Phytochemistry, 1976, Vol. 15, pp 2016–2017. Pergamon Press. Printed in England.

XANTHONES AND TRITERPENOIDS FROM TIMBER OF *CALOPHYLLUM INOPHYLLUM**

V. KUMAR, S. RAMACHANDRAN and M. U. S. SULTANBAWA*
Department of Chemistry, University of Sri Lanka, Peradeniya Campus, Peradeniya, Sri Lanka

(*Received* 30 *April* 1976)

Key Word Index—*Calophyllum inophyllum*; Guttiferae; xanthones; jacareubin; 1,7-dihydroxy-3,6-dimethoxyxanthone; 6-desoxyjacareubin; 6(3-methyl-2-butenyl)-1,5-dihydroxyxanthone; triterpenes; chemotaxonomy.

Plant. Calophyllum inophyllum L., Guttiferae. *Source.* Central Sri Lanka, identified by S. Balasubramaniam. Department of Botany, University of Sri Lanka, Peradeniya Campus. *Previous work.* The heartwoods of *Calophyllum* species [1–6] have all been reported to contain jacareubin, apart from a South Indian sample of *Calophyllum inophyllum* [7]. The heartwood of this sample was reported to contain 1,5,6-trihydroxyxanthone and 6-(3-methyl-2-butenyl)-1,5-dihydroxyxanthone. A sample from the Malagasy Republic [1] was found to contain jacareubin, 6-desoxyjacareubin and 2-(3-methyl-2-butenyl)-1,3,5,6-tetrahydroxyxanthone while an Australian specimen [2] contained in addition 1,7-dihydroxyxanthone, 1,5,6-trihydroxyxanthone, 1,6-dihydroxy-5-methoxyxanthone and 2-(3-methyl-2-butenyl)-1,3,5-trihydroxyxanthone.

Present work. It has been suggested [8] that the presence of jacareubin or its putative isoprenyl precursor, 2-(3-methyl-2-butenyl)-1,3,5,6-tetrahydroxyxanthone may be of taxonomic value in identifying *Calophyllum* species. In the light of the reported absence of these matabolites from the South Indian sample, it was of interest to determine whether jacareubin or its precursor was present in a sample from Sri Lanka, since Sri Lanka is in close proximity to South India. Extraction of the powdered timber with hot petrol followed by hot $CHCl_3$ gave extracts which were chromatographed on Si gel. Elution of the petrol extract with petrol–C_6H_6 mixtures gave the triterpenes friedelin, friedelan-3β-ol and the xanthone, 6-(3-methyl-2-butenyl)-1,5-dihydroxyxanthone. Elution with C_6H_6 gave 6-desoxyjacareubin and sitosterol while a $CHCl_3$–C_6H_6 mixture eluted 1,7-dihydroxy-3,6-dimethoxyxanthone. The structure of the latter was established as follows. The xanthone was methylated with CH_2N_2 to give 1-hydroxy-3,6,7-tri-methoxyxanthone. The identical trimethoxyxanthone was obtained by methylating 1,3,6,7-tetrahydroxyxanthone. The absence of NaOAc shifts in the UV-maxima of the xanthone ruled out the presence of OH groups at C-3 or C-6. IR, NMR and MS were in agreement with the proposed structure. Elution with $CHCl_3$–MeOH gave jacareubin.

Chromatography of the $CHCl_3$ extract on Si gel similarly gave 6-desoxyjacareubin and jacareubin while a hot petrol extract of the bark afforded friedelin, friedelan-3β-ol, sitosterol and β-amyrin.

The presence of jacareubin in the Sri Lanka sample is in agreement with the suggestion by Scheinmann *et al.* [8] that jacareubin may be used as a chemotaxonomic marker for the genus *Calophyllum*. Studies on *C. tomentosum* in these laboratories [9] have shown that although jacareubin was present in timber obtained from the trunk, it was absent in timber obtained from the branches of certain plants investigated, suggesting that it was found only in the older timber. This could provide an explanation for the reported absence of jacareubin in the Indian sample [7]. If the presence of jacareubin is indeed age-dependent, this additional factor may have to be considered before it can be accepted as a chemotaxonomic marker.

EXPERIMENTAL

IR spectra were in Nujol and rotations in $CHCl_3$. TLC was performed with Si gel G. All mps are uncorrected. Comparison with authentic samples were carried out using mmps, IR and TLC.

Extraction of Calophyllum inophyllum. Powdered timber (6.75 kg) was extracted with hot petrol for 4 days and hot $CHCl_3$ for 36 hr. The resulting extracts were concentrated to dryness to give brown gums (22 g and 21.2 g respectively). Extraction of the bark (1 kg) with hot petrol for 2 days gave the bark extract (5.8 g).

