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MONOTERPENE GLUCOSIDES AND OTHER CONSTITUENTS FROM *PERILLA FRUTESCENS*

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Key Word Index—*Perilla frutescens*; Labiatae; monoterpene glycoside; perilloside B; (−)-perillic acid; perilloside C; perilloside D; *trans* and *cis*-dihydroperillyl alcohol; β-sitosteryl *O*-β-D-glucopyranoside.

Abstract—Three new monoterpene glucosides named perilloside B–D have been isolated from the fresh leaves of *Perilla frutescens*. The structures were determined on the basis of spectral and chemical evidence.

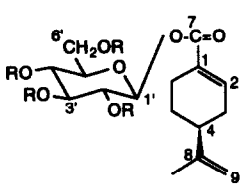
INTRODUCTION

In a previous study, we reported on the isolation and characterization of a new monoterpene glucoside named perilloside A, along with eugenyl *O*-β-D-glucopyranoside (=citrusin C) from the leaves of *Perilla frutescens* Britton *forma viridis* Makino (Japanese name; aojiso) [1]. We have now isolated three new monoterpene glucosides named perilloside B–D and other constituents from this plant.

RESULTS AND DISCUSSION

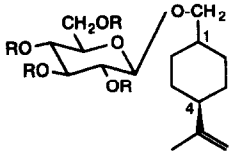
By using a combination of preparative TLC and HPLC, three new glucosidic compounds (**1a**, **2a**, **3**), the known β-sitosteryl *O*-β-D-glucopyranoside [2], and the two phenolics, protocatechuic aldehyde and methyl ferulate, were isolated from a methanolic extract of the fresh leaves of the plant.

Compound **1a**, named perilloside B, was obtained as needles. Its IR spectrum showed absorption bands due to hydroxyl groups (3400 and 1080 cm^{-1}) and carbonyl and olefinic groups (1720, 1700, 1650 and 1260 cm^{-1}). Its UV spectrum showed absorption maximum at 220.5 nm (log ε 4.03). These findings indicated that one conjugated ester was present in the molecule. The molecular formula was established as $C_{16}H_{24}O_7$ by SI mass spectroscopy (*m/z* 329 $[M+H]^+$) and elemental analysis (found: C, 58.50; H, 7.25, required: C, 58.53; H, 7.37%). The ^1H and ^{13}C NMR spectra were assigned based on the 2D NMR spectra (^1H–^1H and ^{13}C–^1H COSY, etc.). The ^1H NMR spectrum revealed the presence of an isopropenyl moiety [δ1.76 (3H, *s*, H-10), 4.74 (1H, *br s*, H-9a) and 4.76 (1H, *t*, *J* = 1.5 Hz, H-9b)] and another olefinic proton [δ7.14 (1H, *br d*, *J* = 4.9 Hz, H-2)]. Additionally, three signals due to a sugar moiety were observed at δ3.67 (1H, *dd*, *J* = 4.3, 12.2 Hz, H-6'a), 3.83 (1H, *dd*, *J* = 1.8, 12.2 Hz, H-6'b) and 5.53 (1H, *d*, *J* = 7.6 Hz, anomeric proton), the coupling constant of which indicated β-linkage with the aglycone. The ^{13}C NMR spectrum (Table 1) showed signals due to D-glucopyranoside. The signal of the anomeric carbon was attributed to an ester-type glucoside as it was upfield shifted like other known acyl glucosides [3]. Acetylation of **1a** yielded tetraacetate **1b** as a powder. The molecular formula of **1b** was confirmed by elemental analysis ($C_{24}H_{32}O_{11}$). The ^1H NMR spectrum of **1b** exhibited four signals due to acetyl groups at δ2.02, 2.03, 2.04 and 2.08 (each 3H, *s*) and an anomeric proton signal at δ5.75 (1H, *d*, *J* = 7.9 Hz). On hydrolysis with potassium hydroxide, **1a** gave an aglycone which was characterized as (−)-perillic acid. Thus, perilloside B was characterized as 1-β-D-glucopyranosyl (−)-perillate; the structure of **1a** was further confirmed by the following synthesis.



