New Acylated Glucosides of Chalcone from the Leaves of *Bidens frondosa*

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Five new acylated glucosides of okanin, okanin 4-*O*-(6″-*O*-acetyl-2″-*O*-caffeoyl-β-D-glucopyranoside), okanin 4-*O*-(2″-*O*-caffeoyl-6″-*O*-*p*-coumaroyl-β-D-glucopyranoside), 4-*O*-methylokanin 4′-*O*-(6″-*O*-*p*-coumaroyl-β-D-glucopyranoside), 4-*O*-methylokanin 4′-*O*-(6″-*O*-acetyl-β-D-glucopyranoside), 4-*O*-methylokanin 4′-*O*-(6′-*O*-acetyl-2″-*O*-caffeoyl-β-D-glucopyranoside), have been isolated from the fresh leaves of *Bidens frondosa*. These structures have been elucidated on the basis of spectral data and chemical correlation.

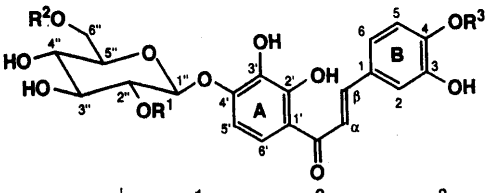
Keywords *Bidens frondosa*; Compositae; chalcone glucoside; phenylpropanoid derivative

Bidens frondosa (Compositae), native to North America, was distributed in temperate regions, and naturalized in Japan. Previously, we investigated the chemical constituents of the leaves of *B. pilosa* and isolated aurone glucosides and phenylpropanoid glucosides.[1] In a continuation of the phytochemical studies on the plant of *Bidens* species, we have now investigated the leaves of *B. frondosa*. It was reported that *B. frondosa* contained chalcones (okanin and butein), chalcone glucosides (mareine and coreopsine), aurones (maritimetin and sulufretin), aurone glucosides (maritimein and sulfurein), luteolin, and quercitrin.[2] Our investigation led to the isolation of five new acylated glucosides of chalcone, okanin 4′-*O*-(6″-*O*-acetyl-2″-*O*-caffeoyl-β-D-glucopyranoside) (**1**), okanin 4′-*O*-(2″-*O*-caffeoyl-6″-*O*-*p*-coumaroyl-β-D-glucopyranoside) (**2**), 4-*O*-methylokanin 4′-*O*-(6″-*O*-*p*-coumaroyl-β-D-glucopyranoside) (**3**), 4-*O*-methylokanin 4′-*O*-(6″-*O*-acetyl-β-D-glucopyranoside) (**4**), and 4-*O*-methylokanin 4′-*O*-(6″-*O*-acetyl-2″-*O*-caffeoyl-β-D-glucopyranoside) (**5**), together with known compounds, okanin 4′-*O*-(6″-*O*-*p*-coumaroyl-β-D-glucopyranoside) (**6**),[3] okanin 4′-*O*-(6″-*O*-acetyl-β-D-glucopyranoside) (**7**),[4] okanin (**8**),[5,6] (*Z*)-6″-*O*-*p*-coumaroylmaritimein (**9**),[1] (*Z*)-6″-*O*-acetylmaritimein (**10**),[1] apigenin (**11**),[7] luteolin (**12**),[7] luteolin 7-*O*-β-D-glucopyranoside (**13**),[7] and kaempferol 3-*O*-β-D-glucopyranoside (**14**).[7] The determination of the structures of **1**—**5** are described here.

