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PHENOLIC COMPOUNDS FROM THE HEARTWOOD OF *GARCINIA MANGOSTANA**

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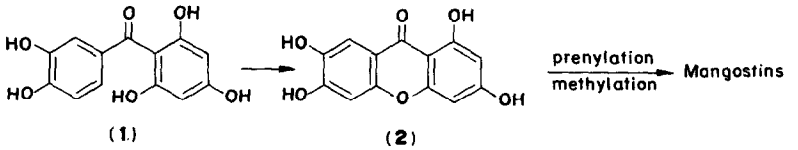
Key Word Index—*Garcinia mangostana* L.; Guttiferae; maclurin; 1,3,6,7-tetrahydroxyxanthone *O*-glycoside.

Plant. Garcinia mangostana L. (Guttiferae). *Source.* Heartwood supplied by Tropical Products Institute, London, and obtained from Coutallam and Ponmundi Estates in Kerala, South India. The samples were collected and identified by Mr. Rajendra Babu, M.Sc., Curator, Government Botanical Gardens, Trivandrum, Kerala. *Previous work.* The bark, fruit hulls and dried latex contain the 3 di-isoprenyl-1,3,6,7-tetraoxygenated xanthones, mangostin [1], β-mangostin and γ-mangostin [2,3].



(1) (2)

Present work. The mangostins were required for further synthetic work and the heartwood of *G. mangostana* was supplied as a possible source of these metabolites. However the heartwood was devoid of the isoprenylxanthones and instead 1,3,6,7-tetrahydroxyxanthone (**2**) [1] and an *O*-glucoside of this xanthone was isolated by extraction with hot $CHCl_3$. In addition the pentahydroxybenzophenone, maclurin (**1**) [4], was present in the extract and isolated as the pentamethyl ether. 1,3,6,7-Tetrahydroxyxanthone (**2**) was identified by direct comparison with an authentic sample and conversion with CH_2N_2 to 1-hydroxy-3,6,7-trimethoxyxanthone [5]. The glucoside of the xanthone was readily hydrolysed with dil. HCl to give glucose and (**2**). The sugar residue is therefore *O*-linked but not at C-1 since the NMR s of the glycoside shows the presence of an intramolecular hydrogen bonded OH group at τ-3·1. Due to lack of material it was not possible to establish which *O* was glucosylated.

Although isoprenylxanthones of the mangostin series are absent from this sample of the heartwood of *G. mangostana*, it is interesting to note that maclurin (**1**) and 1,3,6,7-tetrahydroxy are their postulated precursors (as shown). The presence of an *O*-glycoside suggests that the insoluble yellow polyhydroxyxanthones may be transported in the plant as their glycosides prior to hydrolysis.

EXPERIMENTAL

All UV spectra were determined in MeOH, IR spectra as Nujol mulls. NMR spectra were measured on a Varian HA100 instrument and MS with A.E.I. MS12 and MS9 spectrometers. TLC and PLC were carried out with silica gel (Merck Kieselgel G).

Extraction of *G. mangostana*. Twigs and branches of *G. mangostana* (1·2 kg) were planed to give fine shavings and continuously extracted with hot $CHCl_3$ (15 l) for 48 hr. The filtrate was concentrated and dark brown tar deposited (20 g) which contained mainly polar components (TLC). Crude tar was methylated (Me_2SO_4–K_2CO_3) and the major component isolated by TLC R_f 0·65 (C_6H_6–EtOAc, 14:6) gave pentamethylmaclurin, mp 165–6°, (lit. [4] 165–6°) as pale yellow needles (MeOH). (Found: M^+, 332·343. Calc. for $C_{18}H_{20}O_6$ M, 332·343). Presence of maclurin in the crude extract was confirmed by TLC with an authentic sample and the identity of the pentamethyl ether was also confirmed by direct comparison (MMP, IR, UV, NMR).

* Part 30 in the Series "Extractives from Guttiferae". For Part 29 see Quillinan, A. J. and Scheinmann, F. (1975) *J. Chem. Soc. Perkin* **1**, 241.

