

with moulting hormone activity, mp 258—259°, which is now designated as lemmasterone, from *L. microphyllum*. Although the ecdysterones isolated from *N. ensata* and *L. microphyllum* are identical with authentic ecdysterone in behavior on thin-layer chromatography (showing a single spot) and in their infrared and nuclear magnetic resonance spectra, their melting points are rather higher and of wider range than authentic ecdysterone. Acetylation of each ecdysterone produced, along with ecdysterone triacetate, a small amount of a less-polar acetylated impurity, existence of a similar substance in each plant being indicated.

In the insect (*Sarcophaga*) test, lemmasterone exhibits the high moulting hormone activity. Lemmasterone, as with the other insect-moulting substances (*i.e.*, ponasterone A, pterosterone, ecdysterone, inokosterone, and cyasterone),³⁾ shows also the high accelerating effect on the protein anabolism in mouse liver.

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A Mangiferin Monomethyl Ether from *Mangifera indica* L.

Mangiferin, a xanthone C-glycoside first isolated from *Mangifera indica* L. and later found in several different families of plants,¹⁻³⁾ has been studied extensively by many research groups,^{1,4-8)} and the structure has quite recently been established as 2-C- β -D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone. However, so far none of the corresponding methyl ethers in nature has been reported.⁹⁾

A new compound which was isolated from a sample of mangiferas has now been found to be one of them, named homomangiferin (I), and characterized as mangiferin 3-methyl ether.

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- 9) P.E. Nott and J.C. Roberts¹⁾ have reported that mangiferin, mp 270° (decomp.), obtained from mango bark (*Mangifera indica*) showed two spots (*Rf* 0.4 (major), and 0.6) on thin-layer of "Kieselgel H nach Stahl" (Merck) but that attempted separation of the components failed even by column chromatography on "Polyamidpulver nach Stahl" (Merck).

Mangiferin,¹⁰⁾ decomposed over 250° without melting, $[\alpha]_D^{25} +28.7^{\circ 11)}$ obtained from mango bark (*Mangifera indica* L.) collected in Taipei in November, showed two spots (*Rf* 0.38, 0.15) on thin-layer of polyamide powder (Ube Industries, Ltd.) (solvent: MeOH). It was subjected to column chromatography on polyamide to give pure mangiferin (45% yield), mp 273° (decomp.), $[\alpha]_D^{25} +35.5^{\circ}$, *Rf* 0.15 (identified with authentic sample¹²⁾) and I (15% yield) as yellow needles (dioxane-H₂O), decomposed over 250° without melting, $[\alpha]_D^{25} +8.7^{\circ}$, *Rf* 0.38, C₁₉H₁₇O₁₀(OCH₃)·1.5H₂O.¹³⁾ I shows the UV spectrum which is hardly distinguishable from that of mangiferin,⁴⁾ and afforded on acetylation a heptaacetate (II), mp 173—174° (MeOH), C₃₄H₃₄O₁₈·1.5H₂O. The NMR spectrum¹⁴⁾ of II indicates the presence of three protons (7.99(1H, s), 7.35(1H, s), 6.80(1H, s)) and one methoxyl group (4.04 (3H, s)) on aromatic ring. On treatment with hydrochloric acid I was recovered unchanged, while with hydroiodic acid I gave 1,3,6,7-tetrahydroxyxanthone (identified as tetraacetate (III)) and on ferric chloride oxidation according to Hay, *et al.*¹⁵⁾ arabinose and glucose were provided. Methylation of I with diazomethane in a mixture of dimethylformamide and methanol gave a product (IV), mp 184—187°, C₂₃H₂₆O₁₁·H₂O, which was acetylated to afford an acetate (V), mp 201°, C₃₁H₃₄O₁₅·1/2H₂O. The procedures were duplicated with mangiferin to give tetramethyl ether, mp 185—186°, and tetramethyl ether tetraacetate, mp 202°, which were identical with IV and V, respectively. The long wave length UV absorption of I was significantly shifted bathochromically on addition of boric acid and sodium acetate suggesting the existence of ortho-diphenol function^{16,17)} (at C-6 and C-7) and the similar shift observed in the presence of aluminum chloride¹⁶⁾ or sodium acetate^{16,17)} implies that the hydroxyl groups at C-1 and C-6 or C-3 are free. Comparison of the NMR spectrum of II with those of III, V, 1-acetoxy-3,6,7-trimethoxyxanthone¹²⁾ and mangiferin or xanthone derivatives reported in the literatures^{1,6,7)} indicates that the three singlets at 6.80, 7.35 and 7.99 of II are respectively due to the protons at C-4, C-5 and C-8, and that methoxyl group is located at the C-3 position and acetoxy groups at C-1, C-6 and C-7.

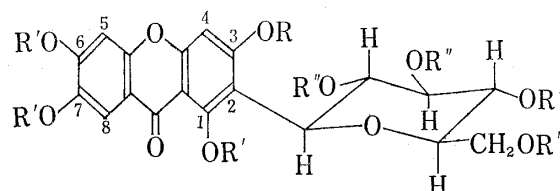
Accordingly I is considered to be mangiferin 3-methyl ether.

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mangiferin : R=R'=R''=H
 homomangiferin (I) : R=Me, R'=R''=H
 II : R=Me, R'=R''=Ac
 IV : R=R'=Me, R''=H
 V : R=R'=Me, R''=Ac

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- 10) Kindly furnished by Prof. T. Tsukamoto to whom the authors' thanks are due.
- 11) Melting points were taken in capillary and are uncorrected. Optical rotation were determined in pyridine with a Jasco automatic polarimeter Model DIP-SL.
- 12) Kindly furnished by Prof. S. Iseda to whom the authors' thanks are due.
- 13) Analytical values are in agreement with the molecular formulae indicated.
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