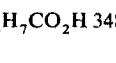
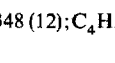
Dichrographe Mark III, R. J. Die lufttrockenen Wurzeln (Herbar-Nr. 77/183, gesammelt im Februar 1977 in Natal) wurden grob zerkleinert und mit Et_2O–Petrol 1:2 extrahiert. Diese erhaltenen Extrakte trennte man zunächst grob durch SC (Si gel, Akt.-St. II) und weiter durch DC (Si gel, GF 254). Als Laufmittel dienten Et_2O–Petrol-Gemische. 300 g Wurzeln lieferten 60 mg **1** (Et_2O–Petrol 1:1), 3 mg **5** (Et_2O–Petrol 1:1) und 25 mg **4** (Et_2O–Petrol 1:3).

8β-Angeloyloxy-senoxyri-4-en-3-on (**1**): Farbloses Öl, IR: C=C CO_2R, C=C CO 1710, 1645 cm^{-1}. UV: λ_{max}^{EtO} = 227 nm. MS: M^+ *m/e* 316.204 (3%) ($C_{20}H_{28}O_3$); —•OCOR217 (8); —$C_4H_7CO_2H$ 216(5); 216—•Me 201 (4); $C_4H_7CO^+$ 832 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+44.1 \quad +45.9 \quad +51.8 \quad +83.0°} (c = 3.06N).$$

CD-Maxima (Et_2O): $\Delta\varepsilon_{343}$ −0.1; $\Delta\varepsilon_{329}$ −0.2; $\Delta\varepsilon_{313}$ −0.2; $\Delta\varepsilon_{303}$ −0.15; $\Delta\varepsilon_{232}$ −1.8; $\Delta\varepsilon_{200}$ +2.6. 10 mg **1** in 2 ml MeOH erwärmte man 1 hr mit 10m g KOH in 0.5 ml H_2O auf 70°. Nach DC (Et_2O–Petrol 1:3) erhielt man 5 mg **2**, farbloses Öl, IR: OH 3600; C=C—CO 1710, 1640 cm^{-1}. MS: M^+ *m/e* 234.162 (8%) ($C_{15}H_{22}O_2$); —•Me 219 (8); —H_2O 216 (3); 219 —CH_2= C=CO 177 (100).

5β, 8-Diangeloyloxy-2β, 3β, 10, 11-diepoxy-4β-hydroxy-7, 14-dehydrobisabolan (**4**): Farbloses Öl, IR: OH 3590; C=CCO_2R 1720, 1650 cm^{-1}. MS: M^+ *m/e* 448.246 (1%) ($C_{25}H_{36}O_7$); —H_2O 430 (2); —  377 (1); —$C_4H_7CO_2H$ 348 (12); C_4H_7-CO^+ 83 (100);  71 (12); 83—CO 55 (37).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ cm}{-17.5 \quad -18.2 \quad -21.3 \quad -37.7°} (c = 0.88).$$

20 mg **4** in 2 ml $CHCl_3$ erwärmte man nach Zusatz von 30 mg 4-Pyrrolidinopyridin und 2 ml Ac_2O 1 hr zum Sieden. Nach üblicher Aufarbeitung erhielt man nach DC (Et_2O–Petrol 1:1) 15 mg **5**, identisch mit den Naturstoff.

4β-Acetoxy-5β, 8-diangeloyloxy-2β, 3β, 10, 11-diepoxy-7, 14-dehydrobisabolan (**5**): Farbloses Öl, IR: OAc 1750, 1240; C=C CO_2R 1720, 1660 cm^{-1}. MS: M^+ *m/e* 490.257 (0.5%) ($C_{27}H_{38}O_8$); —AcOH 430 (1); —$C_4H_7CO_2H$ 390 (4); 390 —$C_4H_7CO_2H$ 290 (2); $C_4H_7CO^+$ 83 (100).

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VEADEIROL AND VEADEIROIC ACID, TWO NOVEL DITERPENES FROM *VELLOZIA FLAVICANS*

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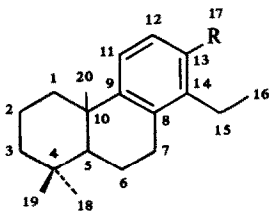
Key Word Index—*Vellozia flavicans*; Velloziaceae; diterpenes; veadeirol; veadeiroic acid.

Two novel diterpenes, veadeirol (**1**) and veadeiroic acid (**2**), have been isolated from the hexane extract of the stem of *Vellozia flavicans* Martius ex. Schultz. To date only one other natural product with the same abnormal cleistanthane skeleton has been reported [1–3].

Examination of the IR spectrum of **1**, $C_{20}H_{30}O$, established the presence of a hydroxyl group (3220 cm^{-1}) and a tetrasubstituted aromatic ring (1480–1420 and 820 cm^{-1}) [4]. The PMR spectrum showed two aromatic protons, δ 7.18 (2H, *s*), and a singlet at δ 4.68 (2H), assigned to a benzylic alcohol grouping ($ArC\underline{H}_2OH$). Signals for three tertiary methyl groups at δ 0.94 (3H, *s*), 0.98 (3H, *s*), and 1.20 (3H, *s*) together with an ethyl group at δ 1.18 (3H, *t*, J = 7 Hz, $ArCH_2C\underline{H}_3$) and 2.70 (2H, *q*, J = 7 Hz, $ArC\underline{H}_2CH_3$) were readily identified.

