Chemistry

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Abstract

Full Text

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Complete Synthesis of the Triglycerides of Soybean Oil

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The glycerides of soybean oil, according to data from physicochemical methods of analysis, contain, in various combinations, residues of linolenic, linoleic, oleic, stearic, and palmitic acids. The experimentally determined glyceride structure of the oil (^{1}) agrees with the results obtained on the basis of distribution theory (^{2}). In order to refine the glyceride composition of soybean oil and to study physicochemical properties, we synthesized triglycerides with allowance for possible positional isomers (scheme 1). Starting from isopropylideneglycerol, we obtained 5 monoglycerides: α-monolinolenin (XLVI), α-monolinolein (XLVII), α-monoolein (XLVIII), α-monostearin (XLIX), and α-monopalmitin (L). Conversion of the latter into triglycerides was carried out either in one stage: α-linolenoyl-β,α'-distearin (VII), α-linoleoyl-β,α'-distearin (XVI), α-linoleoyl-β,α'-dipalmitin (XVII), triolein (XXVII), α-oleoyl-β,α'-distearin (XXVIII), α-stearoyl-β,α'-diolein (XL), tristearin (XLI), α-palmitoyl-β,α'-dilinolenin (XLII), α-palmitoyl-β,α'-dilinolein (XLIV), tripalmitin (XLV), or in two stages: α-oleoyl-β-stearoyl-α'-linolein (XXIII), α,α'-dioleoyl-β-stearin (XXVI), α-stearoyl-β-oleoyl-α'-linolein (XXXIV), α-stearoyl-β-linoleoyl-α'-olein (XXXVI), α,α'-distearoyl-β-linolenin (XXXVII), α,α'-distearoyl-β-linolein (XXXVIII), α,α'-distearoyl-β-olein (XXXIX), α-palmitoyl-β-linoleoyl-α'-linolein (XLIII), via α,α'-diglycerides: α-oleoyl-α'-linoleoylglycerol (LI), α,α'-dioleoylglycerol (LII), α-stearoyl-α'-linoleoylglycerol (LIII), α-stearoyl-α'-oleoylglycerol (LIV), α,α'-distearoylglycerol (LV), and α-palmitoyl-α'-linoleoylglycerol (LVI).

The triglycerides obtained were purified by adsorption chromatography on silicic acid, and paper chromatography was used for their identification. The physicochemical data for the triglycerides are presented in Table 1.

The triglycerides trilinolenin (I), α,α'-dilinolenoyl-β-linolein (II), α,α'-dilinolenoyl-β-olein (III), α,α'-dilinolenoyl-β-stearin (IV), α-linolenoyl-β,α'-dilinolein (V), α-linolenoyl-β,α'-diolein (VI), α-linoleoyl-β,α'-dilinolenin (VIII), trilinolein (IX), α-linoleoyl-β-oleoyl-α'-linolenin (X), α-linoleoyl-β-stearoyl-α'-linolenin (XI), α-linoleoyl-β,α'-diolein (XII), α,α'-dilinoleoyl-β-linolenin (XIII), α,α'-dilinoleoyl-β-olein (XIV), α,α'-dilinoleoyl-β-stearin (XV), α-oleoyl-β,α'-dilinolenin (XVIII), α-oleoyl-β-linoleoyl-α'-linolenin (XIX), α-oleoyl-β-stearoyl-α'-linolenin (XX), α-oleoyl-β,α'-dilinolein (XXI), α-oleoyl-β-linolenoyl-α'-linolein (XXII), α,α'-dioleoyl-β-linolenin (XXIV),

α,α'-dioleoyl-β-linolein (XXV), α-stearoyl-β,α'-dilinolenin (XXIX), α-stearoyl-β-linoleoyl-α'-linolenin (XXX), α-stearoyl-β-oleoyl-α'-linolenin (XXXI), α-stearoyl-β,α'-dilinolein (XXXII), α-stearoyl-β-linolenoyl-α'-linolein (XXXIII), α-stearoyl-β-linolenoyl-α'-olein (XXXV), which are present in both soybean and linseed oil, were obtained by us previously (^{3}).