Isolation of 1,3,6,7-*tetrahydroxyxanthone and an* O-*glucoside.* The remainder of the crude tar from the $CHCl_3$ extraction was dissolved in the minimum of MeOH. Addition of H_2O dropwise, pptd a brown solid which separated into 2 bands by PLC (C_6H_6–EtOAc, 3:2). From the band at R_f 0·4 a yellow solid was isolated which crystallised from EtOAc–light petrol as a yellow amorphous solid, mp 245–8° (ch.). The MS of the metabolite resembled 1,3,6,7-tetrahydroxyxanthone and NMR spectrum suggested an *O*-glycoside of this xanthone. Xanthone glycoside was hydrolysed with dil. HCl and the sugar identified as glucose by PC (BuOH–EtOH–H_2O: 4,1,5). From the band R_f 0·2, 1,3,6,7-tetrahydroxyxanthone was isolated as a pale yellow solid, mp 290° decomp (lit. 300° [1]) identical with an authentic sample (mmp, UV, IR). (Found: M^+, 260·192 Calc. for $C_{13}H_8O_6$ 260·203). Structure of the metabolite was confirmed by methylation (CH_2N_2) which gave 1-hydroxy-3,6,7-trimethoxyxanthone, mp 222–224°, identical with an authentic sample (mmp, UV, IR, NMR) (Found: M^+ 302·280. Calc. for $C_{16}H_{14}O_6$ 302·282).

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REFERENCES

1. Yates, P. and Stout, G. H. (1958) *J. Am. Chem. Soc.* **80**, 1691.
2. Yates, P. and Bhat, H. B. (1968) *Can. J. Chem.* **46**, 3770.
3. Jefferson, A., Quillinan, A. J., Scheinmann, F. and Sim, K. J. (1970) *Australian J. Chem.* **23**, 2539.
4. Locksley, H. D., Moore, I. and Scheinmann, F. (1967) *Tetrahedron* **23**, 2229.
5. (a) Jefferson, A. and Scheinmann, F. (1966) *J. Chem. Soc.* 175; (b) Quillinan, A. J. and Scheinmann, F. (1973) *J. Chem. Soc.* Perkin **1**, 1329.
6. Quillinan, A. J. (1972) University of Salford, Ph.D. Thesis. (We thank Dr. Quillinan for authentic samples.)

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HYDROQUINONE DIACETATE FROM *RHYNCHOSIA MINIMA*

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Key Word Index—*Rhynchosia minima*; Leguminosae; seed germination; seed; pericarp; hydroquinone diacetate.

In the leguminous weed *Rhynchosia minima* DC., Rangaswamy *et al.* [1] observed a prominent brown–black halo around seeds sown for germination on moist filter paper. The halo formation was attributed to the leaching of known phenolic substances from the seed coats. Further chemical examination has shown that the pericarp and seeds of *R. minima* contain hydroquinone diacetate.

The ether-soluble fraction of the alcoholic extract of the pericarp yielded, besides sitosterol, gallic acid, and protocatechuic acid. A fourth component **R** crystallized from petroleum as needles, mp 123–24°. **R** is a neutral compound; its IR spectrum indicated it to be an acetate (ν_{max}^{KBr} 1770 cm^{-1} and 1212 cm^{-1}) and aromatic (ν_{max}^{KBr} 1504 cm^{-1} and 855 cm^{-1}); its NMR spectrum ($CDCl_3$) contains 2 singlets, one at 7·05 δ (aromatic protons) and the other at 2·2 δ (–O–CO–Me) in the ratio 2:3. These data showed that **R** could be hydroquinone diacetate and its identity with an authentic sample was confirmed by co-TLC, mmp (undepressed), and superimposable IR and NMR spectra. On acid hydrolysis **R** gave hydroquinone.

To our knowledge this is the first report of occurrence of hydroquinone diacetate in a plant species, and it constituted as much as 1% of dry wt. of pericarp of *Rhynchosia minima*. The only other hydroquinone derivative reported in the Leguminosae is arbutin in *Lathyrus clymenum* var. *articulatus* [2]. Besides the well-known gallotannins and lichen depsides [3], the only other aryl esters known to occur naturally are the rare fungal metabolites, protoleucomelone and aurantiacin leucodibenzoate [4].

Hydroquinone diacetate was not found in the seed kernel nor was hydroquinone detected in either seeds or pericarp. Hydroquinone is known to occur free [5–7], as monoglucoside [2,5,7] and as monomethyl, dimethyl and diethyl ethers [8] in many taxa. Whether or not hydroquinone diacetate is involved in halo formation during seed germination of *R. minima* is being investigated. Our voucher specimen of *Rhynchosia minima* tallies with the type specimen no. 321 (J. K. Maheshwari) of the Herbarium of the University of Delhi.

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