65. *The Seed Fat of* Parinarium laurinum. *Part II.* *Component Glycerides of the Seed Fat.*

By J. P. Riley.

The glyceride composition of the seed fat of *Parinarium laurinum* has been determined by a combination of low-temperature crystallisation and spectrophotometry. The principal glycerides are triparinarin 22%, elæostearo-diparinarin 27%, oleo-elæostearo-parinarin 16%, saturated-elæostearo-parinarin 15%, and dielæostearo-parinarin 7%. The component acids, except parinaric acid, appear to be combined in the glycerides according to the " rule of even distribution." In the case of parinaric acid, however, far more triparinarin is present than would be accounted for on either " even " or " random " distribution principles.

In Part I of this series (*J.*, 1950, 12) the component acids of a specimen of the seed fat of *Parinarium laurinum* were shown to consist principally of parinaric (*ca.* 53%) and α-elæostearic (*ca.* 30%) acids, together with minor amounts of linoleic, oleic, and saturated and conjugated dienoic acids. In the present paper the component glycerides of the fat will be described.

The only fat containing parinaric acid whose glycerides have so far been studied is the seed fat of *Impatiens Roylei Walpers* (Kaufmann and Keller, *Ber.*, 1948, **81**, 152). These workers were able to isolate from the fat, whose mixed acids contain 42% of parinaric acid and 10% of acetic acid, a rather impure sample of acetodiparinarin. After isomerisation of the glycerides of the α-parinaric acid to the β-isomer with a trace of iodine, they were able to obtain an unstable yellow-white solid—aceto-di-β-parinarin, m. p. 66—67°—whose analysis agreed well with theory.

Oil from *P. laurinum* seeds from near Suva (Fiji) was neutralised, and the neutral oil submitted to crystallisation according to the scheme on p. 292. The seven fractions thus obtained were analysed spectrographically as described in Part I, with results which indicated that the approximate amounts of the principal component glyceride categories of the oil were (see Table II, p. 293) : (*a*) no parinaro-group 6%, one 42% and two parinaro-groups 30%, triparinarin 22%; (*b*) no elæostearo-groups 26%, one 68% and two elæostearo-groups 6%; (*c*) monosaturated-diunsaturated 18%, triunsaturated 82%. Further calculation shows that the most probable principal component glycerides of the fat are : triparinarin 22%, elæostearo-diparinarin 27%, oleo-elæostearo-parinarin 16%, saturated-elæostearo-parinarin 15%, and di-elæostearo-parinarin 7%.

Continued crystallisation of the triparinarin-containing fraction (A in the scheme) yielded a glyceride fraction (J), whose mixed acids contained 95% of parinaric acid, indicating a content of at least 85% of triparinarin in the glycerides. Further attempts to purify the compound were unsuccessful owing to the extreme ease with which it polymerised.

Although the mixed acids of the fat contain only 54% of parinaric acid, there are present in the glycerides 22% of triparinarin and 6% of glycerides containing no parinaric groups. It is evident therefore that we have here an exception to the " rule of even distribution " (Hilditch, " The Chemical Constitution of Natural Fats," 2nd Edn., 1947) since the latter would predict only negligible proportions of triparinarin, and virtual absence of glycerides having no parinaric acid. The only notable exceptions to the rule so far observed among seed fats are those of *Myristica malabarica* (Collin, *J. Soc. Chem. Ind.*, 1933, **52**, 100T) which contains 16—19% of fully saturated glycerides but only 52% of saturated acids (chiefly myristic), and of *Laurus nobilis* (Collin, *Biochem. J.*, 1931, **25**, 95) in which there are 34% (wt.) of fully saturated glycerides (principally trilaurin) although its component acids contain lauric 43%, palmitic 6%, oleic 32%, and linoleic 19% (wt.). If the parinaric acid in *P. laurinum* oil were combined in

the glycerides according to a purely random distribution then there should be about 16% of triparinarin present, which is considerably less the experimentally determined amount.

On the other hand, it appears probable that the α-elæostearic and other component acids of the *Parinarium* oil are arranged in the glycerides according to the " rule of even distribution." Thus, for example, the oil contains 28% of elæostearic acid and there are present only 7% of di-elæostearo-glycerides, a figure which accords well with the graphs published by Hilditch and Seavell (*J. Oil & Colour Chemists Assoc.*, 1950, **33**, 41) relating the amounts of dilinoleo-glycerides in linolenic-rich oils to their content of linolenic acid. It is interesting that the fatty acids (other than lauric) in *Laurus nobilis* (*vide supra*) seem to be evenly distributed in the glycerides.