Compound **1** was obtained as an orange powder. Its secondary ion mass spectrum (SI-MS) showed $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 677 and 655, respectively. The ^1H- and ^{13}C-nuclear magnetic resonance (^1H- and ^{13}C-NMR) spectra of **1** suggested that **1** was okanin glucoside having two acyl groups, an acetyl and a caffeoyl. Because the ^{13}C-NMR signals due to okanin moiety of **1** were identical with those of okanin 4′-*O*-β-D-glucopyranoside,[3,5] two acyl groups were attached to the glucose moiety. In the ^{13}C-NMR spectrum of **1**, the sugar carbons assignable to the C-1″, C-3″ and C-5″ positions were shifted to a higher field than those of methyl β-D-glucopyranoside. These shifts suggested that the C-2″ and the C-6″ hydroxyls of the glucose were acylated. In order to determine the position of the acetyl and the caffeoyl groups, long-range selective proton decoupling (LSPD) experiments were carried out. The long-range coupling between the acetyl carbonyl and the H-6″ and between the caffeoyl carbonyl and the H-2″ were observed. Thus, the structure of **1** was determined to be okanin 4′-*O*-(6″-*O*-acetyl-2″-*O*-caffeoyl-β-D-glucopyranoside).

Compound **2** was obtained as an orange powder. Its SI-MS showed $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 781 and 759, respectively. In the ^1H- and ^{13}C-NMR spectra of **2**, the signals assignable to okanin and glucose moieties were closely related to those of **1**. The difference between **1** and **2** was the presence of a *p*-coumaroyl group in **2** instead of the acetyl group in **1**. The acyl groups bearing to the C-2″ and the C-6″ hydroxyls of the glucose moiety were determined by the same reason mentioned for **1**. As the result of alkaline methanolysis of **2** with 0.03% NaOMe[8] affording methyl caffeate and **6**, the position of the caffeoyl and the *p*-coumaroyl groups were confirmed to be the C-2″ and the C-6″ hydroxyls, respectively. Thus, the structure of **2** was established to be okanin 4′-*O*-(2″-*O*-caffeoyl-6″-*O*-*p*-coumaroyl-β-D-glucopyranoside).

Compound **3** was obtained as an orange powder. Its SI-MS showed $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 633 and 611, respectively. The ^1H- and ^{13}C-NMR spectra showed signals corresponding to okanin, glucose, *p*-coumaroyl and methoxyl moieties. The ^{13}C-NMR signals due to the B-ring moiety of okanin in **3** resembled those of 4-*O*-methylokanin 4′-*O*-β-D-glucopyranoside,[4] while the signals of the A-ring moiety corresponded to those of **1**. The positions of the methoxyl and the glucosyl moieties, therefore, were assumed to be at the C-4 and C-4′ positions of okanin, respectively. This was confirmed by the presence of nuclear Overhauser effects (NOE) between the anomeric proton and the H-5′ and between the methoxyl proton and the H-5. The ^{13}C-NMR signal due to the C-6″ of **3** appeared at the same position as in **6** and **7**, the C-6″ hydroxyls of the glucose was acylated. Thus, **3** was determined to be 4-*O*-methylokanin 4′-*O*-(6″-*O*-*p*-coumaroyl-β-D-glucopyranoside).



	R^1	R^2	R^3
1	caffeoyl	Ac	H
2	caffeoyl	*p*-coumaroyl	H
3	H	*p*-coumaroyl	Me
4	H	Ac	Me
5	caffeoyl	Ac	Me
6	H	*p*-coumaroyl	H
7	H	Ac	H

