Phytochemistry, Vol. 26, No. 8, pp. 2427–2429, 1987.
Printed in Great Britain.

0031-9422/87 \$3.00 + 0.00

BENZOXANTHENONE DERIVATIVES FROM *POLEMANNIA MONTANA*

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(*Revised received* 24 *December* 1986)

Key Word Index—*Polemannia montana*; Umbelliferae; isoapiol; benzoxanthenones derivatives.

Abstract—In addition to known compounds three benzoxanthenones were isolated. The structures were elucidated by using several high field NMR techniques which allowed the determination of the substitution pattern and the assignment of all signals.

INTRODUCTION

The small genus *Polemannia* (Umbelliferae) in the subfamily Apioideae has not previously been examined for its chemical constituents. In the present study we have investigated *P. montana* Schlechter et H. Wolff., collected in Natal.

The root extract of this plant gave the acetylenic compounds **1** and **2**, which are widespread in this family [1], 4α-hydroxygermacra-1(10)*E*,5*E*-diene, nerolidol and two aromatic compounds (**3** and **8**) while the aerial parts gave germacrene D, squalene, δ-cadinene, linalol, δ-cadinol, 4α-hydroxygermacra-1(10)*E*,5*E*-diene, **1** and three aromatic compounds, the benzoxanthenones **7–9**.

The NMR data of **3** (Tables 1 and 2) indicated the presence of apiol or isoapiol. The relative position of the oxygen functions was determined by NOE difference spectroscopy. Saturation of one methoxy signal caused clear effects with the other methoxy group and with one of the olefinic protons. As the data of isoapiol [2] are not reported in the literature we have added these in Tables 1 and 2.

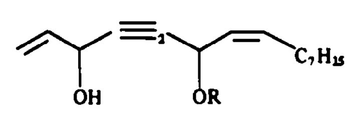
The ^{1}H NMR spectra of **7–9** (Table 1) were in part very similar. In addition to small shift differences it was obvious that compound **8** had two, compound **7** four and compound **9** six methoxy groups. Furthermore, **8** had two and **7** one dioxymethylene group. In the case of **7** spin decoupling allowed the assignment of the sequences H-6′ H-7, H-8 (H-9), H-8′ (H-9′), H-7′. The chemical shift of the latter required a neighbouring keto group while that of H-6 was close to that of H-6 in **3**. Thus a preliminary structure could be deduced from these data. However, the relative position of the oxygen functions had to be determined. This was achieved by NOE difference spectroscopy (Table 3), which also allowed the determination of the relative configurations at C-7, C-8 and C-8′. The ^{13}C NMR spectrum of **7** (Table 2) also supported the proposed structure. However, the complete assignment of the NMR spectral data required in addition to spin decoupling, NOE difference spectroscopy, two dimensional hetero-correlated spectra and selective INEPT spectra by using the long range couplings [3] (INEPT,

Table 1. ^{1}H NMR spectral data for **3** and **7–9** (400 MHz, $CDCl_3$, δ-values)

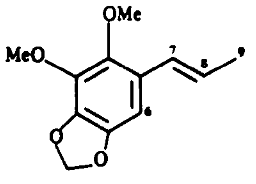
	3*	**7**	**8**	**9**
H-6	6.62 *br s*	6.62 *br s*	6.52 *br s*	6.59 *br s*
H-7	6.60 *dq*	3.31 *br dd*	3.27 *br dd*	3.24 *br dd*
H-8	6.06 *dq*	2.57 *br dq*	2.50 *br dq*	2.57 *br dq*
H-9	1.88 *dd*	1.16 *d*	1.14 *d*	1.13 *d*
H-6′	—	3.21 *ddd*	3.18 *ddd*	3.10 *ddd*
H-7′	—	7.05 *ddd*	7.06 *ddd*	6.99 *ddd*
H-8′	—	2.23 *br ddq*	2.23 *br ddq*	2.19 *br ddq*
H-9′	—	0.65 *d*	0.71 *d*	0.65 *d*
3-OMe	4.01 *s*	3.79 *s*	3.93 *s*	3.85 *s*
4-OR }	5.89 *s*	3.85 *s* }	5.90 *d*	3.86 *s*
5-OR }		3.81 *s* }	5.86 *d*	3.81 *s*
3′-OMe	—	3.97 *s*	3.97 *s*	3.78 *s*
4′-OR	— }	5.68 *s* }	5.78 *s*	4.21 *s*
5′-OR	— }	5.65 *s* }	5.75 *s*	3.45 *s*

*2-OMe: 3.75 *s*.