1a R = H

1b R = Ac



2a R = H (1,4-*trans*)

2b R = Ac (1,4-*trans*)

3 R = H (1,4-*cis*)

An authentic sample of 1-β-D-glucopyranosyl (−)-perillate was prepared from (−)-perilloyl chloride derived from (−)-perillic acid and 2,3,4,6-tetraacetyl D-glucose. Saponification of the synthetic tetraacetylglucoside (**1b**) with methanolic barium oxide by the method of Kasai *et al.* [3] gave the glucoside in low yields and methyl perillate as the major product, since saponification took place in preference to deacetylation. The two pairs of compounds had the same melting point, and were identical in every respect examined. Perilloside B was, thus, inferred to be 1-β-D-glucopyranosyl (−)-perillate.

Table 1. ^{13}C NMR spectral data for **1a**–**3** and **4** (δ values)

C	1a	1b	2a	2b	3	4†
1	130.4	128.6	39.3	37.7	35.2	135.4
2	142.3	142.5	31.1*	29.7*	27.9*	125.9
3	32.2	31.3	32.5	31.0	28.0*	31.6
4	41.2	39.8	46.9	45.3	45.4	42.3
5	28.1	26.8	32.5	31.0	28.0*	28.7
6	25.3	24.2	31.0*	29.5*	27.9*	27.4
7	167.2	164.8	76.4	75.7	72.8	74.3
8	159.9	148.4	151.9	150.6	151.1	150.9
9	109.8	109.3	108.7	108.1	109.2	109.2
10	20.9	20.5	21.1	20.6	21.5	21.0
1′	95.7	91.8	104.6	101.1	104.6	102.8
2′	73.9	70.1	75.2	71.4	75.2	74.9
3′	78.6*	72.7*	78.1	72.8	78.1	78.0
4′	70.9	67.9	71.7	68.5	71.7	71.5
5′	77.9*	72.6*	77.9	71.8	77.9	77.7
6′	62.2	61.5	62.8	62.0	62.8	62.7
CO		170.5		170.7		
		170.0		170.3		
		169.4		169.4		
		169.2		169.2		
Me		20.7		20.9		
		(2 × C)		20.7		
		20.5		20.6		
		(2 × C)		(2 × C)		

All spectra were measured in CD_3OD, except for **1b** and **2b**, which were measured in $CDCl_3$.

*Values in each column may be interchangeable.

†Perilloside A.

Compound **2a**, named perilloside C, was obtained as needles. Its IR spectrum showed absorption bands due to hydroxyl groups (3350, 1070 and 1030 cm^{-1}) and an olefinic group (1640 cm^{-1}). The molecular formula was established as $C_{16}H_{28}O_6$ by SI mass spectroscopy (*m/z* 317 $[M+H]^+$) and elemental analysis (found: C, 60.61; H, 8.77; required: C, 60.74; H, 8.92%). The ^{1}H NMR spectrum revealed the presence of an isopropenyl moiety [δ1.70 (3H, *s*, H-10), 4.65 (1H, *t*, J = 1.5 Hz, H-9a) and 4.66 (1H, *br s*, H-9b)], and an oxygenated methylene [δ3.34 (1H, *dd*, J = 7.0, 9.5 Hz, H-7a) and 3.73 (1H, *dd*, J = 6.6, 9.5 Hz, H-7b)]. Additionally, three signals due to a sugar moiety were observed at δ3.66 (1H, *dd*, J = 5.2, 11.9 Hz, H-6′a), 3.86 (1H, *dd*, J = 1.8, 11.9 Hz, H-6′b) and 4.23 (1H, *d*, J = 7.6 Hz, anomeric proton), which indicated β-linkage with the aglycone. Its ^{13}C NMR spectrum (Table 1) showed signals due to D-glucopyranoside. These findings indicated that the structure of **2a** was similar to perilloside A, except for the presence of a double bond in a cyclohexene ring. On enzymatic hydrolysis with β-glucosidase, **2a** gave an aglycone which was characterized as *trans*-dihydroperillyl alcohol (= *trans*-shisool, *trans*-8-*p*-menthen-7-ol) [4, 5]. These were identified by TLC, GC and/or GC-MS. The sugar moiety was identified as D-glucose by GC comparison of the trimethylsilyl derivatives of the hydrolysed product and authentic D-glucose. Acetylation of **2a** yielded tetraacetate **2b** as a powder. The molecular formula of **2b** was confirmed by elemental analysis ($C_{24}H_{36}O_{10}$). The ^{1}H NMR spectrum of **2b** exhibited four signals due to acetyl groups at δ2.01, 2.02, 2.04, 2.09 (each 3H, *s*) and an anomeric proton signal at δ4.47 (1H, *d*, J = 7.9 Hz). Thus, perilloside C was characterized as *trans*-dihydroperillyl 7-*O*-β-D-glucopyranoside; the structure of **2a** was further confirmed by the following synthesis.

