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A GERANYL NEROL DERIVATIVE AND OTHER CONSTITUENTS FROM *BLAINVILLEA LATIFOLIA*

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Key Word Index—*Blainvillea latifolia*; Compositae; sesquiterpene lactones; guaianolides; heliangolides; diterpene; geranyl nerol derivative.

Abstract—The aerial parts of *Blainvillea latifolia* afforded in addition to widespread compounds the heliangolides zoapatanolide A and B, the guaianolide subacaulin and a new one as well as a further derivative of geranyl nerol. The structures were elucidated by high field ^{1}H NMR studies.

INTRODUCTION

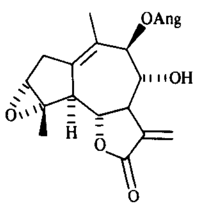
The genus *Blainvillea* (Compositae, tribe Heliantheae) is placed in the subtribe Ecliptinae [1, 2]. So far two species have been investigated chemically. Both gave melampolides and some other sesquiterpene lactones [3, 4]. We now have studied a sample of *B. latifolia* L. The results are discussed in this paper.

RESULTS AND DISCUSSION

The extract of the aerial parts afforded, after separation, in addition to widespread compounds (see Experimental), subacaulin **1** [5], zoapatanolide A and B (**3** and **4**) [6] and the new guaianolide **2** as well as the geranyl nerol derivative **5**.

The structure of **2** could easily be deduced from the ^{1}H NMR spectrum which was close to that of dehydroleucodin [7] and in part to that of **1** [5]. Accordingly, a 5-desoxypumilin was present. The configuration at C-8 and C-9 followed from the observed couplings and the relative position of the ester group from the chemical shifts of H-8 and H-9.

The ^{1}H NMR spectrum of **5** (see Experimental) clearly showed that derivative of geranyl geraniol or nerol was present as signals for three olefinic methyls and three oxygenated methyls were visible, two being hydroxymethylene and one an acetoxy methylene group. Thus two problems had to be solved, the relative position of the oxygen functions and the configurations of the double bonds. Only in deuteriobenzene were the signals sufficiently separated to allow spin decoupling experiments. The protons of the oxygen bearing carbons led to a broadened singlet at δ4.10 (2H), a broadened doublet at δ4.11 (2H), a pair of doublets at δ4.90 and 4.82 (2H) and a triplet at 4.25 (1H). Furthermore, four broadened triplets for olefinic protons were visible. The irradiation at δ5.35 sharpened the methyl singlets at 1.74 and 1.64. Accordingly, H-14 was assigned. Starting with this signal H-13 and H-12 could be determined. As the irradiation at δ5.52 sharpened the pair of doublets and the H-12 triplet also H-18 and H-10 could be assigned. Only by using Gauss multiplication the coupling of H-19, H-6 and H-1 becomes clear to obtain the necessary further assignements of H-19 and H-20. NOE difference spectroscopy established the configurations of the double bands. Clear effects were observed between H-17 and H-13 (5%), between H-16 and H-14 (10%), between H-20 and H-2 (10%), between H-18 and H-9, between H-19 and H-5 (3%) as well as between H-12 and H-10 (10%). Thus the structure was settled. Geranyl nerol derivatives may be characteristic for parts of the subtribe Ecliptinae as these compounds have been isolated from *Aspilia* [8], *Balsamorhiza*



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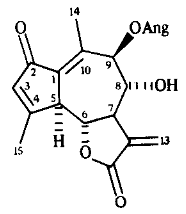

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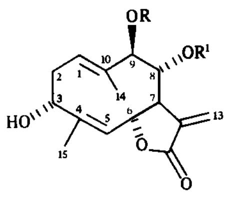
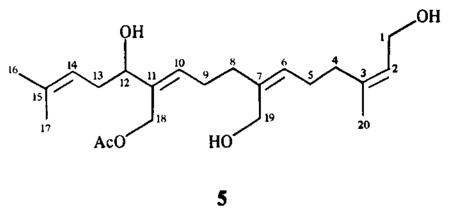


3 R = H, R¹ = Ang
4 R = Ang, R¹ = H



5

Table 1. ^{1}H NMR spectral data of **2** (400 MHz, $CDCl_3$, δ values)

