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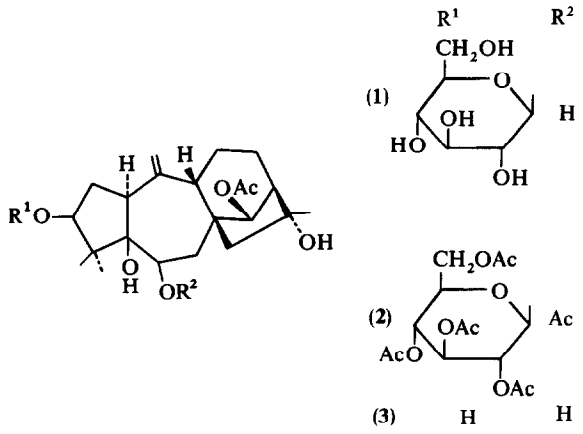
Key Word Index—*Leucothoe grayana*; Ericaceae; diterpene glucoside; grayanoside A.

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.



In general, carbinyl carbon (α-carbon) signals of aglycone alcohols are displaced by +7.0 ppm on glucosidation [3, 4]. The C-3 signal of the aglycone **3** was observed at δ 80.8, and the corresponding C-3 signal of the glucoside **1** was observed at δ 88.4. On the other hand, all other carbinyl carbon signals scarcely shifted on the glucosidation. Therefore, β-D-glucose must be attached at C-3 of **3**.

From these results, we can conclude that grayanoside A(**1**) is 5β,6β,16α-trihydroxy-14β-acetyloxy-3β-(β-D-glucopyranosyl)oxy-A-nor-B-homo-ent-kaur-10(20)-ene.

EXPERIMENTAL

Mps were uncorr. PMR spectra were measured at 100 MHz. ^{13}C-NMR spectra were measured at 15 MHz. Plants were collected at Hokkaido (northern island of Japan).

Extraction and isolation of **1**. Dry leaves and stems (4.3 kg) were extracted first with hot C_6H_6 and then with hot MeOH. The methanolic extracts were diluted with 3 litres of H_2O. The ppt was filtered off and then saturated lead subacetate soln was added to the filtrate. The resulting ppt was filtered and H_2S gas was bubbled into the filtrate. PbS was separated. The soln was concd *in vacuo* to 700 ml, and then extracted with $CHCl_3$, EtOAc and *n*-BuOH, successively. The *n*-BuOH extract was chromatographed on a column of activated charcoal. The MeOH–H_2O (60:40 to 65:35) eluate was concd to dryness and chromatographed on a Si gel column. The MeOH–$CHCl_3$ (15:85) eluate gave a syrup (2 g). The syrup (700 mg) was applied to a silanized Si gel column in MeOH–H_2O (20:80 to 40:60) to give **1** (100 mg).

Grayanoside A (**1**). Viscous syrup. $[\alpha]_D^{25}$ − 19.1 (MeOH c = 2.35), HPLC: JASCO FLC-150; 20% MeOH in H_2O 1.5 %/min gradient 0.75 ml/min, 50 cm × 2.1 mm φ, JASCO-DAC SV-02, UV detector operating at 204 nm (JASCO UVIDEC 100), retention time 5 min.

Pentaacetylgrayanoside A (**2**). Treatment of **1** with Ac_2O–Py for 15 hr at room temp. gave **2**; mp 196–199 (Et_2O); (Found: C 59.30; H 7.08. Calc. for $C_{38}H_{54}O_{16}$ C 59.52; H 7.10%).

Acid hydrolysis of **1**. A soln of **1** in dioxane (1 ml) and 5% H_2SO_4 (2 ml) was heated for 2.5 hr on a water bath. The mixture was cooled, diluted with H_2O (2 ml) and then extracted with EtOAc. The EtOAc extract was evapd *in vacuo* to give a complex mixture. The aq. layer was treated with Amberlite CG-4B-(OH^-) and evapd *in vacuo*. The sugar was converted to the TMSi derivative and identified as TMSi-D-glucose by GLC. The analysis of the TMSi-sugar was performed on a GLC equipped with FID and a stainless column, packed with 5% OV-1 (2 m × 3 mm) at 155°. Identification was made by comparison of the R_t with an authentic standard.

Enzymatic hydrolysis of **1**. To a soln of **1** (31 mg) dissolved in HOAc–NaOAc buffer (pH 4.1, 10 ml) crude naringinase 'SANKYO' (100 mg) was added and the reaction mixture was incubated for 16 hr at 40°. The product was extracted with EtOAc and the extract was purified by Si gel PLC (2 mm) with MeOH–$CHCl_3$ (1:9). The aglycone (**3**) was detected by I_2 vapor, and was eluted with MeOH–EtOAc (1:9), to yield crystals (6 mg). Compound **3** was identified as grayanotoxin IV by TLC, IR and mmp.

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NEW PHENOLIC DIGLYCERIDES FROM *AEGILOPS OVATA**

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Key Word Index—*Aegilops ovata*; Gramineae; phenolic fraction; scopoletin; *p*-coumaric acid; phenolic diglycerides; 1,3-diferulylglycerol; 1-ferulyl-3-*p*-coumarylglycerol; CMR spectroscopy.

Abstract—Two novel phenolic diglycerides have been isolated from *Aegilops ovata* together with scopoletin and *p*-coumaric acid. Spectroscopic evidence and a synthesis confirmed the proposed structures which are presented together with the CMR data for these diglycerides and related model compounds.

INTRODUCTION

The genus, *Aegilops* (Gramineae), is considered to be one of the ancestors of the cultivated wheat [1], *Triticum aestivum*. The genus *Triticum* has recently been examined for its flavonoid constituents [2]. During our studies on wild progenitors of wheat for the presence of naturally occurring germination inhibitors, an examination of the phenolic constituents of *Aegilops ovata* L. was undertaken [3, 4]. We now wish to report some other phenolics of *Aegilops ovata*.

*Part II in the series "*Constituents of the Gramineae*". For Part I see [3].