## KAMLOLENIC ACID FROM THE SEED FATS OF *MALLOTUS DISCOLOR* AND *M. CLAOXYLOIDES*\*

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The seed fat of *Mallotus philippinensis* Muell. Arg. (Euphorbiaceae), a tree native to south-east Asia, is remarkable in that it contains  $\alpha$ -kamlolenic acid (18-hydroxyoctadeca-*cis*-9,*trans*-11,*trans*-13-trienoic acid) (Aggarwal *et al.* 1948; Gupta, Sharma, and Aggarwal 1951; Calderwood and Gunstone 1953; Crombie and Tayler 1954). The tree is also a native of northern New South Wales and coastal Queensland, and Hancox and Hatt (1955) found that the seed fat ("kamala oil") from Australian material was comparable with that from Indian seed and contained from 47 to 60% of kamlolenic acid.

Recently, Toyama and Takai (1955) reported the presence of the acid in the seed fat of M. *japonicus* Muell. Arg., and stated that the amount present there seemed to be less than in kamala oil. We have since isolated kamlolenic acid from the seed fats of two other species native to Australia, M. *discolor* F. v. M. and M. *claoxyloides* Muell. Arg. From spectroscopic examination the seed fats from M. *discolor* and M. *claoxyloides* were estimated to contain 70 and 65% respectively of  $\alpha$ -kamlolenic acid.

The seeds of M. discolor were smaller than those of M. philippinensis. Only one small sample of seeds of M. claoxyloides was available and it may not have been representative, but by contrast these seeds were much larger. Their kernels contained some 50% fat (see Experimental).

The fact that M. claoxyloides is a shrub and has much larger fruits than either of the other two *Mallotus* species makes it of interest as a possible source of kamlolenic acid.

## Experimental

(a) General.—Microanalyses were made by the C.S.I.R.O. and University of Melbourne Microanalytical Laboratory.

(b) Identification of Kamlolenic Acid.—One sample of M. classyloides fruit was collected at Brookfield, N.S.W., in February 1956 and two samples of M. discolor fruit from the Queensland south coast area in January 1956. They were examined a few weeks after collection.

The kernels were gently crushed and extracted with ether in the presence of nitrogen and with the exclusion of light. After evaporation of the ether, samples of the fat (3 g) were saponified by standing with ethanolic KOH (5%; 100 ml) for 24 hr at room temperature with occasional shaking. The mixture was then warmed slightly and extracted with light petroleum (b.p. 40–60 °C) to remove any unsaponifiable material. Following removal of the alcohol by distillation (under nitrogen), acidification with dil. H<sub>2</sub>SO<sub>4</sub> and extraction with ether, the dried, filtered, ether extract was allowed to stand at 0 °C until the kamlolenic acid had crystallized from solution. It was recrystallized once from ether.

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*Hydrogenation.*—The acid (140 mg) was hydrogenated in methyl acetate with platinum oxide as catalyst. When absorption of gas had ceased the catalyst was filtered off and washed with hot methyl acetate. Hydrogenation of the acids from both *Mallotus* species gave 18-hydroxystearic acid, m.p. 98–99 °C (crystallized from methyl acetate).

The p-bromophenacyl esters of the unsaturated acids were prepared in the usual manner and recrystallized once from ethanol.

The analytical results and other data obtained from the examination of the kamlolenic acid from both species were identical within the limits of experimental error and hence only those for M. classyloides are reported below.

Melting point 75-76 °C (lit. 77-78 °C) (Found : C, 73  $\cdot$ 7; H, 10  $\cdot$ 2%. Calc. for  $C_{1s}H_{30}O_3$ : C, 73  $\cdot$ 5; H, 10  $\cdot$ 3%). Moles of hydrogen absorbed per mole of acid, 3  $\cdot$ 1.

*p*-Bromophenacyl ester, m.p. 85–86 °C (lit. 86 °C) (Found : Br,  $16 \cdot 3\%$ . Calc. for  $C_{26}H_{36}O_4Br$  : Br,  $16 \cdot 3\%$ ).

The acid in ethanol showed maxima:  $\lambda_{max}$ , 260 m $\mu$  ( $\varepsilon$ , 39·4×10<sup>3</sup>); 270 m $\mu$  ( $\varepsilon$ , 51·9×10<sup>3</sup>); 281 m $\mu$  ( $\varepsilon$ , 40·7×10<sup>3</sup>) (lit.  $\lambda_{max}$ , 261 m $\mu$ ) ( $\varepsilon$ , 40·5×10<sup>3</sup>); 271 m $\mu$  ( $\varepsilon$ , 52·0×10<sup>3</sup>); 282 m $\mu$  ( $\varepsilon$ , 42·0×10<sup>3</sup>).

(c) The Estimation of  $\alpha$ -Kamlolenic Acid in the Seed Fat.—The method of determining the  $\alpha$ -kamlolenic acid was the same as that used previously (Hancox and Hatt 1955) and is based on the strong absorption shown by the acid in carbon tetrachloride ( $E_{1 \text{ cm}}^{1\%}$ : 1420) at 274 mµ.

These results, together with other analytical data, are presented in the following table :

|                                   | M. discolor    |               | M. claoxyloides |
|-----------------------------------|----------------|---------------|-----------------|
|                                   | Sample I       | Sample II     |                 |
| Percentage fat in kernels         | 57.3           | 48.6          | 53.8            |
| Percentage kamlolenic acid in fat | $70 \cdot 8$   | $69 \cdot 8$  | $65 \cdot 4$    |
| Iodine value (Wijs; 2 hr)         | 171            | 168           | 166             |
| $n_{\rm D}^{40}$                  | $1 \cdot 5260$ | $1\cdot 5250$ | $1 \cdot 5210$  |

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