# New Phenylpropanoid Diglycosides from *Viburnum furucatum*

**IWAGAWA Tetsuo, EGUCHI Satoshi, OKAMURA Hiroaki, NAKATANI Munehiro and HASE Tsunao**

*Department of Chemistry and Bioscience, Faculty of Science, Kagoshima University 1-21-35 Korimoto, Kagoshima 890-0065 Japan*

**Abstract**

Two new phenylpropanoid diglycosides, 3-phenyl-(2*E*)-propenyl *O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**1**) and 4-allylphenyl *O*-α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside (**2**), have been isolated from *Viburnum furcatum*, along with the previously known 4-allyl-2-methoxyphenyl *O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (**3**) and 3-phenyl-(2*E*)-propenyl *O*-α-L-arabinofuranosyl-(1→6)-β-D-glucopyranoside (**4**).
**Key words**: Caprifoliaceae, phenylpropanoid diglycosides, *Viburnum furcatum*

## Introduction

In previous papers, we reported the isolation of two known flavonoid glycosides, isoquercitrin and kaempferol-7-*O*-α-L-rhamnoside-3-β-*O*-glucoside, from a methanol extract of *V. furcatum* (IWAGAWA *et al.* 1983). In addition three new bitter iridoid glycosides, together with α-amyrin palmitate, β-amyrin acetate, chavicol, sitosterol, ursolic acid, *p*-coumaric acid, succinic acid, sitosteryl β-D-glucopyranose, and 1-*O*-*p*-coumaroyl-β-D-glucopyranose were isolated (HASE *et al.*, 1985). The structure of furcatin was revised also to be 4-allylphenyl *O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (HASE and IWAGAWA, 1985). Further investigation of the same plants resulted in isolation of two new phenylpropanoid diglycosides (**1-2**) together with two known phenylpropanoid diglycosides, 4-allyl-2-methoxyphenyl *O*-β-apiofuranosyl-(1→6)-β-D-glucopyranoside (**3**) (MACHIDA *et al.*, 1991) and 3-phenyl-(2*E*)-propenyl *O*-α-L-arabinofuranosyl-(1→6)-β-D-glucopyranoside (**4**) (COMTE *et al.*, 1996). In this report, we describe the isolation and characterization of the glycosides.

## Materials and Methods

**Plant Material**: Leaves of *Viburnum furcatum* were collected in Miyazaki Prefectures in May of 1994 (collection no. 201). The late Dr. SAKO, Faculty of Agriculture of Kagoshima University, kindly provided the species determination. A voucher specimen has been deposited in the herbarium of the Faculty of Agriculture, Kagoshima University, Japan.

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E-mail: iwagawa@sci.kagoshima-u.ac.jp

**General Experimental Procedures**: UV and IR spectra were recorded on UV-210 and JASCO FT/IR 5300 spectrometers, respectively. NMR spectra were recorded in $CD_3OD$ or $CDCl_3$ as solvent on a JEOL JNM-GX 400 spectrometer using TMS as internal standard.

**Extraction and isolation**: Fresh leaves (2.6 kg) of *V. furcatum* were twice extracted with MeOH. The combined solutions were evaporated to dryness *in vacuo* to give a residue. The residue was dissolved in $H_2O$ and extracted with $CH_2Cl_2$, EtOAc, and *n*-BuOH successively. A portion (10.5 g) of the EtOAc extract (11 g) was absorbed on silica gel and subjected to chromatography on silica gel packed in $CH_2Cl_2$, fractions (100 ml) being collected as follows: 1-3 (MeOH-$CH_2Cl_2$, 1:19), 4-7 (MeOH-$CH_2Cl_2$, 1:9), 8-13 (MeOH-$CH_2Cl_2$, 1:4), 14-15 ($H_2O$-MeOH-$CH_2Cl_2$, 0.1:1:9), 16-20 ($H_2O$-MeOH-$CH_2Cl_2$, 2:7:13), and 21 (MeOH). Fractions 8-10 (2.65 g) was again chromatographed on silica gel using MeOH with $CH_2Cl_2$ (13:87) to afford a residue (88 mg). Reversed-phase $C_{18}$ chromatography (ODS-HPLC) of the residue yielded **(3)** (2.9 mg). The *n*-BuOH extract (10 g) was chromatographed on a column of activated charcoal (100 g), fractions being collected as follows: 1 ($H_2O$), 2-3 (MeOH-$H_2O$, 1:1), 4-5 (MeOH-$H_2O$, 1:4), 6-7 (MeOH), 8-9 ($CH_2Cl_2$-MeOH, 1:1), and 10 ($CH_2Cl_2$). The fraction 8 (1.53 g) was chromatographed on silica gel with MeOH-$CH_2Cl_2$ with increasing proportions of MeOH. The fractions eluted with MeOH-$CH_2Cl_2$ (1:4) were further subjected to HPLC with MeOH-$H_2O$ (19:31) to give (2)(28.7mg). Compounds (**1**) (3.8 mg), (**4**) (3.1 mg), and furcatin (55 mg) were obtained from the fraction 9 (739 mg) which was chromatographed on silica gel with MeOH-$H_2O$ (1:4) and then applied to HPLC with MeOH-$H_2O$ (9:11).