Fig. 1

TABLE I. ^{13}C-NMR Spectral Data[a] of 1–7

	1	2	3	4	5	6	7
Okanin moiety							
1	128.4	128.3	129.4	129.5	129.5	128.3	128.4
2	116.1	116.3	116.1	115.4	115.5	116.4	116.1
3	146.9	146.8	148.0	148.1	148.1	146.8	146.9
4	150.2	150.3	152.0	152.0	152.0	150.2	150.2
5	116.7	116.6	112.9	112.6	112.7	116.6	116.6
6	123.9	123.8	123.2	123.9	123.8	123.6	123.9
C=O	149.7	194.6	194.5	194.6	194.7	194.6	194.7
α	118.4	118.1	119.1	119.3	119.4	118.2	118.3
β	147.0	147.0	146.5	146.5	146.5	146.9	147.0
1′	117.8	117.7	117.5	117.5	117.8	117.5	117.6
2′	150.9	150.9	151.6	151.6	151.0	151.4	151.5
3′	136.7	136.9	136.1	136.0	136.9	136.1	136.1
4′	154.1	154.1	154.0	154.0	154.1	154.0	154.0
5′	109.1	109.1	108.4	108.1	109.1	108.4	108.2
6′	122.1	122.1	122.5	122.6	122.2	122.4	122.4
Glucose moiety							
1″	100.8	100.7	102.5	102.5	100.8	102.6	102.6
2″	75.2	75.2	74.8	74.8	75.2	74.8	74.8
3″	75.8	75.9	77.6	77.4	75.8	77.6	77.4
4″	71.6	71.9	72.0	71.6	71.6	72.0	71.6
5″	76.1	76.2	75.9	75.7	76.1	75.8	75.7
6″	64.6	64.4	64.7	64.7	64.6	64.6	64.7
Methyl							
			56.6	56.5	56.5		
Acetyl							
	172.8			172.8	172.8		172.8
	20.7			20.8	20.8		20.8
p-Coumaroyl moiety							
1		127.1	127.2			127.2	
2		131.2	131.2			131.1	
3		117.0	117.1			117.0	
4		161.3	161.3			161.3	
5		117.0	117.1			117.0	
6		131.2	131.2			131.3	
α		114.9	115.1			115.0	
β		147.0	146.9			147.0	
C=O		169.0	169.0			168.9	
Caffeoyl moiety							
1	127.9	127.8			127.9		
2	115.4	115.4			115.4		
3	146.8	146.8			146.8		
4	149.7	149.7			149.7		
5	116.6	116.8			116.6		
6	123.1	123.1			123.1		
α	115.0	115.0			115.0		
β	147.7	147.7			147.7		
C=O	168.7	168.7			168.7		

a) Spectra were measured at 100 MHz in CD_3OD. Data were given in δ value.

Compound **4** was obtained as an orange powder. Its SI-MS showed no $[M+Na]^+$ or $[M+H]^+$ ions. In the electron impact(EI)-MS of **4**, an $[aglycon]^+$ ion was observed at *m/z* 302. The ^{1}H- and ^{13}C-NMR signals assignable to the okanin and glucose moieties of **4** were closely identical with those of **3** except for the presence of an acetyl group in **4** instead of the *p*-coumaroyl group in **3**. Thus, **4** was determined to be 4-*O*-methylokanin 4′-*O*-(6″-*O*-acetyl-β-D-glucopyranoside).

Compound **5** was obtained as an orange powder. Its SI-MS showed $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 691 and 609, respectively. The ^{1}H- and ^{13}C-NMR data of **5** indicated that **5** was *O*-methylokanin glucoside having acetyl and caffeoyl groups. The ^{13}C-NMR signals of the okanin moiety of **5** were neary identical with those of **3** and **4**, and the signals of the glucose moiety with those of **1**. The differential NOE experiment confirmed that the glucosyl and methyl groups were attached to the C-4′ and the C-4 hydroxyls, respectively. The LSPD experiment showed the long-range couplings between the acetyl carbonyl and the H-6″ of glucose and between the caffeoyl carbonyl and the H-2″ of glucose. Thus, the structure of **5** was 4-*O*-methylokanin 4′-*O*-(6′-*O*-acetyl-2″-*O*-caffeoyl-β-D-glucopyranoside).

Experimental

Measurements of optical rotation were carried out on a Jasco DIP-360 digital polarimeter. Infrared (IR) spectra were recorded on a Hitachi 260-36 and a Perkin-Elmer 1710. Ultraviolet (UV) spectra were obtained with a Hitachi 557 spectrometer. MS were measured on a Hitachi M-80. NMR spectra were measured on a Bruker AM-400 spectrometer.

