



A TRIOXYGENATED DIPRENYLATED CHROMENXANTHONE FROM *CALOPHYLLUM MOONII*

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Key Word Index—*Calophyllum moonii*; clusiaceae (Guttiferae); root bark; dombakinaxanthone; calozeyloxanthone; friedelin; taraxerol; taraxerone; sitosterol.

Abstract—A cold hexane extract of the root bark of *Calophyllum moonii* afforded a new trioxxygenated diprenylated chromenxanthone (dombakinaxanthone) [5,8-dihydroxy-2,2-dimethyl-7,12-di(3-methyl-2-but-1-enyl)-2H,6H-pyrano-(3,2-b)xanthene-6-one], calozeyloxanthone, friedelin, taraxerol, taraxerone and sitosterol. © 1997 Elsevier Science Ltd

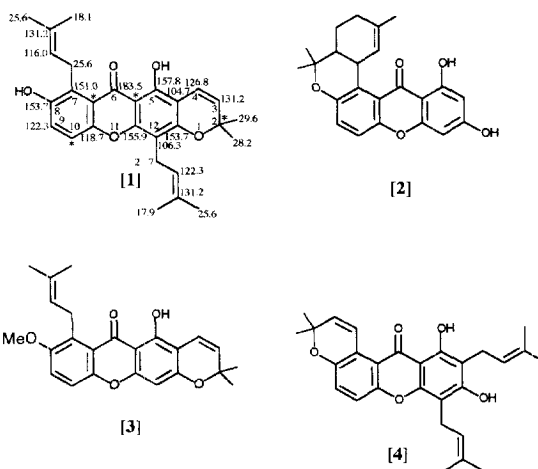
INTRODUCTION

During the past 40 years, a large number of xanthenes have been reported from natural sources. Xanthenes from higher plants have been obtained mainly from the families Clusiaceae (Guttiferae), Gentianaceae, Moraceae and Polygalaceae. In general, prenylated xanthenes are widely distributed in the Clusiaceae [1]. So far nearly 50 xanthenes have been reported from *Calophyllum* species in this family. Of these, 34 xanthenes are reported to be present in Sri Lankan *Calophyllum* species [2]. Prenylated xanthenes have been reported to show antibacterial and antifungal activities [3].

Calophyllum moonii (local name: Domba Kina) is an endemic tree which grows in the lowland, evergreen and wet zone forests in Sri Lanka. It was previously known as *C. soullattri* and later revised as an endemic species *C. moonii* [7]. Five xanthenes, two chroman acids, four triterpenoids, two pyranocoumarins and sitosterol have been previously reported from the stem, stem bark, [4, 5] and leaves [6] of this species. In this communication, we report the isolation and structural elucidation of a new trioxxygenated diprenylated chromenxanthone (dombakinaxanthone), together with other known compounds, from the cold hexane extract of the root bark of *C. moonii*.

RESULTS AND DISCUSSION

Dried and milled root bark was extracted with cold hexane to give the extract. Medium pressure liquid



chromatography (MPLC) of this afforded a new compound dombakinaxanthone (1), calozeyloxanthone (2), friedelin, taraxerol, taraxerone and sitosterol. Calozeyloxanthone (2) was previously reported from *Calophyllum zeylanicum* [8] but it is rare in nature.

Dombakinaxanthone (1), shown by UV and IR spectra to be a xanthone of $[M]^+ m/z$ 446, was isolated as a minor constituent. The 1H NMR (200 MHz) of 1 in $CDCl_3$ showed the presence of a chelated hydroxyl group at δ 13.45 (1H, s). This and the signal of δ 5.41 (1H, s) were exchangeable with D_2O , confirming the presence of two free hydroxyl groups in 1. The singlet at δ 1.47 (6H, 2 $\times$ Me), doublets at δ 5.58 (1H, J = 10 Hz) and 6.75 (1H, J = 10 Hz) suggested the presence of a 2,2-dimethyl-2H-pyrano ring. The methyl singlets at δ 1.88, 1.87, 1.77 and 1.68 for four olefinic methyl groups, two 2H doublets at δ 3.44 (J = 7.33 Hz) and δ 4.29 (J = 6.68 Hz) due to four benzylic protons and

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a 2H multiplet at δ 5.34 for two olefinic protons, suggested the presence of two 3-methyl-2-butenyl (isoprenyl) side-chains in **1**. The compound also had two adjacent aromatic protons and the expanded ^1H NMR spectrum showed two doublets at δ 7.19 ($J = 9$ Hz) and δ 7.25 ($J = 9$ Hz) due to them. The absence of any other high-field aromatic protons in **1** indicated that, the electron-rich phloroglucinol ring of the xanthone was fully substituted. The direct comparison of ^1H NMR and ^{13}C NMR spectra of **1** with calabaxanthone (**3**) [9], batukinaxanthone (**4**) [10] and trapizifolixanthone [11] suggested a linearly fused position for the 2,2-dimethyl-2H-pyrano ring in **1**. One of the two isoprenyl side-chains should be attached to C-4 of the xanthone nucleus, which is the only available position of the phloroglucinol ring of the xanthone. The remaining isoprenyl side-chain should be attached to the C-8 position of the xanthone nucleus. The 2H doublet due to two benzylic protons of this isoprenyl side-chain, appeared at a higher chemical shift. This shift must be due to the anisotropic effect of the neighbouring carbonyl group of the xanthone nucleus. From the above observations, **1** was identified as 5,8-dihydroxy-2,2-dimethyl-7,12-di(3-methyl-2-butenyl)-2H,6H-pyrano-(3,2-b) xanthone-6-one. ^{13}C NMR data further confirmed its structure and the complete ^{13}C NMR (50 MHz) chemical shifts (in CDCl_3) are given in the formula.

