453 $[M-PMAra]^+$ (61.6), 262 $[RDA]^+$ (47.4), 203 $[RDA-COOMe]^+$ (100), 175 $[PMAra]^+$ (33.4).

The permethylether (10 mg) was refluxed in 5% HCl–MeOH (3 ml) for 5 hr. The reaction mixture was poured onto ice, filtered and the ppt was crystallized from MeOH to give methyl oleanolate, mp 201–202° (mmp, co-TLC). The filtrate was extracted with $CHCl_3$. The $CHCl_3$ soln was evaporated. The residue was found to be methyl-2,3,4-tri-*O*-methyl-L-arabinopyranoside by GC (column, 5% NPGS, 4 mm × 1.5 m; column temp., 180°; injector temp., 200°; N_2, 45 ml/min; R_t, 3.6 min).

Hydrolysis of compound **5**. A soln of **5** (20 mg) in 5% HCl–MeOH (5 ml) was refluxed for 5 hr and concd under red. pres. to remove MeOH. After addition of H_2O the resulting ppt was filtered and crystallized from MeOH to yield a sterol mixture, mp 128–131°; MS *m/z* (rel. int.): 414 $[M_1]^+$ (100), 400 $[M_2]^+$ (37.8), 329 $[M_1-C_5H_9O]^+$ (100), 315 $[M_2-C_5H_9O]^+$ (27.1), 303 $[M_1-C_7H_{11}O]^+$ (47.6), 289 $[M_2-C_7H_{11}O]^+$ (20.4), 275 $[M_1-C_9H_{15}O]^+$ (22.7), 273 $[M-\text{side chain}]^+$ (79.6), 261 $[M_2-C_9H_{15}O]^+$ (11.1), 255 $[M-\text{side chain}-H_2O]^+$ (76.9), which was found to consist of sitosterol (64.5%, R_t 3.4 min) and campesterol (35.5%, R_t 2.8 min) by GC (column, 3% OV-I, 4 mm × 1.5 m; column temp., 270°; injector temp., 300°; N_2, 45 ml/min). The filterate was hydrolysed with conc. HCl, neutralized with Ag_2CO_3 and subjected to TLC (cellulose; pyridine–EtOAc–HOAc–H_2O, 36:36:7:21); only D-glucose (R_f 0.27) was detected.

Acid hydrolysis of compound **6**. Acid hydrolysis of **6** (50 mg) under the same conditions as for **3** yielded **2** and L-arabinose.

Acetylation of compound **6**. Acetylation of **6** (50 mg) under the same conditions as for **3** gave the same acetate as that prepared from **3**.

Permethylation of compound **6** *followed by methanolysis*. Permethylation of **6** (30 mg) according to the method of ref. [5] gave a permethylated product, mp 163–165°; MS *m/z* (rel. int.): 674 $[M]^+$ (0.24), 483 $[M-PMAra]^+$ (26.2), 262 $[RDA]^+$ (64.3), 203 $[RDA-COOMe]^+$ (100), 175 $[PMAra]^+$ (43.2); ^1H NMR ($CDCl_3$): δ 0.68–1.09 (Me × 6), 3.3, 3.41, 3.47, 3.55, 3.6 (3H each, *s*, OMe × 5), 4.17 (1H, *d*, J = 7 Hz, anomeric H).

The product (10 mg) was hydrolysed with 5% HCl–MeOH as above to yield 23-*O*-methylhederagenin methylester, mp 203–206°, identified by direct comparison with an authentic sample. By GC under the same conditions as above, methyl-2,3,4-tri-*O*-methyl-L-arabinopyranoside was detected in the filtrate freed from the genin.