An authentic sample of *trans*-dihydroperillyl 7-*O*-β-D-glucopyranoside was prepared from *trans*-dihydroperillyl alcohol and acetobromoglucose by a modified Koenigs–Knorr synthesis [1], followed by saponification of the corresponding synthetic tetraacetyl glucoside with methanolic potassium hydroxide. The two pairs of compounds had the same melting point and were identical in every respect examined. Perilloside C was, thus, shown to be *trans*-dihydroperillyl 7-*O*-β-D-glucopyranoside.

Compound **3**, named perilloside D, was obtained as a minor constituent. Its IR spectrum showed absorption bands due to hydroxyl groups (3350, 1070 and 1030 cm^{-1}) and an olefinic group (1640 cm^{-1}). The molecular formula was established as $C_{16}H_{28}O_6$ by SI-MS (*m/z* 317 $[M+H]^+$). The ^{1}H and ^{13}C NMR spectra showed the presence of an isopropenyl moiety [δ1.71 (3H, *s*, H-10), 4.69 (2H, *br s*, H-9) and 151.9 (C-8), 110.0 (C-9) and 22.3 (C-10), respectively] and an oxygenated methylene group [δ3.51 (1H, *dd*, J = 7.6, 9.5 Hz, H-7a) and 3.90 (1H, *dd*, J = 7.6, 9.5 Hz, H-7b) and 73.6 (C-7), respectively]. Additionally, three signals due to a sugar moiety were observed at δ3.67 (1H, *dd*, J = 5.2, 11.9 Hz, H-6′a), 3.87 (1H, *dd*, J = 1.8, 11.9 Hz, H-6′b) and 4.25 (1H, *d*, J = 7.6 Hz, anomeric proton), which indicated β-linkage with the aglycone. Its ^{13}C NMR spectrum (Table 1) also showed signals due to D-glucopyranoside, as well as **2a**. Its HPLC R_t approximated to that of **2a** and hence these findings revealed that the structure of **3** was similar to **2a**, and indicated that the aglycone moiety of **3** was the 1,4-*cis* isomer of dihydroperillyl alcohol, while that of **2a** was that of the 1,4-*trans* isomer. Therefore, the aglycones of **3** and **2a** were stereoisomers. On enzymatic hydrolysis with β-glucosidase, **3** gave an aglycone which was characterized as *cis*-dihydroperillyl alcohol (= *cis*-shisool, *cis*-8-*p*-menthen-7-ol). This was identified by TLC, GC and/or GC-MS, and then the sugar moiety was identified as D-glucose by the above method. Perilloside D was, thus, established to be *cis*-dihydroperillyl 7-*O*-β-D-glucopyranoside.

