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THREE IRIDOID GLYCOSIDES FROM *VIBURNUM FURCATUM*

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Key Word Index—*Viburnum furcatum*; Caprifoliaceae; valeriana iridoid; furcatosides A–C; bitter principles.

Abstract—Three new bitter iridoid glycosides having an 8,10,11-oxygen substituted iridoid skeleton with an isovaleryl moiety at C-1, have been isolated from the ether and ethyl acetate soluble fractions of the leaves of *Viburnum furcatum*. Two of them had a glucose moiety at C-11 of the iridoid skeleton and a *p*-coumaroyl group linked to C-6 of the sugar, and they were found to be geometrical isomers about the double bond of the *p*-coumaroyl† moiety. The third one was characterized as a alloside of the same aglycone.

INTRODUCTION

The shrub *Viburnum furcatum* Blume is widely distributed in Honshu and Kyushu islands in Japan and its leaves are remarkably bitter. The previous investigation [1] of the leaves of this shrub reported the isolation of a bitter phenolic glycoside named furcatin and identified as *p*-vinylphenyl glycoside. But, recently, this structure has been revised [2] and it was pointed out that furcatin was not bitter and contained a *p*-allylphenol instead of *p*-vinylphenoyl moiety as an aglycone. In a continuation of the investigation on the bitter constituents of the genus *Viburnum*, the bitter components of the leaves of the plant were studied. Three new bitter iridoid glycosides named furcatosides A (**1**) and B (**2**), which were considered to be geometrical isomers of each other and furcatoside C (alloside) (**3**), were isolated. These all have the same 8,10,11-oxygen substituted iridoid skeleton with an *iso*-valeroyl group at C-1. Besides these compounds, 10 known components were isolated and characterized.

RESULTS AND DISCUSSION

The methanol extract of fresh leaves of *Viburnum furcatum* was dissolved in water and extracted with ether followed by ethyl acetate. Chromatography of both extracts led to the isolation of the new glycosides (**1–3**) from fractions eluted with methanol–chloroform (1:19).

Furcatoside A (**1**) was obtained as a hygroscopic amorphous powder with a molecular formula $C_{32}H_{42}O_{14}\cdot 1.5\ H_2O$, $[\alpha]_D -103°$. It turned slightly green when kept for a long time in the air and a preliminary test with hydrochloric acid suggested it to be an iridoid. It showed UV spectral absorptions at λ_{max} nm: 213, 228, 300 sh and 314, and gave IR spectral bands at ν_{max} cm^{-1}: 3400 (OH), 1720 (COOR), 1670 (C=C), 1630 (conjugated C=C), 1600, 1585, 1510, 980 and 830 (*p*-disubstituted benzene). The ^1H NMR (CD_3COCD_3) spectrum contained absorptions at δ0.88 (6H, *d*, J = 7 Hz, methyl protons of isopropyl), 1.93 (3H, *s*, acetoxyl), 5.00 (1H, *d*, J = 8 Hz, sugar-H-1), 6.18 (1H, *d*, J = 6 Hz, iridoid H-1) and 6.48 (1H, *br s*, iridoid H-3). Two doublets (2H each, J = 9 Hz) centred at δ7.02 and 7.68 were assigned to the AA'BB' system of the aromatic protons of a *p*-coumaroyl group which showed two *trans*-olefinic proton resonances at δ6.42 and 7.82 (1H each, *d*, J = 16 Hz). Upon acid hydrolysis, **1** gave glucose which was identified by PC. These spectral data and the hydrolysis result suggest the presence of a non-conjugated iridoid enol ether system, *trans*-*p*-coumaroyl, acetyl and isopropyl groups and a glucose moiety. The presence of an isopropyl group in the ^1H NMR spectrum of **1** suggested a possible similarity of this compound with suspensolide A and its aglycone [3], and other iridoids [4, 5]. These compounds have been reported to possess an isovaleroyl group at C-1 of the iridoid skeleton instead of glucose. Also, in suspensolide A, the glucose moiety was found to be attached to the 11-oxymethylene as found with the iridoids from *Valeriana* species [5, 6].

Acetylation of **1** formed an amorphous penta-acetate **1a**, $C_{40}H_{50}O_{18}$. Its ^1H NMR ($CDCl_3$) displayed resonances for five acetyl groups at δ2.04, 2.14, 2.23 and 2.35 (3H × 5, *s*) due to three acetyl groups of the glucose moiety and a signal for an aromatic acetyl group, in addition to the previous acetyl group. The IR spectrum revealed the presence of a tertiary hydroxyl group at 3500 cm^{-1}.

