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A NAPHTHALENIC NORDITERPENE FROM VELLOZIACEAE

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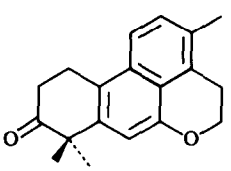
Key Word Index—*Vellozia epidendroides*; *V. phalocarpa*; Velloziaceae; naphthalenic norditerpene.

Abstract—The isolation of a new naphthalenic nor-cleistanthane diterpene from *Vellozia epidendroides* and *V. phalocarpa* is described.

Recently we described two naphthalenic diterpenes (**1** and **2**) from *Vellozia stipitata* L. B. Smith et Ayensu and *V. declinans* Goethart et Henrard [1]. In the present communication we report the isolation of a new naphthalenic nor-cleistanthane diterpene (**3**) from a hexane extract of roots, stem and leaf-sheaths of *V. epidendroides* Martius ex Schultes and *V. phalocarpa* Pohl.

The molecular formula of **3**, $C_{19}H_{22}O$, was determined by mass spectrometry ($[M]^+$ obs. 266.1673 (71%) req. 266.1665). The IR spectrum of **3** revealed the presence of an aromatic ring system (1574, 815 and 784 cm^{-1}) and strong absorptions for an ether linkage (1260 and 1033 cm^{-1}). The UV spectrum showed the presence of a substituted naphthalene (λ_{max}^{EtOH} 241, 306, 322 and 336 nm). The ^1H NMR spectrum, in $CDCl_3$, showed one singlet for a geminal dimethyl group at δ 1.36 (6H); an aromatic methyl substituent at δ 2.38 (3H, *s*); three aromatic protons: two *ortho* with respect to each other at δ 7.26 (1H, *d*, J = 8.5 Hz) and δ 7.70 (1H, *d*, J = 8.5 Hz) and a third one, a singlet at δ 6.92 (1H) for the hydrogen *ortho* to the alkoxy group. Two triplets at δ 3.10 (2H, J = 5Hz) and δ 4.36 (2H, J = 5 Hz) were assigned to an $ArCH_2CH_2O$– moiety suggesting that the oxygen of **3** belongs to a dihydropyran ring fused to the aromatic nucleus. These data and biogenetic considerations are consistent with structure **3** for the naphthalenic nor-cleistanthane diterpene.



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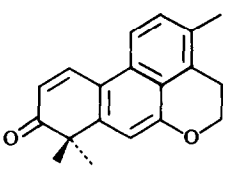

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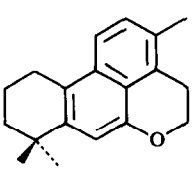

3

The Wolff–Kishner reduction of **1** afforded a product that was identical in all aspects with natural naphthalenic norditerpene **3**.

EXPERIMENTAL

Mps are uncorr. UV spectra were recorded in 95% EtOH IR spectra in KBr discs. ^1H and ^{13}C NMR spectra were recorded at 100 and 25.2 MHz, respectively, and chemical shifts (δ-values, ppm) measured from TMS as int. standard.

Isolation of **3**. Chromatography of the hexane extract of the trunk, roots and leaf-sheaths of *V. epidendroides* and *V. phalocarpa* collected in Diamantina, Minas Gerais, Brazil, yielded the naphthalene norcleistanthane **3**, mp 136–138°; ν_{max}^{KBr} cm^{-1}: 1574, 1450, 1388, 1366, 1318, 1272, 1231, 1163, 1111, 1032, 934, 892, 847, 815 and 784. UV λ_{max}^{EtOH} nm: 241, 306, 322 and 336. ^1H NMR (100

MHz, $CDCl_3$): δ 1.36 (6H, *s*), 1.55 at 2.06 (4H, *m*), 2.38 (3H, *s*), 2.98 (2H, *t*, J = 6 Hz), 3.10 (2H, *t*, J = 5 Hz), 4.36 (2H, *t*, J = 5 Hz), 6.92 (1H, *s*), 7.26 (1H, *d*, J = 8.5 Hz) and 7.70 (1H, *d*, J = 8.5 Hz). ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 18.3 (*q*), 19.5 (*t*), 26.2 (*t*), 26.6 (*t*), 31.4 (*q*), 31.4 (*q*), 34.1 (*s*), 38.8 (*t*), 65.5 (*t*), 108.3 (*d*), 120.2 (*s*) 121.2 (*d*), 123.0 (*s*), 127.3 (*s*), 128.6 (*d*), 128.6 (*s*), 131.3 (*s*), 142.4 (*s*) and 150.5 (*s*). MS *m/z* (rel. int.): 266 $[M]^+$ (71), 251 (100), 236 (14), 221 (16), 210 (9) and 207 (8).