Chromatographic separation of light petroleum extract of timber. The extract (5 g) was chromatographed on Si gel (150 g). Elution with petrol–C_6H_6 (9:1) gave friedelin (195 mg) which recrystallised from $CHCl_3$ as needles, mp 263–264°, $[\alpha]_D^{25}$ $-24°$ (lit. [5] 259-261°, $[\alpha]_D^{25}$ $-21°$) and freidelan-3β-ol (15 mg), colourless plates from $CHCl_3$, mp 280–282°, $[\alpha]_D^{25}$ $+21.8°$ (lit. [10] 280–282°, $[\alpha]_D^{21}$ $+21°$) both identical with authentic samples. Elution with petrol–C_6H_6 (3:1) yielded 6-(3-methyl-2-butenyl-1,5-dihydroxyxanthone (450 mg) which recrystallised from Me_2CO as yellow needles, mp 206° (lit. [4] 205–208°) identical with authentic sample. Elution with C_6H_6 gave 6-desoxyjacareubin (310 mg), yellow needles from Me_2CO, mp 209–210) (lit. [1] 211–213°) identical with authentic specimen. Further elution with C_6H_6 afforded sitosterol (20 mg), white needles from $CHCl_3$, mp 136–137°) Lit. [5] 136–137°). Elution with C_6H_6–$CHCl_3$ (1:1) gave 1,7-dihydroxy-3,6-dimethoxyxanthone (25 mg) which recrystallised from Me_2CO as light yellow needles, mp 268–269° (C:62.2, H:4.3, $C_{15}H_{12}O_6$ requires C:62.3, H:4.2); λ_{max} 238 (log ϵ 4.36), 256 (4.24), 315 (3.77) and 372 (4.18) nm. Addition of $AlCl_3$ shifted λ_{max} to 231 (log ϵ 4.32), 263 (4.29), 333 (4.13) and 396 (3.86). Addition of NaOAc or NaOAc–H_3BO_4 showed no significant shifts in λ_{max}. IR ν_{max} 3230, 1655 and 1610 cm^{-1}. PMR τ (DMSO-d_6) -3.07 (*s*, chelated OH), 2.63 (*s*, H-8), 3.14 (*s*, H-5), 3.51 and 3.72 (*ds* with *J* 2 Hz, H-2 and H-4), 6.14 and 6.17 (*s*, OMe); MS *m/e* 288 (100%), 273 (27), 259 (35), 258 (26) and 245 (54). Elution with $CHCl_3$–MeOH (49:1) gave

---

* Part 19 in the series "Chemical investigation of Ceylonese Plants". For Part 18 see Bandaranayake, W. M., Selliah, S., Sultanbawa, M. U. S. and Ollis, W. D. (1975) *Phytochemistry* **14**, 1878.

jacareubin (30 mg) which recrystallised from Me_2CO as yellow plates, mp 254–255° (lit. [4] 254–256°) identical with authentic sample.

Chromatographic separation of $CHCl_3$ extract of timber. The extract (6 g) was chromatographed on Si gel (150 g) to give 6-desoxyjacareubin (22 mg), mp 208–210° and jacareubin (1.57 g), mp 253–255°.

Chromatographic separation of light petroleum extract of bark. The extract (5 g) was chromatographed on Si gel (100 g) to give a mixture of friedelin and friedelan-3β-ol (288 mg) on elution with petrol–C_6H_6 (9:1) Separation of the mixture (100 mg) by preparative-TLC [3 × petrol–C_6H_6 (9:1)] gave friedelin (74 mg), mp 262–264° and friedelan-3β-ol (10 mg), mp 278–281°. Elution with petrol–C_6H_6 (1:1) yielded β-amyrin (120 mg), mp 199–200°, $[\alpha]_D^{25}$ + 85.1 (lit. [11] mp 197–197.5°), $[\alpha]_D^{19}$ + 88.4°) while elution with C_6H_6 gave sitosterol (230 mg), mp 137°.

1-*Hydroxy*-3,6,7-*trimethoxyxanthone.* (a) 1,3,6,7-Tetrahydroxyxanthone (30 mg) was methylated with CH_2N_2–Et_2O to give 1-hydroxy-3,6,7-trimethoxyxanthone (32 mg), mp 218–219° (lit. [12] 219.5–221°). (b) 1,7-Dihydroxy-3,6-dimethoxyxanthone (8 mg) was methylated similarly to give 1-hydroxy-3,6,7-trimethoxyxanthone (6 mg), mp 217–219°, identical with the above sample.

Acknowledgements—We thank Prof. R. H. Thomson, University of Aberdeen for NMR and MS and Dr. S. Balasubramaniam of the Department of Botany, University of Sri Lanka, Peradeniya Campus for help in the collection and identification of the plant specimen. This work was supported in part by a grant made by the United States Department of Agriculture under P. L. 480.

