cold diazonium solution prepared as above. The mixture was stirred for 30 minutes, neutralized with a solution of 15 per cent sodium hydroxide, and the stirring continued for another 30 minutes. The dye was obtained by ether extraction in about the same yield and purity as for β-naphthol-azo-phenylstearic acid.

In the dyes made from the arylstearic compounds, the aromatic nucleus is in the middle of the fatty acid chain. It was of interest to compare these dyes with a dye similarly prepared from a compound having the aromatic nucleus at the end of a fatty acid chain. Compounds having such a structure are the alkyl aryl ketones described by Ralston and Christensen (7). For our purpose 4′-nitro-4-phenoxyphenyl heptadecyl ketone was selected, since it may be prepared directly from p-nitrodiphenyl ether and stearoyl chloride, by means of the Friedel and Crafts reaction.

We have followed the procedure described for preparing the ketone and have obtained a colorless crystalline product in a yield of 75 per cent, melting at 74-75° C. It is reported in the literature (7) that the compound resulting from this condensation melts at 177-178° C. The per cent of $—NO_2$ in the compound prepared in the present investigation was found to be 9.29 per cent (calculated for $C_{30}H_{43}O_4$ N, 9.56 per cent) as determined by titration with standard titanium trichloride solution. This corresponds to a purity of 97.5 per cent. A control experiment using stearophenone showed that the carbonyl group consumed no titanium trichloride solution. The compound was also analyzed for nitrogen by a semi-micro Kjeldahl method with the following results: Calculated for $C_{30}H_{43}O_4$ N, 2.91 per cent N. Found, 2.77 per cent, 2.87 per cent. To corroborate the point of attachment of the fatty acid part of the molecule to the aromatic part, the compound was oxidized by means of sodium dichromate and sulfuric acid. Pure p-nitrophenoxybenzoic acid was isolated in a yield of 10 per cent. It had a melting point of 235-236° C. (literature, 236° C. [8]) and a neutralization equivalent of 255 (calculated for $C_{13}H_9O_5$ N, 259). From this nitro compound a dye was prepared by the procedure previously described, except that the amine was a solid and could be separated by filtration. β-Naphthol was used as the second component. The dye obtained was a red solid, soluble in organic solvents and readily soluble in cottonseed oil, on heating. The purity of the dye was found to be 64 per cent.

Summary

The preparation of mononitration products of arylstearic compounds derived from U.S.P. oleic acid has been described. Oil-soluble azo dyes have been prepared from the nitroarylstearic compounds by reduction, diazotization, and coupling with β-naphthol or β-naphthylamine.

4′-Nitro-4-phenoxyphenyl heptadecyl ketone has been prepared by the Friedel and Crafts reaction and an azo dye has been prepared from the ketone.

BIBLIOGRAPHY

(1) Stirton, A. J., and Peterson, R. F., Ind. Eng. Chem. *31*, 856 (1939).
(2) Stirton, A. J., Peterson, R. F., and Groggins, P. H., Ind. Eng. Chem. *32*, 1136 (1940).
(3) Nicolet, B. H., and deMilt, C. M., J. Am. Chem. Soc. *49*, 1103 (1927).
(4) Harmon, J., and Marvel, C. S., J. Am. Chem. Soc. *54*, 2515 (1932).
(5) Knecht, E., and Hibbert, E., "New Reduction Methods in Volumetric Analysis," Longmans, Green & Co. (1925).
(6) Vobach, A. C., U. S. Patents 2,081,075 (1937) and 2,095,538 (1937).
(7) Ralston, A. W., and Christensen, C. W., Ind. Eng. Chem. *29*, 194 (1937).
(8) Haussermann, C., and Bauer, E., Ber. *29*, 2083 (1896).

Ceylon Candlenut Oil
Aleurites moluccana (Linn.) Willd

REGINALD CHILD
Bandirippuwa Estate, Lunuwila, Ceylon

Barry (5), reporting on a sample of Candlenut or Lumbang oil and of the corresponding seeds from Malaya, stated that the iodine values of the oils (the original and that extracted from the seeds) were considerably lower than those recorded by Lewkowitsch (12) and Gardner (7) for Philippine oils. The present author, in connection with a survey of Ceylon vegetable oils, has examined a sample of seeds of *Aleurites moluccana* (Linn.) Willd. (known locally as "tel-kekuna"), grown at Peradeniya, Ceylon. The oil from this source had Iodine value (Wijs) of 160.0.

