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SPIROCYCLIC NORTRITERPENES FROM THE BULBS OF *VELTHEIMIA VIRIDIFOLIA**†

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Key Word Index—*Veltheimia viridifolia*; Hyacinthaceae; 22-acetoxy-15-deoxo-eucosterol and 22-acetoxy-15-deoxo-eucosterol pentaglycoside.

Abstract—A new spirocyclic nortriterpene, 22-acetoxy-15-deoxo-eucosterol, was isolated together with a corresponding pentaglycoside from the bulbs of *Veltheimia viridifolia*. The structures of the isolated compounds were elucidated by spectroscopic methods including 1D- and 2D-^{1}H NMR, ^{13}C NMR, 1D-INEPT, 1D- and 2D-TOCSY, HSQC, HMBC, ROESY experiments, FAB- and HRESI-mass spectrometry.

INTRODUCTION

Veltheimia viridifolia belongs to the family of the Hyacinthaceae and is indigenous to South Africa. In a previous publication [1] we reported on the homoisoflavanones, isolated from *V. viridifolia* bulbs. In this paper we describe two structures belonging to the nortriterpene family extracted from this material. The structure elucidations of the nortriterpene **1** and of its pentaglycoside **2**, obtained from the petrol and from the chloroform-2-propanol extract, respectively, were achieved by means of spectroscopic methods including 1D- and 2D-^{1}H NMR, ^{13}C NMR, 1D-INEPT, 1D- and 2D-TOCSY, HSQC, HMBC, ROESY experiments, FAB mass and HRESI spectrometry.

RESULTS AND DISCUSSION

The freeze dried bulbs of *Veltheimia viridifolia* were extracted successively with petrol, diethylether, chloroform, chloroform–2-propanol and methanol. Compounds **1** and **2** were isolated from the crude petrol and the crude chloroform–2-propanol extracts, respectively. Further details of the extraction procedures are given in the Experimental.

The HRESI mass spectrum of **1** provided a molecular ion, m/z 516.3434, in accordance with the molecular formula $C_{31}H_{48}O_6$ containing eight double bond equivalents. Efforts to obtain a HR-mass spectral analysis of **2** were unsuccessful. The positive ion FAB-mass spectrum (LR-MS) of **2** showed a molecular ion + Na^+, m/z 1289 accounting for the molecular formula $C_{59}H_{94}O_{29}$ and a main fragment at m/z 499 (92% rel. int.), indicating that **1** was a substructure of compound **2**. This was confirmed by the ^{13}C NMR spectrum of **1** which was nearly identical to a part of the spectrum of compound **2**. Only one methylene, one methine and one quaternary carbon signal of compound **1** could not be assigned properly to signals of **2** indicating the partial structure probably involved in the linkage to a glycosidic chain.

The ^{13}C NMR spectrum of **1** showed 31 carbon signals which could be resolved by a DEPT experiment into seven methyl, 10 methylene, five methine and eight quaternary carbons, respectively, the chemical shift data of which are shown in Table 1. The protonated carbon signals were assigned to the corresponding proton signals by means of a Heteronuclear Single-Quantum Correlation (HSQC) experiment. The low field shifted signals at δ 209.6, 169.9, 134.2 and 135.0, respectively, were correlated with one carbonylic carbon, one ester carbonyl and with two quaternary carbons of a double bond.

The five remaining double bond equivalents were assumed to account for a pentacyclic structure probably consisting of a steroid skeleton with an addition ring E. Some structural elements of the molecule were determined by combining the results of the HSQC with those of the 2D-H-H-COSY spectrum. Six spin systems could be identified as shown in Fig. 1.

* Part 2 in the series 'Constituents of *Veltheimia viridifolia*' [1].

† Dedicated to Prof. Gottfried Blaschke on the occasion of his 60th birthday.

