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THE SEED FAT OF *MALLOTUS PHILIPPINENSIS* (KAMALA OIL)—AN EXAMINATION OF SOME AUSTRALIAN MATERIAL.

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SUMMARY.

Australian samples of seeds of Mallotus philippinensis, **a tree which has recently received much attention in India as a source of a seed oil possessing drying properties very similar to those of tung oil, have been examined.**

The Australian oil is shown to be comparable with the Indian.

Obstacles to economic production are harvesting difficulties, smallness of the fruit, variability in the quality of the oil, and the need to use solvents other than the usual light petroleum for extraction.

Mallotus philippinensis, which belongs to the family Euphorbiaceae, is a tree distributed widely over South-East Asia and also occurring in Australia (coastal Queensland and northern New South Wales). In India, it has long been of minor economic value because of the red dye "kamala" with which the fruits are coated. Recently much attention has been paid there to the seed fat termed "kamala oil," which has powerful drying properties like those of tung oil (Aggarwal, Bhatnagar, Narain and Karimullah 1948; Sharma and Aggarwal 1952). These are due to the presence, as major constituent acid, of kamlolenic acid which like elaeostearic acid of tung oil has a system of three conjugated double bonds, and differs from it only in the possession of a terminal hydroxyl group (Gupta, Sharma and Aggarwal 1951; Calderwood and Gunstone 1953; Crombie and Taylor 1954).

In view of the wide Australian occurrence of *M. philippinensis* (and several other *Mallotus* species), and the fact that it is one of the very few native plants known to produce a drying oil, it was considered highly desirable to examine some material of local origin and compare it with Indian material.

It is obvious that for commercial exploitation to be feasible many problems must first be overcome, not the least of which are those calling for botanical study. The tree is said to grow to a height of 50 ft., but is often small

and bushy. Whether there could be found a dwarf form amenable to mechanical harvesting of the fruits is of first importance. It is also apparent from the present work that the seed needs to be harvested at the correct stage of maturity. No information on these points has been reported in the Indian literature. Of six recent samples received from Queensland, one was useless because of immaturity, and in two others the seeds, though well-developed and to outward appearance sound, were either quite empty or contained only shrivelled remnants of kernel. This may have been due to too late harvesting, poor soil or climatic conditions. There were also evidences of insect attack. Obviously, these points would have to be clarified before supplies of seed of uniform quality could be assured.

The usable Australian material examined consisted of three samples of fruits—two from Gordonvale (near Cairns) harvested in successive years, and the other from Imbil, near Gympie. The latter when received was two years old, and hence some deterioration was to be expected. Two Indian samples of seeds were obtained for comparison, through the courtesy of Dr. Aggarwal of the National Chemical Laboratory of India. The Australian seeds were only about half the size of the Indian, and the yield of kernels from seed and of seed from total fruit were both lower, but the yield and quality of the oil from the kernels were comparable—see Table 1.

Table 1.

SUMMARY OF EXAMINATIONS.

—	S. India.	Cairns (1953).	Cairns (1954).	Imbil.
Weight of 100 seeds	2·73g.	1·43g.	1·93 g.	Not determined
Kernels from seed	47·5%	36·2%	40·6%	36·2%
Seed from total fruit	30·9%*	21·2%	27·8%	17·9%
Fat from kernels	44·0%†	49·0%	50·0%	48·4%
Iodine value (Wijs 2 hr.)	160	151	135	124
Acid value	19	20	3	26
Saponification value	193	194	195	198

* Published figure—the fruits were not available for checking.

† The Indian sample had evidently deteriorated in transit, resulting in the development of altered oil which could not be extracted. About 50% of oil is usually present in kernels of Indian seed.

The fruits are small, coated with red kamala dye, which easily rubs off in transit, from $\frac{1}{4}$ in. to $\frac{1}{2}$ in. broad, three-lobed (rarely four), each lobe containing when mature a black spherical seed. The fruits were easily cracked and the seeds suitable for separation on standard seed-cleaning machinery.

