

tween 500, 470, 441 $m\mu$ and 502, 471.5, 442 $m\mu$. (b) To 2.6 mg. of prolycopene in 100 cc. of petroleum ether 12.5 μg . of iodine was added and the solution was chromatographed after thirty minutes of standing at room temperature as described above. The column was developed with benzene. Prolycopene had disappeared and the chromatogram showed only the following three layers which can also be obtained from lycopene by heating or on addition of iodine: (1) lycopene (top; 522.5, 488, 457 $m\mu$), (2) neolycopene A (previously termed "neolycopene," 515.5, 482, 451.5 $m\mu$) and (3) a new neolycopene, now termed "B" (bottom; 508.0, 477.5, 448 $m\mu$); neolycopene A predominated.

Summary

A representative of a new class of natural C_{40} -carotenoids, prolycopene, $C_{40}H_{56}$, has been isolated in crystalline form from the ripe fruits of the tan-

gerine tomato, a *Lycopersicum esculentum* variety. Prolycopene is the chief pigment, its quantity being about 20 mg. per kg. of fresh fruit. It can be separated chromatographically from many minor polyenes. The chromophore of prolycopene probably contains 5 to 7 *cis*-double bonds. The spectrum in different solvents is from 35 to 47 $m\mu$ shorter wave length than that of lycopene, $C_{40}H_{56}$. On addition of iodine, however, a new spectrum appears instantaneously, showing maxima which now differ from those of pure lycopene by a few millimicrons only. A mixture of numerous intermediate stereoisomers is then present which can be differentiated in the Tswett column.

PASADENA, CALIF.

RECEIVED DECEMBER 8, 1941

[CONTRIBUTION OF THE COCONUT RESEARCH SCHEME, BANDIRIPPUWA ESTATE]

The Seed Fat of *Litsea longifolia* Bth. & Hk.

BY REGINALD CHILD AND WILFRED R. N. NATHANAEL

The seed fats of many tropical species of *Lauraceae* are characterized by an unusually high content of combined lauric acid. Of the *Litsea* genus and the closely related *Neolitsea* genus, fairly detailed accounts of the seed fats of three species are available. Puntambekar¹ has described those of *Litsea chinensis* (= *L. glutinosa*, C. B. Rob.) and *L. citrata*, both samples of Indian origin. Gunde and Hilditch² have recorded the fatty acid and glyceride composition of both the seed and fruit coat fats of *Neolitsea involucreta* (Nees.) Merrill (= *Litsea zeylanica*) from Ceylon.

Litsea longifolia, known in Sinhalese as Ratkeliya, is a small tree common in the moist regions of Ceylon up to 3000 ft. Trimen³ refers to the species as *L. cauliflora*, but Alston⁴ with stricter adherence to the rules of nomenclature adopted the present name, giving the following synonymy: *Litsea longifolia* Bth. & Hk. f. Gen. Pl. III, p. 161 (1883). *Tetranthera cauliflora* Moon Cat. p. 69 (1824) nomen. *T. longifolia* Nees. Syst. Laurin. p. 528 (1836).

The sample of seeds used for the present investigation was collected for us by the Forest Department in the Matara district in the South of Ceylon.

(1) Puntambekar, *J. Indian Chem. Soc.*, **15**, 19 (1938).

(2) Gunde and Hilditch, *J. Chem. Soc.*, 1610 (1938).

(3) Trimen, "Handbook of the Flora of Ceylon," Vol. III, 450 (1895).

(4) Alston, *ibid.*, Vol. VI, 248 (1831).

One hundred seeds weighed approximately 6.7 g., and consisted of about 66% kernels and 34% seed coats. The kernels contained 9.8% of moisture and yielded 29.0% (on dry weight) of a solid brown fat when extracted with light petroleum (b. p. 40–60°) in a Bolton-Revis apparatus.

The crude fat had acid value 38 (corresponding to 13.6% free acid as lauric), saponification equivalent 236.0 and iodine value 13.0; 89.0 g. was neutralized by shaking its ether solution several times with 10% aqueous potassium carbonate; the neutral fat recovered (73 g.) had saponification equivalent 233.0 and iodine value 10.1, while the acid fraction (16 g.) recovered from the potassium carbonate washings had saponification equivalent 243.9 and iodine value 25.9.