The leaves of *Bidens frondosa* were collected in Hino-shi, Tokyo in Oct., 1989. The concentrated MeOH extract of the fresh leaves (3.7 kg) of the plant was suspended in water. The suspension was successively extracted with $CHCl_3$ and BuOH. Chromatography of the BuOH phase (*ca.* 3 g) on silica gel (Fuji gel BM360, $CHCl_3$–MeOH system), octadecyl silica (ODS, Kusano CIG column, MeOH–H_2O system), and Diaion HP-20 (MeOH–H_2O system) afforded **1** (24 mg), **2** (26 mg), **3** (20 mg), **4** (20 mg), **5** (15 mg), **6** (100 mg),[3] **7** (22 mg),[4] **8** (78 mg),[5,6] **9** (42 mg),[1] **10** (23 mg),[1] **11** (45 mg),[7] and **12** (2.37 g),[7] **13** (405 mg),[7] **14** (41 mg).[7] The known compounds **6**—**14** gave data identical with that described in previous literature.

Okanin 4′-*O*-(6″-*O*-Acetyl-2″-*O*-caffeoyl-β-D-glucopyranoside) (1) Orange powder. $[\alpha]_D^{30}$ +78° (*c*=0.2, MeOH). SI-MS *m/z*: 677 $[M+Na]^+$, 655 $[M+H]^+$; EI-MS *m/z*: 288, 153. IR ν_{max}^{KBr} cm^{-1}: 3400, 2920, 1700, 1630, 1600, 1560, 1510, 1440, 1370, 1290. UV λ_{max}^{MeOH} nm (log ε): 243 sh (4.25), 305 sh (4.33), 333 (4.45), 380 (4.41); +NaOMe: 260, 310, 385, 440 sh; +$AlCl_3$: 263, 312 sh, 360, 497; +$AlCl_3$/HCl: 244 sh, 286 sh, 332, 427; +NaOAc: 244 sh, 306 sh, 334, 377. ^{1}H-NMR (400 MHz, CD_3OD): okanin moiety δ: 6.74 (1H, d, *J*=9.1 Hz, H-5′), 6.83 (1H, d, *J*=8.2 Hz, H-5), 7.11 (1H, dd, *J*=8.2, 2.0 Hz, H-6), 7.19 (1H, d, *J*=2.0 Hz, H-2), 7.52 (1H, d, *J*=15.3 Hz, H-α), 7.56 (1H, d, *J*=9.1 Hz, H-6′), 7.75 (1H, d, *J*=15.3 Hz, H-β); D-glucose moiety δ:3.55 (1H, t, *J*=9.4 Hz, H-4″), 3.72—3.76 (2H, overlapping, H-3″, -5″), 4.30 (1H, dd, *J*=12.0, 6.1 Hz, H_A-6″), 4.46 (1H, dd, *J*=12.0, 2.1 Hz, H_B-6″), 5.14 (1H, dd, *J*=9.4, 8.0 Hz, H-2″), 5.33 (1H, d, *J*=8.0 Hz, H-1″); caffeoyl moiety δ: 6.32 (1H, d, *J*=15.9 Hz, H-8″), 6.77 (1H, d, *J*=8.2 Hz, H-5″), 6.94 (1H, dd, *J*=8.2, 2.0 Hz, H-6‴), 7.04 (1H, d, *J*=2.0 Hz, H-2‴), 7.61 (1H, d, *J*=15.9 Hz, H-7‴); acetyl δ: 2.07 (3H, s).