The synthesized triglycerides (I–XLV), in their properties, are close to natural—

to soybean oil: d_4^{20} 0.921—0.931, n_D^{20}1.472—475. Iodine value 114–137. The principal starting substances in the synthesis of triglycerides of linseed, walnut, sunflower, soybean, sesame, olive, almond, coconut oils, cocoa-bean oil, butter, egg-yolk fat, and other vegetable oils and animal fats are higher acids of the aliphatic series.

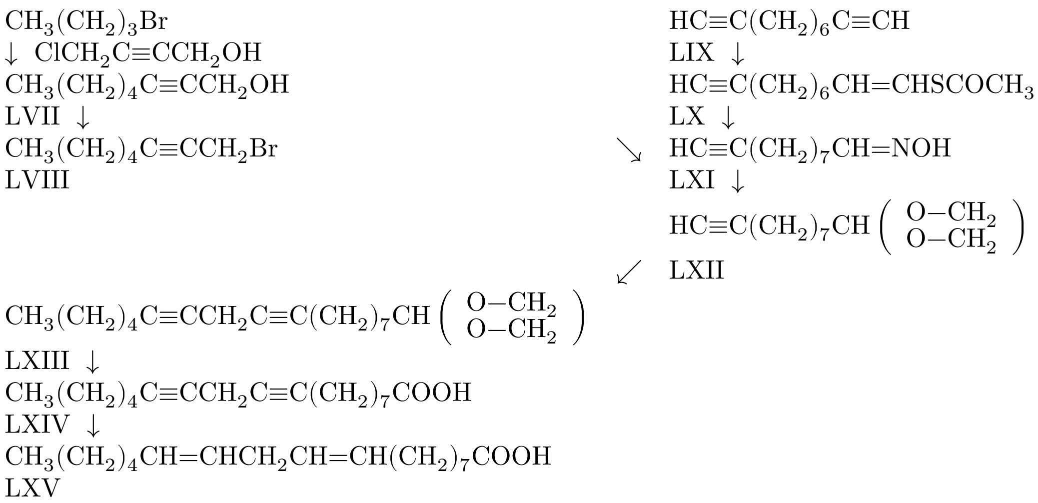
The literature contains descriptions of a number of methods for obtaining linoleic (^{4}), linolenic (^{5}), and other higher fatty acids. Owing to low yields, experimental difficulties, or the absence of accessible raw materials, these methods are, for the most part, of only theoretical interest.

We investigated several possible routes for obtaining higher fatty acids on the basis of products of ethylene telomerization (^{6}), butadiene polymerization (^{7}), and other available types of raw materials (^{8}). The present article gives one of the methods for obtaining linolenic acid, which is also applicable to other compounds of this series.

Octyn-2-ol-1 (LVII, b.p. 98–100°/16 mm, d_4^{20} 0.8916, n_D^{20} 1.4551, MR_D 38.37. $C_8H_{14}OF$. Calculated 38.61), obtained by condensation of butyl bromide and 1-chlorobutyn-2-ol-4, is converted by reaction with phosphorus tribromide into 1-bromooctyne-2 (LVIII). Yield 80.4%. B.p. 69–72°/5 mm, d_4^{20} 1.2095, n_D^{20} 1.4859, MR_D 44.88. $C_8H_{13}BrF$. Calculated 44.84.

The second component, ethylene acetal of decyn-9-al-1 (LXII) (^{13}), was obtained from decadiene-1,9 (LIX, b.p. 76–77°/18 mm, d_4^{20} 0.8376, n_D^{20} 1.4532, MR_D 44.33. $C_{10}H_{14}F_2$. Calculated 44.25. IR spectrum 331 (s.), 2125 (m.) cm^{-1}), synthesized in 80.7% yield from 1,6-dibromohexane (b.p. 110.8–112°/14 mm, d_4^{20} 1.5737, n_D^{20} 1.5055, MR_D 45.49. $C_6H_{12}Br_2$. Calculated 45.44). Decadiene-1,9 (LIX) is converted by reaction with thioacetic acid into decyn-9-en-1-thiol-1 acetate (LX, yield 79.3%, b.p. 95.3–96.4° at 0.12 mm, d_4^{20} 0.9746, n_D^{20} 1.5022, MR_D 63.42. $C_{12}H_{18}OSFF$. Calculated 62.85), from which, via decyn-9-aldoxime-1 (LXI, yield 88.4%, m.p. 79.1–79.5°), ethylene acetal of decyn-9-al-1 (LXII) is obtained. Yield 67.1%.

