singlet on irradiation at δ 2·92; methylene protons (δ 1·78; 2H, *m*; C_6) which collapsed to a broad singlet on irradiation at δ 4·82; methylene protons at δ 4·47 (1H, *m*; H_7) and δ 4·92 (1H, *m*; H_7) which collapsed to an *AB* quartet ($J \simeq 5{\cdot}00$ Hz) an irradiation at δ 1·78; and a tertiary hydroxyl group (δ 3·75; 1H, *s*).

The above spectroscopic data suggested that acetylramosin *C* was tetra-acetylswertiamaroside [2]. This was confirmed by direct comparison of the IR and NMR spectra of the two compounds and a mixed m.p. determination.

EXPERIMENTAL

The IR spectrum was measured as a KBr disc, the UV spectrum in EtOH, and the NMR spectrum in $CDCl_3$. The MS was recorded on a Hitachi Perkin Elmer RMU 6 single focussing spectrometer, and the optical rotation on a Perkin Elmer 141 MC polarimeter.

Acknowledgements—We wish to thank Professor M. Koch, University of Paris, for the sample of tetra-acetylswertiamaroside, and Mr. J. Dougan for the MS.

REFERENCES

1. Hussain, S. F., Khattak, M. I. and Warsi, S. A. (1968) *Pak. J. Sci. Ind. Res.* **11**, 352.
2. Koch, M., Platt, M. and Le Men, J. (1964) *Bull. Soc. Chim., France* 403.

Phytochemistry, 1975, Vol. 14, pp. 298–299. Pergamon Press. Printed in England.

XANTHONES FROM THE HEARTWOOD OF CALOPHYLLUM RAMIFLORUM*

SUBRAMANIAM BHANU and FEODOR SCHEINMANN

The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England

and

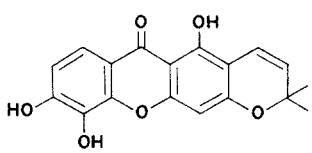
ALAN JEFFERSON

Department of Chemistry, Western Australia Institute of Technology, Bentley 6102, Perth, W. Australia

(*Received* 14 *May* 1974)

Key Word Index—*Calophyllum ramiflorum*; Guttiferae; xanthones; jacareubin; 2-(3-methylbut-2-enyl)-1-hydroxy-3,5,6-trimethoxyxanthone; euxanthone; 1,7-dihydroxyxanthone; 1-hydroxy-6,7-dimethoxyxanthone; chemotaxonomy.

Plant. Calophyllum ramiflorum Schwarz, Guttiferea. *Source.* W. Australia, identified by N. Byrnes, Botanist, Primary Industries Branch, Northern Territory Administration, Darwin, and confirmed by the Royal Botanic Gardens and National Herbarium of South Yarra, S.E.1, Victoria. *Previous work.* None on this species, but previous studies on the pigments from Guttiferae heartwoods [1,2] identify largely xanthones, biflavanoids [3] and coumarins [4]. *Calophyllum* species, apart from the Indian variety [5], contain jacareubin (**1**).

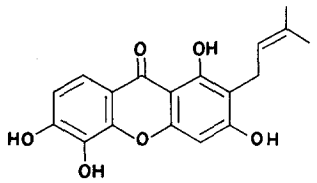


1

Present work. It has previously been suggested [2,6] that the presence of jacareubin (**1**) and/or the putative isoprenyl precursor 2-(3-methyl-2-butenyl)-1,3,5,6-tetrahydroxyxanthone (**2**) may be of taxonomic value in identifying *Calophyllum* species. Only in the Indian variety of *C. inophyllum* L. are these metabolites absent [5]. Further *Calophyllum* species are under examination for the presence of jacareubin (**1**) since this metabolite is required as a synthetic relay in the preparation of morellin analogues [7].

Extraction of the powdered heartwood of *Calophyllum ramiflorum* Schwartz with hot $CHCl_3$ and concentration of the extract gave a solid which contained largely jacareubin. Removal of the solvent from the filtrate gave a mixture which was washed with light petroleum to remove sitosterol, oils and waxes and the residue then chromatographed on silica. Elution $CHCl_3$–EtOAc led to isolation of 1,7-dihydroxyxanthone (euxanthone) and jacareubin (**1**) and a mixture of xanthones which were separated by methylation and further chromatography. Jacareubin dimethyl ether, 2-(3-methylbut-2-enyl)-1-hydroxy-3,5,6-trimethoxyxanthone and 1-hydroxy-6,7-dimethoxy-xanthone were identified by isolation and comparison with authentic specimens.

* Part XXVII in the series "Extractives from Guttiferae". For Part XXVI see Ref. 1.



2

These results support earlier suggestions that jacareubin (**1**) and its putative isoprenyl precursor (**2**) can be expected in the heartwood of *Calophyllum* species regardless of the geographic origin of the sample [2,6].