Octaacetate (1a) of 1 Acetylation of **1** (5.4 mg) with Ac_2O/C_5D_5N gave **1a** (5.1 mg). Colorless powder. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000, 2920, 1770, 1640, 1600, 1500, 1370, 1260, 1200, 1180, 1100. ^{1}H-NMR (400 MHz, $CDCl_3$): okanin moiety δ: 7.06 (1H, d, *J*=8.8 Hz, H-5′), 7.09 (1H, d, *J*=15.9 Hz, H-α), 7.23 (1H, d, *J*=8.3 Hz, H-5), 7.40 (1H, d, *J*=2.1 Hz, H-2), 7.43 (1H, dd, *J*=8.3, 2.1 Hz, H-6), 7.53 (1H, d, *J*=15.9 Hz, H-β), 7.60 (1H, d, *J*=8.8 Hz, H-6′); D-glucose moiety δ: 3.96 (1H, m, H-5″), 4.22 (1H, dd, *J*=12.3, 2.5 Hz, H_A-6″), 4.30 (1H, dd, *J*=12.3, 5.5 Hz, H_B-6″), 5.17—5.48 (4H, overlapping, H-1″, -2″, -3″, -4″); caffeoyl moiety δ: 6.22 (1H, d, *J*=8.4 Hz, H-5‴), 6.35 (1H, d, *J*=16.0 Hz, H-8‴), 7.36 (1H, d, *J*=1.8 Hz, H-2‴), 7.41 (1H, dd, *J*=8.4, 1.8 Hz, H-6‴), 7.62 (1H, d, *J*=16.0 Hz, H-7‴); acetyls δ: 2.00, 2.06, 2.10, 2.20, 2.22, 2.29, 2.29, 2.30, 2.31.

Okanin 4′-*O*-(2″-*O*-Caffeoyl-6″-*O*-*p*-coumaroyl-β-D-glucopyranoside) (2) Orange powder. $[\alpha]_D^{26}$ −66° (*c*=0.2, MeOH). SI-MS *m/z*: 781 $[M+Na]^+$, 759 $[M+H]^+$; EI-MS *m/z*: 288, 153, 152. IR ν_{max}^{KBr} cm^{-1}: 3420, 1680, 1630, 1600, 1510, 1440, 1260. UV λ_{max}^{MeOH} nm (log ε): 232 sh (4.42), 319 (4.62), 380 (4.37); +NaOMe: 250 sh, 312, 372, 440 sh; +$AlCl_3$: 266, 315, 360 sh, 496; +$AlCl_3$/HCl: 250 sh, 321, 426; +NaOAc: 318, 374. ^{1}H-NMR (400 MHz, CD_3OD): okanin moiety δ: 6.74 (1H, d, *J*=9.2 Hz, H-5′), 6.83 (1H, d, *J*=8.2 Hz, H-5), 7.40 (1H, dd, *J*=8.2, 2.0 Hz, H-6), 7.11 (1H, d, *J*=2.0 Hz, H-2), 7.34 (1H, d, *J*=15.3 Hz, H-α), 7.44 (1H, d, *J*=9.1 Hz, H-6′), 7.69 (1H, d, *J*=15.3 Hz, H-β): D-glucose moiety δ: 3.60 (1H, t, *J*=9.2 Hz, H-4″), 3.75—3.85 (2H, overlapping, H-3″, -5″), 4.39 (1H, dd, *J*=11.8, 6.1 Hz, H_A-6″), 4.61 (1H, dd, *J*=11.8, 2.1 Hz, H_B-6″), 5.18 (1H, dd, *J*=9.2, 7.8 Hz, H-2″), 5.36 (1H, d, *J*=7.8 Hz, H-1″); caffeoyl moiety δ: 6.31 (1H, d, *J*=15.9 Hz, H-8‴), 6.77 (1H, d, *J*=8.2 Hz, H-5‴), 6.95 (1H, dd, *J*=8.2, 2.0 Hz, H-6‴), 7.05 (1H, d, *J*=2.0 Hz, H-2‴), 7.59 (1H, d, *J*=15.9 Hz, H-7‴); *p*-coumaroyl moiety δ: 6.33 (1H, d, *J*=16.0 Hz, H-8⁗), 6.74 (2H, d, *J*=8.6 Hz, H-3⁗, -5⁗), 7.40 (2H, d, *J*=8.6 Hz, H-2⁗, -6⁗), 7.62 (1H, d, *J*=15.9 Hz, H-7⁗).

Partial Alkaline Methanolysis of 2 with NaOMe Alkaline methanolysis of **2** (9.0 mg) with 0.03% of methanolic NaOMe (N_2, room temperature, 6 h), followed by treatment with Amberlite IR-120 (H-form) and separation with ODS column chromatography, afforded methyl caffeate, identical with an authentic sample (TLC), and **2a** (2.1 mg). **2a**, orange powder, was completely identical with **6** (TLC, IR, ^{1}H-NMR).

