PERGAMON

Phytochemistry 53 (2000) 917–919

PHYTOCHEMISTRY

www.elsevier.com/locate/phytochem

A cleistanthane diterpene lactone from *Vellozia compacta*

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Received 3 April 1999; received in revised form 22 September 1999

Abstract

8,11,13-cleistanthatrien-7-one-19,20β-olide and six other previously described diterpenes were isolated by silica gel chromatography of the ethyl alcohol extract of *Vellozia compacta*. The structure of the cleistanthane lactone was deduced on the basis of spectral data analysis.

Keywords: *Vellozia compacta*; Velloziaceae; Structural elucidation; Cleistanthane type diterpene

1. Introduction

Although plants in the Velloziaceae family live under conditions of high solar irradiation and low water availability, they show surprising longevity. Gilbert (1977) suggests that the longevity of this family may be due to the presence of terpenoid compounds that provide chemical defense.

As part of a continuing study of the secondary metabolite chemistry of the Velloziaceae family, we report here the results of chemical studies of *Vellozia compacta* Martius ex Schults. This investigation led to the isolation of a new diterpene lactone with a cleistanthane skeleton (**1**) from the ethanol extract of this species.

2. Results and discussion

The ethanol extract of roots, stem and leaf sheaths of *Vellozia compacta* yielded a series of known compounds the diterpenes 7,11-dioxisopimar-8(9),15-diene, 18-acetyl-7β,8β-dihydroxy-isopimar-15-ene, 12β-hydroxy-7-oxo-isopimar-8(9),15-diene, 8,11,13-cleistanthatrien-7-one, 7,16-oxy-1,5,6,8,11,13-cleistanthahexaen-3-one, 7α,16:7β,20-diepoxy-1,8,11,13-cleistanthatetraen-3-one (Pinto & Borges, 1983; Pinto, Patitucci, da Silva, Queiroz & Kelecom, 1983; Pinto, Pinchin, Zocher & Lopes, 1979a; Pinto, Pereira & Antunes, 1985a; Pinto, Silva, Mayer & Braz Fº, 1979b) and the triterpene 11α,12α-epoxy-14-taraxaren-3-one. These compounds were identified based on comparisons with literature data.

The molecular formula $C_{20}H_{24}O_3$ of diterpene **1** was deduced by MS in combination with ^{13}C NMR spectroscopic analysis. Its IR spectrum showed two strong bands at 1724 and 1681 cm^{-1}, due to stretching vibrations of the carbonyl groups of a δ-lactone and a cyclohexanone carbonyl conjugated to an aromatic ring; one band at 1453 cm^{-1} was assigned to aromatic C–C stretching vibrations, and an absorption at 833 cm^{-1} was attributed to an out of plane C–H vibration of a 1,2,3,4-tetrasubstituted aromatic ring (Ponchert, 1975).

The ^1H NMR spectrum of **1** revealed the presence of an ethyl group attached to the aromatic ring (δ 1.20, 3H, *t*, $J = 8$ Hz and δ 2.98, 2H, *q*, $J = 8$ Hz), and two methyl groups on quaternary carbons, one of which (δ 2.38) is bonded to the aromatic ring and the other (δ 1.30) to an sp^3 carbon. The ^1H NMR spectrum also suggested a methylene functionality, adjacent to the carbonyl group. This methylene, in turn, is

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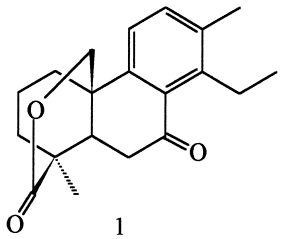
0031-9422/00/$ - see front matter
PII: S0031-9422(99)00579-8

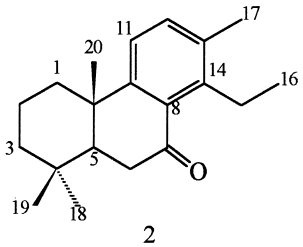
adjacent to a methyne group, and consists of one AB system at δ 4.46 (1H, *d*, $J = 12$ Hz) and δ 4.34 (1H, *d*, $J = 12$ Hz), which was assigned to the protons of C-20; the two doublets at δ 7.18 (1H, *d*, $J = 7$ Hz) and δ 7.32 (1H, *d*, $J = 7$ Hz) were due to the *ortho* related aromatic protons.

The ^{13}C NMR spectrum, in combination with DEPT experiments, showed the presence of three methyl, six methylene, three methyne (1 sp^3, 2 sp^2) groups and seven non-protonated carbon atoms (2 sp^3, 5 sp^2 including 2 carbonyls). The data indicate that this diterpene is of the cleistanthane type. The assignment of the chemical shifts of the carbons of (**1**) was made by comparison to the ^{13}C NMR spectral data of 8,11,13-cleistanthatrien-7-one (**2**) (Pinto et al., 1985a) and the kaurane diterpene (**3**) (Chen et al., 1992).

