

SHORT REPORTS

A CLERODANE LACTONE AND A TREMETONE DERIVATIVE
FROM *BAHIANTHUS VISCIDUS**

FERDINAND BOHLMANN,† RAJINDER K. GUPTA,† ROBERT M. KING‡ and HAROLD ROBINSON‡

† Institute for Organic Chemistry, Technical University of Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, West Germany;

‡ Smithsonian Institution, Washington, DC 20560, U.S.A.

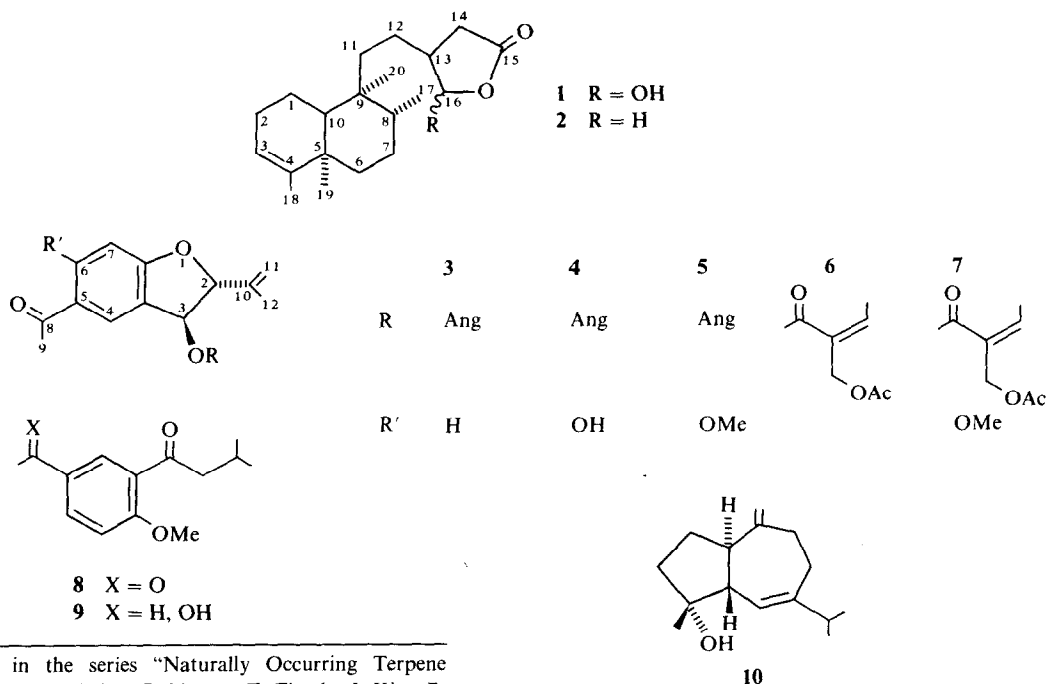
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Key Word Index—*Bahianthus viscidus*; Compositae; diterpene; new clerodane lactone; benzofuran; new tremetone derivative.

The monotypic genus *Bahianthus* is placed in the *Gyptis* group of the tribe Eupatorieae (Compositae) near *Agrianthus* [1]. It was of interest, therefore, to determine whether the chemistry shows relationships between these two genera. The aerial parts of *B. viscidus* (Baker) K. et R. afforded, in addition to germacrene C and D, caryophyllene, α -humulene, euparin, the angelate **3** [2] and the lactone **1** [3], a further clerodane derivative. The ^1H NMR data (Table 1) indicated the presence of **2**, the 16-desoxy derivative of **1**. Spin decoupling showed that the double doublets at δ 4.44 and 3.91 were coupled with a broad multiplet at 2.44, which was further coupled with a double doublet at 2.65 and a three-fold doublet at 2.15. This clearly indicated that we were dealing with the protons H-13, H-14 and H-16, as the other signals were very similar to those of **1**. This is further supported by the

typical fragment m/e 191 ($\text{C}_{14}\text{H}_{23}^+$) in the mass spectrum of **2**, which is formed by splitting the 9,11-bond. The configuration at C-13 was not determined. Comparing the optical rotation with those of similar diterpenes favoured the presence of a clerodane derivative, a type which is widespread in the tribe Eupatorieae. The roots contained the widespread tridecapentaynene, germacrene C and D, α -humulene, caryophyllene, euparin, the tremetone derivatives **4** [4], **5** [5] and **6** [4], the diketone **8** [2], the corresponding carbinol **9** [2] and the carbinol **10** [2] as well as a new compound, the acetoxangelate **7** its spectral data being very similar to those of **6** (Table 2).

This investigation showed that the chemistry of *Bahianthus* is not closely related to that of *Agrianthus* [4]. However, relationships to the *Acritopappus* group are obvious.



