

SESQUITERPENE KETONES FROM *GERANIUM MACRORRHIZUM*

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Key Word Index—*Geranium macrorrhizum*; biomimetic photosynthesis; germarane, a new sesquiterpene skeleton.

Abstract—Two novel stereoisomeric tricyclic sesquiterpene ketones were isolated from *Geranium macrorrhizum*.

A recent study on the photochemical behaviour of isogermacrone (1)‡ resulted in the isolation and identification of several products [1]. Among them was found the sesquiterpene ketone germazone (2) previously isolated [2] from the essential oil of *Geranium macrorrhizum*. A further examination [1] of the same essential oil revealed the presence of 1, which led us to study in greater detail the petrol extract of the aerial parts of the plant.

The extract contained very small amounts (i.e. ca 0.001 %) of 1 as well as of compounds 2, 3 and 4. The presence of compounds 2-4 in the extract together with 1 suggests the possibility that a direct photochemical step in their formation from 1 takes place in the plant. An *in vivo* confirmation, however, with an appropriately isotopically labelled sample of 1 is of course necessary. Similar assumptions suggesting that a photochemical step takes place in the plant to afford either alkaloids or sesquiterpenes directly from appropriate precursors have been made earlier [4-6].

The compounds 3 and 4 with a germarane skeleton, now isolated from a plant source, although previously available *in vitro* [1, 7], can now be regarded as representatives of a novel class of naturally occurring sesquiterpene ketones.

EXPERIMENTAL

The plant material (1.73 kg) was the aerial parts of *G. macrorrhizum* in September from the mountain slopes in north Bulgaria. This was extracted (24 hr, room temp.) with petrol, bp 50-70°. The sesquiterpene ketone fraction was separated by prep. TLC [8] using the photolysis products of 1 as marked samples. This fraction was then subjected to GC analyses on glass capillary columns coated with either Carbowax-20M (35 m/0.3 mm) or DEGS (55 m/0.3 mm) and with N₂ as carrier gas at a linear velocity of 20 cm/sec; programmed temperature rise from 130° to 190° at a rate of 3°/min; the temperature of the injector and FID was 260°.

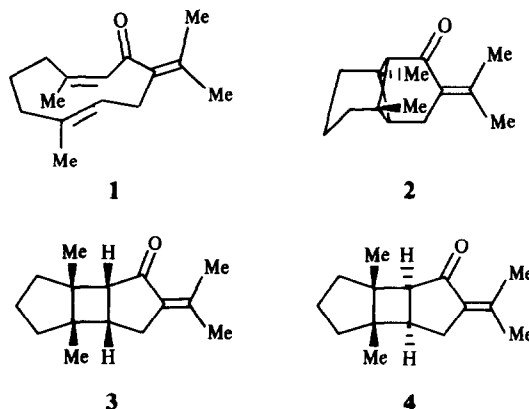
Compound identification was accomplished by *R_s*s and also by injecting simultaneously an authentic sample with the plant

extract. The newly found compounds showed the following *R_s*s: on Carbowax-20M (1 13 min 48 sec; 2 10 min 50 sec; 3 10 min 25 sec; 4 11 min 20 sec) and on DEGS (1 14 min 48 sec; 2 12 min 06 sec; 3 11 min 15 sec; 4 12 min 12 sec).

The ratio of compound 2 to compound 3 was found to be approximately constant when the chromatographic measurements were carried out at initial temperatures of 110° and 170°. The *R_s*s were adjusted by regulating the carrier gas velocity so as to be similar. It can be therefore concluded that 2 and 3 are not products arising from thermal interconversion on the column.

Additional verification concerning the identity of compounds 3 and 4 was obtained from the GC/CIMS analysis of the sesquiterpene ketone fraction. Compound 3 CIMS (iso-butane) 400 eV, *m/z* (rel. int.): 219 [M + H]⁺ (100), 123 [M - 96 + H]⁺ (45). Compound 4 CIMS (iso-butane) 400 eV, *m/z* (rel. int.): 219 [M + H]⁺ (100), 123 [M - 96 + H]⁺ (25) i.e. cyclobutane ring cleavage is observed. No such fragmentation was experienced by the closely related compound 2 which under the same CIMS conditions exhibited solely the *m/z* 219 [M + H]⁺ ion. The GC/CIMS analysis of the ketone extract revealed that compounds with *R_s*s corresponding to 3 and 4 underwent fragmentation under the above CIMS conditions affording the *m/z* 123 ion indicating in this manner cyclobutane fission and corroborating structures 3 and 4.

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‡The C-2-C-3 double bond of this compound has been recently found to be of the Z-configuration on the grounds of ¹H NMR and ¹³C NMR spectra [3].

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A NAPHTHALENIC NORDITERPENE FROM VELLOZACEAE

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

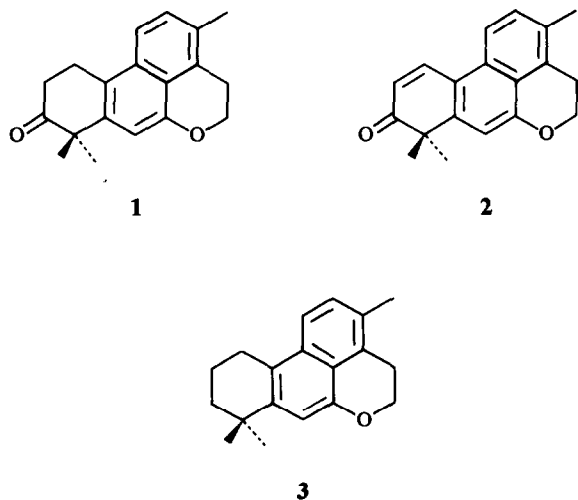
Abstract—The isolation of a new naphthalenic nor-cleistanthane diterpene from *Vellozia epidendroides* and *V. phalocarpa* is described.

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 ($\lambda_{\text{max}}^{\text{EtOH}}$ 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*, $J = 8.5\text{ Hz}$) and δ 7.70 (1H, *d*, $J = 8.5\text{ Hz}$) 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, $J = 5\text{ Hz}$) and δ 4.36 (2H, $J = 5\text{ Hz}$) were assigned to an $\text{ArCH}_2\text{CH}_2\text{O}$ -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.

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° ; $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1574, 1450, 1388, 1366, 1318, 1272, 1231, 1163, 1111, 1032, 934, 892, 847, 815 and 784. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 241, 306, 322 and 336. ^1H NMR (100