Compounds **1a**, **2a** and **3** are new natural compounds which are characterized by having a functional group at the C-7 position of the *p*-menthane skeleton. Compounds **2a** and **3** have a slightly sweet taste, similar to perilloside A, and hydrolyse slowly in the mouth with the evolution of shisool, whilst **1a** is slightly bitter and is not hydrolysed. They seem to be present in the plant as protected and stored forms of their aglycones or perillaldehyde. These shisool glucosides seem to be important precursors of flower flavour [6], since shisools are characteristic constituents of perilla flavour in perilla oils.

EXPERIMENTAL

General. Mp: uncorr.; specific rotations: MeOH; ^{1}H NMR: 270 MHz, using TMS as an int. standard; ^{13}C NMR; 67.8 MHz; SI-MS: matrix, glycerol; HPLC: Chemcosorb 5-ODS-H (4.6 i.d. × 150 mm) column.

Plant material. Plant materials used in the experiment were reported in the previous paper [1].

Isolation. Three frs, 24 (0.98 g), 25 (1.04 g) and 26 (0.77 g), which were obtained from the $CHCl_3$ extract of the plant in the course of a previous study [1], were assumed to contain other monoterpenoid glycosides. Fr. 21 (1.10 g) was assumed to contain sterol glycosides. Frs 24–26 were subjected to prep. TLC ($CHCl_3$–MeOH, 5:1) to give a crude mixt. of monoterpene glycosides (R_f 0.3–0.4). The crude glycoside mixt. was rechromatographed by prep. HPLC using H_2O–MeOH (1:1) and H_2O–MeOH (11:9) on a reversed phase column (Chemcosorb 5-ODS-H), to afford 3 compounds, perilloside B (**1a**, 363 mg), perilloside C (**2a**, 330 mg) and perilloside D (**3**, 30 mg). Fr. 21 was subjected to prep. TLC ($CHCl_3$–MeOH, 10:1) and recrystallized from MeOH–$CHCl_3$ to give β-sitosteryl β-D-glucopyranoside.

Perilloside B (**1a**). Needles, mp 154–155°, $[\alpha]_D^{22}$ −57.1° (MeOH; *c* 0.645). IR ν_{max}^{KBr} cm^{-1}: 3400, 1720, 1700, 1650, 1260 and 1080; UV λ_{max}^{MeOH} nm (log ε): 220.5 (4.03); SI-MS *m/z* 329 $[M+H]^+$; elemental analysis (found: C, 58.50; H, 7.25. $C_{16}H_{24}O_7$ required: C, 58.53; H, 7.37%); ^{1}H NMR (CD_3OD): δ1.50 (1H, *m*, H-5(ax)), 1.76 (3H, *s*, H-10), 1.90 (1H, *m*, H-5(eq)), 3.67 (1H, *dd*, *J* = 4.3, 12.2 Hz, H-6′a), 3.83 (1H, *dd*, *J* = 1.8, 12.2 Hz, H-6′b), 4.74 (1H, *br s*, H-9a), 4.76 (1H, *t*, *J* = 1.5 Hz, H-9b), 5.53 (1H, *d*, *J* = 7.6 Hz, H-1′α), 7.14 (1H, *br d*, *J* = 4.9 Hz, H-2); ^{13}C NMR (CD_3OD): Table 1.

