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XANTHONES AND TRITERPENES OF *CALOPHYLLUM TOMENTOSUM*

SUBADRA KARUNANAYAKE*, SUBRAMANIAN SOTHEESWARAN*‡, M. UVAIS
S. SULTANBAWA* and SINNATHAMBY BALASUBRAMANIAM†

* Department of Chemistry and † Department of Botany, University of Peradeniya, Peradeniya, Sri Lanka

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Key Word Index—*Calophyllum tomentosum*; Guttiferae; xanthones; triterpenes; branch timber; sapwood; heartwood.

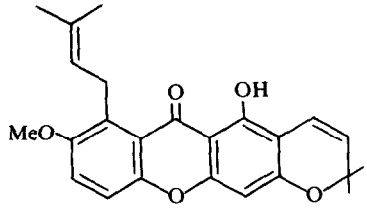
Abstract—The bark, branch timber, sapwood and heartwood extractives of *Calophyllum tomentosum* contain friedelin, friedelan-3β-ol, betulinic acid, taraxerol, taraxerone, calabaxanthone, 6-deoxyjacareubin, 1-5-dihydroxyxanthone, 1,6-dihydroxy-5-methoxyxanthone, 1,7-dihydroxyxanthone, jacareubin and 1,3,5-trihydroxy-2(3-methylbut-2-enyl)xanthone. The heartwood contains only xanthones. Sapwood and branch timber are chemically similar. Calabaxanthone is present in the bark but not in the branch timber which has only triterpenes and sitosterol.

INTRODUCTION

Nigam and Mitra [1] have reported the isolation of friedelin, friedelan-3β-ol and sitosterol from the bark of *Calophyllum tomentosum* T. Anders [1]. Govindachari *et al.* have studied the leaf extractives of the same plant [2] and isolated apetalactone, friedelin and canophyllol. In another study, Nigam and Mitra [3] characterized 4-substituted coumarins from the nuts of *C. tomentosum*. The author citation for *C. tomentosum* reported in these papers is incorrect [4]. *Calophyllum tomentosum* Wight [4], occurring in Sri Lanka, is considered to be morphologically different (A.G.J.H. Kostermans, personal communication) from the species found in India. *C. tomentosum* collected from two different localities in Sri Lanka has been subjected to chemical investigation and the work on the extractives of the bark, branch timber, sapwood and heartwood is reported herein.

RESULTS AND DISCUSSION

The bark extractives yielded, in addition to those reported from the Indian species [1], betulinic acid (0.10% dry wt), taraxerol (0.02%), taraxerone (0.01%) and calabaxanthone (**1**) [5] (0.06%). Calabaxanthone has been isolated from six of eleven Sri Lankan *Calophyllum* species examined to date. The branch timber extractives contained sitosterol, friedelin, friedelan-3β-ol and taraxerol. Calabaxanthone was not present in the branch timber.



1 Calabaxanthone

‡To whom correspondence should be addressed.

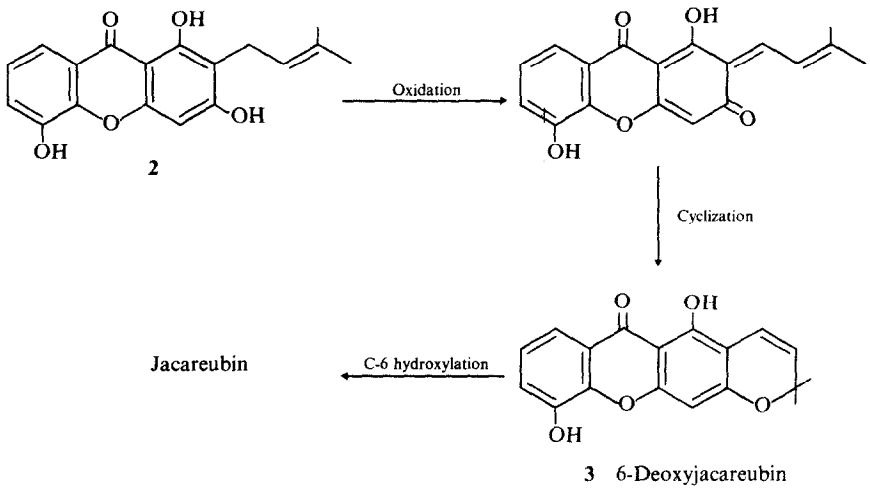
The sapwood extractives were chemically similar to the branch timber extractives. On the contrary, the heartwood had only xanthones. The following have been identified: 6-deoxyjacreubin (0.004%); 1,5-dihydroxyxanthone (0.01%); 1,6-dihydroxy-5-methoxyxanthone (0.042%); 1,7-dihydroxyxanthone (0.02%) and jacareubin (0.01%). Another xanthone (0.24%) isolated as the major product, mp 280°, was shown to be a hydroxyxanthone with an isoprenyl chain by NMR, IR, UV and mass spectral data. The DDQ cyclization gave a xanthone (**3**) which was identified as 6-deoxyjacareubin. These data were compatible with structure **2** for this major product. This is a rare xanthone [6, 7] and when present it has always co-occurred with either jacareubin or 6-deoxyjacareubin. The former is generally regarded as the chemotaxonomic marker [8] for *Calophyllum* species. In *C. tomentosum* all three xanthones are present. 1,3,5-Trihydroxy-2-(3-methylbut-2-enyl)-xanthone (**2**) can be considered [7] as the putative biogenetic precursor of 6-deoxyjacareubin (Scheme 1); C-6 hydroxylation [9] of the latter could yield jacareubin.

