Phytochemistry, 1979, Vol. 18, pp. 2036–2037. Pergamon Press Ltd. Printed in England.

COMPACTONE, A NEW DITERPENOID FROM *VELLOZIA COMPACTA**

Angelo C. Pinto†, Antonio Jorge R. Silva†, Lucia M. U. Mayer† and Raimundo Braz F°‡

† Núcleo de Pesquisas de Produtos Naturais, Centro de Ciências da Saúde, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil; ‡ Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, Itaguaí, RJ, Brazil

(*Received* 9 *February* 1979)

Key Word Index—*Vellozia compacta*; Velloziaceae; compactone; lupenone; triacontan-1-ol; structure elucidation; ^{13}C NMR.

INTRODUCTION

In the course of a continuing phytochemical survey of Brazilian Velloziaceae, we have examined a sample of *Vellozia compacta* Martius ex Schultes, popularly known as 'lily of the rocks' [1], a species occurring in the subtropical regions of the South America, especially in the State of Minas Gerais.

Hexane extracts of the root and stem furnished, besides lupenone and triacontan-1-ol (identified by comparing their spectral properties with authentic samples), a new diterpene named compactone, the 8-hydroxy-7-oxopimar-15-ene. This new pimarene-type diterpenoid was isolated in 0.1% yield from the dry plant.

RESULTS AND DISCUSSION

The molecular formula of compactone (**1a**), $C_{20}H_{32}O_2$, was determined by MS [M^+ obs. 304.2419 (100%), req. 304.2402]. The IR spectrum revealed the presence of carbonyl (1700 cm^{-1}), hydroxyl (3480 cm^{-1}) and vinyl (1640, 980 and 910 cm^{-1}) groups. These data, in combination with comparative analysis of the proton noise decoupled and single frequency off-resonance decoupled ^{13}C NMR (Table 1) spectra, allowed expansions to $C_3(C{=}O)(COH)(CH{=}CH_2)(CH)_2(CH_2)_7(Me)_4$. The ^1H NMR spectrum in $CDCl_3$ showed signals for four tertiary methyl groups (δ 1.22, *s*, 3H; 1.18, *s*, 3H; 0.90, *s*, 6H), one isolated methylene (1.60, *s*, 2H), and one tertiary vinyl (5.78, *dd*, $J = 17$ and 10 Hz; 4.9, *dd*, $J = 17$ and 1.5 Hz; 4.87, *dd*, $J = 10$ and 1.5 Hz) groups and one $-\overset{|}{C}H-CH_2-C{=}O$ system (2.97, *dd*, $J = 13$ and 12 Hz; 2.25, *dd*, $J = 12$ and 3 Hz). These data taken together revealed compactone as a pimarane-type diterpene.

The positions of the carbonyl and hydroxyl groups, located on C-7 and C-8, respectively, were deduced through the preparation of the dideutero-derivative (**1b**, absence of the signals δ 2.97 and δ 2.25; M^+ 306), and formation of two α,β-unsaturated carbonyl compounds by dehydration of **1a** (**2a**, ν_{max}^{Nujol} 1670 cm^{-1}, $\lambda_{max}^{CHCl_3}$ 252 nm (ε 12 000); **2b**, ν_{max}^{Nujol} 1680 cm^{-1}, δ 6.74, *d*, $J = 2$ Hz, H-14).

Significant pyridine-induced solvent shifts of the ^1H NMR signals of compactone were only observed for the 20-Me (Δ 0.14), 17-Me (Δ 0.18) and one 6 β-H (Δ 0.19) [2]. These results in combination with the ^{13}C NMR chemical shifts of the 20-Me and 17-Me [3] and biogenetic considerations are consistent with structure **1a** for compactone.

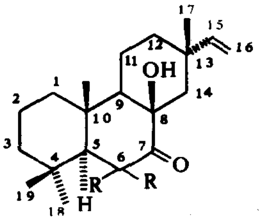
In Table 1 the ^{13}C NMR shifts were assigned by referring to those of pimarane-type diterpenoids [4–7] and comparative analyses of the proton noise decoupled and single frequency off-resonance decoupled spectra.