In order to determine the nature of the acyl group at C-1, the acetate (**1a**) was submitted to an acid methanolysis under nitrogen to yield *iso*-valeric acid recognized by its odour and two oily products (**1b** and **1c**) which were separated by CC. Final purification of the product, **1b**, was achieved by HPLC to afford a colourless oil which gave IR spectral bands at 3075, 1740, 1660 and 950 cm^{-1} due to a saturated ester and exocyclic methylene functions. The prominent ion in the mass spectrum was observed at m/z 254 indicating a molecular formula $C_{13}H_{18}O_5$ when analysed by high resolution mass spectrometry. The ^1H NMR ($CDCl_3$) spectrum contained resonances for acetyl and methoxyl groups at δ2.03 (3H, *s*) and 3.41 (3H, *s*), respectively. The resonances at δ4.19 and 4.46 (1H each, *d*, J = 15 Hz) were attributed to an AB system of methylene protons of an AcO–CH_2– grouping. The exocyclic methylene protons had resonances at δ5.13 and 5.22 (1H each, *d*, J = 3 Hz). Absorptions at δ5.33 (1H, *d*, J = 4 Hz) and 5.42 (1H, *s*) were assigned to protons at C-8 and C-1, respectively. Comparison of these data with those reported for the methanolysis product of suspensolide A acetate [3] suggested that **1b** was

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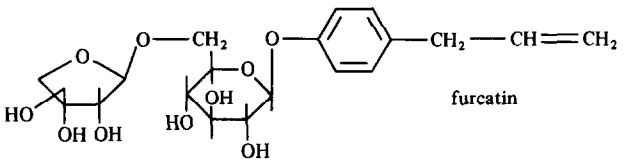
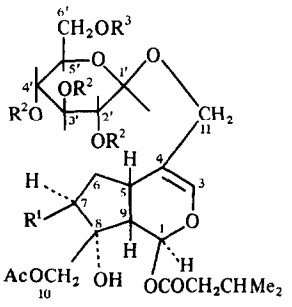
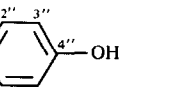
†*p*-Coumaroyl = *p*-hydroxycinnamoyl.

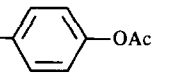


furcatin

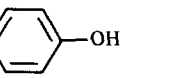




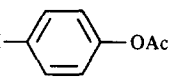
1 $R^1, R^2 = H, R^3 = COCH{=}^{t}CH$–(1″,2″,3″,4″)–OH



1a $R^1 = H, R^2 = Ac, R^3 = COCH{=}^{t}CH$–OAc

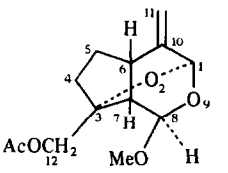


2 $R^1, R^2 = H, R^3 = COCH{=}^{c}CH$–OH

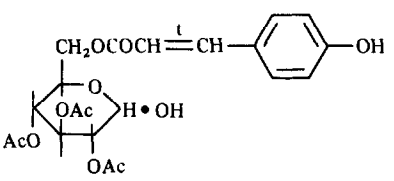


2a $R^1 = H, R^2 = Ac, R^3 = COCH{=}^{c}CH$–OAc

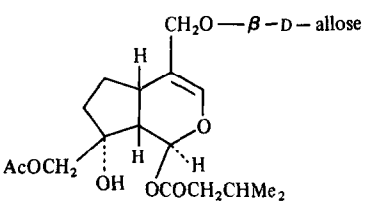
4 $R^1 = OAc, R^2, R^3 = H$



1b



1c



3

3-acetoxymethyl-8-methoxy-10-methylene-2,9-dioxatricyclo(4,3,1,$0^{3,7}$)decane. This structure was further supported by the ^{13}C NMR spectrum (Table 1) in which resonances of 13 carbon atoms were observed. Assuming the usual iridoid stereochemistry at C-5 and C-9, the ready formation of the dioxatricyclo derivative **1b** from **1a** confirms the location at C-8 and the α-orientation of the tertiary hydroxy function in **1a** and, therefore, establishes the relative stereochemistry about C-8 in compound **1**. This is in agreement with the reactivity of an α-oriented hydroxyl group at C-8 towards the centre at C-3 under acid conditions [4, 6, 7]. Furthermore, the ^{13}C NMR spectrum supported this assignment. The diagnostic δ values of C-9 with 8α,10 (δ44.8 ± 1.7) and 8β,10 (δ50 ± 1.5) dihydroxy substituted iridoids have been reported [8] and the chemical shifts of δ46.00 for C-9 in **1** and 43.4 for C-7 (corresponding to C-9 in **1**) in **1b**, agreed with the α-orientation of the OH-8 group in **1**. This was similar to that found for the aglycone of suspensolide A at δ44.8 [3].