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ISOCARNOSOL, A DITERPENE FROM *SALVIA LANIGERA*

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Key Word Index—*Salvia lanigera*; Labiatae; diterpene; isocarnosol.

Abstract—Isocarnosol, a novel diterpene from the leaves of *Salvia lanigera*, has been characterized.

INTRODUCTION

The leaves of *Salvia lanigera* Poir are used as an aromatic tea for a variety of abdominal troubles. A number of diterpenes and diterpene-quinones have been isolated from many *Salvia* species [1–9]. Four diterpene-quinones of the royleanone type have been isolated [10] from *S. lanigera*.

RESULTS AND DISCUSSION

Column chromatography (silica gel) of the petrol extract of the leaves of *S. lanigera* gave a number of fractions. Isocarnosol crystallized out from the chloroform fraction and was recrystallized from methanol to give white crystals, mp 216°. Isocarnosol was given the structure **1** primarily on the basis of ^{1}H NMR data.

Isocarnosol (**1**) $C_{20}H_{26}O_4$ has the same molecular formula as carnosol (**2**) which has been isolated from *Salvia triloba* [11], but the physical properties of the two compounds are different. The IR spectrum of isocarnosol showed a striking resemblance in many of its features to that of carnosol, which exhibits the presence of a 6-membered lactone ring (1730 and 1205 cm^{-1}), an aromatic ring (3050, 1600 and 1500 cm^{-1}) and phenolic hydroxyl groups at 3350 cm^{-1}.

The ^{1}H NMR spectrum of **1** in $CDCl_3$ containing a small amount of DMSO-d_6 indicated the presence of an isopropyl group (δ 1.18, J = 6.7 Hz), two C-methyl (0.85 and 0.89) and a characteristic low field aromatic C–H at 6.63. The aromatic C–H shifted to low field at δ 7.0 in the diacetate derivative indicating its proximity to one of the phenolic hydroxyl groups. The phloroglucinol test for an *o*-diphenol function [12] was negative for isocarnosol, thus leaving the other two isomers (*meta* and *para*) as possibilities. These conclusions were supported by the interpretation of the ^{13}C NMR spectrum of isocarnosol in which the unsubstituted aromatic carbon resonates at δ 111.78. The up-field shift (δ 111.78) for the unsubstituted carbon atom is characteristic of an aromatic carbon adjacent to an oxygen substituent. C-14 in carnosol (**2**) should resonate in the same region as does the same carbon in the diacetate derivative of aethiopinone (**3**) [13] or in carnosolon (**4**) [14] (δ 124.0 and 119.7 respectively).

At this stage the compound was identified as isocarnosol (**1**) or its *meta*-isomer. A structure of the sempervirol type was excluded on biosynthetic grounds as none of the more than 40 diterpene and diterpene-quinones isolated from various *Salvia* species has this structure [15]. However, examination of the IR and NMR data of the oxidation product of **1** showed that this compound was of the *p*-quinonoid type. Thus the IR spectrum of the major product of the bromine oxidation of **1** showed a band at 1660 cm^{-1} (shoulder) typical of the quinonoid structure and an intense band at 1760 cm^{-1} attributable to carbonyl lactone absorption. The appearance of a doublet signal at δ 6.67 ($J \sim$ 1.2 Hz) in the ^{1}H NMR spectrum indicates the structure **5**.

The small coupling constant for proton H-12 ($\sim$ 1.2 Hz) is due to allylic coupling with a hydrogen at C-15, and this situation could not be expected in the *m*-quinonoid type **6** (i.e. H-11 should resonate as a singlet). The ^{13}C NMR spectrum of isocarnosol (Table 1) indicates that one of the C-4 methyl groups is in a 1,3-diaxial relationship with the carboxyl lactone at C-10 and this can happen only if the A/B rings are *trans*-fused [16]. That compounds **1** and **2** have the same absolute configuration