soya (62), and stillingia (90) have the values indicated in parentheses. It must be appreciated that the major polyethenoid glycerides are not the same in all these oils. In linseed oil most glycerides contain two or more linolenic groups, in dog rose and candlenut oil most contain at least one linolenic and one linoleic group, in soyabean oil most contain at least two linoleic groups, and in stillingia most contain at least two linolenic groups or at least one linolenic group and one C_{10} dienoic acid group.

The major glycerides of linseed oil contain 5–9 double bonds (85%) as do those of stillingia oil (88%), whilst those of rose oil have 5–8 double bonds (84%), those of candlenut have 4–8 double bonds (88%), and those of soyabean oil 3–6 double bonds (83%).

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Glyceride Studies. Part IV. The Component Glycerides of Ten Seed Oils Containing Linoleic Acid

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Abstract

The component glycerides of ten seed oils (safflower, tobacco, sunflower, *Argemone mexicana*, maize, cotton, groundnut, *Macadamia ternifolia*, *Gmelina asiatica*, and *Madhuca latifolia*) have been estimated by chromatographic procedures. The results agree with those obtained by lipolysis or calculated directly from the component acids on the basis of the theory of positional distribution.

Introduction

OLEIC AND LINOLEIC are the only unsaturated acids present in many seed oils, including some that are available in large quantities, but information about their component glycerides, apart from a few recent analyses, is based largely on the low temperature crystallisation procedure now considered to be inadequate for the more unsaturated seed oils. We have examined ten seed oils by lipolysis and by chromatographic separation on silica impregnated with silver nitrate. It is convenient to divide these oils into four groups:

(i) Oils with a very high proportion of linoleic acid (> 70%): safflower and tobacco.
(ii) Oils with a high proportion of linoleic acid (50–60%): sunflower, *Argemone mexicana*, maize, and cottonseed.
(iii) Oils with a high proportion of oleic acid (> 50%): groundnut and *Macadamia ternifolia*.
(iv) Oils with a high content of "saturated" acids (> 30%): *Madhuca latifolia* (Mowrah butter) and *Gmelina asiatica*.

Some of the oils fall into more than one category but we have chosen to include them in the group given above rather than in another.

Procedure

Seeds or extracted oils were obtained from J. Bibby and Sons (maize, cottonseed, and groundnut); from the Tropical Products Institute (safflower (var. U.S.A./P2) from Kenya, sunflower from Nigeria (var. Jupiter) and from Bulgaria, *Argemone mexicana* from Jamaica, *Macadamia ternifolia* from Tanganyika, *Madhuca latifolia* from Bombay, and *Gmelina asiatica* from Singapore); from Younghusband, Stephens, and Co. Ltd. (tobacco); and from Dr. C. Y. Hopkins (*M. ternifolia*).

Crushed seeds were thoroughly extracted with boiling petrol ether (bp 40–60C). The extracted oil was neutralised by percolation in chloroform solution through a column of alumina and the triglycerides were subsequently eluted from a column of silica (Whatman chromedia, SG31) with benzene; more polar solvents subsequently removed diglycerides and monoglycerides (1).

Lipolyses were carried out as described in our earlier papers (2,3). The two sunflower oils were examined by low-temperature crystallisation from acetone and methanolic silver nitrate followed by chromatography on columns of silica-silver nitrate (2). The remaining oils were examined by our thin-layer procedure (3,4), developing the plate (20 × 20 cm) with benzene containing 10% of ether. We find the latter procedure to be quicker and more satisfactory. The results are summarised in Tables I and III to V.