Further elution of the column with solvents gave a yellow crystalline compound. This compound was shown by UV and IR spectra to be a xanthone of $[\text{M}]^+ m/z$ 378. ^1H NMR spectra showed the presence of a 2,2-dimethylchroman moiety and an allylic methyl group. Comparison of its spectral and physical data with those in the literature suggested this compound to be calozeyloxanthone (**2**) [8]. In the original publication of calozeyloxanthone (**2**) [8], ^1H NMR signals due to adjacent aromatic protons of (**2**) in acetone- d_6 , were reported as a broad 2H singlet at δ 7.25, but in our spectrum of **2** in CDCl_3 , they appeared as two doublets at δ 7.20 (d , $J = 8.93$ Hz) and δ 7.14 (d , $J = 8.89$ Hz). These spectral data further confirm the structure **2** for calozeyloxanthone.

EXPERIMENTAL

General. Mps: uncorr. ^1H NMR spectra were recorded at 200 MHz for solns in CDCl_3 and are reported in δ values relative to TMS as int. standard.

Plant material. *Calophyllum moonii* Planch and Triana was identified and collected in February 1994 from the Kaneliya forest in the Galle district of Sri Lanka By Mr Shantha Ekanayake (Institute of Fundamental Studies, Kandy). The plant specimen was compared with herbarium specimens (specimen No. 24994) at the Royal Botanic Gardens, Peradeniya, Sri Lanka.

Extraction and isolation. Shade-dried plant material (0.4 kg) was milled and then extracted with cold hexane to yield 0.014 kg (3.5%) of extract. A portion (13

g) was sepd by silica gel CC (120 g, Merk Art 9385) by MPLC with hexane, EtOAc and MeOH as eluants. Further purification of column frs by prep. TLC (Merck Kieselgel 60 F₂₅₄) and flash and medium pressure CC (Merck Kieselgel 60) (230–300 mesh ASTM) with hexane and EtOAc as solvents gave **1** (51 mg, 0.014%), **2** (206 mg, 0.05%), friedelin (117 mg, 0.032%), taraxerol (14 mg, 0.004%) and sitosterol (12 mg, 0.003%).

Dombakinoxanthone (1). Yellow needles, mp 146–147°. UV $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ (log ϵ) nm: 209 (1.150), 231.5 (0.991), 294.0 (2.274), 318 (0.711), 391.5 (0.225). IR $\gamma_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3450, 3400, 2350, 1692, 1610, 1570, 1545, 1525, 1355, 1120, 920. ^1H NMR (200 MHz): δ 13.45 (1H, s, 5-OH), 7.25 (1H, d , $J = 9$ Hz, 10-H), 7.19 (1H, d , $J = 9$ Hz, 9-H), 6.75 (1H, d , $J = 10$ Hz, 4-H), 5.58 (1H, $J = 10$ Hz, 3-H), 5.41 (1H, s, 8-OH), 5.34 (2H, m , 2' and 2''-H), 4.29 (2H, d , $J = 6.68$ Hz, 1''-H), 3.44 (2H, d , $J = 7.33$ Hz, 1'-H), 1.88 (3H, s, Me), 1.87 (3H, s, Me), 1.77 (3H, s, Me), 1.68 (3H, s, Me), 1.47 (6H, s, 2X Me). EI-MS (70 eV) m/z (rel. int.): $[\text{M}]^+$ 446 (4), 376 (24), 375 (14), 360 (11), 361 (12), 333 (6), 332 (5), 306 (6), 307 (6), 167 (5), 67 (12), 42 (12), 41 (10), 26 (100).

Calozeyloxanthone (2). Yellow needles, mp 236–237°, lit. mp 236° [8]. UV $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ (log ϵ) nm: 209 (1.367), 240.5 (1.810), 261.5 (2.401), 313.5 (1.049), 377.5 (0.361). IR $\gamma_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3250, 2925, 2350, 1620, 1610, 1580, 1510, 1455, 1375, 1270, 1200, 1151, 1085. ^1H NMR (200 MHz): δ 12.3 (1H, s, 13-OH), 7.20 (H, d , $J = 8.93$ Hz, 7-H), 7.14 (1H, d , $J = 8.89$ Hz, 8-H), 6.3 (1H, d , $J = 10$ Hz, 10-H), 5.72 (1H, $br m$, 1-H), 4.67 (2H, m , 1'-H), 2.0 (5H, m , 3,4 and 4'-methylenes), 1.63 (3H, s, 2-Me), 1.45 (3H, s, 5-Me), 1.39 (3H, s, 5-Me). ^{13}C NMR (50 MHz): δ 183.2 (C-14), 165.6 (C-13), 162.4 (C-11), 157.9 (C-7a), 134.8 (C-2), 126.6 (C-7), 125.1 (C-8), 123.9 (C-13a), 116.9 (C-1), 98 (C-12), 93.2 (C-10), 77.4 (C-5), 39.8 (C-1a), 33.7 (C-4a), 28.5 (Me), 25.1 (C-3), 23.7 (C-4). EI-MS (70 eV) m/z (rel. int.): $[\text{M}]^+$ 378 (100), 360 (48), 362 (48), 334 (75), 292 (20).

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