EXPERIMENTAL

IR spectra were in Nujol, unless otherwise stated. Analytical TCL was performed with silica-gel G, Stahl (Merck). All m.ps are uncorrected.

Extraction of Calophyllum ramiflorum. Powdered heartwood (1·0 kg) of *C. ramiflorum* was Soxhlet extracted with $CHCl_3$ for 4 days. The extract on concentration deposited a solid (*A*) which was filtered off. The filtrate was evaporated to dryness and the residue (*B*), washed with light petroleum (60–80°) (*C*).

Examination of A: TLC examination (HOAc–$CHCl_3$, 1:9) showed it to consist largely of jacareubin (**1**) which was recrystallized (MeOH) giving yellow plates (8·0 g), m.p. 252–254° (lit.[6] 253–256°), identical with an authentic specimen (m.m.p., IR, NMR and co-TLC). Dimethyl ether (**2**) from acetone–light petroleum (60–80°) as pale yellow prisms, m.p. 190–191° (lit.[8] 192–194°).

Chromatographic examination of B. The solid (2 g) was dissolved in $CHCl_3$ and chromatographed on silica gel (150 g). Elution with $CHCl_3$ followed by increasingly polar mixtures of $CHCl_3$–EtOAc gave several fractions which were combined into three fractions (1–3). Fraction 1 (eluted with EtOAc–$CHCl_3$, 1:9) crystallized from EtOAc to furnish yellow needles (200 mg), m.p. 239° (lit.[9,10] 239°) of euxanthone (m.m.p., IR, UV and NMR). Methyl ether m.p. 127–128° (lit.[10] 129·5°), identical in all respects with 1-hydroxy-7-methoxy xanthone (m.m.p., IR, TLC comparison). Fraction 2 (eluted with EtOAc–$CHCl_3$, 1:19, 1:9, 1:4) yielded jacareubin. Fraction 3 (eluted with EtOAc–$CHCl_3$, 1:3, 2:3) showed on TLC (HOAc–$CHCl_3$, 1:20), a mixture of phenolics ($FeCl_3$). The mixture was methylated [$(CH_3)_2SO_4/K_2CO_3$] and chromatographed on silica gel. Elution with benzene followed by increasingly polar mixtures of C_6H_6–EtOAc gave the following fractions: 2-(3-methylbut-2-enyl)-1-hydroxy-3,5,6-trimethoxyxanthone, crystallized (MeOH) as yellow needles (60 mg), m.p. 168–169° (lit.[8] 166–167°) identical with an authentic sample (m.m.p., IR, NMR and TLC); jacareubin dimethyl ether; and pale yellow prisms, m.p. 186–188° (lit.[4a] 187–189°), identified as 1-hydroxy-6,7-dimethoxy xanthone (m.m.p., IR, NMR and TLC comparison).

Chromatographic examination C. Solvent was removed from (*C*) and the residue $CHCl_3$ was chromatographed on silica gel. Elution with hexane with increasing quantities of EtOAc gave a number of fractions which were combined (TLC) to give sitosterol, m.p. 137° (lit.[8] 136°), MS *m/e* 414 M^+; and a thick yellow oil containing at least four components (TLC), which was not examined further.

Acknowledgement—One of us (S.B.) thanks The Association of Commonwealth Universities for a scholarship.

REFERENCES

1. Owen, P. J. and Scheinmann, F. (1974) *J. Chem. Soc.*, Perkin 1, 1018.
2. Carpenter, I., Locksley, H. D. and Scheinmann, F. (1969) *Phytochemistry*. **8,** 2013.
3. Jackson, B., Locksley, H. D., Scheinmann, F. and Wolstenholme, W. A. (1971) *J. Chem. Soc.* (*C*) 3971.
4. (a) Carpenter, I., Locksley, H. D. and Scheinmann, F. (1969) *J. Chem. Soc.* (*C*) 2421; (b) *idem* (1971); *ibid*, 3783.
5. Govindachari, T. R., Pai, B. R., Muthukumaraswamy, N., Rao, V. R. and Nityananda Rao N. (1968) *Indian J. Chem.* **6,** 57.
6. Scheinmann, F. and Sripong, N.-A. (1971) *Phytochemistry* **10,** 1331.
7. Quillinan, A. J. and Scheinmann, F. (1971) *Chem. Commun.* 966.
8. Jackson, B., Locksley, H. D. and Scheinmann, F. (1966) *J. Chem. Soc.* (*C*) 178.
9. Spoelstra, D. B. and van Royen, M. J. (1929) *Rec. Trav. Chim.* **48,** 370.
10. Locksley, H. D., Moore, I. and Scheinmann F. (1966) *J. Chem. Soc.* (*C*) 2265.