TABLE I

Component Esters (% mol) of the Whole Oil, the 2-Monoglycerides, and the Sum of the Separated Fractions

	14:0	16:0	18:0	16:1	18:1	18:2	18:3[a]
Safflower (extract 30%, triglycerides 91%, iodine value 141)							
Triglyceride	....	6.6	3.4	0.6	12.2	77.0	0.2
Plate (9 fractions)	....	7.0	2.8	0.9	13.0	76.0	0.3
2-Monoglyceride	....	1.0	0.1	0.1	12.5	86.3	....
Tobacco (supplied as crude oil, triglycerides 89%, iodine value 138)							
Triglyceride	....	9.8	3.8	1.0	13.5	70.6	1.3
Plate (9 fns.)	0.1	11.2	4.6	0.6	14.1	68.5	0.9
2-Monoglyceride	....	0.9	0.3	0.2	15.8	82.2	0.6
Sunflower (Nigerian, extract 32%, triglycerides 99%, iodine value 125)							
Triglyceride	0.2	7.1	2.8	0.4	30.0	59.5	....
Columns (13 fns.)	....	8.0	3.5	0.5	32.7	55.3	....
2-Monoglyceride	....	1.1	0.3	....	25.0	73.6	....
Sunflower (Bulgarian, extract 31%, triglycerides 99%, iodine value 129)							
Triglyceride	....	7.0	4.4	0.3	26.0	62.3	....
2-Monoglyceride	....	1.1	0.3	....	23.9	74.7	....
Sunflower (Nigerian, extract 33%, triglycerides 99%, iodine value 112)							
Triglyceride	0.2	5.1	1.8	0.5	50.3	42.1	....
Columns (12 fns.)	....	5.4	2.4	0.4	52.5	39.3	....
2-Monoglyceride	....	1.0	0.2	....	49.9	48.9	....
A. Mexicana (extract 39%, triglycerides 87%, iodine value 117)							
Triglyceride	....	12.3	4.2	0.3	28.1	55.1	....
Plate (9 fns.)	....	12.7	4.6	1.2	27.6	53.9	....
2-Monoglyceride	....	2.2	....	0.5	35.0	62.3	....
Maize (supplied as crude oil, triglycerides 93%, iodine value 120)							
Triglyceride	....	12.6	1.8	0.8	30.0	54.3	0.5
Plate (9 fns.)	....	14.3	2.7	1.1	29.0	51.9	1.0
2-Monoglyceride	....	2.4	....	0.3	29.1	68.2	....
Cotton (extract 20%, triglycerides 86%, iodine value 97)							
Triglyceride	1.1	27.3	3.1	1.4	16.7	50.4	....
Plate (9 fns.)	1.5	27.4	2.9	1.9	17.0	49.3	....
Plate (9 fns.)	1.7	26.6	4.5	2.7	16.7	47.8	....
2-Monoglyceride	0.3	3.6	0.3	0.7	24.5	70.6	....
Groundnut (extract 50%, triglycerides 91%, iodine value 80)							
Triglyceride[b]	....	9.8	3.7	0.4	60.9	18.1	....
Plate (9 fns.)[b]	....	10.5	3.8	0.6	59.9	18.5	....
2-Monoglyceride	....	1.8	0.2	0.4	66.6	31.0	....
M. ternifolia (extract 74%, triglycerides 94%, iodine value 75)							
Triglyceride[c]	0.7	9.3	3.7	27.2	51.9	2.8	....
Plate (7 fns.)[b]	0.7	10.0	3.2	28.3	50.8	3.3	....
2-Monoglyceride	....	0.9	....	23.8	71.0	4.3	....
M. ternifolia (extract 68%, triglycerides 93%, iodine value 69)							
Triglyceride[d]	0.5	10.1	6.2	18.3	55.4	3.4	....
2-Monoglyceride	....	0.8	....	15.5	77.6	6.1	....
G. asiatica (extract 60%, triglycerides 96%, iodine value 96)							
Triglyceride[e]	....	10.1	8.1	0.3	28.8	37.6	....
Plate (12 fns.)[e]	....	10.0	7.5	0.5	29.4	39.7	....
2-Monoglyceride	....	1.6	....	0.9	37.3	60.2	....
M. latifolia (extract 46%, triglycerides 94%, iodine value 58)							
Triglyceride	....	23.7	24.1	0.2	37.6	14.4	....
Plate (9 fns.)	....	22.9	25.8	0.7	37.3	13.3	....
2-Monoglyceride	....	3.1	4.5		60.4	32.0	.