Moreover, the formation of the derivative **1b** confirmed the location at C-1 in **1**, of the *iso*-valeroxyl group which was further identified from peaks at δ172.7 (*s*), 44.5 (*t*), 26.8 (*q*) and 22.7 (*d*) in the ^{13}C NMR spectrum of **1**.

Alkaline hydrolysis of **1b** gave an oily alcohol (**1b′**) with a molecular formula $C_{11}H_{16}O_4$. Its IR spectrum showed absorptions due to a hydroxyl function (3450 cm^{-1}) and an exocyclic methylene group (3075, 1660 and 950 cm^{-1}). No acetyl signals could be seen in the ^1H NMR spectrum of **1b′** and the signals from the AB-system arising from the methoxy group appeared at δ3.83 and 3.63 (J = 12 Hz). When compared with the spectrum of **1b**, this upfield shift ($\Delta\delta ca$ 0.6) confirmed the position of the acetyl group in the latter compound.

Compound **1c** was identified as 2,3,4-tri-*O*-acetyl-6-*O*-*p*-hydroxycinnamoyl-D-glucose by comparison of its IR spectrum with that of an authentic sample. The formation of this compound and the ^{13}C NMR data of **1** showed that the *trans*-*p*-coumaroyl group was attached to C-6 of the sugar moiety and the glycosidic linkage was located at C-11 of the iridoid skeleton.

Table 1. ^{13}C NMR spectral data of compounds **1**, **3** and **1b***

Carbon No.	1	3	1b
1	91.6	92.3	96.8
3	140.5	141.6	81.1
4	115.4	116.1	34.4
5	36.4	37.0	30.4
6	30.7	30.5	38.3
7	38.1	38.7	43.5
8	80.7	81.6	92.8
9	45.7	47.5	—
10	69.9†	72.4†	149.1
11	68.7†	70.5†	108.2
1′	99.2	101.9	65.9 (C-12)
2′	73.6	73.8	—
3′	76.4	73.1	—
4′	71.7	69.7	—
5′	75.7	76.2	—
6′	63.7‡	64.0	—
1″	127.1	—	—
2″,6″	131.3	—	—
3″,5″	117.0	—	—
4″	161.5	—	—
α-C	146.9	—	—
β-C	115.4	—	—
CH_3>$CHCH_2$ CH_3	22.7 × 2, 26.8, 44.5	23.4 × 2, 27.6, 45.1	—
CH_3CO	22.1	21.5	20.9
COO	167.8, 172.7 × 2	173.9, 173.4	170.7
CH_3O	—	—	55.3

*Solvents: **1** and **3**, deuteromethanol; **1b**; deuterochloroform.

†These values may be interchangeable in the vertical column.

‡This value is *ca* δ0.5 smaller than the values of similar compounds described in the lit. [13] but distinct from the values for the free C-6 of the glucose moiety.

Acid methanolysis of **1** itself, also afforded **1b** indicating that the acetyl group in **1** must be at C-10. Thus, on the basis of the above data, the structure of **1** can be represented as shown. The coupling constant ($J = 6$ Hz) between the C-1 and C-9 protons is similar to that previously reported [3] and, hence, supports the *trans*-configuration of these protons.