The free fatty acids are thus more unsaturated than the neutral fat. This phenomenon has been observed by Atherton and Meara⁵ in the fats of *Virola surinamensis* and *Pycnanthus Kombo*, which are rich in myristic acid. Unfortunately, for reasons given below, we were unable to complete further examination of this fraction.

The neutral fat (52.1 g.) was saponified with alcoholic caustic soda. Extraction of the soap solution three times with light petroleum removed 0.72 g. of unsaponifiable matter of iodine value 81.5. It was later found that this treat-

(5) Atherton and Meara, *J. Soc. Chem. Ind.*, **63**, 353 (1939).

ment had failed to remove more than part of the total unsaponifiable matter present, since a further quantity was obtained from the residual fraction of methyl ester distillation. Acidification of the soap solution gave 48.3 g. of mixed acids (I. V. 9.5), which were converted into methyl esters (47.1 g.) in the usual way. Table I shows the fractions obtained by distilling the methyl esters under reduced pressure.

TABLE I

Fraction	Weight, g.	Sap. equiv.	Iodine val.
1	5.27	214.8	0.7
2	3.07	214.1	.2
3	7.00	213.6	.1
4	6.16	214.0	.0
5	6.30	213.6	.1
6	8.54	214.0	.15
7	3.13	217.1	1.7
8 (Residue)	7.51	425.4	53.4
Total	46.98	232.7 (calcd.)	8.80 (calcd.)

It will at once be apparent that fractions 1 to 7 consist almost entirely of methyl laurate (S. E. 214.2). These fractions were bulked and saponified, the soap solutions from the determinations of saponification equivalents being added, and the free acid recovered. In this way from 33.5 g. of methyl ester (the balance, some 6 g., having been used for iodine value determinations) was obtained 31.5 g. of crude lauric acid, m. p. 42.5–43.5°, which after one recrystallization from 70% alcohol had m. p. 43.5°, unchanged when mixed with pure lauric acid.

The acids from the residue (fraction 8), freed from unsaponifiable matter, had saponification equivalent 269.6 and iodine value 44.3. This corresponds to a content of unsaponifiable matter of 33.4% of iodine value (calcd.) about 80 (which agrees with that of 81.5 found for the unsaponifiable matter originally extracted). Assuming oleic acid to be the only unsaturated acid present, fraction 8 also contains 32.8% methyl oleate, 19.8% methyl palmitate and 14.0% methyl stearate. Oxidation of the mixed acids (1.63 g.) with alkaline permanganate gave 1.09 g. of hydroxy acids insoluble in light petroleum, which corresponds to a rather higher content (40%) of oleic ester in fraction 8. Moreover, the hydroxy acids had not a sharp melting point, starting to melt at 129° but not being completely fused until 152° (mixed m. p. with authentic 9,10-dihydroxystearic acid, m. p. 132°, was 129–133°). This points to the presence of a small amount of tetra-

hydroxystearic acid and thus of linoleic acid in the original oil. The differences, however, will be very small when calculated as percentages of the original oil and we have preferred to calculate on the initial assumption made above, including all unsaturated acids as oleic.

Allowance has been made for the small iodine values of fractions 1 to 7 as traces of oleic acid. Apart from this, even in the case of no. 7 we have assumed methyl laurate to be the only ester present, since methyl myristate, if present, can only be in very minor amount. Table II shows the composition of the fatty acids calculated in the manner described.

TABLE II

	% Weight	% Weight (excluding unsaponifiable matter)	% Mol.
Lauric	81.9	88.3	91.2
Palmitic	3.1	3.4	2.8
Stearic	2.2	2.4	1.7
Oleic	5.5	5.9	4.3 (probably includes trace of linoleic)
Unsap.	7.2

Throughout the examination of this fat we had considerable trouble with emulsification when the necessary extractions were carried out at each stage, and vacuum distillation of the methyl esters was much hampered by excessive frothing. This was so much the case with the distillation of the methyl esters prepared from the acids recovered by potassium carbonate from the crude fat, that, after three attempts, we had to abandon further investigation of this material. The persistent emulsifying and frothing agent is associated with the unsaponifiable matter and appears to be difficult to remove in the usual manner by extracting the soaps with light petroleum.