[a] These figures refer to the number of carbon atoms and double bonds per molecule; thus 18:2 represents octadecadienoic acid.

	20:0	22:0	24:0	20:1	22:1
[b] also	1.4	2.7	1.4	1.3	0.3
	1.5	2.8	1.4	0.8	0.2
[c] also	2.4	....	....	2.0	....
	2.8	....	....	0.9	....
[d] also	3.7	....	....	2.4	....
[e] also	2.6	2.4	....	9.9	0.2
	2.6	1.5	....	8.3	0.5

Discussion

Efficiency of Thin-Layer Separation

By the thin-layer procedure we usually separate linoleic-containing oils into nine fractions in which individual glycerides, or groups of closely related glycerides, are separately concentrated. The effectiveness of this separation is apparent in Table II which shows the concentration of each glyceride or group of glycerides in the fraction in which it predominates. Most of these values exceed 80%, many exceed 90%, and lower values generally relate to minor glycerides (5% or below) which could only give high concentrations in smaller fractions than we choose to collect. We believe that if necessary these values could be increased and that chromatography on thin layers of silica containing silver nitrate provides an excellent method for the isolation and purification of glycerides.

In the separation of *Gmelina asiatica* glycerides, which contains about 10% of eicosenoic acid, there is evidence of subfractionation of monoethenoid C_{18} and C_{20} glycerides which was sufficient to distinguish between these two. This was less apparent in the monoethenoid C_{16} and C_{18} glycerides of *Macadamia ternifolia.*

The values quoted in Table I show that there is a reasonable agreement between the sum of the fractions recovered from the plate (or column) and the oil applied, though there is a tendency for the recovery of linoleic acid to be slightly low. The loss is smaller in the plate method than in the crystallisation-column method. We believe this loss arises mainly from the difficulty of completely extracting the more unsaturated glycerides from the silica-silver nitrate mixture.

TABLE II

Concentration (% mol) of Glycerides in Individual Fractions

	222	221	220	211	210	111	200	110	100[a]
Safflower	94	93	90	72	83	55	87	78	61
Tobacco	80	85	93	79	76	67	67	38	....
A. mexicana	92	93	92	84	80	88	71	88	65
Maize	68	82	83	92	92	66	81	41	39
Cotton	74	65	92	57	95	....	87	65	89
Cotton	73	69	90	....	93	....	86	45	81
Groundnut	....	59	69	95	80	86	....	92	79
M. ternifolia	....	....	....	61	48	89	....	78	50
G asiatica	82	91	88	98	94	....	78	95	82
M. latifolia	....	.	.	50	75	40	....	52	94

[a] These figures indicate the number of double bonds in the three acyl chains. Each glyceride category includes all positional isomers.

Safflower and Tobacco

Results for these two oils, both of which contain over 70% of linoleic acid, are given in Table III along with results previously reported for oils of similar fatty acid composition. The high content of linoleic acid is reflected in the large proportion of glycerides containing three linoleic groups (47% and 33%) or two linoleic groups (37% and 43%). The values obtained by thin-layer chromatography agree with those calculated from lipolysis data or directly from the component acids according to a theory of positional distribution proposed by one of us (8). Our results are similar to those of Scholfield and Dutton (6) in their countercurrent distribution study of safflower oil; they do not show good agreement, particularly in respect of individual glycerides, with earlier results obtained by low temperature crystallisation (5,7). This is not surprising as this method is now recognised as unsuitable for oils containing appreciable quantities of more than one unsaturated acid.

Sunflower, Argemone mexicana, Maize, and Cotton

Our results for these oils are quoted, along with previous results where relevant, in Table III. We had three samples of sunflower seed oil, two of which possessed a similar fatty acid composition (Table I); all three samples were examined by lipolysis but only two by the longer crystallisation—chromatography procedure. Though only two of the three samples actually belong to this high linoleic group it is convenient to consider all three together.