Nonaacetate (2b) of 2 Acetylation of **2** (2.5 mg) with Ac_2O/C_5D_5N gave **2b** (5.1 mg). Colorless powder. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 2900, 1760, 1640, 1600, 1500, 1420, 1370, 1190, 1180, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): okanin moiety δ: 7.01 (1H, d, J=15.9 Hz, H-α), 7.08 (1H, d, J=8.8 Hz, H-5′), 7.22 (1H, d, J=8.4 Hz, H-5), 7.37 (1H, br s, H-2), 7.41 (1H, dd, J=8.4, 1.9 Hz, H-6), 7.48 (1H, d, J=15.9 Hz, H-β), 7.53 (1H, d, J=8.8 Hz, H-6′); D-glucose moiety δ: 4.05 (1H, m, H-5″), 4.37 (1H, dd, J=12.3, 5.4 Hz, H_A-6″), 4.45 (1H, dd, J=12.3, 2.5 Hz, H_B-6″), 5.22—5.49 (4H, overlapping, H-1″, -2″, -3″, -4″); caffeoyl moiety δ: 6.35 (1H, d, J=16.0 Hz, H-8‴), 7.22 (1H, d, J=8.4 Hz, H-5‴), 7.37 (1H, br s, H-2‴), 7.39 (1H, dd, J=8.4, 2.1 Hz, H-6‴), 7.63 (1H, d, J=16.0 Hz, H-7‴); p-coumaroyl moiety δ: 6.41 (1H, d, J=16.0 Hz, H-8⁗), 7.09 (2H, d, J=8.6 Hz, H-3⁗, -5⁗), 7.59 (2H, d, J=8.6 Hz, H-2⁗, -6⁗), 7.69 (1H, d, J=16.0 Hz, H-7⁗); acetyls δ: 2.01, 2.07, 2.20, 2.22, 2.29, 2.29, 2.29, 2.30, 2.30.

4-*O*-Methylokanin 4′-*O*-(6″-*O*-*p*-Coumaroyl-β-D-glucopyranoside) (3) Orange powder. $[\alpha]_D^{26}$ −219° (c=0.16, MeOH). SI-MS m/z: 633 $[M+Na]^+$, 611 $[M+H]^+$; EI-MS m/z: 302, 151, 150. IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1720, 1640, 1600, 1560, 1500, 1440, 1260, 1070. UV λ_{max}^{MeOH} nm (log ε): 230 sh (4.34), 270 sh (4.13), 314 (4.53), 373 (4.39); +NaOMe: 248, 358; +$AlCl_3$: 280 sh, 317, 426; +$AlCl_3$/HCl: 280 sh, 316, 416; +NaOAc: 270 sh, 314, 370. ^{1}H-NMR (400 MHz, CD_3OD): okanin moiety δ: 6.79 (1H, d, J=9.1 Hz, H-5′), 6.97 (1H, d, J=8.3 Hz, H-5), 7.10 (1H, dd, J=8.3, 2.0 Hz, H-6), 7.12 (1H, d, J=2.0 Hz, H-2), 7.36 (1H, d, J=15.4 Hz, H-α), 7.44 (1H, d, J=9.1 Hz, H-6′), 7.72 (1H, d, J=15.4 Hz, H-β); D-glucose moiety δ: 3.43—3.62 (3H, overlapping, H-2″, -3″, -4″), 3.78 (1H, ddd, J=9.1, 7.2, 2.3 Hz, H-5″), 4.35 (1H, dd, J=11.9, 6.2 Hz, H_A-6″), 4.60 (1H, dd, J=11.9, 2.3 Hz, H_B-6″), 5.00 (1H, d, J=7.5 Hz, H-1″); p-coumaroyl moiety δ: 6.34 (1H, d, J=16.0 Hz, H-8‴), 6.74 (2H, d, J=8.6 Hz, H-3‴, -5‴), 7.43 (2H, d, J=8.6 Hz, H-2‴, -6‴), 7.62 (1H, d, J=16.0 Hz, H-7‴): methyl δ: 3.93 (3H, s).