A fairly wide survey of the literature, summarized in Table I, has failed to reveal any significant difference in the range of the iodine value and other constants between oils from Malaya, the Philippines, and other sources. Certain earlier records have been omitted from the table since some doubt must attach to their reliability. Thus that of Lach, quoted by Mitchell (23), clearly refers to some other species, the iodine value of 118 being much below the usual range and the acids having the unusually high solidification point of 56°C. Fendler (24) again, referring to a sample of oil from the Cameroons, gives an iodine value of 114.2 and here, too, the reference is possibly to some other species, although the other particulars recorded (including the percentage oil in the kernels) are more normal; whilst Lespinasse (25) has reported the unusual saponification value of 175 and an iodine value of 137; and also states that 100 kilos of "nuts" give 7-10 kilos of kernels, though this percentage of 7-10 may be based on the weight of the fruits and not that of the seeds.

It is not thought that abnormally low iodine values are usually to be explained by assuming that the samples suffered deterioration from long storage, since a sample of oil I.V. 160.0, kept in an ordinary stoppered bottle without special precaution, had after two years I.V. 156.1.

Additional confusion has crept into the chemical literature concerning the botanical nomenclature of

the species, some of the standard text-books on oils and fats referring to *A. moluccana* Willd. and *A. triloba* Forst. as different species. Alston (26) gives the following synonymy:

> "*A. moluccana* Willd. Sp. Pl. IV, p. 590 (1805); Pax, Euphorbiaceae in Engl. Pflanzenreich IV, 147, p. 129 (1910). *Croton moluccanus* Linn. Sp. Pl. p. 1005 (1753) pp.; Merr. Interp. Rumph. p. 319 (1917). *Jatropha moluccana* Linn. Sp. Pl. p. 1006 (1753). *Aleurites triloba* Forst. Char. Gen. p. 112 t. 56 (1776)."

Dr. J. C. Haigh, Botanist of the Department of Agriculture, has informed the writer that the Ceylon "tel-kekuna," both herbarium and field specimens, agrees with the description of Philippine *A. moluccana* given by West and Brown (27) and by West and Smith (28).

TABLE I

Summary of Literature Survey on Candlenut Oil

MALAYA

Observer	Ref.	I. V.	Sap. Val.	Density (15.5°C.)
C. D. V. Georgi	1	163.1	191.4	0.9257
C. D. V. Georgi	2	149.0	193.3	0.9293
C. D. V. Georgi	2	148.4	194.0	0.9237
C. D. V. Georgi	3	152.8	....	....
B. Eaton and C. D. V. Georgi	4	158.5	....	....
T. H. Barry	5	151.5	192.1	0.9264
Averages		153.9	192.7	0.9263
Standard deviation		5.78	....	....

PHILIPPINES

Observer	Ref.	I. V.	Sap. Val.	Density (15.5°C.)
G. F. Richmond and M. V. del Rosario	6	150.2	193.5	0.9260
H. A. Gardner	7	162.0	192.3	0.9270
R. M. Aguilar	8	154.0	188.0	0.9261
		157.0	193.0	0.9253
		160.0	194.0	0.9237
R. M. Aguilar	9	150.4	193.0	0.9252
A. O. Cruz and A. P. West	10	152.7	191.7	....
G. S. Jamieson and R. S. McKinney	11	151.7	190.8	....
Averages		154.8	192.0	0.9256
Standard deviation		4.45	....	....

OTHER SOURCES

Source	Observer	Ref.	I. V.	Sap. Val.	Density (15.5°C.)
South Sea Islands	J. Lewkowitsch	12	163.7	192.6	0.92565
Fiji	Kassler	13	152.8	189.5	0.9248
Hongkong	Imperial Institute	14	139.7	204.2	0.9274
Mauritius	Imperial Institute	15	151.0	192.7	0.9270
Cook Is., N. Z.	Imperial Institute	16	158.5	194.8	0.9280
Ceylon	Imperial Institute	17	161.9	191.2	0.9275
Ceylon	R. Child	....	160.0	193.4	0.9251
New Caledonia	P. Amann	18	154.0	196.0	0.9279
Japan	I. Miura, *et al.*	19	146.3	195.1	0.9267
.....	Amer. Soc. Testing Materials	20	151.6	188.2	0.9276
.....	E. R. Bolton and C. Revis	21	164.0	190.3	....
			143.8	202.5	
Hawaii	J. L. Riebsomer and N. Foote	22	162.0	191.3	....
Average			154.6	194.0	0.9267
Standard deviation			7.94	....	....

Average (all samples) I.V. 154.3, Sap. Val. 193.3, Density 0.9263.

Hilditch (29) referred to Candlenut or Lumbang oil as *A. moluccana* syn. *trisperma*, the latter erroneously for *triloba*, but corrected this in a later publication (30). *Aleurites trisperma*, Blanco, is a different species known in the Philippines as "bagilumbang;" it has been grown experimentally in Malaya (cf. B. Bunting and J. N. Milsum, Guide Gov. Exper. Plantat. Serdang, 1930, 120), but appears to be unknown in Ceylon. Unlike that of *A. moluccana*, the oil of *A. trisperma* resembles tung oils in containing a notable percentage of elaeostearic acid (31).