Studies on sunflower glycerides, apart from the present work and that of Kaufmann (26), are confined to low temperature crystallisation studies and again there is poor agreement between the old and new results. The limitations of the early work have already been mentioned and our results show that a greater variety of glycerides is present in sunflower seed oil than was recognised before; thus three to five glyceride groups were differentiated by crystallisation, but eight by chromatography.

Our results for maize oil, though different from those obtained by low temperature crystallisation, resemble the incomplete analysis by countercurrent distribution (11) and results obtained by two different oxidation procedures (12,13). The component glycerides of *Argemone mexicana* have not been reported

TABLE III

Component Acids and Glycerides (% mol) of Seed Oils Containing Linoleic Acid

Reference	Safflower					Tobacco				Sunflower														*A. mexicana*		
	(5)	(6)	A[a]	B	C[e]	(7)	A[a]	B	C[e]	(5)	B[a]	C[e]	A[a]	B	C[e]	(26)	(5)	(5)	A[a]	B	C[e]	(9)		A[a]	B	C[e]
Component acids																										
16:0 + 18:0[c]	11	11		10		11		14		13	12			10		14	11	12		7		10			17	
16:1 + 18:1	13	13		13		17		14		24	26			30		28	33	44		51		49			28	
18:2 + 18:3	76	76		77		72		72		63	62			60		58	56	44		42		41			55	
Component glycerides																										
S_2U[d]	....	....	2	2	2	3	7	5	4	2	3	3	2	3	3	....	....	1	1	2	1	....		7	6	6
SU_2	32	....	26	26	26	27	33	32	33	35	28	28	26	25	25	....	32	34	22	18	19	31		38	37	37
U_3	68	....	72	72	72	70	62	63	63	63	79	79	72	72	72	....	68	65	77	80	80	69		55	57	57
322[f]	....	....	....	....	....	....	2	2	2	....	....	....	....	....	....	....	....	....	....	....	....	....		....	....	....
222	31	47	47	45	45	19	33	35	34	7	23	24	14	20	21	19	....	....	4	7	7	....		20	17	17
221	37	26	19	23	23	51	17	22	22	56	31	30	39	32	32	28	61	39	31	27	27	24		18	25	25
220	30	8	18	19	19	23	24	22	23	20	14	14	14	11	11	14	7	....	7	4	4	....		17	16	16
211	....	....	5	4	4	....	5	4	5	.	13	13	19	17	16	14	7	26	29	33	33	45		12	13	13
210	2	....	7	6	6	4	8	9	9	15	12	12	11	11	11	12	25	27	11	9	9	31		16	17	17
111	....	....	1	....	....	....	3	....	....	....	2	2	....	3	3	6	....	....	13	13	13	....		5	2	2
200	....	....	2	2	2	3	7	4	3	2	2	2	1	2	2		....	....	....	1	1	....		5	4	4
110	....	....	1	1	1	....	1	1	1	....	2	2	1	3	3	5	....	7	4	5	5	....		5	4	4
100	....	....	....	....	....	....		1	1	....	1	1	1	1	1	2	....	1	1	1	1	....		2	2	2
000		....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....		....	....	....