Acetylation of perilloside B. Compound **1a** (6.8 mg) on acetylation with Ac_2O–pyridine afforded a tetraacetate as a powder (**1b**, 8.1 mg); mp 135–135.5° (found: C, 58.13; H, 6.38. $C_{24}H_{32}O_{11}$ required: C, 58.06; H, 6.50%); IR ν_{max}^{KBr} cm^{-1}: 1760, 1730(sh), 1370 and 1230; ^{1}H NMR ($CDCl_3$): δ1.74 (3H, *s*, H-10), 2.02, 2.03, 2.04, 2.08 (each 3H, *s*, Ac), 3.88 (1H, *ddd*, *J* = 2.1, 4.6, 9.8 Hz, H-5′), 4.11 (1H, *dd*, *J* = 2.4, 12.5 Hz, H-6′b), 4.30 (1H, *dd*, *J* = 4.6, 12.5 Hz, H-6′a), 4.70 (1H, *br s*, H-9a), 4.76 (1H, *t*, *J* = 1.5 Hz, H-9b), 5.14 (1H, *dd*, *J* = 9.2, 9.8 Hz, H-4′), 5.22 (1H, *dd*, *J* = 7.9, 9.5 Hz, H-2′), 5.29 (1H, *dd*, *J* = 9.5, 9.2 Hz, H-3′), 5.75 (1H, *d*, *J* = 7.9 Hz, H-1′α), 7.10 (1H, *br d*, *J* = 4.0 Hz, H-2); ^{13}C NMR ($CDCl_3$): Table 1.

Saponification of perilloside B. To a soln of **1a** (10.2 mg) in H_2O (5 ml), 20% K_2CO_3 (0.2 ml) was added and the mixt. was stirred for 18 hr at room temp. The reaction mixt. was acidified (pH 5) and then extracted with EtOAc. The extract was worked-up as usual and the residue was purified by prep. TLC to give (−)-perillic acid as a powder (3.6 mg): EI-MS *m/z* 166 $[M]^+$; ^{1}H NMR ($CDCl_3$): δ1.75 (3H, *s*, Me), 4.73 (1H, *br s*, H-9a), 4.76 (1H, *t*, *J* = 1.5 Hz, H-9b), 7.16 (1H, *br d*, *J* = 4.7 Hz, H-2), 12.22 (1H, *br*, COOH).

Identification of the sugar moiety. The H_2O layer, which was obtained by the hydrolysis of corresponding glucosides, was worked-up by the procedure described in ref. [1]. The resulting trimethylsilyl derivatives were subjected to GC for identification of the sugar moiety.

Synthesis of perilloside B. (i) 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl (−)-perillate (**1b**). To a soln of 2,3,4,6-tetra-*O*-acetylglucose (10.0 g) in pyridine (40 ml), (−)-perilloyl chloride prepared from (−)-perillic acid (5.0 g, mp 132–134°, $[\alpha]_D^{25}$ −108.2° (EtOH; *c* 10.0)) and thionyl chloride, was added at 20°, and then the mixt. was stirred for 1 hr at the same temp. The reaction mixt. was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O and satd aq. NaCl, and then H_2O. The extract was dried over dry $MgSO_4$ and evapd *in vacuo*. Repeated recrystallizations from Et_2O–petrol furnished **1b** (7.8 g) as needles, mp 135–135.5°. Other spectral data of **1b** were identical with those of tetracetylperilloside B. (ii) Deacetylation of **1b**. To a soln of **1b** (6.7 g) in MeOH (60 ml), 0.5 M methanolic barium oxide (30 ml) was added at 0° and then the mixt. was stirred for 1 hr at the same temp. After neutralization with AcOH, the reaction mixt. was filtered through silica gel (Wako gel C-200) to remove barium salts. The eluent was worked-up as usual and the residue was chromatographed on silica gel with $CHCl_3$–MeOH (10:1) to give a pale yellow paste (0.33 g). Crystallization for $CHCl_3$–Et_2O furnished **1a** (150 mg) as needles, mp 154–155°. Other spectral data of **1a** was identical with those of perilloside B.