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18-NORSPIROSTANOL DERIVATIVES FROM *TRILLIUM TSCHONOSKII*

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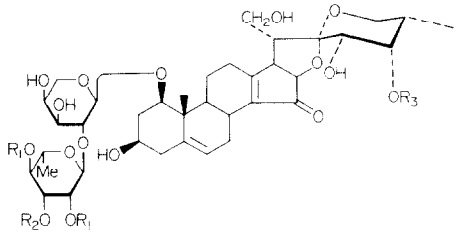
Key Word Index—*Trillium tschonoskii*; Liliaceae; 18-norspirostanol oligoside; acylated glycoside.

Abstract—Three 18-norspironstanol oligoglycosides partly acylated in their sugar moieties were isolated from the underground parts of *Trillium tschonoskii*. Their structures were characterized, as 1-*O*-[2″,3″,4″-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranosyl]-epitrillenogenin-24-*O*-acetate, 1-*O*-[2″,3″,4″-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranosyl]-epitrillenogenin and 1-*O*-[2″,4″-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranosyl]-epitrillenogenin-24-*O*-acetate.

INTRODUCTION

Previously, we reported the structural characterizations of Ts-a (dioscin), Ts-b (methyl proto-dioscin) [1] and Ts-c [2] isolated from the underground parts of *Trillium tschonoskii*. Our continuing study of this plant has led to the isolation of three additional 18-norspirostanol derivatives [3–6]. They are novel steroidal oligosides, designated Ts-d (**1**), Ts-e (**2**) and Ts-g (**3**), and this paper



1 $R_1 = R_2 = R_3 = Ac$ (Ts-d)
2 $R_1 = R_2 = Ac, R_3 = H$ (Ts-e)
3 $R_1 = R_3 = Ac, R_2 = H$ (Ts-g)
5 $R_1 = R_2 = R_3 = H$

deals with the structure elucidations of these compounds.

RESULTS AND DISCUSSION

Ts-d (**1**), a white powder, $[\alpha]_D - 79.6°$ ($CHCl_3$), showed absorptions in the IR spectrum due to an ester (1740 cm^{-1}) and α,β-unsaturated carbonyl (1700, 1625 cm^{-1}) together with a hydroxy group (3550 cm^{-1}). In the mass spectrum, it showed a peak at *m/z* 273 derived from the terminal peracetylated methylpentosyl cation. On acid hydrolysis with 2 N hydrochloric acid–methanol, **1** yielded an 18-norspirostanol derivative, epitrillenogenin (**4**) [5] as an aglycone along with arabinose and rhamnose as sugar components. On alkaline treatment of **1**, it gave a glycoside which was identical with the acetyl-free compound, epitrillenoside C (**5**), derived from epitrillenoside CPA [5] which was previously obtained from *Trillium kamtschaticum*. The ^1H NMR spectrum of **1** exhibited four acetoxyl signals at δ 2.07 (× 2), 2.16 and 2.18 and four methine protons at 5.32 (*dd*, *J* = 2.5, 3.5 Hz), 5.20 (*dd*, *J* = 2, 3 Hz), 5.45 (*dd*, *J* = 3, 10 Hz) and 5.04 (*t*, *J* = 10 Hz) adjacent to their acetoxyl groups, being ascribable to H-24, H-2″, H-3″, and H-4″, respectively. Therefore, the structure of **1** can be represented as 1-*O*-[2″, 3″, 4″-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranosyl]-epitrillenogenin-24-*O*-acetate.

Ts-e (**2**), a white powder, $[\alpha]_D - 121.0°$ ($CHCl_3$), showed a similar IR spectrum [3550 (OH), acetoxyl (1740 cm^{-1}) and α,β-unsaturated carbonyl (1700, 1625 cm^{-1})] to that of **1**. On alkaline treatment, **2** also yielded epitrillenoside C (**5**). The mass spectrum of **2** showed a peak at *m/z* 273 due to the peracetylated methylpentosyl cation. The ^1H NMR spectrum of **2** exhibited three acetoxyl signals at δ 2.16, 2.08 (× 2) and methine protons at 5.20, 5.43 and 5.05 assignable to H-2″, H-3″ and H-4″, respectively, of the rhamnosyl moiety. Therefore, **2** was deduced to be 1-*O*-[2″, 3″, 4″-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranosyl]-epitrillenogenin.