Further support for the suggested structure was obtained from the EI mass spectrum of (**1**), which showed relevant fragments at *m*/*z* 254(66) and at *m*/*z* 197(53). The peak at *m*/*z* 254 results from the loss of bridge between the carbon C-4 and C-10 ($CH_2C(=O)-O$). The fragment at *m*/*z* 197 can be explained by loss of this same bridge followed by loss of the A-ring (Pinto, Rezende, Antunes & Correia, 1996). Compound **1** was therefore identified as cleistantha-8,11,13-trien-7-one-19,20β-olide.



1



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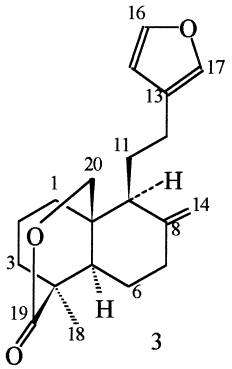

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3. Experimental

Mps are uncorr. (Kofler apparatus), C.C.: Merck silica gel G60 (70–230 mesh), TLC: Merck silica gel PF_{254}. The IR spectrum was recorded in KBr pellets with a Perkin–Elmer 137 apparatus. A low resolution mass spectrum was determined using a VG micromass MM 12F instrument, whereas ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a Varian UNITY-300 apparatus, and recorded in $CDCl_3$ solution using TMS as int. standard. The optical rotation was measured with a Perkin–Elmer 234-B polarimeter.

3.1. Extraction and isolation

Stem, roots and leaf sheaths (1.9 kg) of *V. compacta* (voucher specimen deposited in IB-USP, State of São Paulo, Brazil) collected in Diamantina, State of Minas Gerais, Brazil, were crushed and extracted with hexane (10 l), EtOAc (12 l) and EtOH (10 l) at room temperature, affording after evaporation of the solvents, 137 g (9.1% w/w), 79 g (4.2% w/w), and 62 g (3.3% w/w) crude extracts, respectively.

The ethanol extract (50 g) was redissolved in MeOH (100 ml), adsorbed on silica gel G60 (15 g), and after evaporation of the solvent, placed on top of a column of 500 g of the same adsorbent. Elution was started with hexane and the polarity of the eluant was then increased gradually with EtOAc to give 11 fractions. Fraction 4 (5% EtOAc) yielded 11α,12α-epoxy-14-taraxeren-3-one (10 mg, 0.02%), 7,11-dioxoisopimar-8(9),15-diene (23 mg, 0.05%) (Pinto & Borges, 1983), and 8,11,13-cleistanthatrine-7-one (17 mg, 0.03%) (Pinto et al., 1983); fraction 5 (10% EtOAc) yielded 7,16-oxy-1,5,6,8,11,13-cleistanthahexaen-3-one (30 mg, 0.06%) (Pinto et al., 1979a); fraction 7 (20% EtOAc) yielded 18-acetyl-7β,8β-dihydroxyisopimar-15-ene (15 mg, 0.03%) (Pinto et al., 1979a), 7α,16:7β,20-diepoxy-1,8,11,13-cheistanthatetraen-3-one (18 mg, 0.04%) (Pinto, Patitucci, Zocher & Kelecom, 1985b), and (**1**) (21.7 mg, 0.05%); fraction 8 (20% EtOAc) yielded 12β-hydroxy-7-oxo-isopimar-8(9),15-diene (25 mg, 0.05%) (Pinto & Borges, 1983).

3.2. Cleistantha-8,11,13-trien-7-one-19,20β-olide (*1*)

Colorless crystals from hexane, m.p. 160–162°C. $[\alpha]_D^{25}$: −31° (*c*. 1.23, $CHCl_3$); I.R. ν_{max}^{KBr} cm^{-1}: 2941, 1724, 1681, 1453 and 833; ^{1}H NMR spectral data (300 MHz, $CDCl_3$): 1.20 (3H, *t*, $J = 8$ Hz), 1.30 (3H, *s*), 2.38 (3H, *s*), 2.98 (2H, *q*, $J = 8$ Hz), 4.34 (1H, *d*, $J = 12$ Hz), 4.46 (1H, *d*, $J = 12$ Hz), 7.18 (1H, *d*, $J = 7$ Hz), and 7.32 (1H, *d*, $J = 7$ Hz); ^{13}C NMR spectral data (75 MHz, $CDCl_3$): 14.1 (C-16), 19.4 (C-17), 20.9 (C-2), 22.4 (C-18), 23.9 (C-15), 37.3 (C-6), 37.6 (C-10),

39.1 (C-1), 39.9 (C-3), 43.5 (C-4), 45.4 (C-5), 76.5 (C-20), 122.8 (C-11), 130.4 (C-8), 134.9 (C-12), 137.3 (C-13) 145.9 (C-9), 174.7 (C-19) and 197.5 (C-7); MS m/z (rel. int.): 312[M]$^+$ (100), 297 (14), 268 (6), 267 (27), 254 (66), 239 (75), 225 (36), 211 (35), 197 (53), 181 (21), 128 (12), 115 (12), 91 (12), and 41 (25).

Acknowledgements

We are grateful to Dra. Nanuza L. de Menezes, (IB-USP), for identification of the plants, and Professor Jose Daniel Figueroa-Villar (IME-RJ) for recording the NMR spectra. This work was financially supported by grants from CNPq, FINEP, and FUJB-UFRJ.

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