S 17. *The Component Glycerides of Bacury* (Platonia insignis, *Mart.*) *Seed Fat.*

By T. P. Hilditch and S. P. Pathak.

The seed fat of *Platonia insignis* (Bacury fat) is a yellowish solid which becomes completely liquid at 51—52·5°. Its chief component acids are palmitic (55%) and oleic (32%) acids, with smaller proportions of stearic (6%) and hexadecenoic (3%) acids and probably traces of myristic, arachidic, and linoleic acids. In spite of a total molar content of 35% of unsaturated acids the fat contains over 20% of trisaturated glycerides (largely tripalmitin), and in this respect (as previously noted by Chaves and Pechnik) stands apart from the majority of seed fats. A possible explanation of this seeming anomaly is suggested.

Chaves and Pechnik (*Rev. Quim. Ind.*, 1945, **4**, No. 163; 1946, **15**, No. 165) determined the composition of Bacury fat, the seed fat of *Platonia insignis*, Mart., a member of the Guttiferae family, and found that, whilst its fatty acids were composed of approximately 56% saturated (palmitic and stearic), 39% oleic, and 4% linoleic acids, it contained about 24% of trisaturated glycerides. They drew attention to the unusually high melting point (54—56°) of the fat and to the large proportion of trisaturated glycerides in it, a feature which indicated a considerable departure from the normal, since other seed fats with a similar content of unsaturated acids have been found almost always to contain only insignificant proportions of trisaturated glycerides. Dr. Chaves communicated these results to us and subsequently very kindly placed at our disposal a small specimen of the fat which, in view of its somewhat unusual glyceride structure, we have been glad to examine in our laboratory. It may be said at once that, although our results differ in some details from those of the Brazilian workers, we can fully confirm the presence in Bacury fat of the unusually large proportions of trisaturated glycerides reported by these authors.

The free fatty acid (about 5%) in the crude yellowish Bacury fat was removed (together with some resinous material of high iodine value) and the neutral fat was resolved into three groups by systematic crystallisation from ether at temperatures between 20° and −20° (*cf.* Experimental). The component acids in each group (and, therefrom, in the whole fat) were determined by ester-fractionation. The material available was only sufficient for these analyses and we were therefore unable to determine the proportion of trisaturated glycerides present in them by the method of Hilditch and Lea (*J.*, 1927, 3106). The most insoluble group (A), however, consisted almost wholly of fully-saturated material; but our experience with separated glycerides of similar mean unsaturation to that of the intermediate group (B) (iodine value 30·8) leads us to believe that the latter may have contained small proportions (perhaps up to 10%) of trisaturated glycerides.

The component acids of the whole fat, from the results of these determinations, were approximately as follows: myristic 1, palmitic 55, stearic 6·5, arachidic 0·5, hexadecenoic 3, oleic 32, and linoleic 2% (by wt.). Chaves and Pechnik (*loc. cit.*) observed 56% of saturated and 43% of unsaturated acids, the somewhat higher content of the latter possibly being due to the presence of traces of the resin (iodine value *ca.* 195) which was removed to a greater degree (although probably not completely) in the course of our present work. These authors based their estimate of approximately equal proportions of palmitic and stearic acids upon an observation of the melting point of the saturated acids, but our ester-fractionation data (Tables III, IV) leave no doubt that by far the greater part of the saturated components consists of palmitic acid. These data, moreover (cf., especially Table III, fractions B1—4), indicate the presence of definitely more hexadecenoic acid than is usually encountered in seed fats.

Component Glycerides of Bacury Fat.—The component fatty acid data shown in Table V (Experimental, p. S 90) are consistent with the presence of component glycerides in the proportions shown in Table I.

If group B of the glycerides contained as much as 10% of trisaturated material, the above figures would be altered to trisaturated 23, monounsaturated disaturated 48, and diunsaturated monosaturated 29% (mol.).

