



Soviet-era science, translated into English

Chemistry

1960

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Abstract

Full Text

Chemistry

I. K. Sarycheva, G. A. Serebrennikova, E. N. Zvonkova, T. K. Mitrofanova, M. E. Maurit, O. V. Utkina, and N. A. Preobrazhenskii

Synthesis of the Principal Triglycerides of Linseed Oil

(Presented by Academician A. N. Nesmeyanov, 18 VI 1960)

In recent years, with the aid of methods of fractional crystallization, adsorption chromatography, countercurrent distribution, and spectrophotometry, the glyceride composition of natural fats and oils has been investigated and general rules have been derived for the distribution of glycerides in various fats and oils^(1,2).

For linseed oil it has been shown⁽²⁻⁶⁾ that its glycerides contain residues of the following acids: linolenic, oleic, linoleic, palmitic, and stearic, and that the composition of the glycerides varies depending on conditions, climate, soil, and the method of isolating the oil. At the same time, the experimental data on the composition of the oil proved to be close to those calculated for the triglyceride composition of linseed oil on the basis of Kartcha's distribution theory^(2,5). However, this theory does not permit the possible positions of saturated and unsaturated residues in triglycerides to be determined^(7,8).

- Numbers in parentheses are the serial numbers in Table 1.
** The letter symbols denote acid residues: S –stearic, O –oleic, L –linoleic, Ln –linolenic.

For the investigation of the structure of the triglycerides of linseed oil, we synthesized a series of triglycerides of definite composition and studied their physicochemical properties, in order to establish more precisely the composition of the triglycerides present in linseed oil. The study of the physiological properties of individual triglycerides is also of interest⁽⁹⁾.

The triglycerides synthesized by us are shown in the scheme. The absence from the scheme of triglycerides containing fewer than 4 double bonds is explained by the fact that their presence in linseed oil is very slight, and in investigations of the glyceride composition of linseed oil they have not been isolated in any appreciable amounts. As the saturated acid we introduced a stearic acid residue.

Starting from isopropylidenglycerol, we obtained four monoglycerides: α -monostearin, α -monoolein, α -monolinolein, and α -monolinolenin^(10,11). The

subsequent stages of the synthesis were varied depending on the relative arrangement of the acyls of the triglyceride obtained.

Table 1

No.	Triglyceride	Number of double bonds	n_D^{20}	n_D^{20}	MR_D	MR_D	MR_D	Iodine number	Iodine number	Analysis, found	Analysis, calculated	Analysis, found	Analysis, calculated	M.p. °C	Literature source
										% C	% H	% C	% H		
1	SLnO	4	0.9208	1.4722	268.7	268.5	113.8	114.9	77.60	11.20	77.49	11.64	8.5	(11)	—
															9;
															14
															—
															14.5
2	SLL	4	0.9186	1.4742	270.2	268.5	114.3	114.9	77.52	11.60	77.49	11.64	—	(11, 19)	16)
															—
															18)
3	SOLn	4	0.9211	1.4702	268.1	268.5	112.5	114.9	77.58	11.36	77.49	11.64	—	*	(3
															—
															2)
4	OLO	4	0.9183	1.4722	269.3	268.5	114.4	114.9	77.55	11.77	77.49	11.64	—	(11)	(10
															—
															9)
5	OSLn	4	0.9140	1.4702	269.9	268.5	113.9	114.9	77.31	11.64	77.49	11.64	4.5	(12)	—
															6
6	LOO	4	0.9200	1.4742	269.6	268.5	114.2	114.9	77.69	11.71	77.49	11.64	—	(11)	(2.5
															—
															2)
7	LSL	4	0.9212	1.4742	269.6	268.5	114.8	114.9	77.49	11.79	77.49	11.64	—	(11)	(3.5
															—
															2.5)
8	SLnL	5	0.9335	1.4762	266.4	268.0	142.6	144.0	—	—	77.64	11.44	—	(10)	(45
															—
															40)

No.	Triglyceride	n_D^{20}	n_D^{20}	MR_D	MR_D	Iodine number	Iodine number	Analysis, % C	Analysis, % H	Analysis, % C	Analysis, % H	M.p. °C	Literature source
9	SLLn 5	0.9381	1.4802	266.70	268.05	142.1	144.0	77.38	11.33	77.64	11.44	—	*
												(7	
												—	
												6.5)	
10	OLnO 5	0.9166	1.4742	270.70	268.05	144.7	144.0	77.51	11.52	77.64	11.44	—	*
												48,	
												—	
												27,	
												—	
												15	
11	OLL 5	0.9381	1.4772	268.60	268.05	141.6	144.0	77.75	11.30	77.64	11.44	—	(13)
												(14.5	
												—	
												13)	
12	LOL 5	0.9304	1.4782	268.30	268.05	146.0	144.0	77.90	11.22	77.64	11.44	—	(12)
												(40	
												—	
												38)	
13	LSLn 5	0.9239	1.4792	270.70	268.05	145.6	144.0	77.89	11.19	77.64	11.44	—	(13)
												(27	
												—	
												26),	
												—	
												(10	
												—	
												8.5)	
14	LnOO 5	0.9202	1.4772	270.60	268.05	145.4	144.0	77.83	11.66	77.64	11.44	—	(13),
												(12	(10)
												—	
												10)	
15	SLLnLn6	0.9336	1.4820	268.70	267.59	171.7	173.2	77.70	11.24	77.83	11.23	—	*
												1	
												—	
												0	