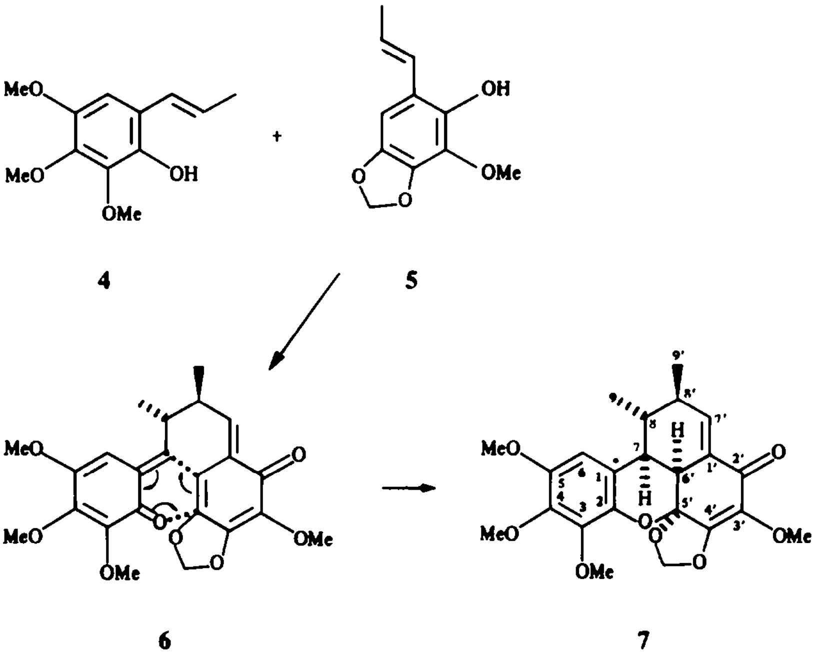
J[Hz]: **3**: 7,8 = 16; 7,9 = 2; 8,9 = 7; **7–9**: 6′,7 = 7.5; 6′,7′ = 6′,8′ = 7,8 = 2.5; 7′,8′ = 1; 8,9 = 7; 8′,9′ = 7.5; 4,5–OCH_2O = 1.5.

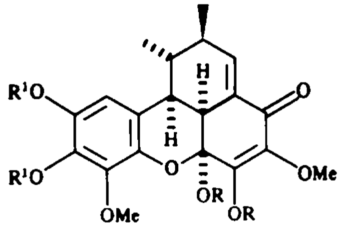


1 R = H
2 R = Ac



3





8 R = R¹ = —CH₂—
9 R = R¹ = Me

refocused, decoupled pulse sequence; typical values: 90° ^{1}H pulse 21 msec (40 DB under 0.2 W); 90° ^{13}C pulse 6.5 sec; $J_{^{13}C,^{1}H} = 5$ Hz). As a clear NOE was observed between one of the dioxymethylene protons and the C-3 methoxy group it was possible to assign both dioxymethylene protons as C-5' showed a coupling with the second one and H-6'. This clearly established the relative position of the oxygen functions at C-3'–C-5'.

Similarly the structures of **8** and **9** could be determined by spin decoupling and NOE difference spectroscopy. Compound **7** was probably formed biogenetically by phenolic oxidation of **4** followed by reaction with **5** leading to **6**, with afforded **7** by the heterodien reaction as shown in the Scheme.

The fragmentation pattern in the mass spectra of **7–9** was characterized by RDA and splitting of the ether function at C-5'. The only known compound of this type is carpanone isolated from a *Cinnamomum* species (Lauraceae) [4] its structure being established by several synthesis [5–7] and by X-ray analysis [5]. The reported ^{1}H NMR data were close to those of **7–9**. The compound with no oxygen functions at C-4, C-5, C-4' and C-5' we have named polemannone. Carpanone and compounds **7–9** are all racemic.

