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Benzyl-2,6-dimethoxy and benzyl-2,3,5,6-tetramethoxybenzoates from *Blainvillea latifolia* Linn.

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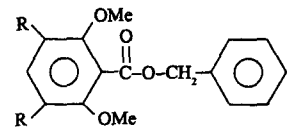
Abstract – Aromatic esters named benzyl-2,6-dimethoxy and benzyl-2,3,5,6-tetramethoxybenzoates along with previously reported compounds were isolated from aerial parts of *Blainvillea latifolia*.

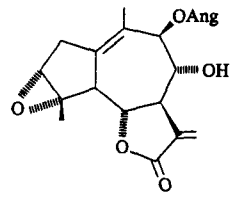
Key words – *Blainvillea latifolia*. Compositae. sesquiterpene lactones. acyclic diterpene. benzyl-2,6-dimethoxybenzoate and benzyl-2,3,5,6-tetramethoxybenzoate.

Introduction

Blainvillea latifolia Linn., an erect annual herb, belongs to the family-Compositae, tribe-Heliantheae and subtribe-Ecliptineae (Stuessy, 1977 and Robinson, 1981). So far three species of this genus namely *Blainvillea dichotoma* (Bohlmann *et al.*, 1981), *B. acmella* (Singh *et al.*, 1985) and *B. latifolia* (Singh *et al.*, 1988, Sawaikar *et al.* 1994, 1997) have been investigated chemically. In pursuing our interest in the constituents of this plant we now report the isolation and characterization of benzyl-2,6-dimethoxybenzoate **1** and benzyl-2,3,5,6-tetramethoxybenzoate **2** from its aerial parts in addition to previously reported subacaulin **3**, 5-desoxy pumilin **4**, zoapatanolide-A **5**, zoapatanolide-B **6** and 18-acetoxy-12,19-dihydroxy geranyl nerol **7**.



1 : R, R = H
2 ; R, R = OMe



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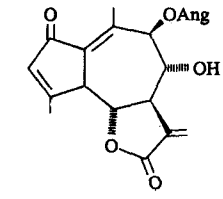

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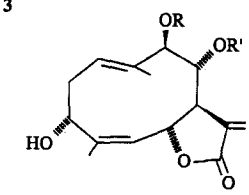
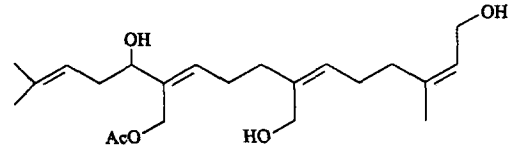


5 : R = H, R' = Ang
6 : R = Ang, R' = H



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Experimental

General-IR – Perkin Elmer 577, Magna-550 FTIR Nicolet spectrometers. UV: Varian Carry 118. ^{1}H NMR: Bruker WH 400 MHz, JEOL FX 90Q. EIMS: Varian Mat 711, Varian CH 7, Hitachi model RMU 6E mass spectrometers. HPLC: Knaufer instrument. $[\alpha]_D$: Perkin

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Elmer polarimeter. CC: Over silica gel (BDH, 60-120 mesh). Prep. TLC: Over Kiesel gel PF_{254}, $^{60}F_{254}$ (E. Merck) plates. Melting points were recorded in soft glass capillaries in an electrothermal m.p. apparatus and are uncorrected. Chemical shifts are reported in ppm.

Plant materials – The aerial parts of *Blainvillea latifolia* were collected from M/s United Chemicals and Allied Products, Calcutta and voucher specimen deposited at RUBL Herbarium, Jaipur.

Extraction and Isolation – The air-dried coarsely powdered aerial parts (2 kg) were extracted with Et_2O-petrol-MeOH (1:1:1) at room temperature for 24 hours. Evaporation of the solvent in vacuo gave a greenish semi-solid mass, it was defatted by dissolving in 200 ml MeOH and leaving over night at 2°. After filtration precipitate was rejected and filtrate was column chromatographed over silica gel and gave fr.1 (petrol), fr.2 (petrol-Et_2O, 4:1), fr.3 (petrol-Et_2O, 1:1), fr.4 (Et_2O) and fr.5 (Et_2O-MeOH, 9:1). Preparative TLC of fr.3 (silica gel PF_{254}) yielded phytol 40 mg, β-sitosterol 50 mg, stigmasterol 20 mg, benzyl-2,6-dimethoxy benzoate **1** 30 mg and benzyl-2,3,5,6-tetramethoxybenzoate **2** 40 mg. Fraction 4 on prep. TLC, Et_2O-MeOH (9:1) afforded subacaulin **3**, 15 mg (R_f 0.4), 5-desoxy pumilin **4**, 12 mg (R_f 0.35), zoapatanolide-A **5**, 20 mg (R_f 0.2) and zoapatanolide-B **6**, 18 mg (R_f 0.15). Fraction 5 on repeated prep TLC gave impure product which was further separated by HPLC (MeOH-H_2O, 7:3, analytical) RP 18 column (R_t 10.8 min). giving a further amount of **5,6** and 18-acetoxy-12-19-dihydroxy geranyl nerol, **7**, 30 mg.