Oxidation of **1** with CrO_3-pyridine furnished an unstable aldehyde which, in the presence of air, was readily converted to an acid, $C_{20}H_{28}O_2$, identical with the acid **2** isolated from the plant. Analysis of the PMR spectrum of **2** demonstrated that the two aromatic protons previously noted for **1** were *ortho* to each other, δ 7.22 (1H, *d*, J = 8 Hz) and 7.88 (1H, *d*, J = 8 Hz). The downfield shifts observed for these two protons upon conversion of **1** to **2**, and also for the methylene protons of the ethyl group, now at δ 3.10, defined the substitution pattern of the aromatic ring.

The structures proposed for **1**, **2**, and the corresponding methyl ester **3**, were confirmed by the comparison of their ^{13}C NMR spectra (Table 1) with the data recorded for several other diterpenes [5, 6].



1 R = CH_2OH
2 R = CO_2H
3 R = CO_2Me

Table 1. ^{13}C NMR spectra of veadeirol (1), veadeiroic acid (2), and its methyl ester (3) ($CDCl_3$, 25.2 MHz, ppm downfield from TMS internal standard)

Carbon No.	(1)	(2)	(3)
1	39.1	39.0	39.0
2	19.0	19.1	19.0
3	41.4	41.3	41.3
4	33.2	33.3	33.3
5	49.5	49.2	49.3
6	19.3	19.3	19.3
7	27.3	27.4	27.3
8	134.9	134.1	133.9
9	150.2	155.2	154.1
10	37.9	38.5	38.4
11	122.1	122.1	121.9
12	125.9	128.6	127.4
13	133.2	125.8	128.6
14	140.1	144.7	143.2
15	21.3	22.6	22.7
16	14.2	14.4	14.0
17	63.3	173.9	168.7
18	21.4	21.6	21.6
19	33.2	33.1	33.1
20	24.8	24.6	24.6
CO_2CH_3	—	—	51.6

EXPERIMENTAL

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

Isolation of **1** *and* **2**. Chromatography of the hexane extract (90 g) of the trunk, roots, and leaf sheaths (3.5 kg) of *Vellozia flavicans*, collected on the Chapada dos Veadeiros, Goiás Brazil, yielded veadeirol (**1**) (2 g), mp 138–139°, ν_{max}^{KBr} cm^{-1}: 3220, 2980, 1480, 1450, 1420, 1370, 1010, and 825. λ_{max}^{EtOH} nm (log ε): 270 (2.79) and 208 (4.70). PMR (100 MHz, $CDCl_3$): δ 0.94 (3H, *s*), 0.96 (3H, *s*), 1.18 (3H, *t*, J = 7 Hz), 1.20 (3H, *s*), 1.68 (1H, *s*, exchangeable with D_2O), 2.70 (2H, *q*, J = 7 Hz), 4.68 (2H, *s*), and 7.18 (2H, *s*). MS (probe) 70 eV *m/e* (rel. int.): 286 M^+ (60), 271 (80), 201 (35), 189 (92), 175 (100), and 69 (77); and veadeiroic acid **2** (600 mg), mp 226–227°, ν_{max}^{KBr} cm^{-1}: 3400–2800 (*br*), 1695 *vs* (—CO_2H), 1580, 1560, 1450, 1410, 1270, 830, 790, and 760. λ_{max}^{EtOH} nm (log ε): 242 (3.87) and 211 (4.66). PMR (100 MHz, $CDCl_3$): δ 0.96 (3H, *s*), 0.98 (3H, *s*), 1.22 (3H, *t*, J = 7 Hz), 1.23 (3H, *s*), 2.9–3.1 (4H, *m*), 7.22 (1H, *d*, J = 8 Hz), and 7.80 (1H, *d*, J = 8 Hz). MS (probe) 70 eV *m/e* (rel. int.): 300 M^+ (34), 285 (42), 203 (100), and 69 (38).

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GRAYANOSIDE A, A NEW DITERPENE GLUCOSIDE FROM *LEUCOTHOE GRAYANA*

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Key Word Index—*Leucothoe grayana*; Ericaceae; diterpene glucoside; grayanoside A.

A number of diterpenoids with A-nor-B-homo(−)-kaurane skeleton have been isolated from *Leucothoe grayana* [1], but their glycoside has not been reported. Now we report the isolation and structural determination of an A-nor-B-homo-(−)-kaurane glucoside from the methanolic extract of the plant, for which we suggest the name grayanoside A.

The PMR spectrum of grayanoside A (**1**) indicated the presence of three tertiary methyls (δ 1.20, 1.48, 1.63), a secondary acetoxyl (δ 2.02, 5.52), a vinylidene group (δ 5.04, 5.08) and the expected signals for a D-glucopyranosyl moiety (δ 3.8–4.6). Acetylation of **1** with Ac_2O–Py gave a pentaacetate (**2**). Acid hydrolysis of **1** yielded only a glucose and attempts to isolate the aglycone part were not successful. However, enzymatic hydrolysis of **1** with naringinase gave the genuine aglycone (**3**). The PMR spectrum suggested that **3** was one of the grayanotoxins, and in fact, **3** was identified as grayanotoxin IV [2] by TLC, IR, and mmp.

From the PMR coupling constants (δ 4.85, *d*, J = 8 Hz) of the anomeric protons of **1** and **2**, **1** must be a β-glucoside. The position of glucosidation in the aglycone **3** was determined by ^{13}C-NMR. The ^{13}C-NMR signals were assigned by means of single-frequency off-resonance decouplings, by selective proton decouplings, and by comparing the spectra of several model compounds.