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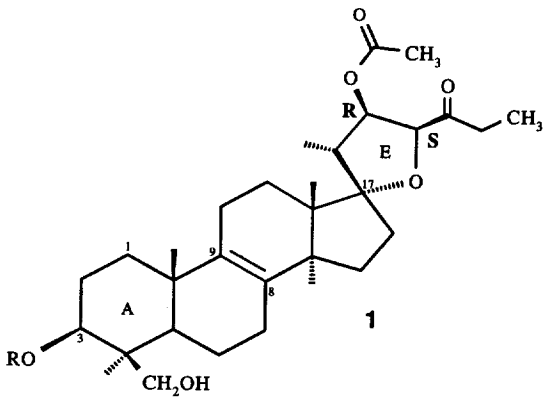
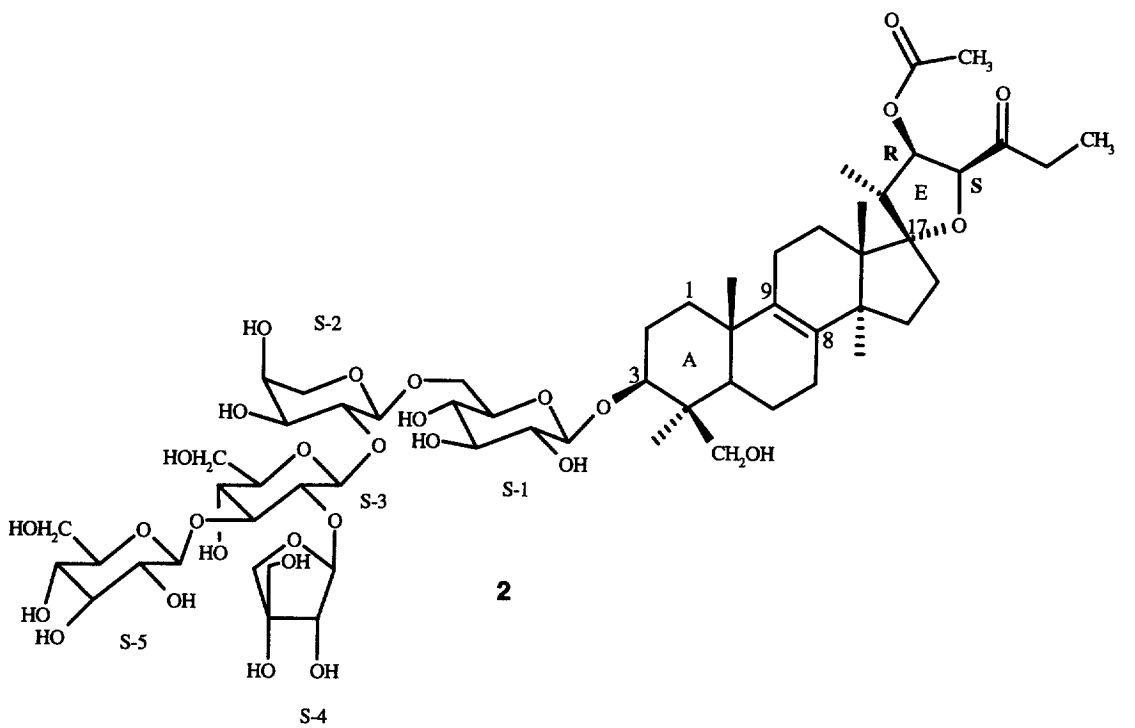


1



2

The cross peak between H-20 and H-22 was missing because of a dihedral angle of about 90°. Nevertheless, the connection between C-21 and C-20 was unequivocally demonstrated by HMBC and ROESY experiments as shown in Table 2 and Figs. 2 and 3.

The structural elements derived from the COSY experiment were combined with those from HMBC experiments done at 10 and 7 Hz, respectively, in order to identify both 2-bond and 3-bond H-C correlations. The data are given in Table 2, all derived hetero spin systems are shown in Fig. 2.

The two quaternary carbons C-8 and C-9 were coupled with the singlets H_3-22 and H_3-19, respectively, the latter of which showed also a cross-peak to C-10 and therefore links C-19 with C-9. On the other hand C-13/C-14 showed cross-peaks with H_3-18, Hβ-12, and Hα-15 demonstrating the connection between the structural elements Hα,β-11, Hα,β-12 and Hα,β-15, Hα,β-16. Additionally the quaternary C-17 showed couplings with Hα-16 and H_3-18, respectively. This information established the structures of ring C and D of the postulated steroidal skeleton. An unequivocal assignment of the signals at δ 50.0 and 50.4 (δ 49.9 and 50.4 for compound **2**) to C-13 and C-14, respectively, could not be decided because of identical LR-couplings but this problem was solved by means of 1D-INEPT experiments with compound **2**, as discussed below.

The extremely low field shifted sp^3-C-17 of **1** showed cross-peaks with H-20, H_3-21, and H-22, as C-23 does with H-20 and C-22 with H-20, H-21, respectively. These results established the furan ring E. Ring E was substituted with a 21-methyl group at C-20 and with an acetoxy substituent at the adjacent C-22, the ester carbonyl signal of which was found at δ 189.9 and showed cross-peaks with the methyl proton signal at δ 2.0 and with H-22, respectively. Since the second carbonylic carbon C-24 (δ 208.8) coupled to

Table 1. ^{13}C and ^{1}H NMR and HETCOR data of compounds **1** and **2** (aglycone part) (75.425 MHz, pyridine-d_5)