Examination of Ceylon Seeds

A parcel of nuts from the same source as that now reported was examined by the Imperial Institute, London, in 1931. Their figures, which have not hitherto been published, are included by courtesy of the Director of Agriculture, Ceylon, and the Director of the Imperial Institute.

The seeds were shelled by hand, and the kernels ground and dried. The dry kernels were extracted with light petroleum (B.P. 40-60°C.) in Bolton Revis extractors, and afforded a clear, very pale straw-colored oil of characteristic odor.

TABLE II

Extraction Analysis

		Imperial Institute figures
Average weight of "nut"	7.08 g.	7.0 g.
Percentage of shells	65.4	68.0
Percentage of kernels	34.6	32.0
Per cent moisture in kernels	5.2	5.4
Per cent oil in kernels	61.0	62.2
Per cent (dry weight)	64.3	65.8
Per cent (whole nuts)	21.1	19.9

These figures are very similar to those recorded elsewhere (*e.g.* Jamieson and McKinney, ref. 11).

TABLE III

Examination of the Oil

		Imperial Institute figures
Density $d^{15.5°}_{15.5°}$	0.9251	0.9275
Refractive Index $n^{30°}_{D}$	1.4733	....
$n^{40°}_{D}$	1.4701	1.4700
Dispersive Power ω	0.0212	....
Acid value	1.97	16.3
Saponification value	193.4	191.2
Iodine value (Wijs)	160.0	161.9
Thiocyanogen value (25 hrs.)	102.6	....
Reichert-Meissl value	0.15	....
Unsaponifiable matter	0.35	0.3
Titre test (fatty acids)	12-13°C.	....
Per cent saturated acids (corrected) (as percentage of the oil)	5.0	....

Halogen Absorption of the Oil

The iodine value by the semi-micro bromine vapor absorption method of Toms (32) was 163. The agreement between this value and that determined by Wijs method is an indication that elaeostearic acid is absent, the oil thus differing markedly from tung oils of the species *Aleurites fordii* and *A. montana*, and also from the oil of *Aleurites trisperma (vide supra)*.

Thiocyanogen absorption, using a reagent prepared as described by Jamieson (33) and the technique of Wiley and Gill (34), was followed with the following results:

	SCN iodine value
After 1 hour	82.4
After 5 hours	92.2
After 18 hours	97.4
After 20 hours	99.9
After 25 hours	102.6

The Fatty Acids of Candlenut Oil

Analyses based on the preparation of the bromo-derivatives of the unsaturated acids have been re-

corded by West and Montes (35), by Cruz and West (10), and by Riebsomer and Foote (22). There is now no doubt that linolenic acid is much underestimated by the insoluble hexabromide method (cf. Griffiths and Hilditch [36]) and Jamieson and McKinney (11) have reported a thiocyanometric analysis of Philippine lumbang oil. The present results are in excellent agreement with theirs and can be regarded as confirming the correspondence of samples of Philippine and Ceylon origin.

TABLE IV

Comparison With Philippine Sample

	Ceylon sample Per cent	Philippine sample (Jamieson & McKinney) Per cent
Saturated acids	5.0	8.9
Oleic acid	28.6	27.7
Linoleic acid	42.6	41.7
Linoleic acid	23.8	21.7
	100.0	100.0

Both of the above compositions have been calculated, using Kaufmann's theoretical values for the thiocyanogen values of linoleic and linolenic acids. Recent studies of the thiocyanometric method have, however, shown that the experimental values differ considerably from those postulated by Kaufmann. Hilditch and Murti (37) provisionally adopt figures of 95.9 for linoleic acid and 162.5 for linolenic acid, and other authors, whose work is reviewed by Hilditch and Murti, give results not widely different. At the same time it is not clear why the only alternative method of obtaining information on fats of considerable linolenic acid content, that of elaidinising the oleic glycerides (Griffiths and Hilditch [36]) should have given results in such close agreement with those afforded by the usual Kaufmann calculation. Uncertainty still attaches to the thiocyanometric method and accordingly the present results are calculated in the usual manner.

Saturated Acids

The saturated acids separated by the Twitchell method in the present examination (5.0 per cent) had, after correction for oleic acid, M.W. 280.0, corresponding to palmitic 0.7, stearic acid 4.7 per cent.

Birosel (38) has made the surprising claim to have isolated 37.9 per cent of heptadecoic acid, m.p. 57.5° C., from Philippine lumbang oil. He suggests that the acid is identical with the "daturic acid" of Meyer and Beer (39). This may be regarded as true, since Verkade and Coops (40) have shown the latter to be a simple mixture of palmitic and stearic acids, whilst Jamieson and McKinney (11) have, by the ester-fractionation method, shown the saturated acids of Philippine lumbang oil to contain palmitic 52.18, stearic 46.84, and arachidic acid 0.98 per cent.

