Phytochemistry, Vol. 28, No. 9, pp. 2393–2396, 1989.
Printed in Great Britain.

0031–9422/89 $3.00 + 0.00

IRIDOID GLYCOSIDES FROM *VIBURNUM SUSPENSUM*

TETSUO IWAGAWA and TSUNAO HASE

Department of Chemistry, Faculty of Science, Kagoshima University, Korimoto 1-21-35, Kagoshima 890, Japan

(*Received in revised form* 26 *January* 1989)

Key Word Index—*Viburnum suspensum*; Capriforiaceae; iridoid glycosides; suspensolides A, B, C; suspensolide aglucone; *p*-coumaric acid; sitosteryl β-glucoside; scopolin; bitter principles.

Abstract—Three iridoid glycosides of an aglucone having a 7,8,10,11-tetraoxygenated iridoid skeleton with an isovaleryl group at C-1 have been isolated from the leaves of *Viburnum suspensum*, along with *p*-coumaric acid, sitosteryl β-glucoside and scopolin. Two of the iridoid glycosides, suspensolides A and C, and the suspensolide aglucone are bitter to the taste. Suspensolide C is the third example of an iridoid D-ribohexo-3-ulopyranoside.

INTRODUCTION

Viburnum suspensum L. is an evergreen shrub distributed in the subtropical zone of Japan. The leaves are intensely bitter. Previous investigations on the methanolic extract of the leaves of the plant led to the isolation and structural characterization of quercitrin, hyperin [1] and a new coumarin acetylglucoside, 2′,6′-diacetylscopolin [2]. In a preliminary paper, we have reported the presence of suspensolide A (**1**) and suspensolide aglucone (**4**) [3]. We have now isolated two more iridoid glycosides, suspensolide B (**2**) and C (**3**), from the plant.

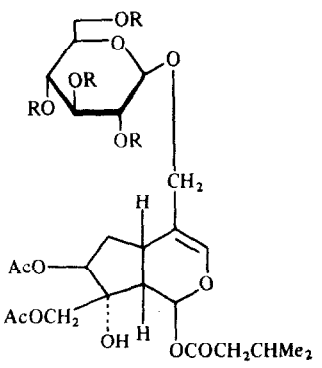
RESULTS AND DISCUSSION

Compound **1**, suspensolide A, was isolated as a bitter hygroscopic powder, with the molecular formula $C_{25}H_{38}O_{14}\cdot 1/2\ H_2O$. It emitted an odour of isovaleric acid on standing and turned black like other iridoids when treated with hydrochloric acid. It exhibited UV absorption at 204 nm and IR absorption at 1760 cm^{-1} characteristic of a non-conjugated iridoid. The ^1H NMR spectrum was similar to that reported for opulus iridoid II [4]. It contained signals of an isovaleroxyl group at δ 0.95 (6H, *d*, $J = 6$ Hz) and two acetoxyl groups at δ 1.98 (3H × 2, *s*). A double doublet at δ 2.40 (1H, $J = 6$ and 10 Hz) was due to a proton at C-9, a doublet at δ 6.16 (1H, $J = 6$ Hz) was assignable to an acylated acetal proton at C-1 and a broad singlet arising from a proton at C-3 appeared at δ 6.44. A triplet at δ 5.06 (1H, $J = 4$ Hz) was assignable to a proton at C-7 with an acyl group. The ^{13}C NMR spectrum of **1** confirmed that C-1 (δ 91.39), C-7 (δ 81.16) and C-10 (δ 68.19) were acylated and β-glucopyranose was attached to C-11 (δ 69.82) (Table 1). Treatment of **1** with acetic anhydride in pyridine yielded a hexa-acetate (**5**), $C_{33}H_{46}O_{18}$, which showed a tertiary hydroxyl band at 3550 cm^{-1} in the IR spectrum. The β-configuration of the hydroxyl group at C-8 was assumed from the chemical shift of C-9 (δ 45.29) in the ^{13}C NMR spectrum of **1** (Table 1) [15].