C	**1*** δ (ppm)	**2*** δ (ppm)	HETCOR with H	**1** δ (ppm)	**2** δ (ppm)
1	35.8 (*t*)	35.8 (*t*)	1α	1.23	1.20
			1β	1.73	1.76
2	28.9 (*t*)	27.5 (*t*)	2α	1.97	2.34
			2β	2.06	2.05
3†	79.9 (*d*)	89.1† (*d*)	3	3.65	3.61
4	43.2 (*s*)	44.4 (*s*)	—	—	—
5	51.6 (*d*)	51.8 (*d*)	5	1.32	1.31
6	18.9 (*t*)	18.8 (*t*)	6α	1.87	1.84
			6β	1.55	1.52
7	26.8 (*t*)	26.9 (*t*)	7a	2.06	2.05
			7b	2.10	2.09
8	134.9 (*s*)	135.1 (*s*)	—	—	—
9	134.7 (*s*)	134.8 (*s*)	—	—	—
10	37.1 (*s*)	36.8 (*s*)	—	—	—
11	21.1 (*t*)	21.2 (*t*)	11α	2.17	2.22
			11β	2.03	2.03
12	25.2 (*t*)	25.3 (*t*)	12α	2.42	2.44
			12β	1.48	1.51
13	50.0 (*s*)	49.9 (*s*)	—	—	—
14	50.4 (*s*)	50.4 (*s*)	—	—	—
15	32.5 (*t*)	32.6 (*t*)	15α	1.53	1.51
			15β	1.77	1.76
16	40.0 (*t*)	40.1 (*t*)	16α	2.64	2.62
			16β	2.02	2.00
17	97.4 (*s*)	97.5 (*s*)	—	—	—
18	19.3 (*q*)	19.3 (*q*)	18	0.94	0.92
19	20.1 (*q*)	19.7 (*q*)	19	1.06	0.98
20	49.5 (*d*)	49.5 (*d*)	20	2.43	2.40
21	15.4 (*q*)	15.4 (*q*)	21	1.12	1.10
22	82.0 (*d*)	82.0 (*d*)	22	5.43	5.40
23	84.9 (*d*)	85.0 (*d*)	23	4.98	4.98
24	208.6 (*s*)	208.8 (*s*)	—	—	—
25	33.3 (*t*)	33.3 (*t*)	25a, b	2.55	2.57
					2.57
26	7.5 (*q*)	7.6 (*q*)	26	1.07	1.09
30	23.3 (*q*)	23.1 (*q*)	30	1.56	1.56
31	64.3 (*t*)	63.2 (*t*)	31a	3.75	3.66
			31b	4.59	4.44
32	26.4 (*q*)	26.5 (*q*)	32	1.58	1.59
$\underline{C}H_3COO$-	20.8 (*q*)	20.8 (*q*)	$\underline{C}H_3COO$-	1.99	2.00
$CH_3\underline{C}OO$-	169.8 (*s*)	169.8 (*s*)	—	—	—

* Carbon multiplicities from DEPT experiments.
† Glycosidation site.

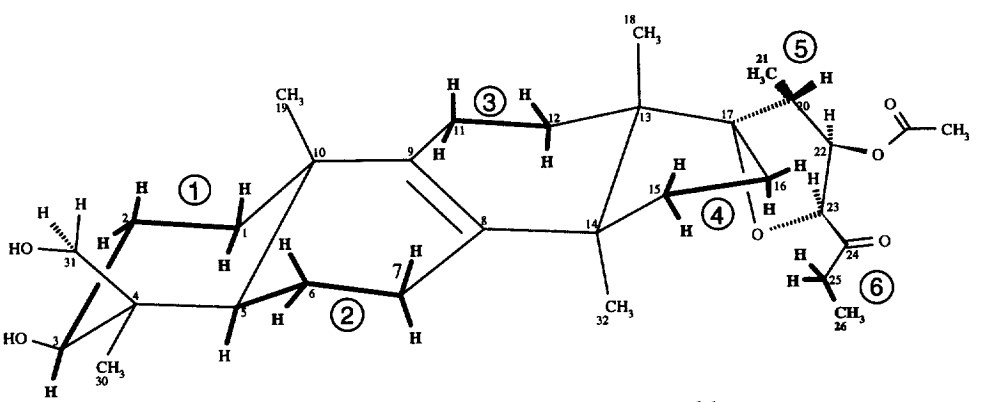


Fig. 1. 2D-H-H-COSY-correlations of compound **1**.

Table 2. HMBC data of compounds **1** and **2** (agyclone part) (75.425 MHz)

C	**1** with 7 Hz H (pyridine-d_5)	**1** with 10 Hz H ($CDCl_3$)	**2** with 7 Hz H (pyridine-d_5)
1	19	19	19; 5; 26
2	—	—	1α, β; 3
3	30	30; 31a	1β; 2α; 5; 30; 31a, b; 1.1*
4	6β	—	2α; 3; 5; 6α; 30; 31a, b
5	19; 30	19	1β; 6α; 19; 30; 31a
6	—	—	5
7	—	5	5; 6α; β
8	32	32	32
9	19	19	6α; 12β; 19
10	19	19	1α, β; 2α; 5; 6α; β; 19
11	—	—	12α, β
12	18	18; 20	18
13	18; 32	18; 12β; 15α	12α, β; 15α; 16α; 18; 32
14	18; 32	18; 12β; 15α	12β; 15α, β; 16β; 18; 32
15	32	32	16α, β; 32
16	—	—	15β; 20
17	18; 21	16α; 18; 20; 21; 22; 23	12α, β; 15α; 16α; 18; 20; 21; 22; 23
18	—	—	12α, β
19	—	1α; 5	1α, β; 5
20	21	21	16β; 21; 22
21	20	20; 22	20; 22
22	20; 21	20; 21	21; 20
23	20	20	20; 22
24	25; 26	23; 25; 26	23; 25; 26
25	26	26	26
26	25	25	25
30	—	31a, b	3; 5; 31a, b; 1.1*
31	30	30	3; 5; 31
32	—	—	15α, β
$\underline{C}H_3COO$-	—	—	—
$CH_3\underline{C}OO$-	$C\underline{H}_3COO$-	22; $C\underline{H}_3COO$	$C\underline{H}_3COO$-; 22

* Proton of sugar unit **S–1**.