Furcatoside B (**2**) was obtained as a hygroscopic amorphous powder with a molecular formula $C_{32}H_{42}O_{14}\cdot H_2O$, $[\alpha]_D - 26.6$ and it turned slightly green when kept for a long time in air, as reported for **1**. A preliminary test suggested it to be an iridoid. Its UV spectrum (λ_{max} nm: 204, 227, 300 sh and 312), IR absorption bands (ν_{max} cm^{-1}: 3400, 1720, 1670, 1600, 1510 and 850) and ^1H NMR ($CDCl_3$) spectrum were very similar to those of **1**. The only difference between **1** and **2** in their spectra were as follows. In the UV spectra, an absorption at 312 nm (ε15 000) in **2** showed a bathochromic shift to 314 nm (ε30 000) in **1**. IR absorption bands at 1630 and 830 cm^{-1} for **1** shifted to 1620 (sh) and 850 cm^{-1} for **2** and the band at 980 cm^{-1} in **1** disappeared in **2**. In the ^1H NMR spectra, the coupling constants between olefinic protons of the *p*-coumaroyl moiety were 16 Hz in **1** and 14 Hz in **2**. These differences showed that **1** and **2** are geometrical isomers of each other and **1** has the *trans*-, while **2** has the *cis*-configuration. Compound **2**, on heating at 60°, afforded a mixture of **1** (predominant) and **2** indicating this isomeric relationship.

On acetylation, **2** afforded a penta-acetate (**2a**) which also showed a residual tertiary hydroxyl group band at 3500 cm^{-1} in the IR spectrum. Acid methanolysis of **2a** gave **1b** and **1c** as in the case of **1**. The formation of these compounds from **2**, which has the *cis*-configuration of the *p*-coumaroyl group, can be explained by a *cis–trans* isomerization during the reaction. Compound **2** was identified as being the *cis*-isomer of **1**.

From the ether extract, besides **1** and **2**, suspensolide A (**4**) [3], α-amyrin palmitate, β-amyrin acetate, chavicol, sitosterol, ursolic acid, *p*-hydroxycinnamic acid, succinic acid, sitosteryl-β-D-glucopyranoside [9] and 1-*O*-*p*-coumaroyl-β-D-glucopyranose [10] were isolated and identified.

Furcatoside C (**3**) was obtained from the ethyl acetate extract as a hygroscopic amorphous powder, $[\alpha]_D - 58.5°$, with a molecular formula $C_{23}H_{36}O_{12}\cdot 2H_2O$. Its UV spectrum ($\lambda_{max}$ nm: 204) and IR absorption bands (ν_{max} cm^{-1}: 3400, 1730, 1665, 1240 and 930) showed it to be an iridoid. Compound **3** was acetylated to give a penta-acetate, with a formula $C_{31}H_{44}O_{16}$, which also showed a residual tertiary hydroxyl absorption band at 3500 cm^{-1}. The ^1H NMR (CD_3COCD_3–D_2O) spectrum of **3** indicated that it was a glycoside having the same 8,10,11-

trioxygenated iridoid skeleton as **1** and **2**. Upon methanolysis, **3** afforded **1b**, as was obtained from **1** and **2**, and a sugar which was identified as D-allose by PC. Thus, **3** should have the structure shown and its ^{13}C NMR spectrum was consistent with this [11].

EXPERIMENTAL

All mps are uncorr. IR and UV spectra were recorded on Shimadzu IR-408 and UV-210A spectrophotometers, respectively. ^1H NMR spectra were obtained on JEOL MH-60 and MH-100 spectrometers, using solvents indicated with TMS as int. standard. MS were recorded on a JEOL D-300 mass spectrometer. ORDs were measured on a Nihonbunko J-20 recording spectropolarimeter. HPLC was performed on a Millipore Waters Associates liquid chromatograph using a μ-Bondapak column.

Extraction and isolation of components. Fresh leaves of *V. furcatum* (12 kg), from Kagoshima city, were extracted with MeOH (150 l.). The extracts were evaporated to dryness *in vacuo* to give a residue (1 kg) which was dissolved in H_2O and extracted with Et_2O and EtOAc successively. Combined Et_2O solns were concd to dryness to give a dark-green residue (150 g) which was applied to a silica gel column. Sequential elution with $CHCl_3$ and MeOH–$CHCl_3$ with increasing MeOH content, gave fractions which were combined according to their R_f on TLC and their IR spectra. They were repeatedly chromatographed until pure.

Elution with $CHCl_3$ led to the isolation of α-amyrin palmitate, β-amyrin acetate, chavicol, sitosterol and ursolic acid. *p*-Coumaric acid was obtained from fractions eluted with MeOH–$CHCl_3$ (3:97). Compounds **1** and **2**, succinic acid, sitosteryl-β-D-glucopyranose and 1-*O*-*p*-coumaroyl-β-D-glucopyranose were isolated from fractions eluted with MeOH–$CHCl_3$ (1:19) and suspensolide A (**4**) from MeOH–$CHCl_3$ (1:9).