Perilloside C (**2a**). Needles, mp 125.5–126.5°, $[\alpha]_D^{22}$ −32.3° (MeOH; *c* 0.600). IR ν_{max}^{KBr} cm^{-1}: 3350, 1640, 1070 and 1030; SI-MS *m/z* 317 $[M+H]^+$; elemental analysis (found: C, 60.61; H, 8.77. $C_{16}H_{28}O_6$ required: C, 60.74; H, 8.92%) HPLC: R_t 34 min (H_2O–MeOH, 11:9, 1.0 ml min^{-1}); ^{1}H NMR (CD_3OD): δ1.70 (3H, *s*, H-10), 3.17 (1H, *dd*, *J* = 8.2, 8.5 Hz, H-2′), 3.34 (1H, *dd*, *J* = 7.0, 9.5 Hz, H-7a), 3.66 (1H, *dd*, *J* = 5.2, 11.9 Hz, H-6′a), 3.73 (1H, *dd*, *J* = 6.6, 9.5 Hz, H-7b), 3.86 (1H, *dd*, *J* = 1.8, 11.9 Hz, H-6′b), 4.23 (1H, *d*, *J* = 7.6 Hz, H-1′α), 4.65 (1H, *t*, *J* = 1.5 Hz, H-9a), 4.66 (1H, *br s*, H-9b); ^{13}C NMR (CD_3OD): Table 1.

Acetylation of perilloside C. Compound **2a** (4.9 mg) on acetylation with Ac_2O–pyridine afforded a tetraacetate as a powder (**2b**, 6.0 mg), mp 94.0–94.5°, elemental analysis (found: C, 59.73; H, 7.50, $C_{24}H_{36}O_{10}$ required: C, 59.49; H, 7.49%); IR ν_{max}^{KBr} cm^{-1}: 1750, 1735(sh), 1380, 1220 and 1040; ^{1}H NMR ($CDCl_3$): δ1.71 (3H, *s*, H-10), 2.01, 2.02, 2.04, 2.09 (each 3H, *s*, Ac), 3.26 (1H, *dd*, *J* = 7.0, 9.5 Hz, H-7a), 3.68 (1H, *ddd*, *J* = 2.4, 4.6, 9.8 Hz, H-5′), 3.73 (1H, *d*, *J* = 5.8, 9.5 Hz, H-7b), 4.14 (1H, *dd*, *J* = 2.4, 12.2 Hz, H-6′b), 4.27 (1H, *dd*, *J* = 4.6, 12.2 Hz, H-6′a), 4.47 (1H, *dd*, *J* = 7.9 Hz, H-1′α), 4.66 (2H, *br s*, H-9), 4.99 (1H, *dd*, *J* = 7.9, 9.5 Hz, H-2′), 5.08 (1H, *dd*, *J* = 9.5, 9.8 Hz, H-4′), 5.21 (1H, *t*, *J* = 9.5 Hz, H-3′); ^{13}C NMR ($CDCl_3$): Table 1.

Enzymatic hydrolysis of perilloside C. To a soln of **2a** (4.0 mg) in H_2O (5 ml), β-glucosidase (5.0 mg) was added. The mixt. was stirred for 5 hr at 37° and then extracted with Et_2O. The extract was worked-up as usual and the residue was purified by prep. TLC to give *trans*-dihydroperillyl alcohol as an oil (1.0 mg): EI-MS *m/z* 154 $[M]^+$.

Synthesis of perilloside C. Compound **2a** was prepared from *trans*-dihydroperillyl alcohol, which was rectified by