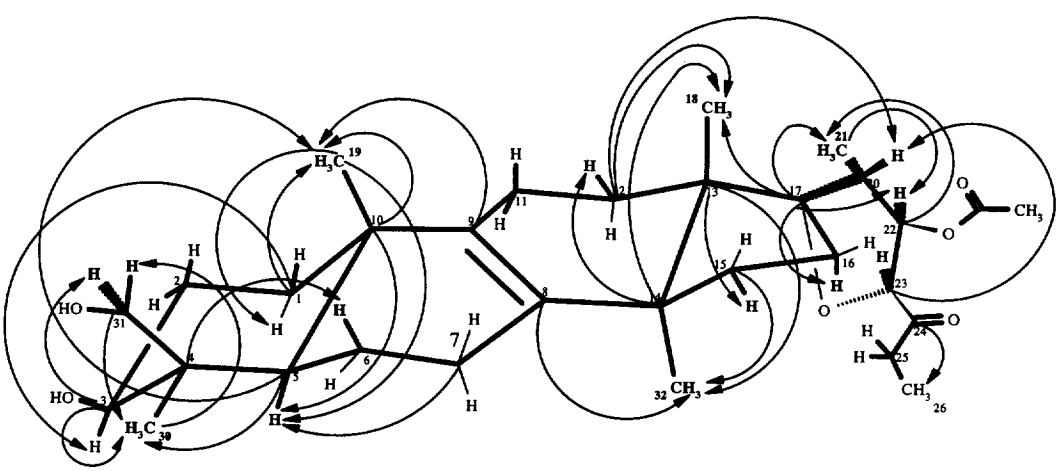


Fig. 2. HMBC-correlations of compound **1**.

H-23, H_2-25 and H_3-26, respectively, the substituent at C-23 was identified as a propionyl moiety. In addition to the evidence on rings C, D, and E of the skeleton and the demonstration of the connections between C-9, C-10 and the methyl C-19 it was also observed that C-10 showed a cross-peak with H-5 thus connecting the structural element of H-5, Hα,β-6, and Hα,β-7. The long-range coupling of C-1 with H_3-19

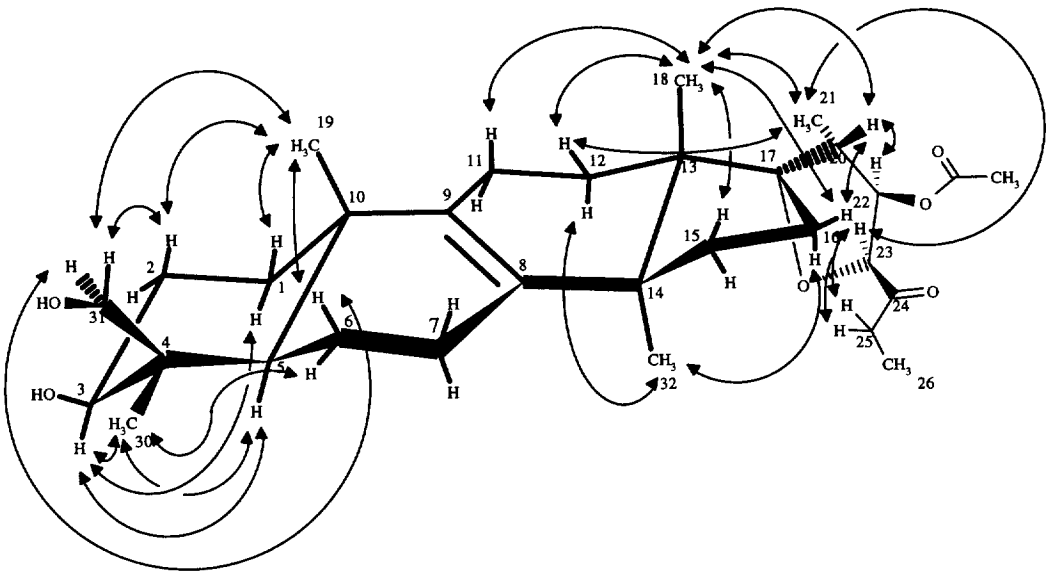


Fig. 3. 2D-ROE-correlations of compound **1**.

fixed the connection between C-10 and C-1, which was further linked to the hydroxylated C-3 via the C-2-methylene. The quaternary C-4 showed a long-range cross-peak with Hβ-6, which imposed not only the closure of ring A between C-3 and C-5, via C-4 but also the connection of ring A and the closure of ring B between C-7 and C-8. The substituent at C-4 was determined via cross-peaks between C-5 and H_3-30, C-3 and H_3-30, Ha-31, respectively, which were also observed for C-30 and Ha,b-31 as well as for C-31 and H_3-30. Taken together the steroidal skeleton with a C-16, C-17-annellated ring E was established for compound **1**.