Table 2. ^{13}C NMR data for 3 and 7–9 (100.7 MHz, $CDCl_3$, δ-values)

	3*	7	8	9
C-1	124.9	118.3	116.8	119.2
C-2	125.1	138.9	137.9	139.1
C-3	137.5	142.8	135.8	142.1
C-4	136.4	141.7	133.6	141.3
C-5	143.8	148.1	143.7	147.5
C-6	98.3	106.1	100.6	106.2
C-7	124.7	33.7	34.1	33.8
C-8	145.0	35.4	35.6	35.7
C-9	18.7	21.4	21.4	21.5
C-1′	—	126.3	126.4	127.2
C-2′	—	183.1	183.2	183.3
C-3′	—	131.4	131.5	138.7
C-4′	—	151.5	151.5	161.4
C-5′	—	102.2	101.4	97.1
C-9′	—	35.1	35.1	35.3
C-7′	—	142.9	143.1	142.1
C-8′	—	36.3	36.3	36.5
C-9′	—	21.1	21.1	21.2
3-OR	60.0	61.4	60.2	61.3
4-OR	101.1	61.3	101.1	61.3
5-OR		56.4		56.4
3′-OR	—	59.8	59.8	60.6
4′-OR	—	98.8	98.8	61.1
5′-OR	—			53.3

*2-OR: 61.4.

EXPERIMENTAL

Plant material of *P. montana* (voucher 77/112, deposited in the Herbarium of the Botany Department of the University of Natal) was collected on the road to Drakensberg Garden, Natal, RSA. Air-dried aerial parts (190 g) were extracted with Et_2O–petrol, 1:2, at room temp. Silica gel CC and prep. TLC (silica gel, PF 254) gave 20 mg germacrene D, 10 mg squalene, 7 mg δ-cadinene, 9 mg linalol, 5 mg δ-cadinol, 20 mg 4-hydroxygermacra-1(10)*E*,5*E*-diene, 10 mg **1** and a polar fraction, which gave by prep. TLC ($CHCl_3$, two developments), 15 mg **8** (R_f 0.5), 24 mg **9** (R_f 0.4) and 25 mg **7** (R_f 0.3). The roots (40 g) were extracted and the compounds separated as above to give 10 mg **3**, 13 mg 4α-hydroxygermacra-1(10)E,5E-diene, 10 mg **2**, 30 mg nerolidol, 25 mg **1** and 6 mg **8**. Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic samples.

Isoapiol (**3**). MS m/z (rel. int.): 222.089 $[M]^+$ (100) (calc. for $C_{12}H_{14}O_4$: 222.089), 207 (8), 177 (40), 149 (20).

4,5-*Dimethoxy-4′,5′-methylendioxypolemannone* (**7**). Colourless crystals, mp 197°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1680 (C=O); MS m/z (rel. int.): 430.162 $[M]^+$ (100) (calc. for $C_{23}H_{26}O_8$: 430.162), 400 (25), 246 (40), 223 (70), 192 (60).

4,5,4′,5′-*Bismethylendioxypolemannone* (**8**). Colourless crystals, mp 170°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1690 (C=O); MS m/z (rel. int.): 414.130 $[M]^+$ (100) (calc. for $C_{22}H_{22}O_8$: 414.130), 384 (20), 246 (25), 207 (60), 177 (56), 149 (20), 121 (10).

4,5,4′,5′-*Tetramethoxypolemannone* (**9**). Colourless crystals, mp 140°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1690 (C=O); MS m/z (rel. int.): 446.195 $[M]^+$ (70) (calc. for $C_{24}H_{30}O_8$: 446.195), 414 (60), 399 (40), 385 (40), 226 (15), 223 (100), 192 (65).

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Table 3. NOE values for 7 and 9 (% in parenthesis)

Saturation	7				9	
H-9	H-8′ (7)	H-6′ (7)	H-7 (6)			
H-9′	H-8 (4)	H-7′ (5)				
H-8	H-6 (12)	H-7 (5)	H-8′ (3)	H-9′ (4)		
3-OMe	4′,5′—OCH_2–O (5.65)βH (2)					
5-OMe	H-6 (8)				H-6 (10)	
5′-OMe					4′-OMe (3)	3-OMe (4.5)
4′-OMe					5′-OMe (2.5)	3′-OMe (6)