Ts-g (**3**), a white powder, $[\alpha]_D - 96.7°$ ($CHCl_3$), gave on alkaline treatment epitrillenoside C (**5**). The ^1H NMR spectrum of **3** showed three acetoxyls at δ 2.16, 2.12 and 2.06 and their acetoxyl methine protons at 5.30, 5.08 and 4.86 ascribable to H-24, H-2″ and H-4″, respectively. Consequently, **3** was deduced to be 1-*O*-[2″,4″-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranosyl]-epitrillenogenin-24-*O*-acetate.

EXPERIMENTAL

Isolation of Ts-d (**1**), *Ts-e* (**2**) *and Ts-g* (**3**). The MeOH extractives (316 g) of underground parts of *Trillium tschonoskii* Max. (3.5 kg) were partitioned between *n*-BuOH and H_2O (each 200 ml). The organic layer was evaporated under red. pres. to give a residue (126 g) which was chromatographed on Si gel using $CHCl_3$–MeOH (50:1–30:1) to afford Ts-d (460 mg), Ts-e (32 mg) and Ts-g (27 mg).

Ts-d (**1**). A white powder, $[\alpha]_D^{22} - 79.6°$ ($CHCl_3$; *c* 1.10). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (OH), 1740 (ester), 1700, 1625 (α, β-unsatd ketone). UV λ_{max}^{EtOH} nm: 247 (ε = 7970). FDMS (*m/z*): 923 $[M+H]^+$, 561, 519 $[923-(ara+rha\cdot 3Ac)]^+$, 405 $[ara+rha\cdot 3Ac]^+$, 273 $[rha\cdot 3Ac]^+$. EIMS (*m/z*): 584 $[C_{28}H_{40}O_{13}]^+$, 566, 542 $[C_{26}H_{38}O_{12}]^+$, 524, 500 $[C_{24}H_{36}O_{11}]^+$, 447, 417, 355, 273 $[rha\cdot 3Ac]^+$. ^1H NMR ($CDCl_3$): δ 0.82 (3H, *d*, *J* = 7 Hz, Me-27), 1.05 (3H, *s*, Me-19), 2.07 (OAc × 2), 2.16, 2.18 (OAc × 2), 4.47 (1H, *d*, *J* = 7 Hz, H-16), 5.04 (1H, *t*, *J* = 10 Hz, H-4″), 5.20 (1H, *dd*, *J* = 2, 3 Hz, H-2″), 5.32 (1H, *dd*, *J* = 2.5, 3.5 Hz, H-24), 5.43 (1H, *br s*, H-1″), 5.45 (1H, *dd*, *J* = 3, 10 Hz, H-3″), 5.59 (1H, *m*, H-6). [Epitrillenogenin penta-acetate; 0.82 (3H, *d*, *J* = 6 Hz, Me-27), 1.12 (3H, *s*, Me-19), 1.94, 2.02, 2.05, 2.07, 2.15 (OAc × 5), 3.45 (1H, *dd*, *J* = 6, 11 Hz, H_{eq}-26), 3.93 (1H, *dd*, *J* = 11, 11 Hz, H_{ax}-26), 4.11 (1H, *dd*, *J* = 9, 11 Hz, H-21), 4.42 (1H, *d*, *J* = 6 Hz, H-16), 4.43 (1H, *dd*, *J* = 4, 11 Hz, H′-21), 4.73 (1H, *dd*, *J* = 4, 11 Hz, H-1), 4.96 (1H, *d*, *J* = 3.5 Hz, H-23), 5.26 (1H, *dd*, *J* = 2.5, 3.5 Hz, H-24).] ^{13}C NMR ($CDCl_3$): δ aglycone part: 84.1, 37.2, 68.1, 42.5, 139.4, 124.8, 29.7, 31.7, 47.5, 42.1, 25.2, 28.0, 176.0, 138.7, 204.3, 81.7, 45.9, 13.6, 48.6, 61.5, 111.6, 71.7, 67.7, 34.1, 63.8, 12.1 (C-1–C-27); sugar moiety: 97.4, 75.1, 74.5, 69.9, 67.3 (arabinosyl C-1′–C-6′), 100.0, 70.2, 70.1, 72.7, 66.2, 17.8 (rhamnosyl C-1″–C-6″).