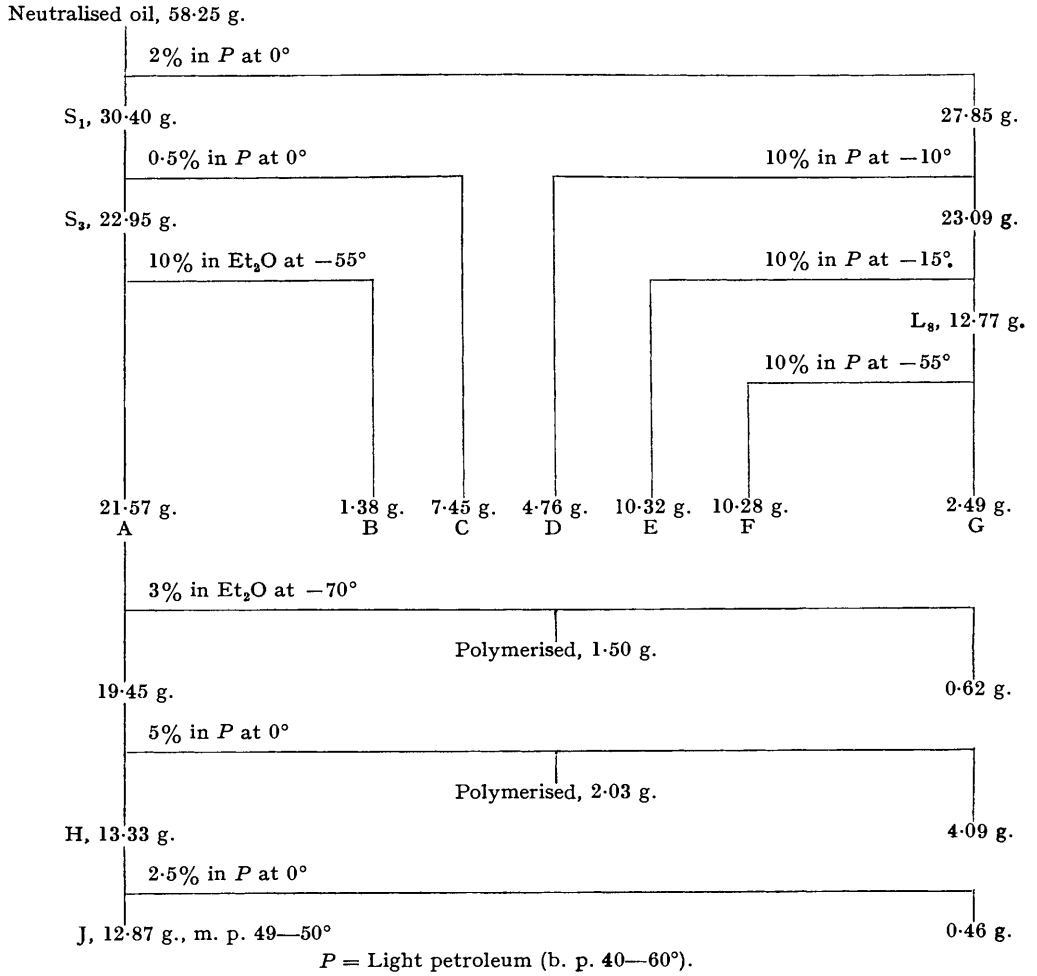
It is not yet known whether the anomalously large amount of triparinarin present in *P. laurinum* oil is due to the development of parinaric acid in a different part of the seed, or at a different time from the other acids.

Experimental.

P. laurinum seeds were extracted with light petroleum, and the resultant solid fat (yield, 12%; free acidity, 4·5%) was neutralised with alcoholic potassium hydroxide. The components of the neutralised fat were found to be parinaric 55·3%, α-elæostearic 28·3%, conjugated dienoic 1·4%, linoleic 2·0%, oleic 4·9%, saturated acids 7·2%, with unsaponifiable matter 0·9% (wt.). The neutralised fat was crystallised

Crystallisation of the mixed glycerides of P. laurinum *seed oil.*

(Soluble fractions shown on the right at each crystallisation stage.)