fine distillation, according to a method given in the lit. [1]. (i) *trans*-Dihydroperillyl 2,3,4,6-tetra-*O*-acteyl-β-D-glucopyranoside (**2b**). To a soln of acetobromoglucose (13.3 g) and *trans*-dihydroperillyl alcohol (5.0 g) in C_6H_6, mercuric cyanide (8.5 g) was added, and then the mixt. was stirred for 90 min at 50°. The reaction mixt. was filtered off and the ppt. washed with EtOAc. The filtrate was washed with H_2O (30 ml) and satd aq. Na_2CO_3 and then H_2O. The extract was dried over dry $MgSO_4$ and evapd *in vacuo*. The residue was rechromatographed on silica gel with hexane–EtOAc (5:1) to give **2b** as a pale yellow paste (11.1 g). Crystallization from MeOH furnished **2b** (5.0 g) as needles, mp 94.0–94.5°. Other spectral data of **2b** were identical with those to tetraacetylperilloside C. (ii) Deacetylation of **2b**. To a soln of **2b** (5.5 g) in MeOH (20 ml), 10% methanolic KOH (40 ml) was added, and then the mixt. was stirred for 5 hr at room temp. After removal of the MeOH by distillation, the residue was dissolved in H_2O and the soln extracted with $CHCl_3$. The extract was worked-up as usual and the residue was chromatographed on silica gel with $CHCl_3$–MeOH (10:1) to give **2a** as pale yellow paste (1.53 g). Crystallization from $CHCl_3$–Et_2O furnished **2a** (0.63 g) as needles, mp 125.5–126.5°, $[\alpha]_D^{25}$ −24.6° (MeOH; *c* 0.439). Other spectral data of **2** were identical with those of perilloside C.

Perilloside D (**3**). Amorphous powder, IR ν_{max}^{KBr} cm^{-1}: 3350, 1640, 1070 and 1030; SI-MS *m/z* 317 $[M+H]^+$; HPLC: R_t 30 min (H_2O–MeOH, 11:9, 1.0 ml min^{-1}); ^1H NMR (CD_3OD): δ1.71 (3H, *s*, H-10), 3.17 (1H, *dd*, *J* = 7.6, 8.8 Hz, H-2′), 3.51 (1H, *dd*, *J* = 7.6, 9.5 Hz, H-7a), 3.67 (1H, *dd*, *J* = 5.2, 11.9 Hz, H-6′a), 3.87 (1H, *dd*, *J* = 1.8, 11.9 Hz, H-6′b), 3.90 (1H, *dd*, *J* = 7.6, 9.5 Hz, H-7b), 4.25 (1H, *d*, *J* = 7.6 Hz, H-1′α), 4.69 (2H, *br s*, H-9); ^{13}C NMR (CD_3OD): Table 1.

β-*Sitosteryl* β-D-*glucopyranoside*. Amorphous powder, mp 283–286° (dec.) (lit. 285–288° (dec.)) [2]. IR ν_{max}^{KBr} cm^{-1}: 3550 and 1080; ^1H NMR (C_5D_5N): δ0.67, 0.95 (each 3H, *s*, H-18, 19), 0.87, 0.88, 1.02 (each 3H, *d*, *J* = 6.4 Hz, H-21, 26, 27), 0.91 (3H, *t*, *J* = 6.7 Hz, H-29), 4.45 (1H, *dd*, *J* = 5.2, 11.6 Hz, H-6′a), 4.60 (1H, *dd*, *J* = 2.1, 11.6 Hz, H-6′b), 5.09 (1H, *d*, *J* = 7.6 Hz, H-1′α), 5.37 (1H, *br d*, *J* = 5.2 Hz, H-6); ^{13}C NMR (C_5D_5N): δ12.0 (*q*), 12.2 (*q*), 19.1 (*q*), 19.3 (*q*), 19.5 (*q*), 20.0 (*q*), 21.3 (*t*), 23.4 (*t*), 24.6 (*t*), 26.4 (*t*), 28.6 (*d*), 29.5 (*d*), 30.3 (*t*), 32.1 (*d*), 32.2 (*t*), 34.2 (*t*), 36.4 (*d*), 37.0 (*t*), 37.5 (*t*), 39.4 (*d*), 40.0 (*t*), 42.5 (*s*), 46.1 (*d*), 50.4 (*d*, C-9), 56.3 (*s*, C-17), 56.9 (*t*, C-14), 78.1 (*d*, C-3), 122.0 (*d*, C-6), 140.9 (*s*, C-5), 62.9 (*t*, C-6′), 71.7 (*d*, C-4′), 75.4 (*d*, C-2′), 78.6 (*d*, C-5′), 78.7 (*d*, C-3′), 102.6 (*d*, C-1′).

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