

The Structure of Triglycerides in Selected Oils Containing Erucic Acid^{1,2}

H. GRYNBERG and H. SZCZEPAŃSKA, Institute of General Chemistry, Warsaw, Poland

Abstract

The fatty acid compositions of 7 oils containing different amounts of erucic acid (1.4 to 57.2%) have been investigated. Fatty acid distribution between the 1,3- and 2-positions of the glyceride molecules was estimated by the pancreatic lipase splitting technique. On the basis of this experimental data, it is possible to speculate on the rules governing glyceride composition in the oils investigated.

Introduction

THE FATTY ACID COMPOSITIONS of various oils containing erucic acid have been reported in the literature. However, very little information is available on the distribution of erucic acid in the triglycerides of these oils. In this paper, the results of an investigation of seven seed oils containing 1.4 to 57.2% erucic acid are reported.

Experimental

The following seed oils were investigated: *Crambe abyssinica*, *Sinapis alba*, *Brassica napus*, *Lunaria annua*, *Eruca sativa*, *Brassica juncea*, and *Camelina sativa*. All seeds except *Brassica napus* and *Camelina sativa* (of Polish origin) were from the experimental cultivations of the Northern Regional Research Laboratory, Peoria, Ill. All oils were extracted with cold ethyl ether using the procedure of Grynberg et al. (1).

Pancreatic lipase hydrolysis of each oil was carried out by the method of Szczepańska (2) using "Steapsin" (Difco Laboratories, Detroit, Mich.). The proper

¹ Presented at the AOCs Meeting in Houston, April 1965.
² Part of the T. P. Hilditch Symposium on Analysis of Natural Fat Triglycerides (JAOCs, September through December, 1965).

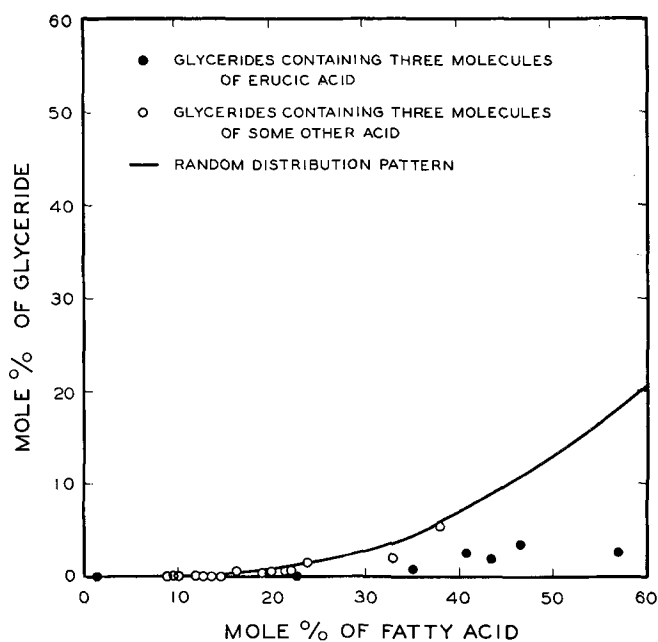


FIG. 1. Distribution pattern for monoacid glycerides in oils containing erucic acid.

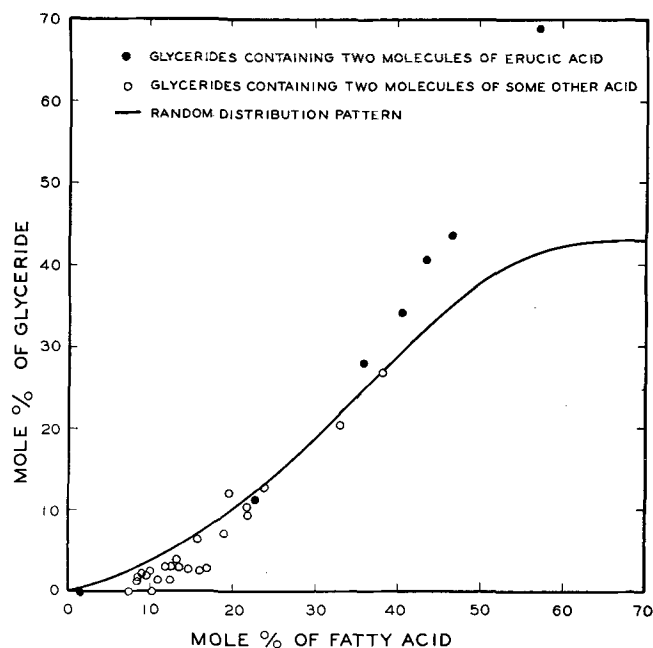


FIG. 2. Distribution pattern for diacid glycerides in oils containing erucic acid.

time of lipolysis was determined for each oil. Following lipolysis, the lipid material was extracted with ethyl ether and fractionated by silicic acid chromatography according to the method of Kaufmann and Wessels (3). The fatty acid composition of the 2-mono-glyceride fraction was determined by gas-liquid chromatography (GLC). The fatty acids in the mono-glycerides were esterified using direct methanolysis according to the method described in IUPAC (4) as