The relative configuration of **1** and the assignments to the α- or β-position of the protons were made by 2D-^{1}H-^{1}H-ROESY experiments. The results are demonstrated in Fig. 3. The assignments of C-13 and C-14 could only be achieved by 1D-INEPT experiments with compound **2**. Hα-11 was chosen for the first set of experiments since its signal was apart from all other signals susceptible to showing long-range couplings with either C-13 or C-14. Hα-11 itself could only couple via three bonds with C-13. The experiments were done with 10 Hz settings and shift values of δ 2.16, 2.21 and 2.25, respectively, which enclose the shift value of δ 2.22 belonging to Hα-11. They should cause signals of the coupling carbons with nearly the same intensity in each of the three experiments whereas the interfering protons Hα-2, Hβ-16, and C$\underline{H}_3$COO- should cause signals with varying intensities. Accordingly the signal at δ 49.9 was assigned (refers to δ 50.0 of compound **1**) to C-13. Secondly, experiments with 6 and 10 Hz settings, respectively, were performed with the shift centre at δ 2.07 of the Ha,b-7 signal-groups for the identification of the C-14 signal. As a result both spectra showed a carbon signal at δ 50.4 (refers to δ 50.4 of compound **1**) which was unambiguously assigned to C-14. In summary compound **1** and the aglycone moiety of compound **2** were identified as the new spirocyclic nortriterpene 22-acetoxy-16-deoxo-eucosterol (**1**).

The structure of the glycosidal chain of compound **2** was determined as follows. Subtraction of the aglycone C-signals from the ^{13}C NMR spectrum of compound **2** left six methylene, 21 methine, and one quaternary carbon signals accounting for the glycosidal moiety. Five anomeric carbon signals at δ 111.0, 106.1, 104.5, 103.6 and 101.8 were correlated via a HETCOR spectrum to the anomeric proton signals at δ 6.22, 4.98, 5.14, 5.06 and 5.10, respectively. The complex sugar portion of the 500 MHz ^{1}H NMR spectrum was analysed by 1D-TOCSY [2] experiments using appropriate mixing times in order to identify the structures and configurations of the five contained monosaccharides. With five separate experiments, each starting with one of the anomeric proton signals, it was possible to extract the proton spin systems for each of five sugar moieties. The spectra are shown in Fig. 4.

For unambiguous assignment of the 1D-TOCSY signal groups to the corresponding protons of a single sugar, 2D-TOCSY spectra with different mixing times had to be recorded simultaneously showing the coupling protons of each spin system one by one. From these spectra, proton signals and coupling constants of the first, second, third and fifth sugar moieties could be assigned as the corresponding carbon signals were determined accordingly from the HETCOR spectrum. From these combined experiments the five sugars were identified as three glucose and two pentose units.

The structure of the fourth sugar could not be elucidated solely by the 1D-TOCSY spectra since it showed only one coupling of H-4.1 at δ 6.22 to H-4.2 at δ 4.70 but at least giving a hint for a quaternary C-4.3. Taking into account the proton signal groups of sugar one to three as well as of sugar five there were only two doublet signals left at δ 4.32 and 4.79 for one