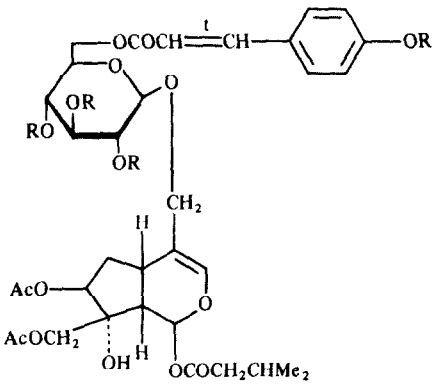
Alkaline hydrolysis of **1** gave isovaleric acid. On hydrolysis with 2 M hydrochloric acid, compound **1** afforded a black polymeric product and glucose. Enzymatic hydrolysis of **1** with β-glucosidase gave D-glucose and an aglycone (**4**), $C_{19}H_{28}O_9$, which was also isolated from the plant. Acetylation of **4** with acetic anhydride in pyridine gave a crystalline triacetate (**6**), the IR spectrum of which showed a tertiary hydroxyl absorption band at 3450 cm^{-1}.

To determine the nature of the acyl group at C-1, the acetate **5** was subjected to methanolysis with methanol containing a catalytic amount of conc. hydrochloric acid. This gave a di-acetate (**7**), $C_{15}H_{20}O_7$, and a mono-acetate (**8**), $C_{13}H_{18}O_6$. The ^1H NMR spectrum of **7** was identical with that of 4-acetoxy-3-acetoxymethyl-8-methoxy-10-methylene-2,9-dioxatricyclo[4, 3, 1, 0, 3, 7] decane prepared from dihydrovaltrate [4]. The isovaleryl group in **1** (and **4**) must, therefore, be located at C-1 and the two acetoxyl groups at C-7 and C-10. The stereochemistry at C-7 and C-8 was also assigned as shown. Thus, the structure of **1** and its aglycone (**4**) can be represented by formulae **1** and **4**. This was further supported by the ^{13}C NMR data.

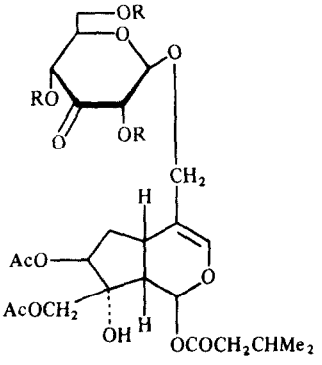
Compound **2**, suspensolide B, was obtained as crystals with the molecular formula $C_{34}H_{44}O_{16}\cdot H_2O$. The IR spectrum showed absorption bands of a hydroxyl group at 3400 cm^{-1}, an ester carbonyl at 1740 cm^{-1} and a double bond at 1640 cm^{-1} together with those of a *p*-substituted phenyl group at 1610, 1520 and 835 cm^{-1}. The ^1H NMR spectrum was similar to that of **1**, except for additional signals due to a *p*-coumaroyl group. The presence of the *p*-coumaroyl group was evident from signals of *trans* olefinic protons at δ 6.32 and 7.62 (AX, *d*, $J = 16$ Hz), *p*-substituted phenyl protons at δ 6.88 and 7.52 (A_2B_2, $J = 8$ Hz) and a phenolic proton at δ 8.22 (1H, *m*). On acetylation with acetic anhydride in pyridine, compound **2** gave a hexa-acetate (**9**), the IR spectrum of which showed an absorption band at 3500 cm^{-1} typical of a tertiary hydroxyl group. Compound **9**, as well as **5**, formed **7** and a mixture of acetylated glucose on acid methanolysis. The mixture was acetylated with acetic anhydride in pyridine to give a single tetra-acetate, the IR and ^1H NMR spectra of which were identical with those of 1,2,3,4-tetra-*O*-acetyl-*p*-acetyl-6-*O*-acetoxycinnamoyl-β-glucose (see Experimental) [17]. Furthermore, the position of the *p*-coumaroyl group at C-6 of the glucose was supported by the facts that methylation of **2** by the Purdie method followed by acid hydrolysis gave 2,3,4-tri-*O*-