No.	Triglyc- ceride	n_D^{20}	n_D^{20}	MR_D	MR_D	Iodine num- ber,	Iodine num- ber,	Analysis, found,	Analysis, found,	Analysis, found,	Analysis, found,	M.p. °C	Literature source
16	OLnL 6	0.9230	1.4792	270.2	267.5	172.3	173.2	77.52	11.41	77.83	11.23	—	(12) (37 — 35.5), — (25 — 24)
17	OLLn 6	0.9269	1.4792	269.1	267.5	172.7	173.2	77.63	11.31	77.83	11.23	—	(10, (30.515) — 29)
18	LLL 6	0.9272	1.4792	269.0	267.5	171.5	173.2	78.01	11.28	77.83	11.23	—	(13) (44 — 43)
19	LOLn 6	0.9367	1.4802	266.8	267.5	171.4	173.2	77.85	10.94	77.83	11.23	—	(10) (29 — 28)
20	LnSLn 6	0.9401	1.4812	266.6	267.5	174.0	173.2	77.67	11.29	77.83	11.23	—	(13), (10)
21	OLnLn 7	0.9301	1.4832	269.6	267.1	200.6	202.5	77.95	10.98	78.03	11.02	—	(12) (16 — 14)
22	LLnL 7	0.9334	1.4842	268.9	267.1	201.8	202.5	78.01	11.07	78.03	11.02	—	*
23	LnLL 7	0.9494	1.4902	267.4	267.1	200.0	202.5	78.06	11.01	78.03	11.02	—	(10)
24	LnOLn 7	0.9248	1.4762	267.6	267.1	201.8	202.5	78.37	10.62	78.03	11.02	—	*

No.	Triglyceride	n_D^{20}	n_D^{20}	MR_D	MR_D	Iodine number	Iodine number	% C	% H	% C	% H	M.p. °C	Literature source
				found	calculated	found	calculated	found	calculated	found	calculated		
25	LLnLn8	0.9318	1.4832	268.4	266.6	431.3	232.1	78.28	11.03	78.21	10.82	—	(12, 53), (15)
26	LnLLn8	0.9319	1.4772	265.7	266.6	434.1	232.1	78.31	10.81	78.21	10.82	—	(16, 15)
27	LnLnLn	0.9591	1.4972	266.0	266.1	256.5	261.6	78.19	10.56	78.39	10.62	—	(46, 44), (26, 24)

* Unpublished data.

Monoacid triglycerides: trilinolein (LLL) and trilinolenin (LnLnLn) were synthesized by the action of the acid chloride of the corresponding acid on the monoglyceride in chloroform in the presence of an organic base (quinoline, pyridine).

The introduction of two acid residues into the monoglyceride molecule was carried out similarly to obtain **unsymmetrical diacid triglycerides**: α -stearoyl- β , α' -dilinolein (SLL); α -stearoyl- β , α' -dilinoenin (SLnLn); α -oleoyl- β , α' -dilinolein (OLL); α -oleoyl- β , α' -dilinoenin (OLnLn); α -linoleoyl- β , α' -diolein (LOO); α -linoleoyl- β , α' -dilinoenin (LLnLn); α -linolenoyl- β , α' -diolein (LnOO); α -linolenoyl- β , α' -dilinolein (LnLL).

To obtain **symmetrical diacid and triacid triglycerides**, use was made of the different reactivity of the primary and secondary hydroxyl groups of the monoglyceride. At a temperature of 15-20° and under the action of the acid chloride on the α -monoglyceride in the presence of a base (quinoline, pyridine), the α' -hydroxyl reacts predominantly. Thus the following diglycerides were ob-

tained: α, α' -diolein⁽¹¹⁾, α, α' -dilinolein⁽¹⁰⁾, α, α' -dilinolenin⁽¹⁰⁾, α -stearoyl- α' -olein⁽¹¹⁾, α -stearoyl- α' -linolein⁽¹⁰⁾, α -stearoyl- α' -linolenin, α -oleoyl- α' -linolein, α -oleoyl- α' -linolenin⁽¹²⁾, α -linoleoyl- α' -linolenin⁽¹³⁾.

At 40-50° and with the action of the acid chloride in the presence of a base, the β -hydroxyl of the diglyceride reacts. In this way the **symmetrical diacid triglycerides** were obtained: α, α' -dioleoyl- β -linolein (OLO); α, α' -dioleoyl- β -linolenin (OLnO); α, α' -dilinoleoyl- β -stearin (LSL); α, α' -dilinoleoyl- β -olein (LOL); α, α' -dilinoleoyl- β -linolenin (LLnL); α, α' -dilinolenoyl- β -stearin (LnSLn); α, α' -dilinolenoyl- β -olein (LnOLn); α, α' -dilinolenoyl- β -linolein (LnLLn).

The **triacid triglycerides** were obtained analogously: α -stearoyl- β -linolenoyl- α' -olein (SLnO); α -stearoyl- β -linolenoyl- α' -linolein (SLnL); α -stearoyl- β -oleoyl- α' -linolenin (SOLn); α -stearoyl- β -linoleoyl- α' -linolenin (SLLn); α -oleoyl- β -linolenoyl- α' -linolein (OLnL); α -oleoyl- β -stearoyl- α' -linolenin (OSLn); α' -oleoyl- β -linoleoyl- α' -linolenin (OLLn); α -linoleoyl- β -stearoyl- α' -linolenin (LSLn); α -linoleoyl- β -oleoyl- α' -linolenin (LOLn).

The physicochemical constants of the triglycerides obtained are summarized in Table 1. In establishing the purity and structure of the triglycerides, paper chromatography⁽¹⁴⁾ and spectral investigations were used. In some cases, to verify the results obtained, we proceeded in the synthesis from benzylidene glycerol.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

Received
16.VI.1960

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