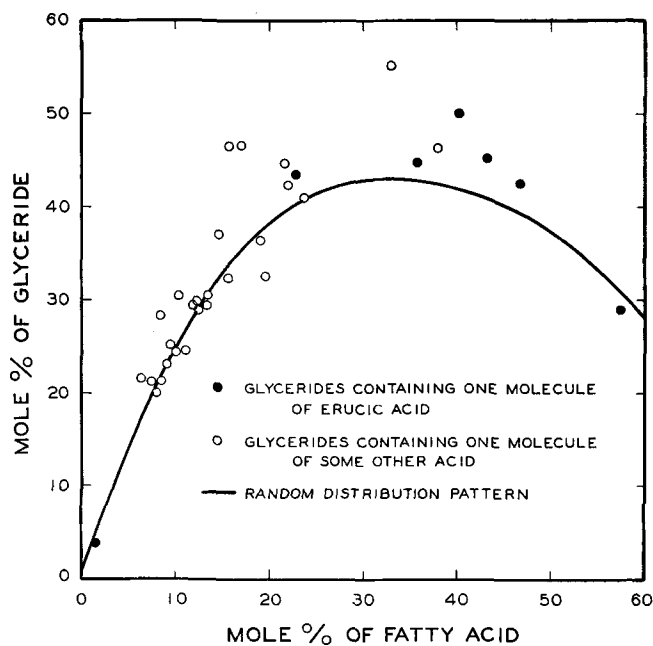


FIG. 3. Distribution pattern for triacid glycerides in oils containing erucic acid.

TABLE I
 Fatty Acid Composition of Oils and 2-Monoglyceride Fractions

Oil	<i>Crambe abyssinica</i>		<i>Sinapis alba</i>		<i>Brassica napus</i>		<i>Lunaria annua</i>		<i>Eruca sativa</i>		<i>Brassica juncea</i>		<i>Camelina sativa</i>	
	A ^a	B	A	B	A	B	A	B	A	B	A	B	A	B
Fatty acid ^b														
C _{14:0}	0.6
C _{16:0}	2.0	0.5	3.0	0.6	4.3	3.2	2.2	0.8	7.2	0.3	2.3	0.1	5.8	2.5
C _{16:1}	0.4	0.4	0.4	0.3	1.0	0.5	0.3	0.3	0.2	0.3
C _{16:2}	0.4	0.2	0.3	0.5	0.4	0.1
C _{16:3}	0.1	Trace	0.8	0.1	0.3
C _{17:1}	0.8
C _{18:0}	0.4	0.9	0.9	1.0	1.5	0.7
C _{18:1}	16.9	44.7	21.9	37.8	12.0	22.1	32.9	61.8	19.0	35.1	23.8	17.5	15.8	15.0
C _{18:2}	8.6	27.6	10.2	29.9	15.9	41.6	9.4	14.5	10.9	26.2	21.7	43.8	19.8	27.5
C _{18:3}	6.4	21.1	7.6	21.9	12.3	22.0	1.5	4.1	12.6	33.7	14.7	35.8	38.1	46.7
C _{20:0}	0.5	0.9	0.8	0.8	1.8
C _{20:1}	3.2	1.3	8.5	2.5	9.1	3.3	Trace	1.3	8.4	0.8	10.0	1.3	13.3	3.8
C _{20:2}	0.2	0.4	Trace	0.7	0.5	1.0	0.3	1.5	0.8
C _{22:0}	2.0	0.7	0.2	0.6	0.2	0.8	2.2
C _{22:1}	57.2	3.3	43.3	4.9	46.4	7.7	40.3	7.7	35.7	1.7	22.7	0.3	1.4
C _{22:2}	0.8	0.2	0.2
C _{24:0}	Trace	1.0	1.9
C _{24:1}	1.4	1.8	0.7	13.6	2.0	1.5	0.5	0.4
C _{24:2}	4.9

^a A, total fatty acid; B, 2-monoglyceride.

^b Mean mole %.

TABLE II

Distribution of Principal Fatty Acids in the 2-Position (mean %)^a

Oil	<i>Crambe abyssinica</i>	<i>Sinapis alba</i>	<i>Brassica napus</i>	<i>Lunaria annua</i>	<i>Eruca sativa</i>	<i>Brassica juncea</i>	<i>Camelina sativa</i>
Fatty acid							
C _{18:0}	8	7	25	12	1	2	16
C _{18:1}	88	58	61	63	62	24	31
C _{18:2}	100	98	87	51	80	67	47
C _{18:3}	100	96	60	91	89	81	41
C _{20:1}	13	10	12	100	3	4	10
C _{22:1}	2	4	5	6	2	0	0
C _{24:1}	0	13	5	0	26

^a The percentage in the 1,3-positions is: 100 - (amt in the 2-position).

modified by Grynberg (5). GLC conditions were: instrument, Pye equipped with a β -ionization detector; column, 0.4 cm by 1.2 meters packed with 80/100 mesh Celite coated with 10% PEGA; carrier gas, 60-100 ml/min argon; column temperature, 180-190C. The fatty acid compositions of the original oils were determined in the same manner.