1 R = H
5 R = Ac



2 R = H
9 R = Ac



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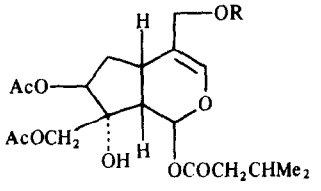
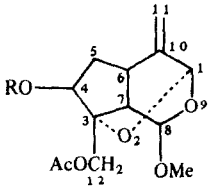
10 R = Ac



4 R = H
6 R = Ac



7 R = Ac
8 R = H

methyl-glucose. The coupling constant ($J = 8$ Hz) of the anomeric proton at δ 4.42 in the ^{1}H NMR spectrum of **2** suggested that the glucosidic linkage is β. Suspensolide B was therefore identified as **2**.

Compound **3**, suspensolide C, was a bitter hygroscopic amorphous powder with the molecular formula $C_{25}H_{36}O_{14}\cdot H_2O$. The ^{1}H and ^{13}C NMR spectra were very similar to those of **1**, except for signals due to sugar. The chemical shifts of C-1′ to C-6′ in the ^{13}C NMR spectrum suggested compound **3** was a D-ribohexo-3-ulopyranoside [8]*. The β-configuration of the sugar was deduced from the coupling constant ($J = 8$ Hz) of the anomeric proton at δ 4.44 in the ^{1}H NMR spectrum. Acetylation of **3** with acetic anhydride in pyridine afforded a penta-acetate (**10**), $C_{31}H_{42}O_{17}$. The IR spectrum of the latter showed a typical tertiary hydroxyl absorption band at 3450 cm^{-1}. Acid methanolysis of **3** yielded **7** as was obtained from **5** and **9**. Thus, compound **3** should have the structure shown. This is the third example of a ribohexo-3-ulopyranose attached to an iridoid aglycone.

*The chemical shift of the CO in dihidroserrulodise was given as δ 179.8, which is abnormally upfield [9]. The wrong value may be explained as a fold in the spectrum.

EXPERIMENTAL

Extraction and isolation. Plant material was collected on the campus of Kagoshima University and identified by Dr S. Sako (Herbarium sample No. 8). Fresh leaves (1.5 kg) of *V. suspensum*

Table 1. ^{13}C NMR spectral data of compounds 1–3 [CD_3OD; 1 and 2 TMS as int. standard; 3 CD_3OD (δ49.8) as int. standard]

C	1	2	3
1	91.39	91.16	92.18
3	140.79	140.40	141.84
4	115.87	115.93	116.30
5	33.64	32.72	34.52
6	36.24	35.96	37.05
7	81.16	81.06	81.90
8	82.20	81.91	83.02
9	45.29	45.69	46.67
10	68.19	67.94	68.93
11	69.82	69.66	70.98
1′	103.54	101.37	105.56
2′	75.19	75.25	79.14
3′	78.17[a]	78.12	207.95
4′	71.79	71.79	74.56
5′	78.00[a]	76.22	79.14
6′	62.91	62.74	63.54
1″		127.21	
2″,6″		131.32	
3″,5″		116.92	
4″		161.34	
α-C		115.32	
β-C		146.96	
$(Me)_2CHCH_2$	22.67 × 2,	22.67, 22.71	23.54 × 2
	26.85, 44.28	26.80, 44.19	27.65, 45.09
MeCO	20.78, 21.08	20.73, 20.94	21.61, 21.90
COO	171.86, 172.68	168.20, 171.60	172.54, 173.37
	173.01	172.53, 172.98	173.66

[a] These values may be interchangeable in the vertical column.