The high Reichert-Meissl value of 17.0 recorded by Riebsomer and Foote (22) has not been confirmed; Jamieson and McKinney (11) failed to detect any acid of lower molecular weight than palmitic.

Composition of the Extraction Residue

The residue after extraction of oil from the kernels had ash 9.1 and nitrogen 10.0 per cent of dry matter. These figures accord with those recorded by other authors; the high nitrogen content being noteworthy.

Summary

A sample of candlenut oil extracted from kernels of Ceylon nuts contained saturated acids 5.0, oleic acid 28.6, linoleic acid 42.6, and linolenic acid 23.8, calculated as percentages of the total acids by the usual Kaufmann method from the iodine and thiocyanogen values and a lead salt separation of the saturated acids. These figures are in good agreement with those recorded by Jamieson and McKinney for a sample from the Philippines.

A review of the literature shows that lumbang or candlenut oils from a variety of sources show similar ranges for iodine values, saponification values and other properties, and are probably all to be ascribed to the species *Aleurites moluccana* (Linn.) Willd.

Unlike those of *A. fordii, A. montana* and *A. trisperma,* the oil contains no elaeostearic acid.

REFERENCES

1. Agric. Bull. F.M.S., 1919, *7*, 162.
2. Malayan Agric. J., 1922, *10*, 202.
3. *Ibid.*, 1926, *14*, 292.
4. *Ibid.*, 358.
5. J.S.C.I., 1929, *48*, 289T.
6. Phil. J. Sci., 1907, *2*, 439.
7. Oil, Paint & Drug Rep., 1917, Feb. 5, *91*, 55.
8. Phil. J. Sci., 1919, *14*, 275.
9. *Ibid.*, 1917, *12A*, 235.
10. *Ibid.*, 1930, *42*, 251.
11. Oil & Soap, 1937, *14*, 203.
12. "Oils, Fats & Waxes," 1922, *II*, 88; J.S.C.I., 1901, *20*, 909A.
13. Seifensieder Zeitung, 1903, *8*, 359. See J.S.C.I., 1903, *22*, 639A.
14. Bull. Imp. Inst., 1907, *5*, 135.
15. *Ibid*, 1912, *10*, 44.
16. *Ibid.*, 1920, *18*, 25.
17. Private communication.
18. Recherches et Inventions, 1935, *16*, 312.
19. J. Chem. Ind., Japan, 1923, *26*, 316. See J.S.C.I., 1923, *42*, 786A.
20. See J.S.C.I., 1914, *33*, 1018A.
21. "Fatty Foods," 1913, p. 251.
22. Proc. Indiana Acad. Sci., 1935, *45*, 116.
23. Lach, Chem. Zeit., 1890, *14*, 871, quoted by A. Wright and C. A. Mitchell, "Fixed Oils," 3rd edition, 1921, p. 465.
24. G. Fendler, Z. Nahr. und Genussm., 1903, 1025; see J.S.C.I., 1904, *23*, 613A.
25. M. Lespinasse, Ann, falsif. et fraudes, 1919, *12*, 152.
26. A. H. G. Alston, Supplement to Trimen's "Handbook of the Flora of Ceylon," 1931, *VI*, 263. See also Index Kewensis, *I*, 75.
27. A. P. West and W. H. Brown, "Philippine Resins, etc.," Bull. No. 20, Philippine Is. Bur. Forestry, Manila, 1920.
28. A. P. West and F. L. Smith, "Commercial Products from Lumbang Oil," Bull. No. 24, Philippine Is. Bur. Forestry, Manila, 1923.
29. T. P. Hilditch in H. Schönfeld, "Chemie und Technologie der Fette und Fettprodukte," 1936, *I*, 76.
30. T. P. Hilditch, "Chemical Constitution of Natural Fats," 1940, p. 134.
31. G. S. Jamieson and R. S. McKinney, Oil & Soap, 1935, *12*, 146.
32. H. Toms, Analyst, 1928, *53*, 69; 1936, *61*, 177.
33. G. S. Jamieson, "Vegetable Fats & Oils," 1932, 345.
34. W. J. Wiley and A. H. Gill, Ind. Eng. Chem. (Anal.), 1934, *6*, 298.
35. A. P. West and Z. Montes, Philippine J. Sci., 1921, *18*, 619.
36. H. N. Griffiths and T. P. Hilditch, J.S.C.I., 1934, *53*, 75T.
37. T. P. Hilditch and K. S. Murti, Analyst, 1940, *65*, 437.
38. D. M. Birosel, Philippine J. Sci., 1931, *45*, 251.
39. H. Meyer and R. Beer, Monatsh., 1912, *33*, 311.
40. P. E. Verkade and I. Coops, Biochem. Zeit., 1929, *206*, 468