Table 1. ^{13}C NMR chemical shifts of compactone*

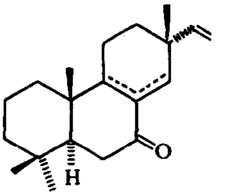
Carbon No.	C	CH	CH_2	Me
1			39.77	
2			18.55	
3			41.96	
4	33.81			
5		56.20		
6			38.31	
7	190.91			
8	76.47			
9		59.12		
10	37.68†			
11			17.10	
12			35.33	
13	36.74†			
14			43.04	
15		151.72		
16			108.66	
17				24.89
18				32.96
19				24.32
20				15.51

*The ^{13}C NMR spectra were taken in $CDCl_3$ solutions and the chemical shifts are expressed as δ ppm from an internal reference of TMS.

†These values may be interchanged.



1a R = H
1b R = D



2a $\Delta^{8(9)}$
2b $\Delta^{8(14)}$

Structures **1a** and **1b** were supported by the interpretation of the MS, the principal fragments being indicated in Table 2. The elemental compositions of these fragments were confirmed by high resolution MS.

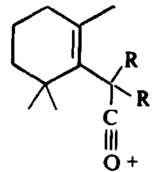
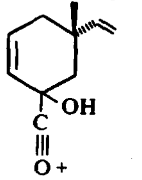
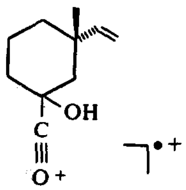
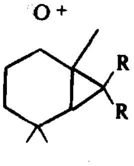
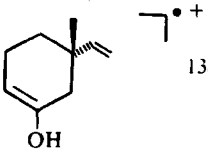
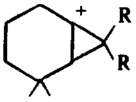
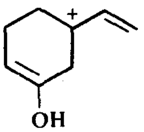
EXPERIMENTAL

Mps are uncorr. UV spectra were measured in $CHCl_3$. ^1H and ^{13}C NMR spectra were recorded at 100 and 25.2 MHz,

---

*Part VI in the series "The Chemistry of S. American Velloziaceae". For Part V see Pinto, A. C., Pinchin, R., Zocher, D. H. T. and Lopes, C. C. (1979) *Tetrahedron Letters* 405.

Table 2. MS fragmentations of compounds **1a** and **1b***

Fragment	**1a** *m/e*	**1a** Relative intensity	**1b** *m/e*	**1b** Relative intensity
	165	26	167	49
	165		165	18
	167	21	167	
	138	53	140	70
	138		138	46
	123	56	125	42
	123		123	59

†The MS were recorded under different conditions.

respectively, and chemical shifts (δ ppm) measured from TMS as internal standard.

Isolation of compactone (**1a**). Chromatography of the hexane extract (60 g) of the trunk, roots and leaf sheaths of *Vellozia compacta* collected in the Serra do Cipó, Minas Gerais, Brazil, yielded compactone (**1a**), mp 217–8°; $\gamma_{\max}^{\text{Nujol}}$ cm^{-1}: 3480, 1700, 1640, 980 and 910. ^{1}H NMR (100 MHz, C_6D_5N): δ 0.86 (3H, *s*), 0.88 (3H, *s*), 1.19 (1H, *dd*, $J = 3, 13$ Hz), 1.30 (3H, *s*), 1.36 (3H, *s*), 1.62 (2H, *s*), 2.24 (1H, *dd*, $J = 3$, 12 Hz), 3.16 (1H, *dd*, $J = 12$, 13 Hz), 4.84 (1H, *dd*, $J = 1, 5$, 10 Hz), 4.93 (1H, *dd*, $J = 1, 5$, 17 Hz), 5.84 (1H, *dd*, $J = 10, 17$ Hz); 6.22 (1H, *s* br, exchangeable with D_2O). MS *m/e* (rel. int.): 304 M$^+$ (100), 286 (18), 167 (20), 165 (24), 138 (52), 123 (56), 109 (28), 95 (35), 81 (34), 69 (40), 67 (30), 55 (38) and 41 (50). CD (c 4.5×10^{-4} g/ml dioxane): $[\theta]_{335}$ 0, $[\theta]_{320}$ -2252, $[\theta]_{307}$ -4188, $[\theta]_{285}$ -2207, $[\theta]_{260}$ 0.

Dideuteration of compactone (**1a**). To a soln of compactone (**1a**, 20 mg) in MeONa (2 ml) was added D_2O (0.5 ml). The mixture was left overnight at reflux, then extracted with $CHCl_3$ (5×6 ml) washed with N HCl, neutralized and dried. After solvent evapn *in vacuo*, a crystalline residue remained (**1b**, 15 mg). M$^+$ 306.