were extracted with MeOH (11 1 × 2). The combined MeOH solns were concd to dryness to afford a dark green residue. The residue was diluted with H_2O, extracted with Et_2O and then EtOAc. The Et_2O extract was further extracted with $CHCl_3$–MeOH (97:3) to give a dark green residue (57 g), which was subjected to CC on silica gel with $CHCl_3$–MeOH with increasing MeOH content. The fractions eluted with $CHCl_3$–MeOH (97:3) gave *p*-coumaric acid (6 mg). Elution with $CHCl_3$–MeOH (93:7) afforded suspensolide B (**2**) (1.45 g). Sitosteryl β-glucoside (44 mg) was isolated as its acetate after acetylation of the part eluted with $CHCl_3$–MeOH (19:1). The EtOAc extract was further extracted with $CHCl_3$–MeOH (19:1) to give a dark brown residue (17 g). The residue was chromatographed on silica gel with $CHCl_3$–MeOH (97:3) to give **4** (30 mg). From the fractions eluted with $CHCl_3$–MeOH (19:1), 2′,6′-*O*-diacetylscopolin (11 mg), scopolin (11 mg), suspensolide C **3** (135 mg) and suspensolide A **1** (150 mg) were afforded successively. Known compounds were identified by their IR and/or ^1H NMR spectra.

Suspensolide A (**1**). A bitter hygroscopic powder; $[\alpha]_D$ −42.9° (MeOH; *c* 0.35), UV λ_{max}^{MeOH} nm (ε): 204 (1880); IR ν_{max}^{film} cm^{-1}: 3450, 1760, 1670; ^1H NMR (100 MHz, CD_3COCD_3): δ 0.95 (6H, *d*, *J* = 6 Hz, isopropyl Me groups), 1.98 (3H × 2, *s*, OAc), 2.40 (1H, *dd*, *J* = 6 and 10 Hz, H-9), 5.06 (1H, *t*-like, *J* = 4 Hz, H-7), 6.16 [(1H, *d*, *J* = 6 Hz; 6.23 (*d*, *J* = 4 Hz) in $CDCl_3$, H-1)], 6.44 (1H, *br s*, H-3); CD $[\theta]_{192}$ −33 500 (MeCN). (Found: C, 52.70; H, 6.92%. Calc. for $C_{25}H_{38}O_{14}\cdot 1/2H_2O$: C, 52.53; H, 6.88%). A soln of **1** (300 mg) in Ac_2O and pyridine was allowed to stand at room temp. overnight. The crude product was chromatographed on silica gel with $CHCl_3$–MeOH (99:1) to give **5** (216 mg), needles from Et_2O, mp 108–110°; IR ν_{max}^{Nujol} cm^{-1}: 3550, 1760, 1670, 1240; ^1H NMR(100 MHz, $CDCl_3$): δ 0.80 (6H, *d*, *J* = 6 Hz), 2.05, 2.08 and 2.12 (3H × 6, *s*), 6.40 (1H, *d*, *J* = 4 Hz), 6.50 (1H, *br s*). (Found: C, 54.13; H, 6.43%. Calc. for $C_{33}H_{46}O_{18}$: C, 54.24; H, 6.36%).

Hydrolysis of **1**. A soln of **1** (27 mg) in MeOH (2 ml) was refluxed with 1 M NaOH (10 ml) for 25 min in a N_2 stream. The reaction soln was acidified with dil. HCl, extracted with Et_2O, washed with H_2O and dried over Na_2SO_4. Removal of the solvent gave isovaleric acid (3 mg); IR ν_{max}^{film} cm^{-1}: 3600–3100, 1730, 940. To a soln of **1** in MeOH, was added 2 M HCl and the mixture was refluxed for 4 hr. The black ppt. was filtered off, and the filtrate neutralized with Amberlite IRA-45. The presence of glucose in the residue was determined by PC [solvent system: EtOAc–pyridine–H_2O–HOAc, 5:5:3:1].