The extraction of the fat has been the subject of much study by the Indian workers (Gupta and Aggarwal 1953). Expression from the kernels appears impracticable, as the fat is solid at room temperature (m.p. ca. 40°C.) and above the melting-point it is much too viscous and sticky to be dealt with in presses. Solvent extraction is therefore necessary, but the range of satisfactory

solvents is limited; the usual cheap petroleum-based solvents give incomplete extraction and the extract is deficient in the all-important kamlolenic acid. Chlorinated hydrocarbons are unsatisfactory because solutions of kamlolenic acid in them are not very stable. Ether is the most satisfactory for laboratory use; its low boiling point minimizes the risk of heat damage to the sensitive kamlolenic acid, and it extracts the fat completely from fresh seed (although deterioration of old seed can result in the presence of altered fat which will not dissolve). The cheapest satisfactory solvent for industrial use appears to be benzene. Because of the susceptibility of kamlolenic acid to aerial oxidation, extraction in an inert atmosphere is necessary. The technical difficulties of solvent extraction on an industrial scale have led Indian workers to propose a process (Mathur 1952) whereby the seeds are expressed along with another vegetable oil—the result is a product in which the drying properties of the "solvent" oil are enhanced by the kamala oil so introduced, but the product is then not comparable with tung oil.

The determination of the kamlolenic acid content of the fat, on which its drying properties depend, is conveniently done spectroscopically, making use of the intense absorption at 270 mμ (alcohol) or 274 mμ (carbon tetrachloride) $E^{1\%}_{1\,cm.}$ alc. : 1750, CCl_4 : 1420). We found it necessary to use carbon tetrachloride as solvent for determinations on the fat, since alcohol would not give complete solution; alcohol is more convenient for determinations on the free fatty acids.

Table 2 shows the kamlolenic acid contents of the oils examined.

Table 2.

KAMLOLENIC CONTENT OF OILS.

Origin.	Kamlolenic Acid.
	%
Northern India ..	66·2
Southern India ..	70·4
Cairns (1953)	62·7
Cairns (1954)	48·4
Imbil	46·5

It is apparent from this table that there is considerable variation in kamlolenic acid content, and hence presumably in drying properties, among the samples examined. The variation between the two Cairns samples obtained in successive years from the same locality is particularly striking. The reason for this variability is another matter calling for study.

Kamlolenic acid was readily isolated from the Australian samples after saponification, the simplest procedure being to crystallize the mixed acids from ether at 0°C., followed by recrystallization from ethyl acetate/petroleum ether to constant extinction coefficient. It had m.p. 77–78°C. and could be hydrogenated to 18-hydroxystearic acid of m.p. 98–99°C.

The kamlolenic acid of *M. philippinensis* has been thoroughly investigated from a structural point of view by other workers (Sharma and Aggarwal 1952; Calderwood and Gunstone 1933; Crombie and Taylor 1954). It differs from elaeostearic acid only in possessing a terminal hydroxyl group. This hydroxyl group appears to have no adverse effect on the drying properties; indeed, the most striking difference of the fat from tung oil is the much shorter gelation time at 280°C. in the Browne Heat Test (tung oil 9–12 min., kamala < 2 min.). The hydroxyl group does have the undesirable effect of raising the melting point of the fat above room temperature. Its presence, however, is responsible for a profound difference between the constitution of the fat itself and that of tung oil and all other fats.

Work at the Paint Research Station of Teddington, England (O'Neill, Dennison and Ahlers 1954) has shown that kamala oil has only one-third of the expected glycerol content of a fat and cannot therefore have a normal triglyceride structure. Instead the kamlolenic acid must be present wholly or in part in the form of a polyester, in which its hydroxyl groups have taken over the functions which those of glycerol perform in a normal fat. This is a feature unique in fat chemistry. The present work confirms O'Neill's findings of abnormally low glycerol content: we found values of 2·8% to 4·8%.

The fact that kamlolenic acid has this terminal hydroxyl group and is prone to form polyesters may well open up a wider field of use than merely as a replacement for tung oil. For example, it provides a source of long-chain hydroxy or dibasic acids of a type otherwise difficultly accessible.

The development of these industrial potentialities obviously depends on the supply of material being adequate, the quality uniform, and the price within reasonable bounds. The fat does not appear to be yet in commercial production in India, where the position is probably more favourable because of lower labour costs and the fact that there is a small industry based on kamala dye. In Australia it would seem that the botanical problems outlined earlier in this note are those which need attention before commercial possibilities could reasonably be assessed. The chemical merits of the material seem sufficient to make such a botanical study worth while.

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