B.p. 73.0–74.5°/16 mm, d_4^{20} 0.9504, n_D^{20} 1.4564, MR_D 56.93. $C_{12}H_{20}O_2$. Calculated 56.61.



$CH_3(CH_2)_3Br$
$\downarrow$ $ClCH_2C{\equiv}CCH_2OH$
$CH_3(CH_2)_4C{\equiv}CCH_2OH$
LVII $\downarrow$
$CH_3(CH_2)_4C{\equiv}CCH_2Br$
LVIII

$HC{\equiv}C(CH_2)_6C{\equiv}CH$
LIX $\downarrow$
$HC{\equiv}C(CH_2)_6CH{=}CHSCOCH_3$
LX $\downarrow$
$\searrow$ $HC{\equiv}C(CH_2)_7CH{=}NOH$
LXI $\downarrow$
$HC{\equiv}C(CH_2)_7CH\left(\begin{matrix}O{-}CH_2\\O{-}CH_2\end{matrix}\right)$
$\swarrow$ LXII

$CH_3(CH_2)_4C{\equiv}CCH_2C{\equiv}C(CH_2)_7CH\left(\begin{matrix}O{-}CH_2\\O{-}CH_2\end{matrix}\right)$
LXIII $\downarrow$
$CH_3(CH_2)_4C{\equiv}CCH_2C{\equiv}C(CH_2)_7COOH$
LXIV $\downarrow$
$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
LXV

Scheme for the synthesis of cis-, cis-octadecadiene-9,12-oic-1 acid

By condensation of 1-bromooctyne-2 (LVIII) with ethylene acetal of decyn-9-al-1 (LXII), ethylene acetal of octadecadiyn-9,12-al-1 (LXIII) is obtained. Yield 57.6%.

B.p. 142.9–144.1°/0.09 mm, d_4^{20} 0.9411, n_D^{20} 1.4789, MR_D 91.73. $C_{20}H_{32}O_2F_2$. Calculated 91.68. Subsequent saponification and oxidation of compound (LXIII) leads to octadecadiyn-9,12-oic-1 acid (LXIV). Yield 39.7%. M.p. 42.6–43.9° (from alcohol). R_f 0.84, system n-butanol : chloroform : 25% aqueous ammonia (10 : 5 : 2).

Table 1

Triglyceride	Empirical formula	Mol. wt.	Number of double bonds	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Iodine number, found	Iodine number, calc.	R_f, chloroform : methyl alcohol 1 : 3	Found, % C	Found, % H	Calculated, % C	Calculated, % H	M.p., °C
(VII)	$C_{57}H_{104}O_6$	885,40	3	–	–	–	–	86,60	86,00	0,23	77,66	11,60	77,32	11,84	24,3–24,5

Triglyceride	Empirical formula	Mol. wt.	Number of double bonds	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Iodine number, found	Iodine number, calc.	R_f, chloroform : methyl alcohol 1 : 3	Found, % C	Found, % H	Calculated, % C	Calculated, % H	M.p., °C
(XVI)	$C_{57}H_{106}O_6$	887,42	2	–	–	–	–	57,00	57,22	0,14	77,62	11,80	77,16	12,03	36–38
(XVII)	$C_{53}H_{98}O_6$	831,31	2	–	–	–	–	60,05	61,11	0,166	76,51	11,98	77,63	11,84	36,5–38
(XXII)	$C_{57}H_{104}O_6$	885,40	3	0,9082	1,4665	270,40	268,48	84,70	86,00	0,228	77,11	11,70	77,32	11,84	–(20–19), –12,16,5
(XXVI)	$C_{57}H_{106}O_6$	887,42	2	–	–	–	–	56,48	57,22	0,15	77,18	12,29	77,16	12,03	14–15,39,5–40,5
(XXVII)	$C_{57}H_{104}O_6$	885,40	3	0,9146	1,4672	268,99	268,48	85,70	86,00	0,24	77,34	11,88	77,32	11,84	–4, –(13–12)
(XXVIII)	$C_{57}H_{108}O_6$	889,43	1	–	–	–	–	29,50	28,58	0,125	77,10	12,29	76,95	12,23	25–27
(XXXIV)	$C_{57}H_{104}O_6$	885,40	3	0,9044	1,4661	269,20	268,48	84,50	86,00	0,18	77,74	11,87	77,32	11,84	–(4–2), –(17–15)