	Maize							Cottonseed										*M. latifolia*				
	A[a]	B	C[e]	(10)	(11)	(12)	(13)	A_1[a]	A_2[a]	B	C[e]	(13)	(14)	(15)	(16)	(17)	(18) A	(18) B[e]	A[a]	B	C[e]	(17)	(20)
Component acids																							
16:0 + 18:0[c]		14		15	13	13	16		32			33	29	27	27	23	....	....		48		43	44
16:1 + 18:1		31		24	27	27	?		18			17	22	16	?	?	....	....		38		?	43
18:2 + 18:3		55		61	60	60	?		50			50	47	57	?	?	....	....		14		?	13
Component glycerides																							
S_2U[d]	6	5	5	2	....	4	5	23	23	22	22	22	13	17	13	13	....	....	52	46	51	47	28
SU_2	38	33	34	41	....	34	34	50	52	48	50	51	59	48	48	44	....	....	39	41	41	36	71
U_3	56	62	61	57	....	62	61	27	25	29	28	27	28	35	39	43	....	....	8	9	8	17	....
322[f]	2	1	1	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
222	14	15	15	1	22	20	....	11	10	12	11	....	..	17	....	....	6	15	....	....	....	....	....
221	20	27	27	49	24	26	....	9	10	12	12	....	28(18)[b]	14	....	....	13	13	....	1	1	....	....
220	17	14	14	34	13	16	....	27	27	26	27	....	18(31)	29	....	....	30	26	3	2	3	....	....
211	14	16	15	7	....	14	....	5	3	4	4	....	...(9)	3	....	....			3	4	4	....	....
210	17	15	16	6	....	15	....	20	20	19	19	....	41(26)	17	....	....	23	18	15	17	16	....	....
111	6	3	3	....	....	2	....	2	2	1	1	....	...(1)	....	....	....			5	4	3	....	....
200	5	3	3	2	....	3	....	17	18	16	16	....	7(10)	12	....	....	23	21	17	15	14	....	....
110	4	4	4	1	....	3	....	3	5	3	4	....	..(2)	3	....	....			21	22	22	....	....
100	1	2	2	....	....	1	....	6	5	6	6	....	6(3)	5	....	....	5	7	35	31	37	....	....
000		....	....	....	....	....	....	....	....	1	....	....	....	....	....	....	....	....	1	4	....	....	....

[a] Present work.
[b] Result recalculated by Gunstone (ref. 8).
[c] See footnote, Table I.
[d] U and S refer to saturated and unsaturated acyl chains.
[e] Results obtained by chromatography (A), by lipolysis (B), and by direct calculation from the component acids (ref. 8,C).
[f] See footnote, Table II.

previously. They are very similar to those of maize oil, thus emphasising the previously accepted view that the glyceride composition of a seed oil depends on its component acids and not on its biological origin.

The component glycerides of cottonseed oil were first examined by Hilditch and Maddison (14) and their results have been reinterpreted and recalculated by Gunstone (8). More recently, Russian investigators (15) examined this oil by adsorption chromatography on alumina, by reverse phase chromatography, and by gas-liquid chromatography (GLC). The oil has also been examined by oxidation methods (13,16,17) and by lipolysis and thin-layer chromatography (TLC) (18). Bearing in mind slight differences in the composition of the oils examined, our results are similar to the more recent studies (only the Russian results are equally detailed) but differ from the earlier results, even after recalculation. Cottonseed oil was one of the first oils we examined by TLC and therefore we did the experiment twice. Both sets of results are given in Table II (A1 and A2); they show good agreement.

Groundnut and Macadamia ternifolia

These two oils are both rich in oleic acid but otherwise they have little resemblance. In groundnut oil (Table IV) four glycerides [211 (see footnote [a], Table II), 210, 111, and 110] make up almost 80% of the total but six minor glycerides are also present. The analysis by crystallisation picked out three major glycerides (211, 210, and 110; almost 80%) and three minor components also. Our results are similar to, but more detailed than, those of Barrett et al. (18), obtained by TLC and by lipolysis.

M. ternifolia seed oil is of interest in that it contains C_{16} and C_{18} monoethenoid acids in appreciable proportions but its component glycerides have not previously been reported. Our chromatographic study did not distinguish between glycerides in which these two acids were interchanged but the total amount in each group of similar glycerides agrees so well with those obtained by lipolysis that the figures for individual glycerides can be taken from the lipolysis results (column B, Table V). Our results show that five major glycerides (111, 11H, 1HH, 110 and H10) comprise over 80% of the oil and are accompanied by ten minor components.

