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SHORT COMMUNICATION

THE ISOLATION OF 6-DESOXYJACAREUBIN, 2-(3,3-DIMETHYLALLYL)-1,3,5,6-TETRAHYDROXYXANTHONE AND JACAREUBIN FROM *CALOPHYLLUM INOPHYLLUM*[1]

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Abstract—The presence of 6-desoxyjacareubin, 2-(3,3-dimethylallyl)-1,3,5,6-tetrahydroxyxanthone, and jacareubin in the heartwood of *Calophyllum inophyllum* L. is reported. The chemotaxonomic significance of the presence of jacareubin is discussed.

THE RECENT paper[2] on the isolation of 1,5,6-trihydroxyxanthone[3] (mesuaxanthone B) (I) and 6-(3,3-dimethylallyl)-1,5-dihydroxyxanthone[4] (calophyllin B) (II) from the heartwood of *Calophyllum inophyllum* L. (Guttiferae) prompts us to report our findings on the metabolites from a heartwood sample of this species obtained from the Malagasy Republic (formerly Madagascar).

Evaporation of the chloroform extract from the powdered heartwood of *C. inophyllum* L. gave a brown solid which was chromatographed on silica gel. Elution with chloroform–ethyl acetate led to the isolation of a yellow pigment which was identified as 6-desoxyjacareubin (III) by comparison (mixed m.p. and i.r. spectrum) with an authentic sample.[5] Later fractions yielded jacareubin (IV) and 2-(3,3-dimethylallyl)-1,3,5,6-tetrahydroxyxanthone (V) identical (mixed m.ps and i.r. spectra) with authentic samples.[1,6] However, the presence of 1,5,6-trihydroxyxanthone (I) and 6-(3,3-dimethylallyl)-1,5-dihydroxyxanthone (II) could not be detected in our extract.

[1] Part XI in the series "Extractives from Guttiferae"; for Part X, see I. CARPENTER, H. D. LOCKSLEY and F. SCHEINMANN, *J. Chem. Soc.* (C), in press.

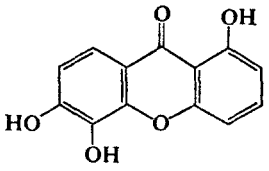
[2] T. R. GOVINDACHARI, B. R. PAI, N. MUTHUKUMARASWAMY, U. R. RAO and N. NITYANANDA RAO, *Indian J. Chem.* **6**, 57 (1968).

[3] 1,5,6-Trihydroxyxanthone has also been found in *Symphonia globulifera* L, see H. D. LOCKSLEY, I. MOORE and F. SCHEINMANN, *J. Chem. Soc.* (*C*), 431 (1966); in *Calophyllum scriblitifolium* Henderson et Wyatt-Smith, see Ref. 5; and in *Mesua ferrea* L., see T. R. GOVINDACHARI, B. R. PAI, P. S. SUBRAMANIUM, U. R. RAO and N. MUTHUKUMARASWAMY, *Tetrahedron* **23**, 243 (1967).

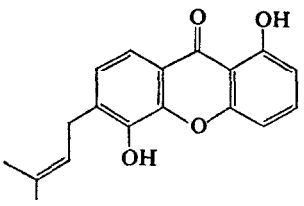
[4] 6-(3,3-Dimethylallyl)-1,5-dihydroxyxanthone has also been isolated from *Calophyllum scriblitifolium* Henderson et Wyatt-Smith, see B. JACKSON, H. D. LOCKSLEY and F. SCHEINMANN, *Tetrahedron* **24**, 3059 (1968); and from *Calophyllum brasiliense* Camb., see O. R. GOTTLIEB, M. TAVEIRA MAGALHÃES, M. OTTONI DA SILVA PEREIRA, A. A. LINS MESQUITA, D. DE BARROS CORRÊA and G. G. DE OLIVEIRA, *Tetrahedron* **24**, 1601 (1968).

[5] B. JACKSON, H. D. LOCKSLEY and F. SCHEINMANN, *J. Chem. Soc.* (C), 2500 (1967).

[6] A. JEFFERSON and F. SCHEINMANN, *J. Chem. Soc.* (C), 175 (1966).



