145Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoated25210.534.65	28	6-Nonenal, 3.7-dimethyl- <sup>d</sup>	1905		0.04	
30Butanoic acid, 2-ethyl-, methyl ester19540.02312-Hydroxyhexadecyl butanoate <sup>d</sup> 19630.03329,12-Octadecadienal, dimethyl acetal <sup>d</sup> 19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy- <sup>d</sup> 20170.0135Linoleic acid, methyl ester210797.586.254.368,11-Octadecadienoic acid, methyl ester (isomer 1)21470.011399,12-Octadecadienoic acid, methyl ester (isomer 2)21920.041396,9,12-Octadecadienoic acid, methyl ester (isomer 2)21920.041396,9,12-Octadecatienoic acid, methyl ester (isomer 2)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.31142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester23500.0143Olealdehyde, dimethyl acetal <sup>d</sup> 23740.020.350.449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.18145Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoate <sup>d</sup> 25210.534.65	29	Tetradecanoic acid, 10.13-dimethyl-, methyl ester <sup>d</sup>	1926	0.00	0.02	0.12
12-Hydroxyhexadecyl butanoated19630.03329,12-Octadecadienal, dimethyl acetald19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy-d20170.0135Linoleic acid, methyl ester210797.586.254.368,11-Octadecadienoic acid, methyl ester21120.590.40379,12-Octadecadienoic acid, methyl ester (isomer 1)21470.01389,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatrienoic acid, methyl ester (isomer 2)21920.04406,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22940.220.416,9,12-Octadecatrienoic acid, methyl ester (isomer 3)^d23200.31142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester23500.0143Olealdehyde, dimethyl acetal (isomer 3)^d24220.181449,12-Octadecadienal, dimethyl acetal (isomer 3)^d24220.534.6545Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecended25210.534.65	30	Butanoic acid. 2-ethyl-, methyl ester <sup>d</sup>	1954		0.02	
329,12-Octadecadienal, dimethyl acetald19700.1233Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy.d20170.0135Linoleic acid, methyl ester210797.586.254.368,11-Octadecadienoic acid, methyl ester21120.590.40379,12-Octadecadienoic acid, methyl ester (isomer 1)21470.01389,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.311441Olealdehyde, dimethyl acetald23740.020.350.42Olealdehyde, dimethyl acetal (isomer 3) <sup>d</sup> 24220.181445Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenated25210.534.65	31	2-Hydroxyhexadecyl butanoate <sup>d</sup>	1963		0.03	
33Methyl (Z)-11-tetradecenoate20010.07343-Hexanone, 1,5,6,6-tetramethoxy.d20170.0135Linoleic acid, methyl ester210797.586.254.368,11-Octadecadienoic acid, methyl ester21120.590.40379,12-Octadecadienoic acid, methyl ester (isomer 1)21470.01389,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.311416,9,12-Octadecatrienoic acid, acid, methyl ester (isomer 3) <sup>d</sup> 23200.31142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]-, methyl ester <sup>d</sup> 23500.0143Olealdehyde, dimethyl acetal (isomer 3) <sup>d</sup> 24220.181449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.534.65	32	9.12-Octadecadienal, dimethyl acetal <sup>d</sup>	1970		0.12	
343-Hexanone, 1,5,6,6-tetramethoxy.d20170.0135Linoleic acid, methyl ester210797.586.254.368,11-Octadecadienoic acid, methyl ester21120.590.40379,12-Octadecadienoic acid, methyl ester (isomer 1)21470.01389,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.311416,9,12-Octadecatrienoic acid, acid, methyl ester (isomer 3) <sup>d</sup> 23200.31142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl]methyl]-, methyl ester <sup>d</sup> 23500.01143Olealdehyde, dimethyl acetal (isomer 3) <sup>d</sup> 24220.1811449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.534.65	33	Methyl (Z)-11-tetradecenoate	2001		0.07	
11111135Linoleic acid, methyl ester210797.586.254.36 $8,11$ -Octadecadienoic acid, methyl ester21120.590.4037 $9,12$ -Octadecadienoic acid, methyl ester (isomer 1)21470.0138 $9,12$ -Octadecadienoic acid, methyl ester (isomer 2)21920.0439 $6,9,12$ -Octadecatrienoic acid, methyl ester (isomer 2)22940.220.40 $6,9,12$ -Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.31142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester23500.0143Olealdehyde, dimethyl acetal d23740.020.350.44 $9,12$ -Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.18145Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenate <sup>d</sup> 25210.534.65	34	3-Hexanone, 1 5 6 6-tetramethoxy- <sup>d</sup>	2017	0.01		