REFERENCES

1. Jackson, B., Locksley, H. D. and Scheinmann, F. (1969) *Phytochemistry* **8**, 927.
2. Al-Jeboury, F. S. and Locksley, H. D. (1971) *Phytochemistry* **10**, 603.
3. Scheinmann, F. and Sripang, N. A. (1971) *Phytochemistry* **10**, 1331.
4. Somanathan, R. and Sultanbawa, M. U. S. (1972) *J. Chem. Soc., Perkin 1* 1935.
5. Dahanayake, M., Kitagawa, I., Somanthan, R. and Sultanbawa, M. U. S. (1974) *J. Chem. Soc. Perkin 1* 2510.
6. Sultanbawa, M. U. S. (1973) *J. Natl Sci. Council Sri Lanka*, **1**, 123.
7. Govindachari, T. R., Pai, B. R., Muthukumaraswamy, N., Rao, V. R. and Nityananda Rao, N. (1968) *Indian J. Chem.* **6**, 57.
8. Carpenter, I., Locksley, H. D. and Scheinmann, F. (1969) *Phytochemistry* **8**, 2813.
9. Karunanayake, S. and Sotheeswaran, S. unpublished results.
10. Sainsbury, M. (1970) *Phytochemistry* **9**, 2209.
11. (1965) *Dictionary of Organic Compounds*, Vol. I, p. 228. Eyre & Spottiswoode, London.
12. Yates, P. and Stout, G. H. (1958) *J. Am. Chem. Soc.* **80**, 1691.

Phytochemistry, 1976, Vol. 15, p 2017. Pergamon Press. Printed in England.

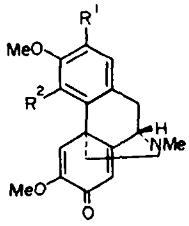
(+)-CORYTUBERINE FROM *CORYDALIS PALLIDA* VAR. *TENUIS*

Tetsuji Kametani, Makoto Takemura and Masataka Ihara
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai, Japan

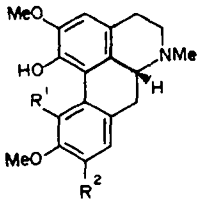
(*Received* 5 *June* 1976)

Key Word Index—*Corydalis pallida* var. *tenuis*; Papaveraceae; aporphine alkaloid; (+)-corytuberine.

In a previous paper [1], we reported the isolation of alkaloids, pallidine (**1**), kikemanine, corydalactam (alkaloid P), sinoacutine (**2**), (+)-isoboldine (**3**), capaurimine, capaurine, (−)-tetrahydropalmatine and protopine, from *Corydalis pallida* var. *tenuis* (Yatabe), which was collected in May 1969, in Sendai. Concurrently, Kaneko and Naruto [2] published the isolation of kikemanine, corydalactam, capaurimine, capaurine, capauridine, (−)-tetrahydropalmatine, protopine, (+)-tetrahydrocorysamine, (−)-scoulerine, (+)-corydaline, dihydrosanguinarine, oxysanguinarine, and ginnol from the same plant gathered in the southern part of Japan. We further studied the alkaloidal fraction of the plant collected in May 1975 in Sendai. Here we wish to report the isolation of (+)-corytuberine (**4**) along with the other alkaloids previously isolated by us. It is of interest that all four possible products from (+)-reticuline, by intramolecular phenol oxidative couplings, pallidine (**1**), sinoacutine (**2**), (+)-isoboldine (**3**) and (+)-corytuberine (**4**), occur in the same plant.



(1) R^1=OH, R^2=H
(2) R^1=H, R^2=OH



(3) R^1=H, R^2=OH
(4) R^1=OH, R^2=H

EXPERIMENTAL

(+)-*Corytuberine.* The basic fraction from 2.5 kg dried material was separated into phenolic and non-phenolic fractions, which were then purified by column chromatography on Si gel as previously reported [1]. Further elution of the phenolic fraction with $CHCl_3$–MeOH (19:1) gave a powder, which was recrystallised from $CHCl_3$ to give (+)-corytuberine (200 mg), mp 238–239° (uncorr.) [lit. [3], mp 240°], $[\alpha]_D^{20}$ +288° (*c* 0.026, EtOH) [lit. [3], $[\alpha]_D$ +282.7° (EtOH)]. *m/e* 327 (M^+), 312. UV: λ_{max}^{EtOH} 305, 270, 223 nm. NMR (CF_3CO_2H, TMS): δ3.37 (3H, *d*, *J* 5Hz, NMe), 4.08 (6H, *s*, 2 × OMe), 6.90 (1H, *s*, 3-H), 7.06 (2H, *s*, 8, 9-H) [4].

REFERENCES

1. Kametani, T., Ihara, M., and Honda, T. (1969) *Chem. Commun.* 1301; (1970) *J. Chem. Soc.* (*C*) 1060.
2. Kaneko, H. and Naruto, S. (1971) *J. Pharm. Soc. Japan* **91**, 101.
3. Kametani, T. (1968) *The Chemistry of the Isoquinoline Alkaloids*, p. 94. Hirokawa, Tokyo and Elsevier, Amsterdam.
4. Jackson, A. H. and Martin, J. A. (1966) *J. Chem. Soc.* (*C*) 2222.