TABLE III
Glyceride Composition

No.	Oil	Fatty acid		Monoacid-glycerides	Diacid-glycerides	Triacid-glycerides
		Symbol	%			
1	2	3	4	5	6	7
1	<i>Crambe abyssinica</i>	C _{22:1}	57.2	2.3	69.2	29.0
		C _{18:1}	16.9	2.7	46.7
		C _{18:2}	8.6	28.3
		C _{18:3}	6.4	21.5
2	<i>Sinapis alba</i>	C _{22:1}	43.3	1.9	40.8	45.2
		C _{20:1}	8.5	1.8	21.0
		C _{18:1}	21.9	0.7	9.5	42.5
		C _{18:2}	10.2	0.1	30.6
	C _{18:3}	7.6	0.1	20.9	
3	<i>Brassica napus</i>	C _{22:1}	46.4	3.3	43.4	42.5
		C _{20:1}	9.1	0.1	2.1	23.1
		C _{18:1}	12.0	0.1	3.1	29.5
		C _{18:2}	15.9	2.5	46.4
	C _{18:3}	12.3	0.1	3.1	29.9	
4	<i>Lunaria annua</i>	C _{24:1}	13.6	0.1	3.1	30.4
		C _{22:1}	40.3	2.5	33.9	50.1
		C _{18:1}	32.9	2.1	20.5	55.3
		C _{18:2}	9.4	0.1	2.1	25.0
5	<i>Eruca sativa</i>	C _{22:1}	35.7	0.5	27.9	44.8
		C _{20:1}	8.4	1.5	20.0
		C _{18:1}	19.0	0.4	7.3	36.6
		C _{18:2}	10.9	1.5	24.5
	C _{18:3}	12.6	1.2	34.0	
6	<i>Brassica juncea</i>	C _{22:1}	22.7	11.2	43.6
		C _{20:1}	10.0	0.1	2.3	24.4
		C _{18:1}	23.8	1.3	12.7	41.0
		C _{18:2}	21.7	0.5	10.3	44.8
	C _{18:3}	14.7	0.1	2.7	36.9	
7	<i>Camelina sativa</i>	C _{22:1}	1.4	3.3
		C _{20:1}	13.3	0.1	4.0	29.5
		C _{18:1}	15.8	0.4	6.4	32.3
		C _{18:2}	19.8	0.7	12.0	32.5
	C _{18:3}	38.1	5.3	26.7	46.2	

Results and Discussion

The fatty acid compositions of the oils investigated and the 2-monoglycerides from lipolysis are given in Table I. The percentage distribution of individual fatty acids on the 1,3- and 2-positions of glycerides was calculated from the data in Table I and is reported in Table II. Glyceride composition was calculated according to the method of Coleman (6), based on the assumption that the 1,3- and 2-positions are occupied by fatty acids in a random manner.

The triglyceride distribution of the oils with respect to erucic and C₁₈ unsaturated acids is presented in Table III. (Only those triglycerides present in amounts greater than 0.05% were considered.)

The percentages of mono-, di-, and triacid glycerides were plotted vs. the content of individual fatty acids. (See Fig. 1-3.) Figure 1 shows that trierucin content is much lower than the values predicted by random distribution. The content of other monoacid-glycerides is in accordance with the random distribution theory. The content of the diacid-glycerides (Fig. 2) without erucic acid is near to the values calculated for random distribution. On other hand dieruco-glycerides are present in greater than random amounts. For the triacid-glycerides, the highest deviation from the random distribution curve is observed.

The following conclusions were drawn from the experimental results: (A) The oils investigated do not conform to the even distribution theory. (B) A great number of glycerides in the oils investigated are present in the amounts predicted by the random distribution theory. There is some limitation on the formation of trierucin, however, similar to the limitations for trisaturated glycerides in Kartha's restricted random distribution theory (7). (C) Certain triglyceride structures were preferentially formed. The erucic acid appears almost completely in the outer positions, and unsaturated C₁₈ acids appear mainly in the inner positions of the glycerides.

ACKNOWLEDGMENT

Supported in part by PL-480 funds granted by the USDA.

REFERENCES

- Grynberg, H., H. Szczepanska and M. Beldowicz, *Oleagineux* 17, 875 (1962).
- Szczepanska, H., *Chemia analityczna* 9, 1083 (1964).
- Kaufmann, H. P., and H. Wessels, *Fette Seifen Anstrichmittel* 66, 81 (1964).
- Annex I-2-1964 of International Union of Pure and Applied Chemistry (IUPAC), Oil and Fat Section.
- Grynberg, H., Annual Report for US Department of Agriculture, Project F.G.P.O. 136 (1964).
- Coleman, M. H., *JAOCS* 38, 685 (1961).
- Kartha, A. R. S., *Ibid* 30, 326 (1953).