Evaporation of the EtOAc extract *in vacuo* gave a residue which was subjected to silica gel chromatography eluting with MeOH–$CHCl_3$ (1:19) followed by re-chromatography eluting with MeOH–Et_2O (1:19) to give pure **3**.

Furcatoside A (**1**). Hygroscopic amorphous powder (680 mg), $[\alpha]_D^{16}$ −103.1° (MeOH; *c* 0.16). UV λ_{max}^{MeOH} nm (ε): 213 (15 000), 228 (15 300), 300 sh and 314 (30 000); IR ν_{max}^{nujol} cm^{-1}: 3400, 1720, 1670, 1600, 1580, 1510, 980 and 830; ^1H NMR (60 MHz, CD_3COCD_3): δ0.88 (6H, *d*, *J* = 7 Hz, isopropyl Me groups), 1.93 (3H, *s*, OAc), 3.3–4.8 (6H, sugar H), 5.00 (1H, *d*, *J* = 8 Hz, glucose H-1), 6.18 (1H, *d*, *J* = 6 Hz, H-1), 6.48 (1H, *br d*, H-3), 6.42, 7.82 (1H each, *d*, *J* = 16 Hz, α-H and β-H), 7.02, 7.68 (2H each, *d*, *J* = 9 Hz, AA′BB′, aromatic H); ^{13}C NMR (25.05 MHz, CD_3OD) see Table 1. (Found: C, 56.58; H, 6.42. $C_{32}H_{42}O_{14}\cdot 1.5\ H_2O$ requires: C, 56.71; H, 6.69%.)

Hydrolysis of **1**. Compound **1** (6 mg) dissolved in EtOH (1.5 ml) and 2 M HCl (0.5 ml) was refluxed for 4 hr. The black polymeric product formed was filtered off and the filtrate diluted with H_2O and extracted with Et_2O. The aq. layer was neutralized over a column of Amberlite IR-45. The eluate was concd *in vacuo* and the presence of glucose was established by PC with pyridine–EtOAc–H_2O–HOAc (5:5:3:1) as solvent. The Et_2O soln was washed with H_2O and a satd soln of NaCl, dried over Na_2SO_4 and evaporated to dryness. A yellowish residue (1 mg) was obtained and identified as *p*-hydroxycinnamic acid.

Acetylation of **1**. Compound **1** (25 mg) was acetylated with Ac_2O–pyridine in the usual manner. After work-up, the acetate was purified by silica gel chromatography to yield 18 mg of a colourless amorphous penta-acetate (**1a**), $C_{40}H_{50}O_{18}$. IR ν_{max}^{nujol} cm^{-1}: 3500, 1735, 1670, 1635, 1600, 1500 and 1040; ^1H NMR (100 MHz, $CDCl_3$): δ0.90 (6H, *d*, *J* = 7 Hz, isopropyl Me groups), 2.04 (6H, *s*, OAc), 2.14, 2.23 (3H each, *s*, OAc), 2.35 (3H, *s*, aromatic OAc), 6.36 (1H, *d*, *J* = 5 Hz, H-1), 6.52 (1H, *br s*, H-3). (Found: C, 58.25; H, 6.22. $C_{40}H_{50}O_{18}$ requires: C, 58.07; H, 6.11%.)

Methanolysis of **1a**. Compound **1a** (77 mg) was dissolved in dry MeOH (2 ml) containing two drops of conc. HCl. The mixture was warmed at 55° until the soln became slightly blue (1 hr). H_2O was added followed by extraction with Et_2O. The crude product was applied to a gel column. Elution with $CHCl_3$ gave a colourless oil mixture which was purified by HPLC [column: μ-Bondapak C_{18}; solvent: MeOH–H_2O (4:6), 1 ml/min, R_t 18 min] to afford (4 mg) **1b**. Elution with MeOH–$CHCl_3$ (3:97) yielded 2 mg **1c**. **1b**: IR ν_{max}^{film} cm^{-1}: 3075, 1740, 1660 and 950; ^1H NMR (60 MHz, $CDCl_3$): δ2.03 (3H, *s*, OAc), 3.41 (3H, *s*, OMe), 4.19, 4.46 (1H each, *d*, *J* = 15 Hz, H-10), 5.13, 5.22 (1H each, *d*, *J* = 3 Hz, H-11), 5.33 (1H, *d*, *J* = 4 Hz, H-8) and 5.42 (1H, *s*, H-1); ^{13}C NMR: see Table 1. (Found: *m/z* 254.1188. $C_{13}H_{18}O_5$ requires 254.1154.) **1c**: amorphous powder, IR ν_{max}^{film} cm^{-1}: 3400, 3030, 1740, 1721, 1630, 1585 and 830. This compound was identified with an authentic sample of 2,3,4-tri-*O*-acetyl-6-*O*-*p*-hydroxycinnamoyl-D-glucose by comparison of IR spectra and TLC.