Triglyceride	Empirical formula	Mol. wt.	Number of double bonds	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Iodine number, found	Iodine number, calc.	R_f, chloroform : methyl alcohol 1 : 3	Found, % C	Found, % H	Calculated, % C	Calculated, % H	M.p., °C
(XXXVI)	$C_{57}H_{104}O_6$	885,40	3	0,9046	1,4652	270,70	268,42	87,10	86,00	0,234	77,18	11,73	77,32	11,84	–(19–18); –(13–11,5)
(XXXVII)	$C_{57}H_{104}O_6$	885,40	3	–	–	–	–	84,85	86,00	0,185	77,67	12,05	77,32	11,84	19,5–20,5, 36
(XXXVIII)	$C_{57}H_{106}O_6$	887,42	2	–	–	–	–	56,32	57,22	0,218	77,25	11,93	77,16	12,03	35–36
(XXXIX)	$C_{57}H_{108}O_6$	889,43	1	–	–	–	–	29,90	28,58	0,13	77,31	12,42	76,95	12,23	22–22,5, 41–42,5, 60–61
(XL)	$C_{57}H_{106}O_6$	887,42	2	–	–	–	–	58,10	57,22	0,20	77,08	11,53	77,16	12,03	21–21,5
(XLI)	$C_{57}H_{110}O_6$	891,45	0	–	–	–	–	–	–	–	76,82	12,63	76,79	12,43	62–63
(XLII)	$C_{55}H_{94}O_6$	850,30	6	0,940	1,4811	258,80	259,21	178,00	178,80	–	76,88	11,36	77,65	11,00	–(11–10)

Triglyceride	Empirical formula	Mol. wt.	Number of double bonds	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Iodine number, found	Iodine number, calc.	R_f, chloroform : methyl alcohol 1 : 3	Found, % C	Found, % H	Calculated, % C	Calculated, % H	M.p., °C
(XLIII)	$C_{55}H_{96}O_6$	853,32	5	0,9221	1,4758	269,02	268,15	141,80	144,00	–	77,97	11,37	77,67	11,43	–(14–13), –(8–7)
(XLIV)	$C_{55}H_{98}O_6$	855,33	4	0,9141	1,4729	261,82	259,21	116,40	118,70	–	77,23	11,36	77,20	11,54	–(4–3)
(XLV)	$C_{51}H_{98}O_6$	807,29	0	–	–	–	–	–	–	–	75,94	12,37	75,93	12,16	64,5–65,5

Scheme 1. Synthesis of soybean-oil glycerides

[The page contains a reaction scheme with compounds labeled (I)-(LXIV), showing triglyceride structures bearing acyl residues denoted P, S, Ol, L, and Ln.]

P–$C_{15}H_{31}CO$ *(palmitoyl)*
S–$C_{17}H_{35}CO$ *(stearoyl)*
Ol–$C_{17}H_{33}CO$ *(oleoyl)*
L–$C_{17}H_{31}CO$ *(linoleoyl)*
Ln–$C_{17}H_{29}CO$ *(linolenoyl)*

By selective hydrogenation of octadeca-9,12-diynoic acid (LXIV), cis,cis-octadeca-9,12-dienoic acid, linoleic acid (LXV), is obtained. Yield 82.6%. B.p. 148.1-150.7°/0.21 mm, d_4^{20} 0.9122, n_D^{20} 1.4715, MR_D 86.10. $C_{18}H_{32}O_2$. F_2. Calculated 85.93. R_f 0.71, system n-butanol : 10% aqueous ammonia (9 : 2).

Found, %: C 77.36; 77.51; H 11.61; 11.63
$C_{18}H_{32}O_2$. Calculated, %: C 77.11; H 11.50

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