368,11-Octadecadienoic acid, methyl ester21120.590.40379,12-Octadecadienoic acid, methyl ester (isomer 1)21470.01389,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatrienoic acid, methyl ester (isomer 1)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22990.380.31416,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.310.3142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester23740.020.350.43Olealdehyde, dimethyl acetal d23740.020.350.0.449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.180.534.65	35	Linoleic acid. methyl ester	2107	97.5	86.2	54.5
379,12-Octadecadienoic acid, methyl ester (isomer 1)21470.01389,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatrienoic acid, methyl ester (isomer 1)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22990.380.38416,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.310.3842Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester23500.0143Olealdehyde, dimethyl acetal d23740.020.350.449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.180.534.65	36	8.11-Octadecadienoic acid, methyl ester	2112	0.59	0.40	
139,12-Octadecadienoic acid, methyl ester (isomer 2)21920.04396,9,12-Octadecatrienoic acid, methyl ester (isomer 1)22940.220.406,9,12-Octadecatrienoic acid, methyl ester (isomer 2)22990.38416,9,12-Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.3142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester23500.0143Olealdehyde, dimethyl acetal d23740.020.350.449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.184.6545Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoate d25210.534.65	37	9.12-Octadecadienoic acid, methyl ester (isomer 1)	2147	0.01		
39 $6,9,12$ -Octadecatrienoic acid, methyl ester (isomer 1)2294 $0.22$ $0.2$ 40 $6,9,12$ -Octadecatrienoic acid, methyl ester (isomer 2)2299 $0.38$ 41 $6,9,12$ -Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 2320 $0.31$ 42Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester2350 $0.01$ 43Olealdehyde, dimethyl acetal d2374 $0.02$ $0.35$ $0.44$ 49,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 2422 $0.18$ $0.53$ $4.65$	38	9.12-Octadecadienoic acid, methyl ester (isomer 2)	2192	0.04		
40 $6,9,12$ -Octadecatrienoic acid, methyl ester (isomer 2) $2299$ $0.38$ 41 $6,9,12$ -Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> $2320$ $0.31$ 42Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester <sup>d</sup> $2350$ $0.01$ 43Olealdehyde, dimethyl acetal <sup>d</sup> $2374$ $0.02$ $0.35$ $0.44$ 44 $9,12$ -Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> $2422$ $0.18$ $0.53$ $4.65$	39	6.9.12-Octadecatrienoic acid, methyl ester (isomer 1)	2294		0.22	0.50
41 $6,9,12$ -Octadecatrienoic acid, methyl ester (isomer 3) <sup>d</sup> 23200.3142Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester23500.0143Olealdehyde, dimethyl acetal <sup>d</sup> 23740.020.350.4449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.180.534.6545Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoate <sup>d</sup> 25210.534.65	40	6.9.12-Octadecatrienoic acid methyl ester (isomer 2)	2299		0.38	
42Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester22500.0143Olealdehyde, dimethyl acetal23740.020.350.4449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.1845Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoate <sup>d</sup> 25210.534.65	41	6.9.12-Octadecatrienoic acid methyl ester (isomer 3) <sup>d</sup>	2320	0.31		
43Olealdehyde, dimethyl acetal23740.020.350.449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.1845Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoate <sup>d</sup> 25210.534.65	42	Cyclopropaneoctanoic acid. 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester <sup>d</sup>	2350	0.01		
449,12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup> 24220.1845Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoate <sup>d</sup> 25210.534.65	43	Olealdehyde, dimethyl acetal <sup>d</sup>	2374	0.02	0.35	0.98
45 Methyl (Z)-12,13-epoxy-11-methoxy-9-octadecenoate <sup>d</sup> 2521 0.53 4.65	44	9.12-Octadecadienal, dimethyl acetal (isomer 3) <sup>d</sup>	2422	0.18	0.00	0.90
	45	Methyl (Z)-12.13-epoxy-11-methoxy-9-octadecenoate <sup>d</sup>	2521	0.53	4.65	
46 Octadecanoic acid 9 10-dihydroxy- methyl ester <sup>4</sup> 2612 0 30	46	Octadecanoic acid 9 10-dihydroxy- methyl ester <sup>d</sup>	2612	0.30		