Enzymatic hydrolysis of **1**. To a soln of **1** (100 mg) in acetate buffer (pH 4.9, 10 ml), was added β-glucosidase (20 mg) in H_2O (2 ml) and the mixture stirred at 37°. After 24 hr, the soln was extracted with Et_2O, washed with H_2O and dried over Na_2SO_4. Removal of the solvent follwed by CC on silica gel with $CHCl_3$–MeOH(97:3) gave an oil **4** (35 mg); $[\alpha]_D$ −56° (MeOH; *c* 0.25), IR ν_{max}^{film} cm^{-1}: 3500, 1750, 1670; ^1H NMR (100 MHz, $CDCl_3$): δ 0.98 (6H, *d*, *J* = 7 Hz, isopropyl Me groups), 2.05 and 2.09 (3H each, *s*, OAc), 2.46 (1H, *dd*, *J* = 4 and 9 Hz, H-9), 3.98 and 4.07 (1H each, AB, *J* = 12 Hz, H-1), 4.24 (2H, *s*, H-10), 5.07 (1H, *t*, *J* = 5 Hz, H-7), 6.31 (1H, *d*, *J* = 4 Hz, H-1), 6.41 (1H, *br s*, H-3). (Found: *m/z* 298.1081. Calc. for $C_{19}H_{28}O_9$–$(Me)_2CHCH_2COOH$: *m/z* 298.1053). Compound **4** was acetylated with Ac_2O in pyridine. The crude product was subjected to CC on silica gel with $CHCl_3$–MeOH (99:1), giving **6**, needles

from Et_2O–petrol, mp 87°; IR ν_{max}^{Nujol} cm^{-1}: 3450, 1740, 1720, 1660; ^1H NMR (100 MHz, $CDCl_3$): δ 0.97 (6H, *d*, $J = 7$ Hz), 2.07 and 2.12 (3H × 3, *s*), 2.42 (1H, *dd*, $J = 4$ and 9 Hz), 4.25 (2H, *s*), 4.42 and 4.58 (1H each, AB, $J = 16$ Hz), 5.12 (1H, *t*-like, $J = 5$ Hz), 6.38 (1H, *d*, $J = 4$ Hz), 6.55 (1H, *s*); MS *m/z*: 382 [M − AcOH]$^+$, 364, 281, 178, 132, 85. (Found: *m/z*: 382.1627. Calc. for $C_{21}H_{30}O_{10}$–AcOH: *m/z*: 382.1627).

Methanolysis of **5**. To a soln of **5** (100 mg) in dry MeOH (5 ml), was added 2 drops of HCl and the mixture stirred at 60° for 30 min in N_2 stream. The reaction soln was dild with H_2O and dried over Na_2SO_4. The crude product was chromatographed on silica gel with $CHCl_3$ to give **7** (24 mg) and **8** (13 mg). Compound **7**, an oil; $[\alpha]_D$ + 46.6° ($CHCl_3$; *c* 0.45), IR ν_{max}^{film} cm^{-1}: 1750, 1240, 950, 860; ^1H NMR (60 MHz, $CDCl_3$): δ 1.99 and 2.07 (3H each, *s*, OAc), 2.47 (1H, *dd*, $J = 3.5$ and 5 Hz, H-7), 3.39 (3H, *s*, OMe), 4.22 and 4.46 (1H each, AB, $J = 12$ Hz, H-12), 4.66 and 4.78 (1H each, AB, $J = 1$ Hz, H-11), 5.06 (1H, *d*, $J = 3$ Hz, H-8), 5.13 (1H, *s*, H-1). (Found: *m/z* 312.1196. Calc. for $C_{15}H_{20}O_7$: *m/z* 312.1208). Compound **8**, an oil; IR ν_{max}^{film} cm^{-1}: 3550, 1760, 1675, 1240, 960; ^1H NMR (60 MHz, $CDCl_3$): δ 2.15 (3H, *s*, OAc), 2.47 (1H, *dd*, $J = 3.5$ and 5 Hz, H-7), 3.36 (3H, *s*, OMe), 4.25 and 4.55 (1H each, AB, $J = 12$ Hz, H-12), 4.80 and 4.90 (1H each, AB, $J = 1.5$ Hz, H-11), 4.95 (1H, *d*, $J = 3$ Hz, H-8), 5.09 (1H, *s*, H-1). Acetylation of **7** gave **8**.