We therefore agree with Chaves and Pechnik that Bacury fat contains somewhat more than 20% of trisaturated glycerides. Since more than 75% of the trisaturated glycerides consist of the simple triglyceride tripalmitin (m. p. 65·5°) and since the " melting point " of a natural fat is not a true melting point, but merely the temperature at which the component of highest melting point passes into solution in the remainder of the mixture of mixed glycerides (already in the liquid phase), we suggest that the unusually high " melting point " of this fat may be

explained by its specific composition, and especially the presence in the whole fat of about 15% of the simple glyceride tripalmitin.

TABLE I.

Component glycerides (approximate) of Bacury seed fat.

Glyceride groups, % (mol.).	*A.* 21·1	*B.* 35·8	*C.* 43·1	Whole fat.
	(Increments % mol.).			% (mol.).
Trisaturated (19·5%) :				
Myristodipalmitin	3·5	—	—	3·5
Tripalmitin	14·7	—	—	14·7
Dipalmitostearin	1·3	—	—	1·3
Monounsaturated disaturated (55·0%) :				
Hexadecenodipalmitin	1·4	5·3	—	6·7
Oleodipalmitin	0·2	20·5	10·2	30·9
Oleopalmitostearin	—	8·2	9·2	17·4
Diunsaturated monosaturated (25·5%) :				
Palmitohexadeceno-olein	—	1·8	1·4	3·2
Palmitodiolein	—	—	15·8	15·8
Palmito-oleolinolein	—	—	6·5	6·5

In the great majority of seed fats, fully saturated triglycerides do not occur in significant proportions unless the unsaturated acid content is below that (about 35%) necessary to permit of each mixed triglyceride molecule containing one unsaturated acyl group. The case of Bacury fat is only the third outstanding exception yet observed to this generalisation, which has come to be referred to as the " rule of even (or widest) distribution " of acyl groups amongst the glycerol molecules of a fat: the other two exceptions (Collin and Hilditch, *Biochem. J.*, 1929, **23**, 1273) are those of the seed fats of *Laurus nobilis* (with 51% of unsaturated acids and 40% of trisaturated glycerides) and of *Myristica malabarica* (with 48% of oleic acid and 16—19% of trisaturated glycerides). The last-mentioned fat is peculiar in other respects, *e.g.*, it apparently contains resin acids as well as fatty acids in combination as mixed glycerides (Collin, *J. Soc. Chem. Ind.*, 1933, **52**, 100T). In laurel-kernel fat (Collin, *Biochem. J.*, 1931, **25**, 95) the 40% of trisaturated glycerides have been shown to consist very largely of trilaurin and to account for at least 75% of the lauric acid present in the total acids of the fat (lauric 43, palmitic 6, oleic 32, linoleic 19%); moreover, the residual lauric acid and the remaining fatty acids are constituted on the usual " mixed " lines and, for example, contain little or no triunsaturated glycerides. This led Collin to suggest that the lauric acid may occur in different parts of the seed, or be predominantly synthesised at a different stage, from the remainder of the seed fatty acids in *Laurus nobilis*.

The case of Bacury fat may be compared with that of other seed fats similarly rich in palmitic as well as in oleic acid, when it will be seen (Table II) that the content of trisaturated glycerides is sometimes negligible and in other instances appreciable, but not so great as in Bacury fat.

TABLE II.

Trisaturated glyceride contents of seed fats rich in palmitic acid.

	[Component acids (% by wt.).] Myristic.	Palmitic.	Stearic.	Unsaturated.	Trisaturated glycerides.
Madhuca butyracea [1] (seed fat)	—	56	4	40	8
Platonia insignis (seed fat)	1	55	7	37	20
Caryocar villosum [2] (seed fat)	1	49	1	49	2
Cameroons palm oil [3] (fruit coat)	1	47	4	48	8

[1] Bushell and Hilditch, *J. Soc. Chem. Ind.*, 1938, **57**, 48.
[2] Hilditch and Rigg, *ibid.*, 1935, **54**, 109T.
[3] Hilditch and Maddison, *ibid.*, 1940, **59**, 67.