<sup>a</sup> Relative concentration of compounds from the linoleic acid sample degraded at 50 °C.

<sup>b</sup> Relative concentration of compounds from the linoleic acid sample degraded at 100 °C.

<sup>c</sup> Relative concentration of compounds from the linoleic acid sample degraded at 150 °C.

<sup>d</sup> Identified with lower probability matching by NIST MS Search algorithm (see supporting information).

<sup>e</sup> Identified with higher probability matching by NIST MS Search algorithm, but they are the same compounds (probably isomers) (see supporting information).

standard deviation value for each case (see supporting information for TEM images).

# 2.8. GC-MS analysis

For the analysis of the methyl esters of fatty acids, a Hewlett–Packard HP 6890 Series gas chromatograph coupled with a Hewlett–Packard 5973 mass spectrometry detector (GC–MS) system was used (see supporting information for full range gas chromatograms).

A HP-5 MS capillary column (30 m length, 0.25 mm i.d., 0.25  $\mu$ m film thickness) was used for the GC system. The temperature programme was set up from 50 to 250 °C at 4 °C/min, both the injector and detector temperatures were



Fig. 3. Gas chromatograms for the linoleic acid samples degraded at 50 °C (top), 100 °C (middle), and 150 °C (bottom) for the KI in the range 2000–2600.

280 °C and He was used as carrier gas. The injection volume was  $2 \mu l$ . For quantification, dodecane was used as external standard.

Ionization energy EI of 70 eV was used for the mass spectrometry detector, with a source temperature of 150 °C, scan range 50–300 amu, scan rate  $1 \text{ s}^{-1}$ . The mass spectra were compared with the NIST/EPA/NIH Mass Spectral Library 2.0 (see supporting information for experimental and NIST database mass spectra).

# 3. Results and discussion

The linoleic acid/ $\alpha$ - and  $\beta$ CD complexes were obtained with good yields of 88% and 74%, respectively. Rhombic crystals with a mean side dimension of 230 ± 57 nm were obtained in the case of the linoleic acid/ $\alpha$ CD complex (revealed by TEM analysis). In the case of the linoleic acid/  $\beta$ CD complex, the same analysis revealed hexagonal crystals with a mean side dimension of 236 ± 86 nm. The differential scanning calorimetry (DSC) analysis revealed that the linoleic acid had a melting point of -12.8 °C, with a transition energy of 0.63 J/g/K. The DSC analyses (Fig. 1) of the complexes, comparatively with those of the pure linoleic acid and  $\alpha$ -/ $\beta$ CD, indicate the formation of the complex, the dehydration energy for the pure  $\alpha$ CD and  $\beta$ CD being 119.2 J/g (in the temperature range 80–130 °C) and 56.35 J/g (in the temperature range 70–115 °C), respectively (Fig. 1). For the linoleic acid/ $\alpha$ CD complex, the interaction energy was 19.44 J/g (in the temperature range 101–130 °C), and for the linoleic acid/ $\beta$ CD complex this energy was 34.13 J/g, corresponding to the decomplexation and/or rearrangement of the fatty acid in the complex (Rysanek, Coquillay, Bourgaux, & Ollivon, 2002).

In order to establish the free and degraded linoleic acid composition, the pure sample and the samples degraded at temperature values in the range 50–150 °C were analyzed by GC–MS. The concentration of the linoleic acid in the raw sample was 98% (as methyl ester), the main impurities being the corresponding 7,10- and 8,11-dien isomers of the linoleic acid, linolenic acid and some geometric isomers (Fig. 2 and Table 3). The Kovats indices (KI) were obtained according to the retention time of the sample compounds by evaluation from the correlational equation



Fig. 4. Gas chromatograms for the degraded (at 50  $^{\circ}$ C – top and 100  $^{\circ}$ C – bottom) linoleic acid/ $\alpha$ CD complexes, recovered, and methyl ester derived samples for the KI values in the range 2000–2600.

corresponding to the  $C_8$ – $C_{20}$  alkane standard solution. These KIs were calculated in order to confirm the MS identification of the main sample compounds, some KIs being previously determined for the pure compounds under the same conditions.

After thermal degradation of the linoleic acid sample at a temperature within the range 50–150 °C (in air at atmospheric pressure, 70% relative humidity), some degradation products can be identified, especially at temperatures above 100 °C, the main compounds being aldehydes (resulting from oxidation), epoxides and vicinal dihydroxy-acids. The concentration of linoleic acid in the sample degraded at 50 °C was 97.5%, the degradation compounds being in low concentrations, while the sample degraded at 100 °C revealed a linoleic acid concentration of 86.2%. The lowest linoleic acid concentration of 86.2%. The lowest linoleic acid concentration was observed for the sample degraded at 150 °C (54.5%) (Table 4).