(I)



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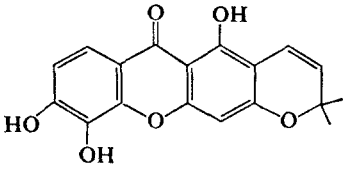

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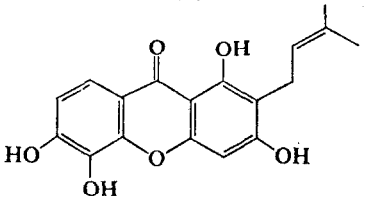
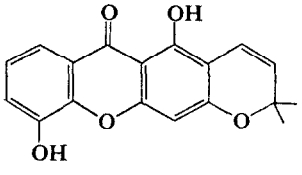


(V)



(III)

In addition to xanthones from *C. inophyllum* L. heartwood, triterpenes from leaves,[7] phenylcoumarins from nuts[8] and leaves,[9] and isoprenylchromanones from the bark resins,[10] have been reported. The heartwood metabolites from six,[1,5,11–13] of the 112 classified *Calophyllum* species[14] have been examined; in every case jacareubin (IV) has been found. Thus, the presence of jacareubin may have considerable taxonomic significance at the generic level. However, jacareubin is not unique to *Calophyllum* since it has recently been isolated[15] from *Kielmeyera ferruginea* A. P. Duarte (sub-family Kielmeyeroideae, family Guttiferae).

EXPERIMENTAL

I.r. spectra as Nujol mulls were recorded with a Perkin–Elmer 137 or Unicam SP 200 spectrophotometer. Analytical and preparative TLC was carried out on silica gel G, Stahl (Merck). M.ps are uncorrected.

Extractives from Calophyllum inophyllum

The ground heartwood (2 kg) was extracted with hot $CHCl_3$ in a Soxhlet for 5 days. The extract afforded a brown solid (7·5 g) on evaporation, which was dissolved in a small amount of ethyl acetate, and chromato-

[7] T. R. GOVINDACHARI, N. VISWANATHAN, B. R. PAI, U. R. RAO and M. SRINIVASAN, *Tetrahedron* **23**, 1901 (1967).
[8] J. POLONSKY, *Bull. Soc. Chim. Fr.* 1079 (1957); 929 (1958).
[9] K. KAWAZU, H. OHIGASHI and T. MITSUI, *Tetrahedron Letters* **19**, 2383 (1968).
[10] G. H. STOUT, M. M. KRAHN and G. D. BRECK, *Tetrahedron Letters* **29**, 3285 (1968).
[11] B. JACKSON, H. D. LOCKSLEY and F. SCHEINMANN, *J. Chem. Soc.* (C), 178 (1966).
[12] F. E. KING, T. J. KING and L. C. MANNING, *J. Chem. Soc.* (C), 3932 (1953).
[13] I. G. MURRAY and H. D. LOCKSLEY, unpublished results on the extractives of *C. fragrans* Ridley.
[14] J. C. WILLIS, *A Dictionary of the Flowering Plants and Ferns*, p. 181, 7th edition, Cambridge University Press (1966).
[15] O. R. GOTTLIEB, personal communications.

graphed on a column of silica gel (500 g) with $CHCl_3$. Four fractions were collected, the cuts being taken according to the number of constituents present (accompanying TLC).

Fraction 1 (eluted with $CHCl_3$/ethyl acetate 19:1). This fraction yielded a yellow solid which crystallized from ethyl acetate affording 6-desoxyjacareubin (III) as yellow prisms, m.p. 211–213° (Lit.[5] 212–214°) identical (mixed m.p. and i.r. spectra) with an authentic sample.[5]

Fraction 2 (eluted with $CHCl_3$/ethyl acetate 9:1). This fraction yielded a yellow solid, which crystallized from ethyl acetate/petroleum ether (b.p. 60–80°) affording jacareubin (IV) (2·1 g) as yellow plates, m.p. 256° (lit.[6] 256°) identical (mixed m.p. and i.r. spectra) with an authentic sample.

Fraction 3 (eluted with $CHCl_3$/ethyl acetate 4:1). The solid which remained after evaporation of the solvent was washed with $CHCl_3$, yielding 2-(3,3-dimethylallyl)-1,3,5,6-tetrahydroxyxanthone (V) as pale cream crystals (1·3 g), m.p. 254–257°, identical (mixed m.p. and i.r. spectra) with an authentic sample (ex. *C. sclerophyllum* Vesq.)[11]

Fraction 4 (eluted with $CHCl_3$/ethyl acetate 1:1). The solid obtained (100 mg) was sensitive to aerial oxidation, and TLC examination showed that one of the components had an R_f value consistent with that of a tetrahydroxyxanthone.[5] This fraction was not examined further.

Acknowledgements—We are indebted to Professor J. Polonsky for a sample of heartwood (and for confirmation of its authenticity) from *C. inophyllum* L. which was obtained from the Malagasy Republic (Madagascar). We also thank the University of Salford for a Demonstratorship (to B. J.) and the S.R.C. for two grants.