The erratic departure, indicated in Table II in varying degrees, from the generalisation closely followed in the great majority of seed and fruit coat fats, in which trisaturated glycerides are not encountered in appreciable amounts unless their content of oleic (or other unsaturated) acid is insufficient to provide one acyl group in each triglyceride molecule, is perhaps more apparent than real. The fat extracted from a seed represents the total quantity of lipid present in the endosperm and/or embryo at maturity, and its observed composition cannot take account either of different types of fat possibly present in different parts of the seed-tissue or of the

component acids being possibly synthesised in different proportions at different stages of development of the fruit. If, for example, in Bacury fat much more palmitic than oleic acid should be synthesised and assembled into triglycerides at certain stages of development, the observed, apparently abnormal, proportions of trisaturated glycerides in the total fat finally produced would be readily accounted for, in the manner suggested by Collin (*loc. cit.*) in the analogous instance of the unexpectedly high trilaurin content of laurel-kernel oil.

Experimental.

The crude Bacury seed fat was a yellow-coloured solid at the ordinary temperature with an acid value of 11·1 (corresponding to 5·3% of free fatty acid at the mean equivalent (267·6) of the total acids in the fat); it became completely liquid at 51—52·5°. The crude fat (61·2 g.) was washed in ether solution with aqueous potassium hydroxide solution which removed 3·7 g. of resinous acidic material (iodine value 155·6) and left a paler yellow solid neutral fat (57·5 g., iodine value 40·4).

The neutral fat was crystallised from 5% solutions in ether, (*a*) first at room temperature and then (*b*) at 0°, which led to the separation of (*a*) 6·0 g., iodine value 4·9, and (*b*) 7·9 g., iodine value 9·3, leaving in solution at 0° 43·6 g., iodine value 51·0. The latter material was further crystallised from ether at −10° and −20°, when 23·5 g., iodine value 66·4, were finally left in solution. The material deposited at −10° and −20° respectively had iodine values of 33·1 and 36·1, whilst further crystallisation from ether at 0° of the two fractions (*a*) and (*b*) originally separated caused the deposition of a fraction A (11·2 g., iodine value 1·0) and left 2·7 g. (iodine value 34·0) in solution. The three intermediate groups with iodine values 32·1, 34·0, and 36·1 were united and once more crystallised from 5% solution in ether at −20°, when a fraction B (19·9 g., iodine value 30·8) separated, leaving 2·9 g. (iodine value 51·7) in solution. The latter was united with the 23·5 g., iodine value 66·4 (above), to form fraction C (26·4 g., iodine value 64·8, containing 1·8 g. of resinous material of iodine value 194·9). All weights in the above description have been corrected (for small amounts withdrawn for analysis) to the original weight taken. The neutral Bacury fat had therefore been separated in the course of these crystallisations into the following groups of mixed glycerides :—

	Wt., g.	Iodine value.	Sapon. equiv.	Glycerides, % (wt.).	% (mol.).
A. Insoluble in ether at 0°	11·2	1·0	267·7	20·1	21·1
B. Insoluble in ether at −20°	19·9	30·8	279·4	35·7	35·8
C. Soluble in ether at −20°	24·6	55·2	287·3	44·2	43·1

Component Acids of the Groups of Mixed Glycerides, A, B, and C.—Fractions A and B were hydrolysed and the respective mixed fatty acids converted into mixed methyl esters which were distilled at 0·2 mm. pressure through an electrically-heated and packed column. The amounts and characteristics of the ester-fractions thus obtained are given in Table III.

Table III.

Fractionation of methyl esters of fatty acids from Bacury glyceride groups A and B.

	Methyl esters from group A.				Methyl esters from group B.			
Fraction.	Wt., g.	B. p.	Sapon. equiv.	Iodine value.	Wt., g.	B. p.	Sapon. equiv.	Iodine value.
1	1·70	100—105°	265·8	0·2	1·92	105—110°	271·8	8·5
2	1·62	105—115	267·1	0·4	2·55	110—115	272·0	9·8
3	1·66	115	269·0	0·5	2·78	115—120	272·4	12·6
4	1·54	115—120	269·4	1·0	3·37	120—122	273·3	12·9
5	1·53	120	271·6	1·2	3·32	122—125	286·2	58·7
6	1·82	Residue	276·8 *	10·4 *	2·76	Residue	305·3 *	82·4 *
	9·87				16·70			

* Residual esters, freed from unsaponifiable matter :

A6, Sapon. equiv. 272·2, iodine value 10·3
B6, ,, ,, 297·8, ,, ,, 79·8

Component fatty acids of Bacury glyceride groups A and B.