Madhuca latifolia and Gmelina asiatica

Our sample of *G. asiatica* (Table IV) contained 23% of saturated acids along with 10% of eicosenoic acid which, like the saturated acids, is largely excluded from the 2-position. This content of "saturated" acids (33%) is interesting, for it is at this value that the difference between widest distribution (requiring 100% of S_2U) and positional distribution (requiring 50% of S_2U) is greatest (8). Our value of 48% is therefore highly significant. The subfrac-

TABLE IV

Component Acids and Glycerides (% mol) of Groundnut Oil and of *G. asiatica* Seed Oil

Ref.	Groundnut						*G. asiatica*		
	A[a]	B	C[e]	(18) A	(18) B[e]	(19) (17)	A[a]	B	C[e]
Component acids									
Sat.		19		....	20	20		23	
16:1 + 18:1[c]		61		....	59	?		29	
20:1 + 22:1		2		....	21	?		10	
18:2		18		....	....	?		38	
Component glycerides									
S_2U[d]	11	10	9	....	7	9	21	24	25
SU_2	40	42	47	....	47	42	48	51	50
U_3	49	48	44	....	46	49	31	25	25
222[f]	....	....	1	....	....		6	4	5
221	5	5	6	8	3	6	10	10	10
22E[g]	....	....	....				6	5	5
211	4	2	2			....	12	11	11
21E	18	20	19				11	9	8
2EE	1	1	1	24	22	34	6	8	7
220	....	....	....				....	1	1
210	14	15	14			16	14	17	17
2E0	....	....	....				7	6	6
111	26	23	22	39	47		4	2	2
11E	....	2	2			6	3	3	3
1EE	....	....	....				....	1	1
200	4	3	2			....	7	7	7
110	21	22	24	26	24	31	7	7	7
E10	2	1	1				3	4	5
100	5	6	6	3	4	7	4	5	5

[a] Present work.
[c–f] Same as footnotes to Table III.
[g] E stands for eicosenoic acid and includes 20:1 and 22:1. In calculating the proportions of S_2U, etc., E is reckoned as a saturated acyl group (see text).

tionation of oleic and eicosenoic glycerides already referred to allowed us to distinguish between their glycerides with the results shown in Table IV. The greater number of acids in this oil means more glyceride categories. Fourteen are distinguished with four (221, 220, 211, and 210) exceeding 10% and a further six each present to the extent of 6 to 7%.

Mowrah butter (*M. latifolia*) with almost 50% of saturated acyl groups is the most saturated fat we examined (Table III). It contains eight categories of glycerides with four of them (210, 200, 110, and 110) comprising nearly 90% of the whole fat. The study of this more saturated material highlights one of the limitations of our chromatographic procedure in that it does not distinguish between the various saturated glycerides. Half of mowrah butter is 100 or 200 glycerides but within each group we cannot distinguish between the dipalmito-, the palmitostearo and the

TABLE V

Component Acids and Glycerides (% mol) of *M. ternifolia* Seed Oil

	A[a]	B	C[e]
Component acids			
Sat.		16	
16:1[c]		27	
18:1 + 20:1		54	
18:2		3	
Component glycerides			
S_2U[e]	5	6	6
SU_2	40	36	37
U_3	55	58	57
220[f]	1	....	....
211	4	2	2
21H[h]		2	2
2HH		1	1
210	4	2	2
2H0		1	1
111	51	15	15
11H		24	23
1HH		12	12
HHH		2	2
200	....	....	....
110	35	15	15
1H0		15	15
HH0		3	4
100	5	4	4
H00		2	2

[a] Same as footnote to Table III.
[c–f] Same as footnotes to Table III.
[h] H stands for hexadecenoic acid.