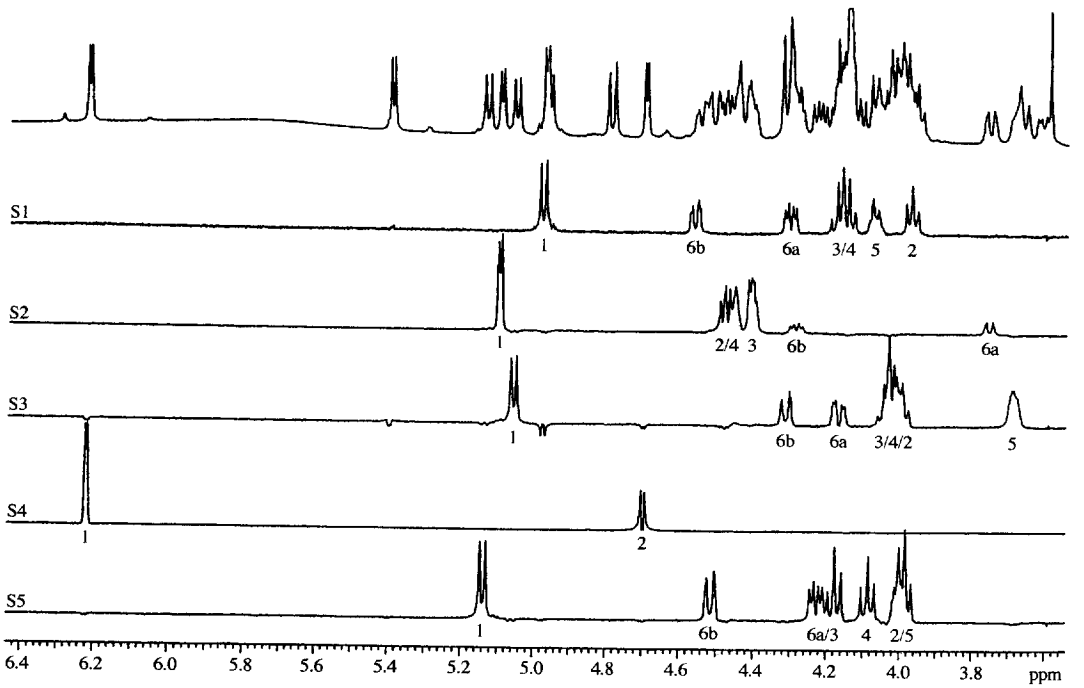


Fig. 4. 1D-TOCSY Spectra of the sugar moiety of compound **2**.

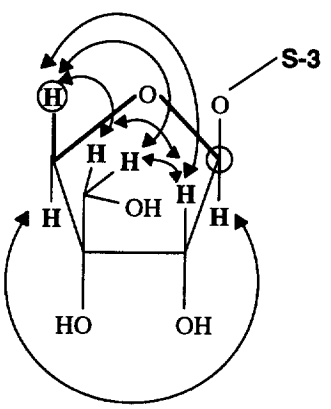


Fig. 5. HMBC-(○–○) and 2D-ROE (↻)-correlations of sugar moiety **S–4**.

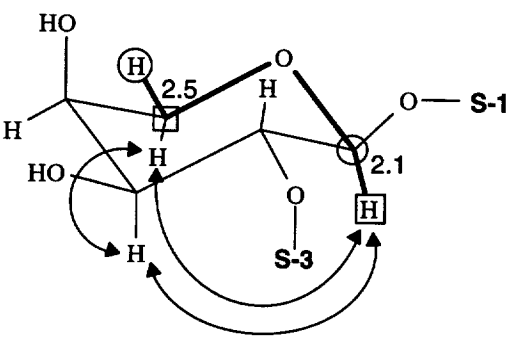


Fig. 6. HMBC-(□–□; ○–○) and 2D-ROE(↻)-correlations of sugar moiety **S–2**.

methylene group and a singlet at δ 4.15 for a second methylene group. Structural support for an apiose came from the HMBC spectrum with cross-peaks of C-4.1 with H-4.2 as well as with the proton signal at δ 4.32, which could be assigned to Ha-4.4 (Fig. 5). Accordingly, the proton signal group at δ 4.79 was attributed to Hb-4.4 and the two proton singlet at δ 4.15 to Ha,b-4.5.

The nature of sugar two was elucidated by HMBC long-range cross-peaks between C-2.1 and Ha,b-2.5 as well as between C-2.5 and H-2.1 (Fig. 6). These three bond couplings are only observed in a pyranoside structure type.

The connections between the single sugar units and the aglycone were deduced from the HMBC spectrum. As a result the aglycone had a C-3 *O*-glycosidal link to C-1.1 of sugar one, C-1.6 to C-2.1 of sugar two, and C-2.2 to C-3.1 of sugar three the glycoside chain branches. The two further links connect C-3.2 with C-4.1 of sugar four and C-3.3 with C-5.1 of sugar five. The data are shown in Table 3.

After complete signal assignments to the single sugar units, as well as the unambiguous elucidation of their connections, the types of sugars including their α, β and D, L-configuration remained to be identified. The coupling constants of the anomeric protons of sugars one, three, and five, 7.4, 7.4 and 7.7 Hz, respectively, were decisive for three β-glucose units. This was proved by RO effects, which are shown in Fig. 7. The RO effects of sugar two are seen in Fig. 6. No cross-peaks between H-2.2, H-2.4, and Hb-2.5 could be observed. Taken together with the results from HMBC, an α-arabinopyranose unit was indicated. The ROE signals of sugar four shown in Fig 5,

Table 3. ^{13}C and ^{1}H NMR-, DEPT-, HETCOR-, ROESY- and HMBC-data of sugar moiety **S-1**–**S-5** of **2** (75.425 MHz, pyridine-d_6)