* Part 304 in the series "Naturally Occurring Terpene Derivatives". For Part 303 see Bohlmann, F., Ziesche, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 263.

Table 1. ^1H NMR spectral data of compound **2** (270 MHz, CDCl_3 , TMS as internal standard)

2-H	2.00 <i>m</i>	16'-H	3.91 <i>dd</i>
3-H	5.19 <i>br. dd</i>	17-H	0.80 <i>d</i>
13-H	2.44 <i>ddddt</i>	18-H	1.58 <i>dd</i>
14-H	2.65 <i>dd</i>	19-H	1.00 <i>s</i>
14'-H	2.15 <i>ddd</i>	20-H	0.73 <i>s</i>
16-H	4.44 <i>dd</i>		

J (Hz): 2,3 ~ 3; 2,18 = 3,18 ~ 2; 8,17 = 6,5; 12,13 = 7; 12,14 = 1,3; 13,14 = 9; 13,14' = 8; 13,16 = 13,16' = 7,5; 14,14' = 17,5; 16,16' = 9.

Table 2. ^1H NMR spectral data of compounds **6** and **7** (CDCl_3)

	6	7
2-H	5.15 <i>d</i>	5.10 <i>d</i>
3-H	6.10 <i>d</i>	6.18 <i>d</i>
4-H	7.89 <i>s</i>	7.92 <i>s</i>
7-H	6.47 <i>s</i>	6.52 <i>s</i>
9-H	2.56 <i>s</i>	2.56 <i>s</i>
11-H	5.08 <i>br. s</i>	5.08 <i>br. s</i>
11'-H	4.99 <i>br. s</i>	4.98 <i>br. s</i>
12-H	1.76 <i>br. s</i>	1.77 <i>br. s</i>
OCOR	6.48 <i>q</i>	6.47 <i>q</i>
	2.09 <i>d</i>	2.10 <i>d</i>
	4.74 <i>br. s</i>	4.70 <i>br. s</i>
OAc	1.98 <i>s</i>	2.00 <i>s</i>
OH	13.04 <i>s</i>	—
OMe	—	3.92 <i>s</i>

J (Hz): 2,3 = 2,5; 3',4' = 7.

EXPERIMENTAL

The air-dried plant material (voucher RMK 8160, collected in Brazil) was extracted with Et_2O -petrol, 1:2. The resulting extracts were separated by column chromatography (SiO_2 , act. grade II) and further by TLC (SiO_2 , GF 254). Known

compounds were identified by comparing their IR and ^1H NMR spectra with those of authentic material. The roots (130 g) afforded 2 mg tridecapentaynene 100 mg germacrene D, 50 mg germacrene C, 2 mg α -humulene, 5 mg caryophyllene, 100 mg euparin, 10 mg **4**, 10 mg **5**, 10 mg **6**, 10 mg **7** (Et_2O -petrol, 1:1), 20 mg **8**, 10 mg **9** and 5 mg **10**, while the aerial parts (440 g) yielded 200 mg germacrene D, 50 mg germacrene C, 10 mg caryophyllene, 5 mg α -humulene, 60 mg euparine, 1 g **1**, 10 mg **2** (Et_2O -petrol, 1:3) and 50 mg **3**.

16-Hydroxy-kolaven-15-oic acid lactone (**2**). Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4} \text{ cm}^{-1}$: 1785 (γ -lactone), 845 ($\text{C}=\text{CH}$); MS m/e (rel. int.): 304, 240 (M^+ , 6) ($\text{C}_{20}\text{H}_{32}\text{O}_2$), 289 ($\text{M} - \text{Me}$, 8), 191 ($\text{C}_{14}\text{H}_{23}^+$, 36), 123 ($\text{C}_8\text{H}_{15}^+$, 92), 55 (C_4H_7^+ , 100).

$$[\alpha]_{24}^c = \begin{array}{cccc} 589 & 578 & 546 & 436 \text{ nm} \\ -29.0 & -31.3 & -36.0 & -60.0 \end{array}$$

($c = 0.3$, CHCl_3).

3 β -[5'-Acetoxylangeloyloxy]-6-methoxytremetone (**7**). Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4} \text{ cm}^{-1}$: 1745 (OAc), 1725 ($\text{C}=\text{CCO}_2\text{R}$), 1675 (PhCO); MS m/e (rel. int.): 388, 152 (M^+ , 80) ($\text{C}_{21}\text{H}_{24}\text{O}_4$), 230 ($\text{M} - \text{RCO}_2\text{H}$, 100), 215 (230 - Me, 78).

$$[\alpha]_{24}^c = \begin{array}{cccc} 589 & 578 & 546 & 436 \text{ nm} \\ -26.2 & -27.5 & -32.0 & -62.0 \end{array}$$

($c = 0.8$, CHCl_3).

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