Synthesis of 2,3,4-*tri*-O-*acetyl*-6-O-p-*hydroxycinnamoyl*-D-*glucose*. 1,2,3,4-Tetra-*O*-acetyl-β-D-glucose (167 mg), mp 128°, $[\alpha]_D^{24}$ +15.3° ($CHCl_3$; *c* 0.021) (lit. [12] mp 128–129°, $[\alpha]_D^{20}$ +12.2°) which was prepared from 1,2,3,4-tetra-*O*-acetyl-6-*O*-trytyl-β-D-glucose according to ref. [12], was treated with *p*-acetoxycinnamoyl chloride prepared from *p*-acetoxycinnamic acid (124 mg) and $SOCl_2$ (0.3 ml) in pyridine for 48 hr. Usual work-up gave 1,2,3,4-tetra-*O*-acetyl-6-*O*-*p*-acetoxycinnamoyl-β-D-glucose (122 mg) needles from MeOH, mp 168–170° $[\alpha]_D^{24}$ −36.4° ($CHCl_3$; *c* 0.011). IR ν_{max}^{nujol} cm^{-1}: no OH absorption, 1767, 1640, 1610, 1508 and 915; ^1H NMR (60 MHz, $CDCl_3$): δ1.99, 2.02, 2.07, 2.16 (3H each, *s*, OAc), 2.28 (3H, *s*, aromatic OAc), near 4.16 (3H, glucose H-5, H-6, H-6′), 4.98–5.76 (3H, glucose H-2–H-4), 5.95 (1H, *d*, *J* = 7.5 Hz, glucose H-1), 6.27 (1H, *d*, *J* = 16 Hz, *trans*-CH=CH), 7.10, 7.56 (2H each, *d*, *J* = 9 Hz, AA′BB′, aromatic H) and 7.73 (1H, *d*, *J* = 16 Hz, *trans*-CH=CH). (Found: C, 56.30, H, 5.25. $C_{25}H_{28}O_{13}$ requires: C, 55.95, H, 5.26%.) This peracylate (100 mg) was dissolved in MeOH (2 ml) and 0.5 M HCl (2 ml), stirred for 1 hr at room temp., H_2O added, extracted with $CHCl_3$ and it was dried and concd to a syrup which was chromatographed on silica gel to give two hydrolysis products. The eluate ($CHCl_3$) was evaporated to give an amorphous solid identified as 2,3,4-tri-*O*-acetyl-6-*O*-(*p*-acetoxycinnamoyl)-D-glucose. Elution with MeOH–$CHCl_3$ (3:97) afforded an amorphous material (22 mg), $[\alpha]_D^{24}$ +83.3° ($CHCl_3$; *c* 0.042), which was identified as 2,3,4-tri-*O*-acetyl-6-*O*-(*p*-hydroxycinnamoyl)-D-glucose with an IR spectrum identical to that of **1c**. ^1H NMR (60 MHz, $CDCl_3$): δ2.00, 2.04, 2.06 (3H each, *s*, OAc), 3.53–3.99 (1H, *m*, glucose H-5), 4.30 (2H, *br s*, glucose H-6), 4.64–5.57 (4H, *m*, glucose H-1–H-4), 6.75, 8.30 (each 1H, *d*, *J* = 17 Hz, *trans*-CH=CH), 7.39 and 7.99 (each 2H, *d*, AA′BB′, *J* = 9 Hz, aromatic H). TLC [silica gel, MeOH–$CHCl_3$ (10:90); R_f **1c** 0.62, synthetic 0.62]. (Found: C, 55.83, H, 5.28. $C_{21}H_{24}O_{11}$ requires C, 55.73, H, 5.35%.)

Hydrolysis of **1b**. Compound **1b** (34 mg) was dissolved in 2 ml MeOH and 0.5 ml 1 M NaOH. The mixture was refluxed gently under N_2 for 20 min at 35°. The reaction product was cooled and H_2O added. Et_2O extraction gave 9 mg **1b′**, an amorphous solid. IR ν_{max}^{film} cm^{-1}: 3450, 3075, 1660, 1072 and 948; ^1H NMR (100 MHz, $CDCl_3$): δ3.63, 3.83 (1H each, *d*, *J* = 12 Hz, AB*q* of $-CH_2OH$); *m/z* $[M]^+$ 212.