The absence of jacareubin in the branch timber of *Calophyllum tomentosum* and its presence only in mature timber is chemotaxonomically significant. The absence [10] of jacareubin in the Indian *Calophyllum inophyllum* species and its presence [8] in the Sri Lankan *C. inophyllum* extractives is probably due to the examination of immature samples by the Indian group.

EXPERIMENTAL

The bark, branch timber, sapwood and heartwood of *C. tomentosum* were collected at Deniyaya and Belihuloya, Sri Lanka. Analytical and prep. TLC were carried out with Si gel (Merck). Column chromatography was carried out using Si gel (Merck, 30–70 mesh). Mps were determined with Kofler hot stage apparatus.

The dried, powdered bark (5.4 kg) was successively extracted with hot petrol, C_6H_6 and MeOH. The petrol (88 g) and C_6H_6 (28 g) extracts were found to be similar. On standing, petrol extract deposited betulinic acid, mp 294° (lit. [11] 306–310°), $[\alpha]_D^{27}$ +8.5°



Scheme 1. Biogenetic relationship between 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)-xanthone, 6-deoxyjacareubin and jacareubin.

($CHCl_3$) (lit. [11] +9°). The filtrate was concd and chromatographed. On elution with C_6H_6–petrol the following were isolated in the order: calabaxanthone, mp 178° (lit. [5] 172°); taraxerone, mp 237° (lit. [12] 245–249°), $[\alpha]_D^{27}$ +28° ($CHCl_3$) (lit. [12] +12°); friedelin, mp 261° (lit. [13] 259°), $[\alpha]_D^{27}$ −20° ($CHCl_3$) (lit. [13] −27.3°); friedelan-3β-ol, mp 260° (lit. [14] 279–283°); taraxerol, mp 278° (lit. [15] 279°), $[\alpha]_D^{27}$ +6° ($CHCl_3$) (lit. [15] +30°); sitosterol, mp 136°.

The dried, powdered timber (4.7 kg) of the branch of *C. tomentosum* gave 5 g of petrol and 12 g C_6H_6 extractives. The two extractives were found to be similar on TLC analysis. The following were isolated by column chromatographic separations. Sitosterol, mp 136°; friedelan-3β-ol, mp 260° (lit. [14] 279–283°); friedelin, mp 261° (lit. [13] 259°), taraxerol 278° (lit. [15] 279°).

The timber of the main trunk was separated into heartwood and sapwood. TLC analysis showed that sapwood was chemically similar to the timber of the branch. The heartwood was powdered (2.5 kg) and on extraction gave 45 g C_6H_6 extract and 330 g MeOH extract. The C_6H_6 extract was stirred in Me_2CO when a yellow ppt., mp 280°, was obtained: M^+ 342 (57.1%); *m/z* at 297 (39), 269 (53), 258 (19), 257 (100); ^1H NMR (DMSO-d_6, 100 MHz): δ 13.1 (1 H, *s*), 7.6 (1 H, *q*), 7.3 (2 H, *m*), 6.4 (1 H, *s*), 5.22 (1 H, *t*, J = 6 Hz), 3.28 (2 H, *d*, J = 6 Hz), 1.78 and 1.68 (6 H, 2*s*); UV λ_{max}^{EtOH} nm (log ε): 235 (4.45), 246 (4.38), 300 (4.39) and 359 (3.80). This xanthone (100 mg) was treated with DDQ (75 mg) [7] in dry C_6H_6 (1 ml). The mixture was heated under reflux for 2 hr. The product was purified by prep. TLC to give a xanthone derivative which was identified as 6-deoxyjacareubin, mp 210° (lit. [16] 211–213°). Hence the original xanthone should be 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)-xanthone. After removing this xanthone, the mother liquor was separated on a column and elution with C_6H_6 gave the following: 6-deoxyjacareubin, mp 210° (lit. [16] 211–213°); 1,5-dihydroxyxanthone, mp 265 (lit. [16] 268–270°); 1,6-dihydroxy-5-methoxyxanthone, mp 246° (lit. [17] 243–246°); 1,7-dihydroxyxanthone, mp 238° (lit. [18] 238°); jacareubin, mp 254° (lit. [19] 254–256°).

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