TABLE VI

Observed and Calculated[a] Proportions (% mol) of S_2U, SU_2 and U_3 Glycerides

Ref.		"Sat." acids[b] (% mol)	Observed S_2U	Observed SU_2	Observed U_3	Calculated S_2U	Calculated SU_2	Calculated U_3
3	Wild rose	5	1	15	84	1	13	86
*	Sunflower	7	1	22	77	1	19	80
3	Linseed	9	1	29	70	2	23	75
3	Candlenut	10	2	28	70	2	26	72
*	Sunflower	10	2	26	72	2	26	72
*	Safflower	10	2	26	72	2	26	72
12	Olive	12	5	33	62	3	30	67
12	Corn	13	4	34	62	4	31	65
*	Tobacco	14	7	33	62	4	34	62
2	*J. gossypifolia*	14	3	35	62	4	34	62
23	Poppy	14	0	32	68	4	34	62
*	Maize	14	6	38	56	4	34	62
16	Olive	15	6	35	59	5	35	60
*	*M. ternifolia*	16	5	40	55	6	36	58
3	Soya	16	6	38	56	6	36	58
16	Soya	17	6	38	56	7	37	56
*	*A. mexicana*	17	7	38	55	7	37	56
2	*J. curcas*	20	10	47	43	9	42	49
*	Groundnut	21	11	40	49	10	43	47
2	*J. multifida*	26	15	51	34	15	48	37
15	Cottonseed	27	17	48	35	16	49	35
*	Cottonseed	32	23	50	27	23	50	27
16	Cottonseed	33	21	49	29	25	50	25
*	*G. asiatica*	33	21	48	31	25	50	25
24	*Erythrina indica*	34	27	48	25	26	50	24
18	Shea	45	52	?	?	46	43	11
*	*M. latifolia*	48	52	39	8	52	40	8
18	Malayan palm	51	47	?	?	59	35	6
12	Cocoa butter	57	81	17	....	73	25	2
16	Cocoa butter	62	81	17	2	86	14	....
25	Cocoa butter	63	94	6	....	89	11	....
18	Cocoa butter	63	80	?	?	89	11	....

[a] Calculated according to Gunstone (8).
[b] 20:1 and 22:1 acids included with saturated acids.
* Present work.

disearo-monounsaturated glycerides. In this respect we consider our procedure to be complementary to that of Youngs et al. (13,16) which distinguishes between saturated but not between unsaturated acyl groups.

Chromatography, Lipolysis and Calculation of Component Glycerides from Component Acids

Results obtained in these three ways have been quoted in this paper and in two of our earlier papers (2,3). The agreement between values calculated from lipolysis data (column B) and those derived directly from component acids (column C) is to be expected and is not greatly significant since both are based on the same *assumption* that acyl groups present in the 2-position are associated statistically with those present in the 1- and 3-positions. They differ in that the lipolysis results allow for minor deviations from the mathematically limiting situation on which the theory is based (8).

The agreement between results obtained by our chromatographic procedures and those obtained by the other two methods is, on the other hand, much more meaningful for it provides support for the assumption adopted in handling lipolysis data and for the essential correctness of the postulates in the theory

TABLE VII

Proportions (% mol) of Polyethenoid Glycerides

	Component acids (% mol)		Component glycerides			
	Pe	X	Pe_3	Pe_2X	PeX_2	X_3[a]
Safflower	77	23	47	37	14	2
Tobacco	72	28	35	41	20	4
J. gossypifolia	69	31	33	48	16	3
Sunflower	60	40	14	53	31	2
A. mexicana	55	45	20	35	33	12
Maize	55	45	16	37	36	11
Cottonseed	50	50	11	36	42	11
J. multifida	49	51	9	38	43	10
Sunflower	42	58	4	38	40	18
G. asiatica	38	62	6	28	45	21
J. curcas	37	63	3	27	46	24
Groundnut	18	82	....	9	37	54
M. latifolia	14	86	....	3	35	62
M. ternifolia	3	97	....	1	8	91

[a] Pe and X refer to polyethenoid and other (monoethenoid and saturated) acyl chains.