Methanolysis of **1**. Compound **1** (26 mg) was dissolved in dry MeOH (2 ml) containing two drops of conc. HCl. The mixture was warmed at 50° until it became slightly blue. After work-up as previously described, **1b** (2 mg) was obtained, indicating an acetoxyl group at C-10 in **1**.

Furcatioside B (**2**). Hygroscopic amorphous powder (105 mg), $[\alpha]_D^{27} - 26.6°$ (MeOH; *c* 0.075). UV λ_{max}^{MeOH} nm (ε): 204 (19 000), 227 (12 300), 300 (sh) and 312 (15 000); IR ν_{max}^{nujol} cm^{-1}: 3400, 1720, 1670, 1623, 1510 and 852; ^{1}H NMR (60 MHz, CD_3COCD_3): δ0.95 (6H, *d*, *J* = 6 Hz, isopropyl Me groups), 2.02 (3H, *s*, OAc), 2.88 (*br s*, OH), 3.3–4.7 (6H, sugar protons), 5.06 (1H, *d*, *J* = 8 Hz, glucose H-1), 6.00 (1H, *d*, *J* = 14 Hz, α-H), 6.28 (1H, *d*, *J* = 6 Hz, H-1), 6.62 (1H, *br s*, H-3), 7.06 (2H, *d*, *J* = 8 Hz, AA'BB', aromatic H), 7.13 (1H, *d*, *J* = 14 Hz, β-H) and 8.02 (2H, *d*, *J* = 8 Hz, AA'BB', aromatic H). (Found: C, 57.68; H, 6.74. $C_{32}H_{42}O_{14}\cdot H_2O$ requires: C, 57.48; H, 6.63%.)

Acetylation of **2**. Compound **2** (60 mg) was treated with Ac_2O–pyridine in the usual way to afford 47 mg of a penta-acetate (**2a**) as an amorphous solid. IR ν_{max}^{film} cm^{-1}: 3500, 1740, 1672, 1635, 1600, 1504 and 1040; ^{1}H NMR (60 MHz, $CDCl_3$): δ0.95 (6H, *d*, *J* = 6 Hz, isopropyl Me groups), 2.00 (3H, *s*, OAc), 2.10 (6H, *s*, OAc), 2.17, 2.31 (3H each, *s*, OAc), 5.80 (1H, *d*, *J* = 14 Hz, α-H), 6.28 (1H, *d*, *J* = 5 Hz, H-1), 6.37 (1H, *br s*, H-3), 7.09, 7.56 (2H each, *d*, *J* = 10 Hz, AA'BB', aromatic H) and 7.69 (1H, *d*, *J* = 14 Hz, β-H).

Methanolysis of **2a**. Compound **2a** (40 mg) was dissolved in dry MeOH and 1 drop of conc. HCl was added. The mixture was warmed at 55° as in the case of **1a**. Extraction with Et_2O and purification by silica gel chromatography gave **1b** (6 mg) and **1c** (3 mg) from the $CHCl_3$ and MeOH–$CHCl_3$ (3:97) eluates, respectively.

Transformation of **2**. Compound **2** (5 mg) in MeOH (1 ml) was refluxed for 1 hr and the soln was evaporated to dryness. The residue was detected by TLC [silica gel, MeOH–$CHCl_3$ (1:19); R_f **1** 0.19, **2** 0.23, transformed product 0.21 (broad)], and the IR spectrum showed that the product was a mixture of **1** and **2**.

α-Amyrin palmitate. Oil (900 mg). IR ν_{max}^{film} cm^{-1}: 1735, 1658, 1175, 991, 830 and 720; ^{1}H NMR (100 MHz, $CDCl_3$): δ0.79–1.06 (total 27H), 2.26 (2H, *t*, *J* = 7 Hz), 4.44 (1H, *t*-like, *J* = 7 Hz) and 5.08 (1H, *m*); EIMS *m/z*: 665 $[M+1]^+$. Hydrolysis of the compound with 2 M NaOH afforded α-amyrin and palmitic acid.

β-Amyrin acetate. White leaflets (53 mg), mp 222–224°. IR spectrum identical to that of an authentic β-amyrin acetate.