Heptaacetate (3a) of 3 Acetylation of **3** (4.2 mg) with Ac_2O/C_5D_5N gave **3a** (5.9 mg). Colorless powder. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000, 2920, 1760, 1640, 1600, 1500, 1440, 1400, 1200. ^{1}H-NMR (400 MHz, $CDCl_3$): okanin moiety δ: 6.94 (1H, d, J=8.5 Hz, H-5), 6.95 (1H, d, J=15.9 Hz, H-α), 7.01 (1H, d, J=8.4 Hz, H-5′), 7.27 (1H, d, J=2.1 Hz, H-2), 7.38 (1H, dd, J=8.5, 2.1 Hz, H-6), 7.48 (1H, d, J=15.9 Hz, H-β), 7.53 (1H, d, J=8.8 Hz, H-6′); D-glucose moiety δ: 4.01 (1H, m, H-5″), 4.35 (1H, dd, J=12.3, 5.3 Hz, H_A-6″), 4.42 (1H, dd, J=12.3, 2.5 Hz, H_B-6″), 5.18—5.36 (4H, overlapping, H-1″, -2″, -3″, -4″); p-coumaroyl moiety δ: 6.39 (1H, d, J=16.0 Hz, H-8‴), 7.04 (2H, d, J=8.6 Hz, H-3‴, -5‴), 7.52 (2H, d, J=8.6 Hz, H-2‴, -6‴), 7.68 (1H, d, J=16.0 Hz, H-7‴); methyl δ: 3.87 (3H, s); acetyls δ: 2.04, 2.07, 2.08, 2.22, 2.28, 2.29, 2.33 (each 3H, s).

4-*O*-Methylokanin 4′-*O*-(6″-*O*-Acetyl-β-D-glucopyranoside) (4) Orange powder. $[\alpha]_D^{26}$ +119° (c=0.20, MeOH). EI-MS m/z: 302 [aglycon]$^+$, 151, 150. IR ν_{max}^{KBr} cm^{-1}: 3430, 1740, 1640, 1580, 1500, 1440, 1280. UV λ_{max}^{MeOH} nm (log ε): 238 sh (4.07), 261 (3.99), 324 sh (4.22), 372 (4.50); +NaOMe: 255, 283, 357, 404 sh; +$AlCl_3$: 244, 270, 336 sh, 415; +$AlCl_3$/HCl: 244, 270, 336 sh, 415; +NaOAc: 238 sh, 261, 324 sh, 371. ^{1}H-NMR (400 MHz, CD_3OD): okanin moiety δ: 6.78 (1H, d, J=9.1 Hz, H-5′), 6.97 (1H, d, J=8.4 Hz, H-5), 7.20 (1H, dd, J=8.4, 2.0 Hz, H-6), 7.25 (1H, d, J=2.0 Hz, H-2), 7.60 (1H, d, J=15.3 Hz, H-α), 7.63 (1H, d, J=9.1 Hz, H-6′), 7.78 (1H, d, J=15.3 Hz, H-β); D-glucose moiety δ: 3.30—3.58 (3H, overlapping, H-2″, -3″, -4″), 3.70 (1H, m, H-5″), 4.26 (1H, dd, J=11.9, 6.3 Hz, H_A-6″), 4.43 (1H, dd, J=11.9, 2.1 Hz, H_B-6″), 4.99 (1H, d, J=7.4 Hz, H-1″); methyl δ: 3.91 (3H, s); acetyl δ: 2.08 (3H, s).