TABLE VIII
Glyceride Categories (% mol) of Linoleic-Containing Oils

	"Sat." acids[a] (% mol)	Number of double bonds						
		7 and 6	5	4	3	2	1	0
Safflower	10	47	19	23	8	3	....	....
Tobacco	14	35	17	29	11	8	....	....
J. gossypifolia	14	33	22	32	9	3	1	....
Sunflower	10	14	39	33	11	2	1	....
Maize	14	16	20	31	23	9	1	....
A. mexicana	17	20	18	29	21	10	2	....
Sunflower	7	4	31	36	24	4	1	....
J. multifida	26	10	15	32	24	15	4	....
J. curcas	20	3	16	26	32	19	4	....
Cottonseed	32	11	9	32	22	20	6	....
G. asiatica	33	6	16	29	28	17	4	....
Groundnut	21	....	5	23	40	27	5	....
M. ternifolia	16	....	....	5	55	35	5	....
M. latifolia	48	....	....	6	20	38	35	1

[a] See footnote, Table VI.

of positional distribution. When first elaborated this theory was tested against results then available which were taken from Hilditch's monograph (21). Whilst agreement in the proportion of U_3, US_2, and S_3 glycerides was fair, agreement for U_2S glycerides was less satisfactory and this has been adversely commented upon (22). In Table VI we compare results for these categories of glycerides calculated on the basis of our theory of positional distribution with recent results obtained by ourselves or by others. These show a much better agreement than the earlier results. It should be noted that these comments apply only to vegetable fats.

Polyethenoid Glycerides

In Tables VII and VIII results obtained from our linoleic-containing oils are classified according to the number of polyethenoid acid groups present in the glyceride and the number of double bonds present in the glycerides. The safflower, tobacco, *Jatropha glandulifera,* and the linoleic-rich sunflower seed oil, each with more than 60% of linoleic acid, contain 67–84% of glycerides having two or three linoleic chains and are the only oils listed here which are likely to show drying properties.

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Glyceride Studies. V. The Distribution of Unsaturated Acyl Groups in Vegetable Triglycerides

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Abstract

The distribution of oleic, linoleic, linolenic, petroselinic, hexadec-9 and 11-enoic, sterculic, four conjugated octadecatrienoic acids, isolinolenic, and octadeca-6,9,12,15-tetraenoic acid in vegetable triglycerides has been studied by hydrolysis with pancreatic lipase. The results, discussed in terms of a selectivity factor, indicate that these unsaturated acids do not compete equally for the secondary hydroxyl group.

Introduction

PANCREATIC LIPASE is known to remove acyl groups attached to the two primary glycerol hydroxyls in preference to those attached to the secondary hydroxyl group and lipolysis of vegetable fats by several investigators (1–6) has shown that in most cases 95–100% of the fatty acids in the 2-position are unsaturated C_{18} acids (oleic, linoleic, and linolenic) even when the total content of these acids is as low as 37 or 38% (see reference 7 for a summary of results). This important result has emphasised the non-random character of acyl group distribution in vegetable glycerides and has led to the wide acceptance of the theory of positional distribution (7–9) in place of the earlier ideas of random and widest distribution, neither of which is entirely acceptable. Gunstone (7) and Mattson and Volpenhein (5) have suggested that the acids found in natural triglycerides fall into two groups: those which are preferentially esterified at the 1- and 3- positions (designated "saturated" by Gunstone and Category I acids by Mattson and Volpenhein) and those which are preferentially esterified at the 2-position ("unsaturated" or Category II acids). Mattson and Volpenhein (4) had earlier shown that though oleic, linoleic, and linolenic acids belong to Category II, the C_{20} and C_{22} monoethenoid acids, which characterise the Cruciferae, belong to Category I, behaving like palmitic and stearic acids. From an examination of the distribution of the three unsaturated C_{18} acids these same authors (5) conclude that there is a slight tendency for there to be more linoleic and less oleic in the 2-position than would be expected from their pro-