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SHORT COMMUNICATION

XANTHONES FROM THE HEARTWOOD OF *CALOPHYLLUM NEO-EBUDICUM*: COMMENTS ON THE TAXONOMIC VALUE OF JACAREUBIN IN *CALOPHYLLUM* SPECIES*

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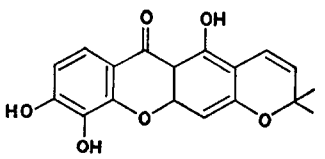
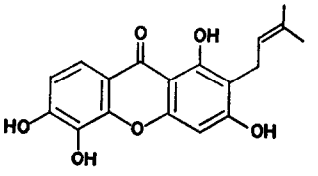
Abstract—From the heartwood of *Calophyllum neo-ebudicum* Guillaumin 6-desoxyjacareubin, jacareubin, and 2-(3,3-dimethylallyl)-1,3,5,6-tetrahydroxyxanthone have been isolated. β-Sitosterol is also present in the heartwood The taxonomic significance of the presence of the xanthones in *Calophyllum* species is discussed.

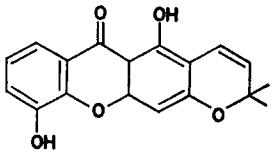
IN A RECENT review on xanthones in higher plants we suggested[1] that the presence of jacareubin (I) and/or a putative isoprenyl precursor, namely 2-(3,3-dimethylallyl)-1,3,5,6-tetrahydroxyxanthone (II) may be of taxonomic value at the generic level in *Calophyllum* (Guttiferae). At that time jacareubin had been found in all of the six species of *Calophyllum* that had been examined. The work of Govindachari *et al.*[2] on *Calophyllum inophyllum* L. collected near Madras, India was exceptional in that neither jacareubin (I) nor its putative isoprenyl precursor (II) were identified, despite the availability of authentic reference compounds.[3] These results are particularly interesting especially since examination of *C. inophyllum* L. obtained from first the Malagasy Republic[4] and later from Australia[5] showed



Jacareubin (I)



(II)



6-Desoxy jacareubin (III)

* Part XX in the series 'Extractives from Guttiferae'. For Part XIX see H. D. LOCKSLEY and I. G. MURRAY, *J. Chem. Soc.* (C), submitted for publication.

[1] I. CARPENTER, H. D LOCKSLEY and F. SCHEINMANN, *Phytochem.* **8**, 2013 (1969).
[2] T. R. GOVINDACHARI, B. R. PAI, N. MUTHUKUMARASWAMY, U. R. RAO and N. NITYANANDA RAO, *Indian J. Chem.* **6**, 57 (1968)
[3] T. R. GOVINDACHARI, personal communication.
[4] B JACKSON, H. D. LOCKSLEY, and F. SCHEINMANN, *Phytochem.* **8**, 927 (1969).
[5] F. S. AL-JEBOURY and H. D. LOCKSLEY, *Phytochem.* **10**, 603 (1971).

that in both cases the heartwood contained jacareubin(I) and its probable biogenetic precursor(II). It now becomes of interest to chematoxonomy to know whether the absence of jacareubin (I) and/or the isoprenylxanthone (II) from the Indian specimen[2] is an isolated observation or whether in fact these substances may also be absent in other *Calophyllum* species.

The availability of *Calophyllum neo-ebudicum* Guillaumin from the New Hebrides in the South Pacific enables us to provide further support to the suggestion that the presence of jacareubin (I) and/or its putative biogenetic precursor (II) is of taxonomic value at the generic level. Thus extraction of the heartwood with hot chloroform led to the isolation of a yellowish brown solid. Trituration with a small amount of cold chloroform gave a soluble extract from which 6-desoxyjacareubin (III) and β-sitosterol were isolated by chromatography. Chromatography of the insoluble residue after trituration led to the isolation of jacareubin (I) and its putative biogenetic precursor (II). These results are in accord with previous work at Salford which show that jacareubin (I) and its isoprenyl xanthone (II) appear to be present in all the samples of *Calophyllum* species regardless of their geographic origin [1,5]

EXPERIMENTAL

I.r spectra were measured as KBr discs and as Nujol mulls. Mass spectra were obtained with A E.I, MS12 single focusing instruments at an ionization potential of 70 eV. Analytical and preparative TLC were carried out using silica gel, Stahl (Merck).

Extraction of Calophyllum Neo-ebudicum *Guillaumin* The timber from the New Hebrides in the South Pacific was kindly supplied by Mr A. G. Kenyon of Tropical Products Institute, London. A sample of the heartwood as wood shavings (105 g) was extracted with hot $CHCl_3$ (6 l) in a Soxhlet for 48 hr. The yellow solution was evaporated to dryness to give a yellowish brown solid (5 g) which was triturated with a small amount of cold $CHCl_3$ to produce suspension, which was filtered to give solid A and filtrate B.