Acid hydrolysis of **1**. Compound **1** (3 mg) in 2 N HCl–MeOH (1 ml) was refluxed for 1 hr, then the soln was neutralized with 3% KOH–MeOH, concd and checked by Si gel TLC to detect epitrillenogenin (**4**) (R_f 0.50, $CHCl_3$–MeOH–H_2O, 8:2:0.2) and methylglycosides of arabinose (R_f 0.34) and rhamnose (R_f 0.41).

Alkaline hydrolysis of **1**. A soln of **1** (320 mg) in 3% KOH–MeOH (12 ml) was refluxed for 50 min. The soln was neutralized with 1 N HCl–MeOH and evaporated to dryness *in vacuo*. The residue was treated with MeOH and the soluble part was passed through a Sephadex LH-20 column (eluent MeOH) to give a glycoside (**5**) as a white powder (139 mg), R_f 0.30 ($CHCl_3$–MeOH–H_2O, 7:3:0.5), $[\alpha]_D^{21} - 135.7°$ (MeOH; *c* 0.71).

Ts-e (**2**). A white powder, $[\alpha]_D^{22} - 121.0°$ ($CHCl_3$; *c* 1.20), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (OH), 1740 (ester), 1700, 1625 (α, β-unsatd ketone). UV λ_{max}^{EtOH} nm: 247 (ε = 6300). FDMS (*m/z*): 903 $[M+Na]^+$. EIMS (*m/z*): 584 $[C_{28}H_{40}O_{13}]^+$, 566 $[C_{28}H_{38}O_{12}]^+$, 524, 482, 459, 417, 381, 355, 273 $[rha\cdot 3Ac]^+$, 231, 217, 189, 171. ^1H NMR ($CDCl_3$): δ 0.95 (3H, *d*, *J* = 7 Hz, Me-27), 1.06 (3H, *s*, Me-19), 2.08 (OAc × 2), 2.16 (OAc), 4.46 (1H, *d*, *J* = 7 Hz, H-16), 5.05 (1H, *t*, *J* = 10 Hz, H-4″), 5.20 (1H, *m*, H-2″), 5.43 (1H, *br s*, H-1″), 5.44 (1H, *dd*, *J* = 3, 10 Hz, H-3″), 5.60 (1H, *m*, H-6). Alkaline treatment of **2** afforded epitrillenoside (**5**).

Ts-g (**3**). A white powder, $[\alpha]_D^{21} - 96.7°$ ($CHCl_3$; *c* 0.90). EIMS (*m/z*): 584, 566, 542, 500, 459, 417, 381, 355, 339, 324, 296, 278, 266, 231, 217, 189, 171, 157. ^1H NMR ($CDCl_3$): δ 0.80 (3H, *d*, *J* = 7 Hz, Me-27), 1.04 (3H, *s*, Me-19), 2.06, 2.12, 2.16 (OAc × 3), 4.47 (1H, *d*, *J* = 7 Hz, H-16), 4.86 (1H, *t*, *J* = 10 Hz, H-4″), 5.08 (1H, *m*, H-2″), 5.30 (1H, *m*, H-24), 5.37 (1H, *br s*, H-1″), 5.60 (1H, *m*, H-6). Alkaline treatment of **3** gave epitrillenoside C (**5**).

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