Benzyl-2,6-dimethoxybenzoate, 1 – Colorless oil, IR ν_{max} (CCl_4): 3000-2800, 1750 (COOR), 1610, 1590 (Ph), 1480, 1400, 1310, 1265, 1125, 1080 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44 (2H, dd, J=7.5, 2 Hz, 2 x Ar-H), 7.36 (3H, m, 3 x Ar-H), 7.26 (1H, d, J=7.5 Hz, 1 x Ar-H), 6.55 (2H, d, J=7.5 Hz, 2 x Ar-H), 5.37 (2H, s, O-$\underline{CH_2}$-Ph), 3.8 (6H, s, 2 x OMe). MS m/z (rel. int.): 272 $[M]^+$ (30) (Calc. for $C_{16}H_{16}O_4$: 272), 181 $[M\text{-}CH_2Ph]^+$ (5), 165 $[C_6H_3(OMe)_2CO]^+$ (100), 149 [181-MeOH]$^+$ (20), 91 $[\text{-}CH_2C_6H_5]^+$ (50).

Benzyl-2,3,5,6-tetramethoxybenzoate, 2 – Colorless oil, IR ν_{max} (CCl_4): 2900-2800, 1735 (COOR), 1590 (Ph), 1380, 1280, 1130, 1100, 1080 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47 (2H, brd, J=7.5 Hz, 2×Ar-H), 7.35 (3H, m, 3 x Ar-H), 6.57 (1H, s, 1 x Ar-H), 5.39 (2H, s, -O-$\underline{CH_2}$-Ph), 3.85 (6H, s, 2 x OMe), 3.74 (6H, s, 2 x OMe). MS m/z (rel. int.): 332.126 $[M]^+$ (90) (*Calc. for $C_{18}H_{20}O_6$: 332.126*), 317 [M-Me]$^+$ (24), 289 [317-CO]$^+$, 225 $[C_6H_1(OMe)_4CO]^+$ (18), 197 [225-CO]$^+$ (18), 91 $[\text{-}CH_2C_6H_5]^+$ (100).

Results and Discussion

Compounds **1** and **2** were isolated as colorless oil. The presence of aromatic ester functions was ascertained by the appearance of strong obsorption bands at 1750, 1610 cm^{-1} and 1735, 1590 cm^{-1} in their IR spectra, respectively. High resolution mass spectrometry has established their molecular formulae. The high field ^1H NMR spectrum of **1** showed the presence of a sharp singlet at δ 5.37 corresponding to benzylic protons. A singlet at δ 3.8 integrated for six protons was assigned to two methoxyl groups. Eight aromatic protons displayed signals in the region of δ 6.55 to 7.44. In the ^1H NMR spectrum of **2** benzylic protons appeared at δ 5.39 as singlet and four methoxy groups exhibited a pair of singlets at δ 3.85 and δ 3.74 each integrated for six protons. Six aromatic protons gave signals in the region δ 6.57 to 7.47. Both compounds showed similar fragmentation behaviour. In the mass spectrum of **1** highly abundant molecular ion peak was observed at m/z 272 along with some important fragments at m/z 181 $[M\text{-}CH_2Ph]^+$, 165 $[C_6H_3(OMe)_2CO]^+$ and 91$[C_6H_5CH_2]^+$ while in the mass spectrum of **2** besides a molecular ion peak at m/z 332, important fragments were observed at m/z 317 [M-Me]$^+$, 225 $[M\text{-}C_6H_1(OMe)_4CO]^+$, 197[225-CO]$^+$, and 91$[C_6H_5CH_2]^+$.

The above spectral data were in close agreement with those reported earlier for **1** by Joshi et al. 1983 and for **2** by Bohlmann et al. 1980.

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