Suspensolide B (**2**). Prisms from $CHCl_3$–Et_2O, mp 132–134°; IR ν_{max}^{film} cm^{-1}: 3400, 1740, 1640, 1610, 1520, 835; ^1H NMR (100 MHz, CD_3COCD_3): δ 0.96 (6H, *d*, $J = 6$ Hz, isopropyl Me groups), 1.88 and 1.92 (3H each, *s*, OAc), 2.36 (1H, *dd*, $J = 4$ and 10 Hz, H-9), 4.42 (1H, *d*, $J = 8$ Hz, H-1′), 4.99 (1H, *t*-like, $J = 4$ Hz, H-7), 6.16 (1H, *d*, $J = 4$ Hz, H-1), 6.32 and 7.62 (1H each, AB, $J = 16$ Hz, α-H and β-H), 6.36 (1H, *br s*, H-3), 6.88 and 7.52 (2H each, A_2B_2, $J = 8$ Hz, aromatic H), 8.92 (1H, *m*, phenolic OH). (Found: C, 56.06; H, 6.50%. Calc. for $C_{34}H_{44}O_{16}H_2O$: C, 56.19; H, 6.38%). Compound **2** (104 mg) was acetylated as described above to give **9** (67 mg), an amorphous powder; IR ν_{max}^{film} cm^{-1}: 3500, 1750, 1670, 1630, 1600,1505, 864, 840; ^1H NMR (60 MHz, $CDCl_3$): δ 1.88, 1.95, 2.00, 2.06 and 2.27 (3H × 6, *s*), 6.16 (1H, *d*, $J = 4$ Hz), 6.45 (1H, *br s*), 6.28 and 7.68 (1H each, AB, $J = 17$ Hz), 7.10 and 7.57 (2H each, A_2B_2, $J = 9$ Hz).

Methanolysis of **2**. To a soln of **2** (100 mg) in dry MeOH (5 ml), was added conc. HCl (1 ml) and the mixture was stirred at 50° for 30 min in a N_2 stream. After the usual work-up, the crude product was subjected to CC on silica gel with $CHCl_3$ to give **7** (8.5 mg); IR ν_{max}^{film} cm^{-1}: 1750, 1240, 950, 860. The fractions eluted with $CHCl_3$–MeOH (97:3) afforded an acetylated glucose, which were acetylated with Ac_2O in pyridine to yield 1,2,3,4-tetra-*O*-acetyl-6-*O*-*p*-acetoxycinnamoyl-β-glucopyranose (14 mg), needles from MeOH, mp 168–170°; IR ν_{max}^{film} cm^{-1}: 1767, 1640, 1510, 915; ^1H NMR (60 MHz, $CDCl_3$): δ 1.99, 2.02, 2.07, 2.16 and 2.28 (3H × 5, *s*, OAc), near 4.16 (3H, H-5′ and 6′), 4.98 – 5.76 (3H, H-2′, 3′ and 4′), 6.27 and 7.73 (1H each, AX, $J =$ 16 Hz, α-H and β-H), 6.32 (1H, *d*, $J = 7.5$ Hz, H-1′), 7.10 and 7.56 (2H each, A_2B_2, $J = 9$ Hz, aromatic H). The spectral data were identical with those of an authentic sample [7].

Methylation of **2** *followed by acid hydrolysis.* Compound **2** (100 mg) was dissolved in DMF (2 ml) and Ag_2O (500 mg) and MeI (0.5 ml) added. The mixture was stirred at 10° for 2 days in the dark, a small amount of $CHCl_3$ added and the mixture filtered. The filtrate was evapd to afford a residue (100 mg; IR ν_{max}^{film} cm^{-1}: no OH absorption) which was refluxed with 2M HCl (2 ml) and MeOH (2 ml) for 2 hr, giving 2, 3, 4,-tri-*O*-methyl-D-glucose (2 mg) whose IR spectrum was identical with that of an authentic sample.