Dehydration of compactone **1a**. 50 mg of **1a** was refluxed for 2 hr with MeOH (3 ml) and HCl (1 ml). After cooling, the mixture was poured into 5% aq. $NaHCO_3$ (5 ml). The aq. soln was extracted with $CHCl_3$ (3×20 ml), washed with D_2O (3×10 ml) dried and concd *in vacuo* to give a residue of two compounds which were immediately chromatographed on PLC (hexane–EtOAc, 9:1, developed 2 ×) to produce **2a** (30 mg) and **2b** (12 mg). The compound **2a** showed IR $\gamma_{\max}^{\text{Nujol}}$ cm^{-1}: 1670, 1640, 1620, 980 and 910. $\lambda_{\max}^{\text{CHCl}_3}$ nm (log ε): 252 (4.07). ^{1}H NMR (100 MHz, $CDCl_3$): δ 0.88 (3H, *s*), 0.90 (3H, *s*), 1.0 (3H, *s*), 1.1 (3H, *s*), 2.1–2.6 (5H, *m*), 4.72–4.98 (2H, *m*) and 5.70 (1H, *dd*, $J = 10$, 17 Hz). MS (probe) 70 eV *m/e* (rel. int.): 286 M$^+$ (53) 271 (22), 245 (100), 201 (22), 189 (23), 163 (74), 147 (25), 123 (25), 121 (30), 109 (24), 105 (25), 91 (40), 69 (30), 55 (35) and 41 (59). Compound **2b** showed IR $\gamma_{\max}^{\text{Nujol}}$ cm^{-1}: 1680, 1620; $\lambda_{\max}^{\text{CHCl}_3}$ nm (log ε): 248 (3.92); ^{1}H NMR (100 MHz $CDCl_3$): δ 0.76 (3H, *s*), 0·78 (3H, *s*), 0.92 (3H, *s*), 1.11 (3H, *s*), 2.35 (1H, *dd*, $J = 5$, 17 Hz), 3.7 (1H, *dd*, $J = 12$, 17 Hz), 4.92–5.12 (2H, *m*), 5.82 (1H, *dd*, $J = 10$, 17 Hz) and 6.72 (1H, *d*, $J = 2$ Hz). MS (probe) 70 eV *m/e* (rel. int.): 286 M$^+$ (64), 271 (16), 162 (48), 149 (50), 148 (64), 133 (66), 123 (75), 105 (68), 91 (54), 55 (51) and 41 (100).

Interconvertion of **2b** *to* **2a**. Compound **2b** (5 mg) was refluxed with MeOH (2 ml) and HCl (0.5 ml) for 20 hr with stirring. After cooling, the reaction mixture was submitted to the same work-up as above only **2a** (3.5 mg) was obtained (IR, ^{1}H NMR, TLC).

Acknowledgements—The authors are indebted to Dr. Nanuza L. de Menezes for identification of the plant species and to the Ministry of Planning (FINEP), The National Research Council (CNPq), and the Research Council of this University (CEPG) for financial assistance.

REFERENCES

1. Corrêa, M. P. (1969) *Dicionário das Plantas Úteis do Brasil*, Vol. IV, p. 671. Ministério da Agricultura, Rio de Janeiro.
2. Demarco, P. V. (1972) *Lloydia* **35**, 362.
3. Zelnik, R., Rabenhorst, E., Matida, A. K., Gottlieb, H. E., Lavie, D. and Panizza, S. (1978) *Phytochemistry* **17**, 1795.
4. Wenkert, E. and Buckwalter, B. L. (1972) *J. Am. Chem. Soc.* **94**, 4367.
5. Polonsky, J., Baskevitch, Z., Bellavita, N. C., Ceccherelli, P., Buckwalter, B. L. and Wenkert, E. (1972) *J. Am. Chem. Soc.* **94**, 4369.
6. Cambie, R. C., Burfitt, I. R., Goodwin, T. E. and Wenkert, E. (1975) *J. Org. Chem.* **40**, 3789.
7. Matsuo, A., Uto, S., Nakayama, M. and Hayashi, S. Yamasaki, K., Kasai, R. and Tanaka, O. (1976) *Tetrahedron Letters* 2451.