H		H	
3	6.22 *br s*	13	6.27 *d* ($J = 2.5$)
5	3.62 *br d* ($J = 8$)	14	2.29 *br s*
6	3.67 *t* ($J = 8, 8$)	15	2.37 *br s*
7	3.20 *tt* ($J = 8, 2.5$)	3	6.29 *qq* ($J = 1.5,7$)
8	3.96 *t* ($J = 8$)	4	2.06 *dq* ($J = 7, 1.5$)
9	5.53 *br d* ($J = 7$)	5	2.02 *dq* ($J = 1.5, 1.5$)
13	6.29 *d* ($J = 2.5$)		

Table 2. ^{1}H NMR spectral data of **5** (400 MHz, C_6D_6, δ values)

H		H	
1	4.11 *dq*	13	2.40 *br d*
2	5.52 *tq*	14	5.82 *br t*
4	2.08 *br t*	16	1.74 *dt*
5	2.13 *br q*	17	1.64 *dt*
6	5.30 *br t*	18	4.10 *br s*
8	2.29 *br t*	19	4.90 *d*
9	2.47 *br q*	19	4.82 *d*
10	5.35 *br t*	20	1.70 *dt*
12	4.25 *t*	OAc	1.78 *s*

J [Hz]: 1,2 = 4, 5 = 5, 6 = 8, 9 = 9, 10 = 12, 13 = 13, 14 ~ 7; 1, 20 = 2, 20 = 10, 12 = 13, 16 = 13, 17 = 14, 16 = 14, 17 ~ 1

[9], *Dimerostemma* [10, 11] *Kingianthus* [12], *Zexmenia* [13] and *Zinnia* [14]. Guaianolides related to 2 are reported from *Balsamorhiza* [9] and *Berlandiera* [5].

EXPERIMENTAL

The air-dried coarsely powdered aerial parts, 500 g (supplied by M/S United Chemicals and Allied Products, Calcutta, voucher deposited in Rajasthan University Botany Herbarium) were extracted with Et_2O-petrol–MeOH (1:1:1) in cold conditions. The concd extract on CC fractionation (silica gel) gave petrol (fr. 1), petrol–Et_2O (4:1) (fr. 2), petrol-Et_2O (1:1) (fr. 3), Et_2O (fr. 4) and Et_2O-MeOH (9:1) (fr. 5) fractions. ^{1}H NMR spectra of the last two fractions showed the presence of some interesting compounds. TLC of fr. 3 (silica gel PF 254) petrol–Et_2O (7:3) yielded phytol 20 mg, β-sitosterol 15 mg, stigmasterol 7 mg and benzyl tetramethoxy benzoate, 2 mg. Fraction 4 on TLC, Et_2O–petrol (9:1) afforded subacaulin (**1**) 3 mg (R_f 0.4), a new guaianolide (**2**) 2 mg (R_f 0.35), zoapatanolide A (**3**), 5 mg (R_f 0.2) and zoapatanolide B (**4**) 2 mg (R_f 0.15). TLC of fraction (5) Et_2O–MeOH (9:1) gave crude UV inactive band which was further separated by HPLC (MeOH–H_2O, 7:3, analytical), RP 18 column (R_t 10.8 min.) affording a further amount of **3**, **4** and a new diterpene **5** (5 mg).

Known compounds were identified by comparing their 400 MHz ^{1}H NMR spectra with those of authentic materials. The purity of all compounds was checked by their homogeneous behaviour on TLC in different solvent systems and by their ^{1}H NMR spectra.

5-Desoxy pumilin (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3500 (OH), 1780 (γ-lactone), 1720 (C=CCO_2R), 1690 (C=C-C=O); MS *m/z* (rel. int.) 358.141 (10) (calc. for $C_{20}H_{22}O_6$ 358.142), 258 $[M - RCO_2H]^+$ (8), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (52); $[\alpha]_D^{24°} = +240$ ($CHCl_3$; *C* 0.08).

18-*Acetoxy*-12,19-*dihydroxy geranyl nerol* (**5**): Colourless oil, IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3520 (OH) 1730 (OAC), 1385, 1270; MS: Molecular ion peak is not visible; *m/z* (rel. int.) 302 $[M - AcOH - H_2O]^+$ (0.05), 86 $[C_5H_{10}O]^+$ (100), 84 $[C_5H_8O]^+$ (100); CIMS-isobutane: 381 $[M + 1]^+$ $[\alpha]_D^{24} = +147$ ($CHCl_3$; *C* 0.1).

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