Suspensolide C (**3**). A bitter hygroscopic amorphous powder; $[\alpha]_D$ −50° (MeOH; *c* 1.0); UV ν_{max}^{MeOH} nm (ε): 205 (2000); IR ν_{max}^{film} cm^{-1}: 3450, 1740, 1660; ^1H NMR (100 MHz, CD_3COCD_3): δ 0.92 (6H, *d*, $J = 6$ Hz, isopropyl Me groups), 1.98 (3H × 2, *s*, OAc), 2.38 (1H, *dd*, $J = 6$ and 10 Hz, H-9), 4.44 (1H, *d*, $J = 8$ Hz, H-1′), 5.00 (1H, *t*-like, $J = 4$ Hz, H-7), 6.12 (1H, *d*, $J = 6$ Hz, H-1), 6.40 (1H, *br s*, H-3); FABMS *m/z*: 583 [M + Na]$^+$. (Found: C, 51.98; H, 6.39%. Calc. for $C_{25}H_{36}O_{14}\cdot H_2O$: C, 51.90; H, 6.62%). Compound **3** (100 mg) was acetylated with Ac_2O in pyridine to give **10** (68 mg), an amorphous powder; IR ν_{max}^{film} cm^{-1}: 3450, 1740, 1660; ^1H NMR (100 MHz, $CDCl_3$): δ 0.96 (6H, *d*, $J = 6$ Hz), 2.02, 2.08 and 2.12 (3H × 5, *s*), 2.20 (1H, *dd*, $J = 4$ and 8 Hz), 4.96 (1H, *t*-like, $J = 4$ Hz), 6.20 (1H, *d*, $J = 4$ Hz), 6.30 (1H *br s*). (Found: C, 53.96; H, 6.08%. Calc. for $C_{31}H_{42}O_{17}$: C, 54.22; H, 6.17%).

Methanolysis of **3**. To a soln of **3** (30 mg) in dry MeOH (3 ml), was added two drops of conc. HCl and the mixture was stirred at 50° for 1 hr. After the usual work-up, compound **7** (1 mg) was obtained. The IR spectrum was identical with that of **7** obtained from **5** and **9**.

p-*Coumaric acid.* Prisms from $CHCl_3$–MeOH, mp 202–205°; IR ν_{max}^{Nujol} cm^{-1}: 3450, 2700–2600, 1690, 1640, 1610, 1520, 980, 940, 830; ^1H NMR (100 MHz, C_5D_5N): δ 6.99 and 8.18 (1H each, AB, $J = 17$ Hz), 7.21 and 7.73 (2H each, A_2B_2, $J = 8$ Hz), 11.23 (1H, *m*); MS *m/z*: 164 [M]$^+$ [10].

Sitosteryl β-glucoside. Acetylation of the crude glucoside gave needles from EtOH, mp 166°; IR ν_{max}^{Nujol} cm^{-1}: 1750; ^1H NMR (100 MHz, $CDCl_3$): δ 1.96, 2.01, 2.03 and 2.05 (3H × 4, *s*), 3.24–5.27 (8H, *m*), 5.39 (1H, *m*) [11].

Scopolin. Acetylation of the crude scopolin gave needles from EtOH, mp 171.5–172°; IR ν_{max}^{Nujol} cm^{-1}: 1780–1750, 1620, 1570. (Found: C, 55.32; H, 5.01%. Calc. for $C_{24}H_{26}O_{13}$: C, 55.17; H, 5.02%).[12].

Acknowledgements—We thank Dr T. Marunaka (Taiho Yakugyo, Co. Ltd) and Drs K. Sibata and T. Miwa (Osaka City University) for the FABMS and the NMR spectra measurements, respectively. We are grateful to Dr S. Eguchi (Hiroshima University) for elementary analysis and Dr S. Sako (Kagoshima University) for identification of the plant material.

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