305. *The Seed and Fruit-coat Fats of* Neolitsea involucrata.

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The seed fat of *Neolitsea involucrata*, like those of several other tropical shrubs belonging to the family *Lauraceae*, is unusually rich in combined lauric acid and, consequently, trilaurin. Its component acids were found to be : *n*-decoic 3, lauric 86, myristic 4, oleic 4, and linoleic 3% (by weight) ; it contained 87% of fully-saturated glycerides (including about 66% of trilaurin). The glyceride structure of the fat follows the usual rule of " even distribution," *i.e.*, maximum formation of mixed, in preference to simple, triglycerides.

The fruit-coat fat, on the other hand, is typical in containing oleic and palmitic acids as major components. The component acids were found to be : lauric 10, palmitic 28, stearic 3, hexadecenoic 5, oleic 44, and linoleic 10% (by weight).

Although the kernel fat is an excellent source of either lauric acid or trilaurin, the yields of either of these obtainable from the fat in the whole fruit (*i.e.*, without " depericarping "—a difficult process in this case) would be reduced by about 20—25%.

THE seed fats of a number of tropical plants belonging to the family *Lauraceae* have from time to time been reported to contain large amounts of the simple triglyceride trilaurin, and their saponfication equivalents indicate very high proportions of lauric acid in their total fatty acids. Most reports of this general nature have concerned members allied to the cinnamon group and belonging to *Cinnamomum*, *Litsea*, and related genera. In one instance only has a more detailed account been given of a seed fat of this nature : Puntambekar and Krishna (*J. Indian Chem. Soc.*, 1933, **10**, 395) state that the kernels of the Indian shrub *Actinodaphne Hookeri* contain 75% of fat which melts at 43—44° and consists very largely of trilaurin, its component acids being 96% lauric and 4% oleic acid. The shell of these seeds contained 25% of a liquid fat, the component acids of which were given as 33% lauric, 49% oleic, and 18% of other (including resin) acids.

By the courtesy of Dr. R. Child (Director, Coconut Research Scheme, Ceylon), we have been able to examine the seed and fruit-coat fats of *Neolitsea involucrata* (Lamk.) Merr., a shrub indigenous to Ceylon, with fruits in the form of small kernels surrounded by a comparatively thin fleshy covering, the average weight of each berry being about 0·2 g. The native name of the plant is Dawul-kurundu, and it appears to be similar to, but not identical with, wild cinnamon (*Cinnamomum* sp.). A preliminary examination of the kernels by Dr. Child gave data as to fat yields and characteristics which were confirmed by our own study, and indicated that the seed fat contained at least 60% of trilaurin.

The fruits supplied to us were composed of, on an average, 64% of kernel and 36% of fruit-coat. The kernels were carefully detached from the fleshy pericarp, and each part of the fruit was ground and extracted with light petroleum (b. p. 40—60°). The kernels contained 66% of a darkish cream-coloured fat, which was solid at room temperature and had the following characteristics: saponification equivalent 223·3, iodine value 22·5, acid value 10·4, unsaponifiable matter 2·1% (with an iodine value of 175·6). The fruit-coat contained 27% of a fat which remained almost liquid at room temperature, with saponification equivalent 277·5, iodine value 69·0, acid value 162·0, unsaponifiable matter 4·3% (with an iodine value of 111·4). Each fat was submitted to detailed analysis as described below.

Component Acids and Glycerides of the Seed Fat.—Component acids. A portion (60 g.) of the fat was hydrolysed, and the mixed acids converted into methyl esters; the unsaponifiable matter present was not removed prior to esterification of the acids, and unfortunately (as will be seen from Table I), part of it was evidently of approximately the same boiling point as methyl laurate and was present in the ester fractions rich in that ester. Table I shows the fractions obtained on distilling the mixed methyl esters at 0·1 mm. pressure through an electrically-heated and packed fractionation column (Longenecker, *J. Soc. Chem. Ind.*, 1937, **56**, 199T).

TABLE I.

Fractional distillation of methyl esters of the seed fat mixed acids.

Fraction No.	Wt., g.	B. p.	Sap. equiv.	Iod. val.
1	2·08	65—67°	193·3	1·7
2	0·81	67—74	207·8	1·2
3	11·22	74—75	216·6	6·2
4	9·25	75	214·7	2·2
5	7·12	75	214·2	1·3
6	2·58	75	214·2	1·2
7	14·96	75—85	215·6	3·1
8	2·29	85—110	273·9	40·3
9	4·21	Residue	310·6	129·2
	54·52			

Certain of the individual ester fractions were examined as follows :

Fraction 1. *n*-Decoic acid (m. p. 30°) was obtained by recrystallisation from 50% aqueous alcohol of the acids obtained by hydrolysis of the esters present.