4-*O*-Methylokanin 4′-*O*-(2″-*O*-Acetyl-6″-*O*-*p*-coumaroyl-β-D-glucopyranoside) (5) Orange powder. $[\alpha]_D^{26}$ +26° (c=0.20, MeOH). SI-MS m/z: 691 $[M+Na]^+$, 669 $(M+H]^+$; EI-MS m/z: 302, 151, 150. IR ν_{max}^{KBr} cm^{-1}: 3420, 2920, 1700, 1630, 1600, 1500, 1440, 1260. UV λ_{max}^{MeOH} cm (log ε): 243 sh (4.27), 304 sh (4.29), 334 (4.39), 360 sh (4.37); +NaOMe: 250 sh, 320 sh, 370; +$AlCl_3$: 265, 374 sh, 376 sh, 421; +$AlCl_3$/HCl: 244 sh, 280 sh, 330, 415; +NaOAc: 236 sh, 304 sh, 336, 360. ^{1}H-NMR (400 MHz, CD_3OD): okanin moiety δ: 6.75 (1H, d, J=9.1 Hz, H-5′), 6.97 (1H, d, J=8.5 Hz, H-5), 7.19 (1H, dd, J=8.5, 2.0 Hz, H-6), 7.24 (1H, d, J=2.0 Hz, H-2), 7.58 (1H, d, J=15.3 Hz, H-α), 7.59 (1H, d, J=9.1 Hz, H-6′), 7.76 (1H, d, J=15.4 Hz, H-β); D-glucose moiety δ: 3.54 (1H, t, J=9.4 Hz, H-4″), 3.72—3.76 (2H, overlapping, H-3″, -5″), 4.29 (1H, dd, J=12.0, 6.1 Hz, H_A-6″), 4.45 (1H, dd, J=12.0, 2.1 Hz, H_B-6″), 5.14 (1H, dd, J=9.4, 7.9 Hz, H-2″), 5.33 (1H, d, J=7.9 Hz, H-1″); caffeoyl moiety δ: 6.32 (1H, d, J=15.9 Hz, H-8‴), 6.76 (1H, d, J=8.2 Hz, H-5‴), 6.94 (1H, dd, J=8.1, 2.0 Hz, H-6‴), 7.04 (1H, d, J=2.0 Hz, H-2‴), 7.61 (1H, d, J=15.9 Hz, H-7‴); methyl δ: 3.93 (3H, s); acetyl δ: 2.07 (3H, s).

Heptaacetate (5a) of 5 Acetylation of **5** (4.0 mg) with Ac_2O/C_5D_5N gave **5a** (3.6 mg). Colorless powder. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000, 2930, 1760, 1640, 1600, 1500, 1370, 1200. ^{1}H-NMR (400 MHz, $CDCl_3$): okanin moiety δ: 6.96 (1H, d, J=8.6 Hz, H-5′), 7.00 (1H, d, J=15.9 Hz, H-α), 7.06 (1H, d, J=8.8 Hz, H-5), 7.28 (1H, d, J=2.1 Hz, H-2), 7.40 (1H, dd, J=8.6, 2.1 Hz, H-6), 7.52 (1H, d, J=15.9 Hz, H-β), 7.59 (1H, d, J=8.8 Hz, H-6′); D-glucose moiety δ: 3.96 (1H, m, H-5″), 4.22 (1H, dd, J=12.4, 2.4 Hz, H_A-6″), 4.30 (1H, dd, J=12.4, 5.4 Hz, H_B-6″), 5.17—5.47 (4H, overlapping, H-1″, -2″, -3″, -4″); caffeoyl moiety δ: 6.35 (1H, d, J=16.0 Hz, H-8‴), 7.22 (1H, d, J=8.4 Hz, H-5‴), 7.36 (1H, d, J=2.0 Hz, H-2‴), 7.40 (1H, dd, J=8.4, 2.0 Hz, H-6‴), 7.63 (1H, d, J=16.0 Hz, H-7‴); methyl δ: 3.87 (3H, s); acetyls δ: 2.00, 2.06, 2.10, 2.19, 2.22, 2.29, 2.29, 2.32 (each 3H, s).

Acknowledgments We thank Dr. Y. Shida and Ms. Y. Kato for MS measurements, and Ms. C. Sakuma for NMR measurements.

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