P = Light petroleum (b. p. 40—60°).

at low temperatures from ether and light petroleum as shown in the scheme. Samples of the fractions A—G were then analysed spectrographically for parinaric, α-elæostearic, conjugated dienoic, and linoleic acids as described in Part I (see Table I). Saturated acids and unsaponifiable matter were determined in the fractions by the Bertram (*Z. deutsch. Oel Fett Ind.*, 1925, **45**, 733) and S.P.A. (*Analyst*, 1933, **58**, 203) procedures respectively. Final calculations are in Table II.

TABLE I.

Characteristics of glyceride fractions.

Fraction.	g.	%.	I.V. (Toms).	$E^{1\%}_{1\,cm.}$ (untreated) at * 305 mμ.	270·5 mμ.	234 mμ.	$E^{1\%}_{1\,cm.}$ (isomerised * at 180°/60 mins.) at 234 mμ.
A	21·57	37·0	—	2236	528	68·8	—
B	1·38	2·4	197·8	1341	659	112·0	161
C	7·45	12·7	148·4	1116	772	115·0	183
D	4·76	8·2	212·9	954	770	156·0	—
E	10·32	17·7	—	1295	777	99·9	—
F	10·28	17·7	201·4	720	894	126·0	170
G	2·49	4·3	191·4	250	675	108·6	224
Total	58·25	100·0					
H	13·33	22·9	—	2220	466	74·1	—
J	12·87	22·1	—	2491	475	62·3	—
S_1	30·40	52·2	—	1713	605	97·9	—
S_3	22·95	39·4	—	2225	557	154·0	—
L_8	12·77	21·9	212·9	642	840	110·0	176

* Expressed as acids.

TABLE II.

Component acids and glycerides of P. laurinum *fat* (*fractions* A—G).

	A.	B.	C.	D.	E.	F.	G.	Total.	H.	J.
Glycerides (% mol.)	37·0	2·4	12·7	8·2	17·7	17·7	4·3	100·0	—	—
Component acids of glyceride fractions (% wt.).										
Parinaric	85·2	51·1	42·5	36·4	49·4	27·4	9·5	55·3	84·6	95·0
Elæostearic	11·2	26·0	34·2	31·5	33·0	44·3	35·8	28·3	7·2	5·0
Conj. dienoic	—	2·6	1·8	5·9	0·5	1·6	2·4	1·4	1·2	—
Linoleic	—	3·8	6·3	—	—	4·4	12·9	2·0	7·0	—
Oleic	0·5	7·1	6·7	23·1	10·9	6·9	31·3	4·9		
Saturated	2·0	7·5	7·2	2·0	5·2	14·5	7·0	7·2		
Unsaponifiable	1·1	1·9	1·3	1·1	1·0	0·9	1·1	0·9		
Component acids of glyceride fractions, excluding unsaponifiable (% mol.).										
Parinaric	86·2	52·1	43·1	37·0	50·0	27·6	9·7	55·8		
Elæostearic	11·2	26·3	34·4	31·9	33·1	44·3	36·2	27·0		
Conj. dienoic	—	2·7	1·8	6·0	0·5	1·6	2·4	1·3		
Linoleic	—	3·9	6·3	—	—	4·3	12·9	2·2		
Oleic	0·5	7·1	6·8	23·0	10·9	6·9	31·4	7·6		
Saturated	2·1	7·9	7·6	2·1	5·5	15·3	7·4	6·1		
Component glyceride categories of fractions (increments % mol.).										
(*a*) No parinaro-	—	—	—	—	—	3·0	3·0	6·0		
Monoparinaro-	—	1·0	9·0	7·3	8·8	14·7	1·3	42·1		
Diparinaro-	15·3	1·4	3·7	0·9	8·9	—	—	30·2		
Triparinarin	21·7	—	—	—	—	—	—	21·7		
(*b*) No Elæostearo-	24·6	0·5	—	0·3	0·1	—	—	25·5		
Monoelæostearo-	12·4	1·9	12·3	7·9	17·6	11·9	3·9	67·9		
Dielæostearo-	—	—	0·4	—	—	5·8	0·4	6·6		
(*c*) Monosatd.-diunsatd.	2·3	0·6	2·9	0·5	2·9	8·1	1·0	18·3		
Triunsaturated	34·7	1·8	9·8	7·7	14·8	9·6	3·3	81·7		

The author thanks Professor T. P. Hilditch, F.R.S., and Dr. M. L. Meara for their advice and valuable criticism, and Mr. G. Winter of the Defence Research Laboratory, Victoria, Australia, for a gift of seeds.

THE UNIVERSITY, LIVERPOOL. [*Received, October 23rd*, 1950.]