C/H	δ_C* (ppm)	δ_C† (ppm)	δ_H‡ (ppm)	ROESY with H	HMBC (7 Hz) with H
S–1		**V–1**			
1.1	106.1 (*d*)	105.5–106.1	4.98	3§; 30§; 1.3; 1.5	3§; 1.2; 1.5
1.2	75.4 (*d*)	75.3–75.6	3.96	1.4	1.3
1.3	78.4 (*d*)	78.2–79.0	4.16	1.1	1.1; 1.2; 1.4
1.4	72.4 (*d*)	71.5–72.6	4.14	1.2; 1.6a, b	1.3; 1.5; 1.6a, b
1.5	76.0 (*d*)	75.5–75.7	4.07	1.1	1.1; 1.4; 1.6a
1.6a	69.0 (*t*)	68.6–68.9	4.30	1.4; 2.1	1.4; 2.1
b			4.55	1.4; 2.1	
S–2		**V–2**			
2.1	101.8 (*d*)	101.1–101.5	5.10	1.6a, b; 2.3; 2.5a	1.6a, b; 2.2; 2.3; 2.5a, b
2.2	80.7 (*d*)	77.8–79.7	4.48	3.1	2.1; 2.3; 2.4; 3.1
2.3	72.4 (*d*)	72.1–72.4	4.40	2.1; 2.5a; 3.1	2.1; 2.2; 2.5a, b
2.4	67.3 (*d*)	66.5–67.2	4.44	—	2.2; 2.5b
2.5a	64.4 (*t*)	63.1–64.8	3.76	2.1; 2.3	2.1
b			4.29	—	
S–3		**V–3**			
3.1	103.6 (*d*)	102.5–103.6	5.06	2.2; 2.3; 3.3; 3.5	2.2; 3.2
3.2	81.1 (*d*)	77.6–81.7	4.00	4.1	3.3; 3.4; 4.1
3.3	88.2 (*d*)	86.3–88.2	4.03	3.1; 4.1; 5.1	3.2; 3.4; 5.1
3.4	69.3 (*d*)	68.9–69.0	4.03	3.6a	3.3; 3.6b
3.5	77.5 (*d*)	77.6–77.8	3.69	3.1	3.6a, b
3.6a	61.9 (*t*)	61.7–62.0	4.17	3.4	3.4
b			4.32	—	
S–4		**V–4**			
4.1	111.2 (*d*)	111.0	6.22	3.2; 3.3; 4.4a; 5.1	3.2; 4.2; 4.4a, b
4.2	77.7 (*d*)	77.9	4.70	4.4b; 4.5a, b; 5.1	4.1; 4.4a, b;
4.3	79.5 (*s*)	80.2	—	—	4.1; 4.2; 4.4a, b; 4.5a, b
4.4a	74.8 (*t*)	75.5	4.32	4.1	4.1; 4.2; 4.5a, b
b			4.79	4.2; 4.5a, b	
4.5a	64.9 (*t*)	65.5	4.15	4.2; 4.4b	4.2; 4.4a, b
b			4.15		
S–5		**V–5**			
5.1	104.5 (*d*)	106.2	5.14	3.3; 4.1; 4.2; 5.3; 5.5	3.3; 5.2; 5.3; 5.5
5.2	75.1 (*d*)	75.8	3.98	—	5.3
5.3	78.3 (*d*)	78.1	4.18	5.1; 5.5	5.2; 5.4
5.4	71.5 (*d*)	70.6	4.09	5.6a	5.3; 5.6a, b
5.5	78.4 (*d*)	77.8	4.00	5.1; 5.3	5.4; 5.6a
5.6a	62.3 (*t*)	62.9	4.22	5.4	5.4
b			4.52	—	

* Carbon multiplicities from DEPT experiment.

† From the lit. [3].

‡ HSQC-correlated.

§ Protons of the aglycone.

V–1: β-D-Gluco-pyranosyl/1,6-connected, **V–2**: α-L-Arabino-pyranosyl/1,2-connected, **V–3**: β-D-Gluco-pyranosyl/1,2,3-connected, **V–4**: β-D-Apio-D-furanosyl/1-connected and **V–5**: β-D-Gluco-pyranosyl/1-connected.

together with the results from HMBC, lead to the structure and configuration of a β-apiofuranose unit.

The absolute configuration of the sugars was derived by comparison of the ^{13}C NMR signals with the literature data [3]. A maximum deviation of 2 ppm gives evidence of identical configurations. Any enantiomeric sugar unit would have given rise to a diastereomeric glycosidal chain with distinctive chemical shift deviations. Summarising, the sugar chain consisted of a β-D-glucose linked to the C-3 of the aglycone via C-1.1 followed by a 6 → 1 link to α-L-arabinose, a 2 → 1 connection to a second β-D-glucose, which bears a 2 → 1 link to a β-D-apio-D-furanose and a 3 → 1 link to a third β-D-glucose.

In conclusion 3β-[*O*-β-D-glucopyranosyl-(1 → 6)-*O*-α-L-arabinopyranosyl-(1 → 2)-*O*-(3-*O*-β-D-gluco-pyranosyl-(1 → 3))-β-D-glucopyranosyl-(1 → 2)-*O*-β-D-apio-D-furanosyl]-(22*R*,23*S*)-22-acetoxy-31-hydroxy-17,23-epoxy-27-nor-5α-lanost-8-en-24-on (**2**), a 22-acetoxy-15-deoxo-eucosterol pentaglycoside to-

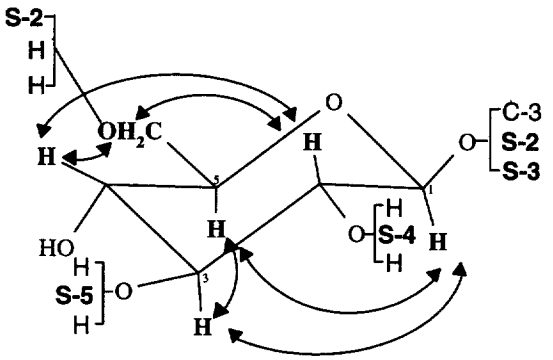


Fig. 7. 2D-ROE-correlations of sugar moieties **S–1**, **3**, **5**.

gether with it's aglycon **1** have been isolated for the first time. Copies of the original spectra can be obtained from the author (AWF).