**Compound (1)**: Amorphous powder, $[\alpha]_D$ 75° (MeOH: *c* 0.21); UV (MeOH) λmax (log ε): 251 (4.17) nm; IR (film) νmax: 3370, 1651, 1597, 1495, 738, 692 $cm^{-1}$; $^1H$ NMR (see Table 1); $^{13}C$ NMR (see Table 1); COLOC: H-5/C-1, H-6/C-1, C-4, H-7/C-2, C-3, C-4, C-8, H-6'/C-4', C-5', H-1"/C-2", H-5"/C-1", C-3"; (+)-FABMS: *m/z* 451 $[M + Na]^+$, (-)-FABMS: *m/z* 427 $[M - H]^+$.

**Compound (2)**: Amorphous powder, $[\alpha]_D$ -47° (MeOH: *c* 0.33), UV (MeOH) λmax (log ε): 222 (3.85) nm; IR (film) νmax: 3372, 1640, 1611, 1510, 830 $cm^{-1}$; $^1H$ NMR (see Table 1); $^{13}C$ NMR (see Table 1); (+)-HRFABMS: *m/z* 429.1759 $[M + H]^+$ (Calcd for $C_{20}H_{29}O_{10}$, 429.1761).

**Acetylation of 2**: Treatment of **2** (4.8 mg) with $Ac_2O$ (one drop) in pyridine (one drop) at r. t. overnight gave a hexaacetate (**6**) (4.8 mg); amorphous powder, IR (film) νmax: 1753, 1540, 1611, 1510, 831 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.86, 2.02, 2.03, 20.4, 2.05, 2.14 (3H each, s, $C\underline{H}_3CO$), 3.35 (2H, d, *J*=6.6 Hz, H-7), 3.55 (1H, dd, *J*=1.5 and 13.2 Hz, H-5"), 3.64 (1H, dd, *J*=7.3 and 11.0 Hz, H-6'), 3.83-3.87 (1H, m, H-5'), 3.91 (1H, dd, *J*=11.0, 1.8 Hz Hz, H-6'), 4.00 (1H, dd, *J*=13.2, 3.1 Hz, H-4"), 4.46 (1H, d, *J*=7.0 Hz, H-1"), 4.97-5.04 (3H, overlapped, sugar-H), 5.06 (2H, m, H-9), 5.16-5.30 (4H, overlapped, sugar-H), 5.89-5.99 (1H, m, H-8), 6.93 (2H, d, *J*=8.6 Hz, H-2, H-6), and 7.15 (2H, d, *J*=8.6 Hz, H-3 and H-5); (+)-FABMS: *m/z* 703 $[M + Na]^+$.

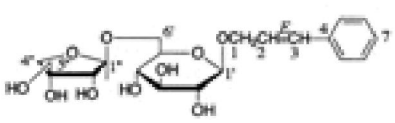
**Compound (3)**: Amorphous powder, $[\alpha]_D$ -53° (MeOH: *c* 0.08); (+)-FABMS: *m/z*

481 $[M + Na]^+$. Compound 3 was identified as 4-allyl-2-methoxyphenyl *O*-D-β-apiofuranosyl-(1→6)-β-D-glucopyranoside by comparing the spectral data with those of an authentic sample (MACHIDA *et al.*, 1991).

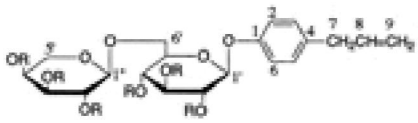
**Compound (4)**: Amorphous powder, $[\alpha]_D$ -68° (MeOH: *c* 0.18); (+)-FABMS: *m/z* 451 $[M + Na]^+$. Compound (**4**) was identified as 3-phenyl-(2*E*)-propenyl *O*-α-L-arabinofuranosyl-(1→6)-β-D-glucopyranoside by comparing the spectral data with those of an authentic sample (COMTE *et al.*, 1996).

## Results and Discussion

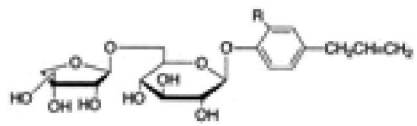
Compound (**1**), $C_{20}H_{28}O_{10}$, had the IR absorptions assigned to a hydroxyl group (3370 $cm^{-1}$) and a mono-substituted phenyl group (1597, 1495, 738, 692 $cm^{-1}$). The $^{13}C$ NMR spectrum was similar to that of furcatin (**5**), except for resonances due to an aglycone (Table 1). In the $^1H$ NMR spectrum, resonances due to a mono-substituted phenyl group [δ 7.22 (1H, br t, *J*=7.3 Hz, H-7), 7.29 (2H, br t, *J*=7.3 Hz, H-6, H-8), 7.42, (2H, d, *J*=7.3 Hz, H-5, H-9)] and to a 3-propenylalcohol derivative [δ 4.31 (1H, ddd, *J*=12.8, 6.2, 1.5 Hz, H-1), 4.50 (1H, ddd, *J*=12.8, 5.5, 1.5 Hz, H-1), 6.37 (1H, dt, *J*=15.8, 6.6, Hz, H-2), 6.69 (1H, br d, *J*=15.8 Hz, H-3) were observed (Table 1). The low-field chemical shifts of the C-1 methylene protons and the large coupling constant (*J*=15.8 Hz) between H-2 and H-3 suggested that compound (**1**) was a glycoside of cinnamic alcohol. The coupling constants of the anomeric protons in the apiose (*J*=2.4 Hz) and glucose (*J*=7.7 Hz) suggested β-glycosidic linkages. The structure of **1** was, therefore, concluded to be 3-phenyl-(2*E*)-propenyl *O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.