Fraction 3. A portion (3·68 g.) gave on redistillation a distillate (2·41 g., b. p. 71—73°, sap. equiv. 217·1, iod. val. 8·4) and a residue (1·27 g., sap. equiv. 214·9, iod. val. 3·4). The acids from the hydrolysed distillate, after removal of unsaponifiable matter, had equiv. 201·0, iod. val. 0·4, from which it appeared that fraction 3 and the succeeding fractions consisted substantially of methyl laurate with small amounts of an unsaponifiable constituent of an unsaturated nature.

Fractions 3—7. The fatty acids obtained during the determination of the equivalents of these fractions were combined, and crystallised from 70% alcohol; they then melted at 43·5° (unchanged when mixed with pure lauric acid).

Fraction 8. The acids present were oxidised with dilute ice-cold alkaline permanganate solution (Lapworth and Mottram, J., 1925, **127**, 1628). Dihydroxystearic acid was not isolated satisfactorily from the products of oxidation, but the portion of the latter soluble in light petroleum yielded, on recrystallisation from 90% alcohol, acids which melted at 50·5°. This m. p. was not raised by further crystallisation, and it was therefore concluded that palmitic acid was not present in detectable amounts.

Fraction 9. This residual fraction contained esters which, when freed from unsaponifiable matter, possessed sap. equiv. 285·3, iod. val. 105·7.

The unsaturated acids present were identified, after as much lauric acid as possible had first been separated from the mixed acids of the whole fat by systematic crystallisation from 70% alcohol. 10·8 G. of the mixed fatty acids yielded (*a*) 5·2 g., iod. val. 3·5, (*b*) 1·2 g., iod. val. 10·4, and (*c*) 4·4 g., iod. val. 18·1. The acids (5 g.) from (*b*) and (*c*) were oxidised in solution in dilute alkali at 0° by potassium permanganate, and the products of oxidation extracted with light petroleum to remove saturated acids. The products insoluble in light petroleum were separated by hot water into an insoluble and a soluble portion. The former fraction yielded, on crystallisation from ethyl acetate, an acid which melted at 130·5° (unchanged when mixed with 9 : 10-dihydroxystearic acid, m. p. 132°), and the latter fraction melted on recrystallisation at 154—155° (no depression when mixed with 9 : 10 : 12 : 13-tetrahydroxystearic acid, m. p. 155°). The unsaturated acids present were therefore the usual Δ^{9}-oleic and $\Delta^{9,12}$-linoleic acids.

With the aid of the above qualitative data, and the equivalents and iodine values of the ester fractions in Table I, the proportions of the component acids (excluding unsaponifiable matter) were calculated to be those given in Table II.

TABLE II.

Component acids of Neolitsea involucrata *seed fat.*

	% (wt.).	% (mol.).
n-Decoic	3·0	3·6
Lauric	85·9	87·7
Myristic	3·8	3·4
Oleic	4·0	2·9
Linoleic	3·3	2·4

Component glycerides. On oxidation in acetone solution with finely powdered potassium permanganate, the neutralised seed fat (82·7 g.) gave fully-saturated glycerides (70·8 g., sap. equiv. 212·2, acid value 0·85, iod. val. 0·3), from which it follows that the seed fat contained 86·7% (wt.) or 88·7% (mol.) of fully-saturated glycerides. The mixed acids (freed from unsaponifiable matter) from the hydrolysis of 51 g. of the latter were converted into methyl esters and fractionally distilled (Table III).

TABLE III.

Fractional distillation of methyl esters of the fully-saturated glyceride mixed acids.

Fraction No.	Wt., g.	B. p.	Sap. equiv.	Iod. val.
1	1·47	54—56°	187·5	—
2	1·37	56—75	198·1	—
3	3·95	75—76	210·8	—
4	11·21	76	215·1	—
5	8·84	76	214·0	—
6	12·41	76	214·9	—
7	3·99	76	216·4	—
8	2·28	Residue	239·3	6·2
	45·52			

The acids present in fraction 1, after recrystallisation from 50% alcohol, melted at 30° (*n*-decoic), those from fractions 3—7, crystallised from 70% alcohol, at 44° (lauric), and those from the residue 8 (from 90% alcohol) at 50°; the last m. p. could not be raised by further crystallisation, which again points to the substantial absence of any saturated acid of higher molecular weight than myristic acid.

The percentage proportions (wt.) of the component acids in the fully-saturated glycerides of *Neolitsea* seed-fat are therefore approximately as follows : *n*-decoic 6, lauric 89, myristic 5%.

The above results indicate that about 87% (wt.) of the fat consists of fully-saturated components, and that 66% (wt.) or more is trilaurin, with up to 21% of dilaurodecoin, dilauromyristin, and possibly a little lauromyristodecoin. The remainder of the fat (about 13%) consists of mixed saturated–unsaturated glycerides in which the average " association ratio " of saturated to unsaturated acids is 1·2 : 1. The seed fat thus conforms to the usual " rule of even distribution "; owing to the very high content of lauric acid in the fat, a large proportion of this acid remains as trilaurin after mixed glycerides have been produced as far as possible by its association with the relatively small proportions of the other fatty acids present in the seed fat.