EXPERIMENTAL

General. Mps. Optical rotations were determined on a Perkin-Elmer 241 polarimeter. ^{1}H NMR 500 MHz and ^{13}C NMR 300 MHz. FAB MS: 70 eV and HRESI-MS on a MAT-95a. CC was performed on Sephadex LH20® (Pharmacia), Lobar B LiChroprep® Si 60 (40–63 μm), Lobar B LiChroprep® RP 18 (40–63 μm) (Merck), HPLC on a LiChrosorb® RP-18 (5 μm; 250 × 4 mm) (Merck), and silica gel 60 F_{254} for TLC (Merck). TLC spots/bands were located/detected with a UV lamp and 40% H_2SO_4 followed by heating at 120° for 5 min, respectively.

Extraction and isolation of the compounds. The plants of *Veltheimia viridiflora* were cultivated from seeds and identified at TU Berlin [4]. Plant material was harvested after a growing period of 4 to 5 years in April 1991. A voucher specimen no. 471 is deposited in the herbarium of the TU Berlin. The cut and freeze dried bulb material (3.8 kg) was successively extracted in a Soxhlet apparatus with petrol (2 × 3 l), Et_2O (2 × 3 l) and $CHCl_3$ (2 × 3 l). The following extraction steps with $CHCl_3$–2-PrOH. (3:2) (10 × 2 l) and MeOH (10 × 2 l), respectively, were performed at room temp. The solns were concd under red. pres. to yield five crude extracts (15.6, 15.4, 12.2, 64.3 and 344.3 g, respectively).

Compound **1** was isolated from the petrol extract which was suspended in 90% MeOH (5 l). After filtration over Celite® the solvent was removed in vacuum yielding 5.3 g extract. A portion (441 mg) of the extract was chromatographed on Lobar B LiChroprep® Si 60 (gradient of *n*-hexane–Et_2O, 4:1 to 0:10; 1 ml min^{-1}) producing 600 frs of 5 ml each. From fr. 569 1.7 mg of **1** could be crystallized. Further purification of frs 565–569 by RP 18 HPLC (gradient MeOH–H_2O 13:7 to 100:0; 0.8 ml min^{-1}) gave pure **1** (2.6 mg) as white needles. The $CHCl_3$–2-PrOH extract was chromatographed in 6 portions of 10 g on Sephadex LH 20® (MeOH; about 2 ml min^{-1}) sampling 10 ml frs. These frs were combined after TLC control to give 15 crude frs. Crude fr. 3 (11.8 g) was further sepd by chromatography on Sephadex LH 20® (MeOH–H_2O, 19:1; about 2 ml min^{-1}) and Lobar B LiChroprep® RP 18 (MeOH–H_2O 13:7; 0.7 ml min^{-1}) which gave 300 mg of **2**. The sepn of 1 g crude fr. 4 (17.2 g) on Lobar B LiChroprep® RP 18 (MeOH–H_2O 13:7; 0.7 ml min^{-1}) yielded another 20 mg portion of **2**.

Compound **1**. (22*R*,23*S*)-22-Acetoxy-3β,31-17,23-epoxy-dihydroxy-27-nor-5α-lanost-8-en-24-one (22-acetoxy-15-deoxo-eucosterol) ($C_{31}H_{48}O_6$). White needles, mp 176°, $[\alpha]_D^{25}$ −17.0° (MeOH; $c = 0.1$). HRESI-MS *m/z*: 516.3434 $[M]^+$ (calcd *m/z*: 516.3451). For NMR data see, Tables 1 and 2.

Compound **2**. 3β-[*O*-β-D-Glucopyranosyl-(1 → 6)-*O*-α-L-arabinopyranosyl-(1 → 2)-*O*-(3-*O*-β-D-glucopyranosyl-(1 → 3))-β-D-glucopyranosyl-(1 → 2)-*O*-β-D-apio-D-furanosyl]-(22*R*,23*S*)-22-acetoxy-31-hydroxy-17,23-epoxy-27-nor-5α-lanost-8-en-24-one ($C_{59}H_{94}O_{29}$). White amorphous powder, mp 206–209° (decomposition), $[\alpha]_D^{25}$ −48.9° (MeOH; $c = 3.4$). FAB MS (positive ion-mode) *m/z*: 1289 $[M+Na]^+$ ($[M]^+$ calculated *m/z*: 1266.6). For NMR data see: Tables 1, 2 and 3.

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