Chromatography of Solid A

The yellowish-brown solid A (3 5 g) was chromatographed on a column of silica gel (250 g). Elution was carried out with $CHCl_3$ containing increasing proportions of EtOAc Aliquots (100 ml) of the eluate were collected, examined by analytical TLC and combined as appropriate to yield five fractions:

Fraction 1 was eluted with $CHCl_3$–EtOAc (24:1) Evaporation of the solvent gave a yellow solid (8 mg) which had the same R_f value (0 8 in $CHCl_3$–EtOAc, 9·1) and colour under u v light (black) as authentic 6-desoxyjacareubin and gave a dark green colour with $FeCl_3$ m p. 197–198°. Comparison with authentic material showed it to be impure 6-desoxyjacareubin (III) This material was also isolated and purified from filtrate B (see below)

Fraction 2 was eluted with $CHCl_3$–EtOAc (24·1); TLC investigation indicated that this fraction is largely a mixture of fraction 1 and fraction 3 and was not examined further

Fraction 3 was eluted with $CHCl_3$–EtOAc (47·3) Evaporation of the fraction to low bulk gave a deep yellow crystalline material (1 g) which had the same R_f (0 6 in $CHCl_3$–EtOAc, 3 2) and colour under u v light (black) as authentic jacareubin and gave a dark green colour with $FeCl_3$ Recrystallization from acetone gave pure jacareubin (I) as yellow needles (0 5 g), m p 253–256° (lit [4] m.p 254–256°) identical by mixed m p with an authentic sample and comparison of the i r spectra NMR (τ values in deuterioacetone): 8 52s (6H, Me_2C<), 3 26d and 4 23d (each 1H, J = 10 Hz, CH=CH chromene), 3 58s (1H, H-4), 2 97d and 2 30d (each 1H, J = 9 Hz, H-7, H-8) Found M (mass spectrometry 326) $C_{16}H_{14}O_6$ requires M326)

Fraction 4 was eluted with $CHCl_3$–EtOAc (9 1). This was largely a mixture of fractions 3 and 5 with trace quantities of some unknown compounds and was not examined further

Fraction 5 was eluted with $CHCl_3$–EtOAc (41 9) Evaporation of the fraction to low bulk gave a pale yellow solid which had the same R_f (0 25 in $CHCl_3$–EtOAc, 3 2) and colour under u v light (black) as authentic 2-(2,3-dimethylallyl)-1,3,5,6-tetrahydroxyxanthone (II) and gave a dark green colour with $FeCl_3$. It was washed twice with a small amount of $CHCl_3$ and gave the isoprenylxanthone (II) as a creamy solid (0 5 g) m p 252–253°, (lit [6] 255–257°) identical mixed m p. and comparison of i r. spectra with an authentic

[6] B JACKSON, H D LOCKSLEY and F. SCHEINMANN, *J Chem Soc.* (C), 178 (1966)

sample, NMR (τ value in deuterioacetone), 8·32s, 8·19s (3H, 3H, Me_2C=) 6·60d (2H, J = 7 Hz, CH_2), 4·63t (1H, J = 7 Hz, CH=), 3·40s (1H, H-4), 2·95d and 2·28d (each 1H, J = 9 Hz, H-7 and H-8), −3·3s, (1H, hydrogen bonded 1—OH). Found M (mass spectrometry) 328. $C_{18}H_{16}O_6$ requires M328.

Chromatography of the Solid from Filtrate B

The $CHCl_3$-soluble brown solid (1 g) was chromatographed on preparative TLC and eluted with $CHCl_3$–EtOAc (9:1) and the various bands removed from silica gel using acetone:

Fraction 1 A yellow oily substance gave a blue colour spot under u.v. light and had R_f (0·82 in $CHCl_3$–EtOAc, 9·1), but no further work was carried out because of insufficient material.

Fraction 2 Evaporating the solvent to small volume and further evaporation gave yellow crystals (30 mg) which had the same R_f (0·8 in $CHCl_3$–EtOAc, 9·1) and colour under u.v. light (black) as authentic 6-desoxyjacareubin and gave dark green colour with $FeCl_3$. The m.p. 211–212° (lit.[7] 212–214°) mixed m.p. and comparison of i.r. spectra with authentic sample confirmed the structure as 6-desoxyjacareubin; NMR (τ value in deuterioacetone)· 8·53s (6H, Me_2C<) 4·23d and 3·26d (each 1H, J=10 Hz, CH=CH chromene), 3·58s (1H, H-4) 2·68c (2H, H-6 and H-7), 2·28q (1H, J=3 and 7 Hz, H-8) Found M (mass spectrometry) 310. $C_{18}H_{14}O_5$ requires M310.

Fraction 3. β-Sitosterol was isolated from the chloroform soluble fraction by preparative TLC on silica gel Elution with $CHCl_3$–EtOAc (49·1) gave the triterpene at R_f 0·65 ($CHCl_3$–EtOAc 9:1 and development with iodine vapour) Removal of β-sitosterol from the silica gel by washing with acetone and recrystallization from ethyl acetate gave β-sitosterol as white needles, m.p. 134–135° (lit[8] m.p. 136°), mixed m.p. undepressed on admixture with a standard The identity of the material was confirmed by comparison of infrared, NMR and mass spectral fragmentation pattern with an authentic specimen purchased from Koch-light Ltd Found: M (mass spectrometry) 414 $C_{29}H_{50}O$ requires M414.

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[7] B Jackson, H D Locksley and F. Scheinmann, *J. Chem. Soc.* (C), 2500 (1967).
[8] B E Nilsen and H Kotod, *Acta Chem Scand.* 17 1161 (1963).