Component Acids of the Fruit-coat Fat.—The fruit-coat fat (35·8 g.), which already contained a large proportion of free fatty acids, was hydrolysed, and as much unsaponifiable matter as possible was removed by extraction with ether from the solution of potassium soaps before the latter were converted into fatty acids (32·8 g.). The lead salts of the mixed fatty acids were separated by crystallisation from alcohol into " solid " acids (from the alcohol-insoluble lead salts, 29·4%) and " liquid " acids (from the alcohol-soluble lead salts, 70·6%). Each group of acids was converted into methyl esters and fractionally distilled at 0·1 mm. pressure as described (Table I) for the seed fat esters. The fractionation data are given in Table IV.

TABLE IV.

Fractional distillation of methyl esters of the fruit-coat fat acids.

Fraction No.	Wt., g.	B. p.	Sap. equiv.	Iod. val.
	(a) *Methyl esters of " solid " acids.*			
1	2·71	106—140°	257·4	1·1
2	3·67	140—141	271·3	1·9
3	3·01	Residue	279·6	7·7
	9·39			
	(b) *Methyl esters of " liquid " acids.*			
1	2·45	68—70°	213·9	1·9
2	2·51	70—112	271·6	57·1
3	3·83	112—116	295·0	97·1
4	3·37	116—126	296·0	103·3
5	3·27	126—128	296·2	102·3
6	3·88	Residue	301·0	93·4
	19·31			

Examination of acids from individual ester-fractions.

Fraction.	Acids identified.
S2	Palmitic, m. p. 62° (crystallisation from 95% alcohol).
L1	Lauric, m. p. 44° (crystallisation from 70% alcohol).
L2	The saponification equivalent and iodine value of this fraction indicate the presence of methyl hexadecenoate.
L5	9 : 10-Dihydroxystearic acid, m. p. 130°, and 9 : 10 : 12 : 13-tetrahydroxystearic acid, m. p. 153° (by oxidation with permanganate in alkaline solution; Lapworth and Mottram, *loc. cit.*), indicating the presence of Δ^{9}-oleic and $\Delta^{9,12}$-linoleic acids.
L6	The residual esters, freed from unsaponifiable matter, had sap. equiv. 298·7 and iod. val. 83·4.

From the data in Table IV, coupled with the qualitative examination of the various fatty acids, it is calculated that the component acids of the fruit-coat fat had the quantitative composition shown in Table V.

TABLE V.

Component acids of Neolitsea involucrata *fruit-coat fat.*

	" Solid " acids (29·4%).	" Liquid " acids (70·6%).	Total.	Component acids (excluding unsaponifiable), % (wt.).	
				% (wt.).	% (mol.).
Lauric	1·54	8·63	10·17	10·2	13·4
Palmitic	23·54	4·60	28·14	28·2	28·9
Stearic	3·12	—	3·12	3·1	2·9
Hexadecenoic	—	4·59	4·59	4·6	4·7
Oleic	1·20	42·24	43·44	43·6	40·5
Linoleic	—	10·27	10·27	10·3	9·6
Unsaponifiable	—	0·27	0·27	—	—

Since the amount of mixed acids studied was small, the final figures for their composition are of an approximate order. It is, however, clear that, in contrast to the seed fat, oleic and palmitic acids are the most prominent components, linoleic and lauric acids being also present, but to a less extent. It has been pointed out elsewhere (Hilditch, *J. Soc. Chem. Ind.*, 1933, **52**, 169T) that the major component acids of all fruit-coat fats yet studied are confined to palmitic, oleic, and linoleic acids, irrespective of whether the corresponding seed fats contain the same mixture of acids or, as very frequently happens, specific fatty acids of widely varying character. This feature is equally well marked in the *Neolitsea* seed and fruit-coat fats, although in the latter it is notable that about 10% of lauric acid appears in addition to the usual fruit-coat fat major components.

The seed fat of *N. involucrata*, like that of *Actinodaphne Hookeri* (*loc. cit.*) and some other species of *Lauraceae*, forms an excellent source of either lauric acid or trilaurin. The separation of the fruit-coat from the small kernels is, however, a very tedious operation, and would hardly be practicable if any quantity of the berries had to be handled. Extraction of the fat from the fruit as a whole would lead, in consequence of the different nature of the fruit-coat fat, to a material the component acids of which would contain only about 70% of lauric acid; whilst the fat itself would contain about 50% of trilaurin, a fair proportion of which might be obtained in the pure condition by crystallisation from acetone.

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