Crystallization of the Neutral Fat.—Crystallization of the fat was also affected by the non-glyceride matter and the fractions separated were all more or less brown colored even when decolorizing charcoal was used. However, direct crys-

TABLE III

FRACTIONS OBTAINED BY CRYSTALLIZATION OF FAT FROM ACETONE						
No.	Wt., g.	%	M. p., °C.	Sap. equiv.	Iodine value	
I	10.54	51.6	45–6	214.1	1.2	
II	4.36	21.3	45–6	217.2	1.55	
III	0.96	4.7	42.5–44	219.1	3.7	
Res. IV	4.58	22.4	Oil	347.3	36.1	
	20.44	100.0	..	235.3 (calcd.)	9.2 (calcd.)	
				233.0 (found)	10.1 (found)	

TABLE IV
Glycerides free from

No.	Wt., g.	Wt., g. of unsap.	Wt., g.	unsap. Sap. equiv. ^a	I. v. ^b	Wt., g. acid.	Wt., g. oleic acid.	Saturated acids	
								Wt., g.	S. E. (calcd.)
I	10.54	0.03	10.51	213.5	0.6	9.88	0.07	9.81	200.4
II	4.36	.07	4.29	213.9	1.4	4.04	0.07	3.97	200.2
III	0.96	.02	0.94	215.4	3.6	0.89	0.04	0.85	201.1
Res. IV	4.58	1.23	3.35	254.0	27.4	3.18	1.02	2.16	225.8
	20.44	1.35	19.09	17.99	1.20	16.59	...

^aCalculated from values determined on the acids, *i. e.*, S. E. (glyceride) = S. E. (acids) + 12.67. ^bI. v. (glycerides) = I. v. (acids) × S. E. (acids)/S. E. (glycerides).

tallization from acetone led to the recovery of about 77% of material which consisted substantially of trilaurin. The neutral fat (about 21 g.) was dissolved in acetone (80 cc.) and kept overnight at 5°. After collection of the first crop of crystals, two further crops were obtained by concentration of the mother liquor, which was finally evaporated to dryness and dried *in vacuo*.

In each case, after saponification, unsaponifiable matter was removed by light petroleum extraction, the acids recovered and their saponification equivalents and iodine values determined.

The percentages of unsaponifiable matter and of oleic acid in the mixed acids (including unsaponifiable matter) of the fat calculated from this data are 7.0 and 6.2, respectively, which are in fair agreement with 7.2 and 5.5 from the ester fractionation data.

The fatty acid composition (excluding unsaponifiable matter) from this crystallization experiment may be expressed as follows:

Lauric acid (from fractions I-III).....	81.3%
Oleic acid.....	6.6
Saturated acids (of S. E. 225.8) from fraction IV..	12.0

Adopting the figure of 88.3% for lauric acid, from the ester fractionation data, the acids from fraction IV contain 7.0% of this acid and 5.0% of

acids of calculated S. E. 275. This corresponds (like the fractionation data) to the presence of palmitic and stearic acids; it must be noted that we have not demonstrated the occurrence of these acids in the fat, but simply inferred their presence from the saponification equivalents of the residual fractions.

Trilaurin.—It is apparent that fractions I-III consist substantially of trilaurin. Correction of the weights on the basis that oleic acid is present in these fractions as oleodilaurin gives the minimum possible trilaurin content. The trilaurin content of the neutral fat so estimated is 75 or 80% of the glycerides.

Summary

The seed fat of *Litsea longifolia* Bth. & Hk. like other seed fats of this group so far investigated, has a high content of lauric acid, the composition of the separated fatty acids being: lauric 81.9, palmitic 3.1, stearic 2.2, oleic acid 5.5 and unsaponifiable matter 7.2%. The component glycerides contain at least 80% trilaurin.

Owing to the comparatively low content of fat in the kernels, and its high percentage of intractable unsaponifiable matter, *Litsea longifolia* seed fat has little economic value.