The main aldehydes identified in the degraded samples (as acetals) were: malondialdehyde at a concentration of 0.1% for the sample degraded at 100 °C and in a higher

concentration of 0.9% in the sample degraded at 150 °C. The same increasing concentrations were observed in the case of hexanal (concentration in the range 0.15-10.5% for the sample degraded at 50–150 °C), heptanal (0–0.3%), 9-oxononanoic acid (0.02–6%), octanedioic acid (0–0.9%), 6-oxooctanoic acid (0.01–0.6%), nonandioic acid (0–8.4%), and some linoleic and linolenic acid isomers (octadecadienoic and octadecatrienoic acids). In the case of the sample degraded at 100 °C, a small concentration of the 12,13-epoxi derivative can be identified.

The GC chromatograms for the raw linoleic acid and for the samples degraded at 50, 100, and 150 °C, corresponding to the Kovats index range of 2000–2600 (oxidation, epoxidation, epoxidation–hydrolysis degradation products) are depicted in Figs. 2 and 3, respectively. At higher temperatures the linoleic acid and some degradation products were probably polymerized.

A higher concentration of linoleic acid (as methyl ester) was detected in the recovered samples from the linoleic acid/ $\alpha$ - and  $\beta$ CD complexes (99.3% and 99.6%, respectively).



Fig. 5. Gas chromatograms for the degraded (at 50  $^{\circ}$ C – top and 100  $^{\circ}$ C – bottom) linoleic acid/ $\beta$ CD complexes, recovered, and methyl ester derived samples for the KI values in the range 2000–2600.

A good protection against the environmental degradation factors (especially against oxygen and humidity at higher temperature) can be observed in the case of nanoencapsulated fatty acid in cyclodextrin matrices. For the linoleic acid/ $\alpha$ CD complex degraded at 50 °C no major degradation product can be identified (only malondialdehyde was present at the low relative concentration of 0.6%). The concentration of the linoleic acid was 99.4% while, for the sample degraded at 100 °C, the concentration of the fatty acid (as mixture of linoleic and one of its geometric isomers) was 98.4%; the main degradation compound was malondialdehyde (1.5%). In the case of the sample degraded at 150 °C, the concentration of linoleic acid was only 80%, this fatty acid being partially polymerized.

In the samples recovered from the linoleic acid/ $\beta$ CD complex degraded at 50 and 100 °C, small relative concentrations of malondialdehyde and hexanal could be identified, the concentrations of the linoleic acid being 94% and 92%, respectively. In the case of the sample degraded at 150 °C, the concentration of the linoleic acid was only 74%.

Figs. 4 and 5 show the gas chromatograms for the linoleic acid/ $\alpha$ - and  $\beta$ CD samples (which can be compared with the gas chromatograms of the raw and degraded linoleic acid samples from Figs. 2 and 3) at the KI values in the range 2000–2600, corresponding to linoleic acid and its superior homologues or similar derivative peaks. The peaks corresponding to the degradation products from the nonencapsulated sample, degraded at 150 °C, can be clearly observed (see Fig. 3).

## 4. Conclusion

Very good yields were obtained for the complexation process, especially in the case of  $\alpha$ CD, probably due to the best fit of the linoleic acid in the  $\alpha$ CD cavity, that provides a higher interaction between the fatty acid and cyclodextrin.

Higher relative concentrations of degradation products can be identified in the case of thermally degraded linoleic acid samples, the main compounds being aldehydes (malondialdehyde, hexanal, heptanal, octanal, nonanal, decanal) probably resulted from oxidation processes, especially at higher temperature, and linoleic acid epoxidation and epoxidation–hydrolysis products.

A relatively high amount of the linoleic acid was transformed (probably by hydration–dehydration processes) to the more stable isomers of linoleic acid, most of them in the case of samples degraded at 100 and 150 °C.

Very good thermal stability was observed for both linoleic acid/ $\alpha$ - and  $\beta$ CD complexes, the relative concentration of the fatty acid recovered from the complex with  $\alpha$ CD being 99.4% and 98.4% in the cases of complexes degraded at 50 and 100 °C, respectively, comparatively with the nonencapsulated samples degraded at the same temperatures, where these concentration were 97.5% and 86.2%. In the case of the complex with  $\beta$ CD, the stability of the linoleic acid was lower, the relative concentrations of the fatty acid being 94% and 92% for the degradation temperatures of 50 and 100 °C, respectively.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.foodchem. 2005.08.012.

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