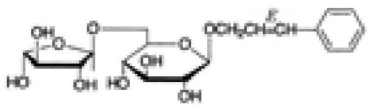
**1**



**2** R=H
**6** R=Ac



**3** R=OMe
**5** R=H



**4**

Table 1. $^{1}H$ and $^{13}C$ NMR Spectral Data of 1 and 2 in $CD_3OD$.[a]

| | 1 | | 2 | |
|---|---|---|---|---|
| **1** | 4.31 (ddd, 12.8, 6.2, 1.5) | 70.9 | | 157.4 |
| | 4.50 (ddd, 12.8, 5.5, 1.5) | 134.0 | | 117.9 |
| **2** | 6.37 (dt, 15.8, 6.6) | 128.8 | 7.04 (d, 8.5) | 130.6 |
| **3** | 6.69 (br d, 15.8) | 138.3 | 7.06 (d, 8.5) | 135.3 |
| **4** | | 127.6 | | 130.6 |
| **5** | 7.42 (d, 7.3) | 129.6 | 7.06 (d, 8.5) | 117.9 |
| **6** | 7.29 (br t, 7.3) | 126.7 | 7.04 (d, 8.5) | 40.4 |
| **7** | 7.22 (br t, 7.3) | 129.6 | 3.31 (br d, 6.6) | 139.2 |
| **8** | 7.29 (br t, 7.3) | 127.6 | 5.89-5.99 (m) | 115.7 |
| **9** | 7.42 (d, 7.3) | | 4.99-5.04 (m) | |
| **1'** | 4.35 (d, 7.7) | 103.4 | 4.87 (d, 7.0) | 102.3 |
| **2'** | | 75.2 | | 74.9 |
| **3'** | | 77.0[b] | | 77.8[b] |
| **4'** | | 71.8 | | 71.5 |
| **5'** | | 78.1[b] | | 77.2[b] |
| **6'** | 3.62 (dd,11.2, 6.2) | 68.8 | 3.82(dd,) | 69.3 |
| | 4,00 (dd, 11.2, 1.8) | | 4.10 (br d, 11.7) | |
| **1"** | 5.03 (d, 2.4) | 111.1 | 4.30 (d, 7.0) | 104.8 |
| **2"** | | 78.1 | | 72.5 |
| **3"** | | 80.6 | | 74.0 |
| **4"** | | 75.0 | | 69.5 |
| **5"** | 3.78, 3.99 (each, 9.5) | 65.7 | 3.42 (m) | 66.7 |
| | | | 3.82 (dd, 3.2, 11.8) | |

[a] δ values in ppm and coupling constants (in parentheses) in Hz.

[b] These values may be interchangeable in any vertical column.

The $^{1}H$ NMR spectral data of **2**, $C_{20}H_{28}O_{10}$, indicated the presence of a 4-allylphenol moiety as in the case of **5** [δ 3.31 (2H, d, *J*=6.6 Hz, H-7), 4.99-5.04 (2H, m, H-9), 5.89-5.99 (1H, m, H-8), 7.04 (2H, *J*=8.5 Hz, H-2, H-6), 7.06 (2H, *J*=8.5 Hz, H-3, H-5)]. Comparison of the $^{13}C$ NMR spectrum with that of **5** showed a close relationship between **2** and **5**, the only difference being resonances due to L-arabinopyranose, instead of D-apiofuranose (Bock, *et al.*, 1983). The coupling constants of H-1' (δ 4.87, 1H, d, *J*=7.0 Hz) and H-1" (δ 4.30, 1H, d, *J*=7.0 Hz) indicated the β-linkage of the D-glucopyranose and α-linkage of the L-arabinopyranose, respectively. The presence of arabinose as a pyranose form in **2** was also supported by the only small difference in the chemical shift (Δ 0.12 ppm) between H-5" of **2** and that of hexaacetate (**6**), $C_{32}H_{40}O_{16}$, obtained by acetylation of **2** with acetic anhydride in pyridine. Thus, compound (**2**) was determined to be 4-allylphenyl *O*-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranoside. This is the fourth isolation of 4-allylphenyl diglucoside, 4-allylphenyl rutinoside

(HERISSEY and LAFOREST, 1932), 4-allylphenyl *O*-α-L-arabinofuranosyl-(1→6)-β-D-glucopyranoside (HIGUCHI *et al.*, 1997). 4-allylphenyl *O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (HASE and IWAGAWA, 1982).

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