Chavicol (169 mg); sitosterol, mp 137–139° (171 mg); ursolic acid, mp 283–285° (476 mg); *p*-hydroxycinnamic acid, mp 210–214° (92 mg); and succinic acid (9 mg) were identified with authentic samples by comparison of IR and ^{1}H NMR spectra.

*Sitosteryl-β-*D*-glucopyranose*. Needles, mp 279–280° (348 mg). IR ν_{max}^{nujol} cm^{-1}: 3350, 1660 and 1105; ^{1}H NMR (100 MHz, C_5D_5N): δ0.60–2.24 (signals of steroid protons), 4.90 (1H, *d*, *J* = 8 Hz, glucose H-1) and 5.32 (1H, *m*). Spectral data of the compound and its acetate were coincident with those in ref. [9].

*1-O-p-Hydroxycinnamoyl-β-*D*-glucopyranose*. Needles, mp 232–233° (37 mg). UV λ_{max}^{MeOH} nm (ε): 214 (11 000), 229 (15 000) and 316 (30 000); IR ν_{max}^{nujol} cm^{-1}: 3550, 3390, 1703, 1635, 1610, 1590, 1515 and 835; ^{1}H NMR (100 MHz, C_5D_5N): δ5.85 (1H, *d*, *J* = 8 Hz), 6.47, 7.80 (1H each, *d*, *J* = 16 Hz) and 7.12, 7.42 (2H each, *d*, *J* = 8 Hz). Upon hydrolysis, this compound gave a sugar identical to D-glucose correspond with reported in ref. [10].

Suspensolide A. Amorphous solid, (acetate mp 108–110°) (23 mg). IR and ^{1}H NMR spectra of the compound were identical with those of an authentic sample isolated from *Viburnum suspensum* [3].

Furcatoside C (**3**). Hygroscopic amorphous powder (180 mg), $[\alpha]_D^{30} - 58.1°$ (MeOH; *c* 0.031). UV λ_{max}^{MeOH} nm (ε): 204 (4600); IR ν_{max}^{nujol} cm^{-1}: 3400, 1732, 1665, 1150, 1090 and 930; ^{1}H NMR (100 MHz, CD_3COCD_3–D_2O): δ0.94 (6H, *d*, *J* = 6 Hz, H-17 and H-18), 2.04 (3H, *s*, OAc), 4.64 (1H, *d*, *J* = 8 Hz, allose H-1), 6.14 (1H, *d*, *J* = 6 Hz, H-1) and 6.42 (1H, *br s*, H-3). (Found: C, 51.16; H, 7.09. $C_{23}H_{36}O_{12}\cdot 2H_2O$ requires: C, 51.10; H, 7.46%.) ^{13}C NMR (25.05 MHz, CD_3OD): see Table 1.

Acetylation of **3**. Compound **3** (52 mg) was treated with Ac_2O–pyridine in the usual manner. After work-up, the product was purified by silica gel chromatography to give a penta-acetate as an amorphous powder (52 mg). IR ν_{max}^{nujol} cm^{-1}: 3500, 1742, 1220, 1095 and 1040; ^{1}H NMR (100 MHz, $CDCl_3$): δ0.96 (6H, *d*, *J* = 6 Hz, H-17 and H-18), 1.98, 2.08, 2.16 (total 15H, OAc), 3.9–5.08 (10H, *m*, H-10, H-11 and sugar protons), 5.63 (1H, *m*, sugar H-3), 6.11 (1H, *d*, *J* = 5 Hz, H-1) and 6.38 (1H, *br s*, H-3).

Methanolysis of **3**. Compound **3** (36 mg) was dissolved in 2 ml dry MeOH containing 1 drop of conc. HCl, warmed at 40° for 15 min under N_2, H_2O added and the mixture extracted with Et_2O. The Et_2O extract was evaporated to dryness and the residue was subjected to silica gel chromatography ($CHCl_3$–hexane, 1:1) to give 6 mg of a compound, $[\alpha]_D^{27} + 37.5°$ ($CHCl_3$; *c* 0.067), which was identical with **1b** from comparison of IR spectra and by HPLC. The H_2O soln was passed through a column of Amberlite IR-45 and concd to a syrup which was identified as D-allose by PC (solvent: EtOAc–pyridine–H_2O–HOAc, 5:5:3:1; R_f 0.58, authentic D-allose R_f 0.58).

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