	Group A (excluding unsaponifiable).			Group B (excluding unsaponifiable).		
Acid.	% (wt.).	% (wt.).	% (mol.).	% (wt.).	% (wt.).	% (mol.).
Myristic	4·9	5·0	5·5	—	—	—
Palmitic	89·9	90·1	89·8	55·0	55·2	57·3
Stearic	2·4	2·4	2·1	7·4	7·5	7·0
Arachidic	—	—	—	0·8	0·8	0·7
Hexadecenoic	2·2	2·2	2·3	6·4	6·4	6·6
Oleic	0·3	0·3	0·3	30·1	30·1	28·4
Unsaponifiable	0·3	—	—	0·4	—	—

It should be mentioned that, owing to the small quantities of material available, none of the minor component acids included in Tables III and IV was identifiable experimentally, their presence being deduced from the equivalents of the fractions. It is, however, evident that the unsaturated acids present in many of these fractions consisted mainly of one with a molecular weight close to that of palmitic acid (methyl palmitate, equivalent 270), *i.e.*, of hexadecenoic acid.

The acids from group C of the mixed glycerides were submitted to crystallisation from 10% solution in ether at −40° before conversion of each fraction so obtained into methyl esters :

	g.	%.	Iodine value.
C*a*. Acids insoluble in ether at −40°	10·55	44·0	2·4
C*b*. Acids soluble in ether at −40°	13·45	56·0	94·5

The ester-fractionation data for both fractions are given in Table IV.

TABLE IV.

Fractionation of methyl esters of fatty acids Ca and Cb.

	Methyl esters from fraction C*a*.				Methyl esters from fraction C*b*.			
Fraction.	Wt., g.	B. p.	Sapon. equiv.	Iodine value.	Wt., g.	B. p.	Sapon. equiv.	Iodine value.
1	1·33	100—105°	270·9	1·1	1·95	105—115°	271·6	79·7
2	1·93	105—110	272·5	1·2	2·29	115—122	280·8	81·9
3	2·31	110—118	275·0	1·3	2·24	122—125	286·1	87·8
4	2·25	118	275·3	1·5	3·18	125	297·7	94·6
5	2·44	Residue	280·1 *	8·8 *	3·34	Residue	320·7 *	98·1 *
	10·26				13·00			

* Residual esters, freed from unsaponifiable matter :

C*a*5, sapon. equiv. 276·9, iodine value 8·5.
C*b*5, ,, ,, 301·6, ,, ,, 95·5.

Component fatty acids of Bacury glyceride group C.

Acid.	C*a*, % (wt.).	C*b*, % (wt.).	Total, % (wt.).	(Excluding unsaponifiable), % (wt.).	% (mol.).
Palmitic	79·7	6·0	38·4	38·9	41·2
Stearic	16·8	—	7·4	7·5	7·1
Hexadecenoic	2·2	—	1·0	1·0	1·1
Oleic	1·0	82·7	46·7	47·4	45·5
Linoleic	—	9·2	5·2	5·2	5·1
Unsaponifiable	0·3	2·1	1·3	—	—

From the fatty acid compositions of the groups A, B, and C the proportion of the fatty acids in the original Bacury fat is that shown in Table V.

TABLE V.

Component fatty acids of Bacury fat.

	A.	B.	C.	Whole fat.	
Glycerides, % (mol.)	21·1	35·8	43·1		
	(Increments, % mol.).			% (mol.).	% (wt.).
Component acids,					
Myristic	1·2	—	—	1·2	1·0
Palmitic	18·9	20·5	17·8	57·2	55·1
Stearic	0·4	2·5	3·1	6·0	6·4
Arachidic	—	0·2	—	0·2	0·3
Hexadecenoic	0·5	2·4	0·4	3·3	3·2
Oleic	0·1	10·2	19·6	29·9	31·7
Linoleic	—	—	2·2	2·2	2·3

THE UNIVERSITY, LIVERPOOL.

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