Full Papers

Flavonol and Chalcone Ester Glycosides from *Bidens andicola*

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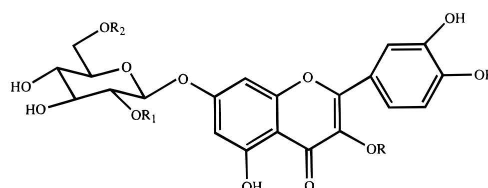
Five new flavonol 7-*O*-glycosides (**1**−**5**), having quercetin or quercetin 3-methyl ether as their aglycons, and sugar chains made up of three or four sugars, including *β*-D-glucopyranose, α-L-rhamnopyranose, and *β*-D-xylopyranose, have been isolated from the aerial parts of *Bidens andicola*, along with a new chalcone ester glycoside (**6**) and five known chalcone ester glycosides. The structures of **1**−**6** were elucidated using a combination of spectroscopic techniques.

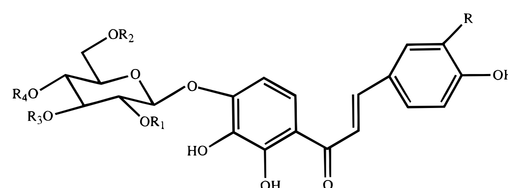
In a continuing search for bioactive compounds from South American medicinal plants, we have examined *Bidens andicola* H. B. K. (Asteraceae), a species used in Peruvian folk medicine.[1] A decoction of the whole plant is claimed to be effective when taken orally as a contraceptive and is employed topically as an antirheumatic. The leaves are used as a food.[1,2]

In the present investigation, 11 compounds were isolated from the methanol extract of the aerial parts of *B. andicola* and comprised five new glycosides (**1**−**5**, Chart 1) having quercetin or quercetin 3-methyl ether as the aglycons and an oligosaccharide portion made up of three or four sugars (glucose, xylose, and rhamnose) linked to C-7. A new chalcone ester glycoside (**6**) having a 4,2′,3′,4′-tetrahydroxychalcone unit, along with five known chalcone ester glycosides possessing okanin as the aglycon moiety, were also obtained from this plant.

Chart 1[a]



	R	R1	R2
1	-CH3	Xyl	Rha-(2—>1)-Rha
2	-CH3	Xyl	Rha
3	-CH3	Xyl	Glc-(2—>1)-Rha
4	-H	Xyl	Rha-(2—>1)-Rha
5	-H	Xyl	Rha



	R	R1	R3	R4	R2
6	H	Ac	H	H	Cinnamoyl

[a] Key: Rha = α-L-rhamnopyranosyl, Glc = *β*-D-glucopyranosyl, Xyl = *β*-D-xylopyranosyl.

Results and Discussion

A Sephadex LH-20 column and reversed-phase HPLC separations of the MeOH extract of the leaves of *B. andicola* provided new compounds **1**−**6**. The molecular formulas $C_{39}H_{50}O_{24}$ for compound **1**, $C_{33}H_{40}O_{20}$ for **2**, $C_{39}H_{50}O_{25}$ for **3**, $C_{38}H_{48}O_{24}$ for **4**, and $C_{32}H_{38}O_{20}$ for **5** were determined by negative-ion FABMS and ^{13}C and DEPT ^{13}C NMR analysis.

Their ^{1}H and ^{13}C NMR spectra indicated that glycosides **1**−**3** had an identical aglycon portion but differed only in the saccharide chains. Acid hydrolysis of **1**−**3** afforded quercetin 3-methyl ether,[3] which was identified by comparing its ^{1}H and ^{13}C NMR data with published values.[4,5] In their ^{1}H NMR spectra, an unusual pattern of 7-O-glycosylation was indicated by downfield shifts of H-6 (ca. +0.32 ppm) and H-8 (ca. +0.33 ppm) with respect to rutin[4] as a model compound. Similarly, in the ^{13}C NMR spectra of **1**−**3** (see the Experimental Section), 7-O-glycosylation was confirmed by the diagnostic[6] upfield shift of C-7 (−2.0 ppm) and by downfield shifts of the ortho-related C-8 (+0.8 ppm) and C-6 (+1.2 ppm) and the para-related C-10 (+1.6 ppm) carbons with respect to rutin.[4] The ^{1}H NMR and ^{13}C NMR data of compounds **4** and **5** indicated that quercetin was the aglycon. The 7-O-glycosylation of compounds **4** and **5** was confirmed by comparison with literature data.[7]

Acid methanolysis of **1** gave glucose, rhamnose, and xylose in a 1:2:1 ratio. FABMS of **1** showed the [M − H]$^-$ ion at *m*/*z* 901 with prominent fragments at *m*/*z* 755 [(M − H) − 146]$^-$ and 623 [(M − H) − (146 + 132)]$^-$,

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Table 1. ^{13}C NMR Data for the Sugar Moieties of Compounds **1**, **3**, and **6** in CD_3OD^a

	1 δ_C	**2** δ_C	**3** δ_C		**6** δ_C
Glc 1	100.0	100.2	100.1	Glc 1″	99.5
2	83.0	83.0	82.8	2″	75.8
3	77.7	77.6	77.8	3″	77.0
4	71.1	71.3	71.1	4″	71.1
5	77.5	77.8	77.8	5″	76.9
6	69.0	69.1	68.8	6″	65.0
Rha I 1	102.0	105.0	104.8	cinnamoyl 1‴	167.5
2	80.0	74.0	74.2	2‴	119.0
3	71.0	72.2	72.0	3‴	146.1
4	75.3	75.3	75.0	4‴	135.4
5	69.2	69.4	69.6	5‴	130.0
6	18.5	17.8	18.2	6‴	128.9
				7‴	131.0
Rha II 1	104.3			8‴	128.9
2	74.0			9‴	130.0
3	72.0			*CH₃*CO	21.8
4	75.3			CH₃*CO*	178.5
5	69.7				
6	18.0				
Xyl 1	107.0	107.1	106.8		
2	76.2	75.9	76.0		
3	78.8	79.0	78.9		
4	73.4	73.2	73.4		
5	67.1	67.0	66.9		
Glc II 1			104.1		
2			82.6		
3			77.4		
4			71.0		
5			78.5		
6			62.5		

[a] Assignments were confirmed by HSQC and HMBC experiments. Glc = β-D-glucopyranosyl, rha = α-L-rhamnopyranosyl, xyl = β-D-xylopyranosyl.

due to the subsequent losses of one deoxyhexose unit and one pentose unit, at *m/z* 477 [(M − H) − (146 + 132 + 146)]⁻, indicative of the subsequent loss of one deoxyhexose unit, and at *m/z* 315 [(M − H) − (146 + 132 + 146 + 162)]⁻, derived from the loss of a hexose unit. Four anomeric protons were evident for **1**. They resonated at δ 5.18 (d, J = 7.5 Hz), 5.00 (d, J = 1.5 Hz), 4.75 (d, J = 1.5 Hz), and 4.60 (d, J = 7.6 Hz) in the ^{1}H NMR spectrum and correlated in an HSQC experiment to carbons at δ 100.0, 104.3, 102.0, and 107.0, respectively. The structure of oligosaccharide chain was assigned in the following manner. By a combination of 1D and 2D TOCSY[8] and 2D DQF-COSY[9] experiments, the 1D-TOCSY subspectrum of the four monosaccharide units could be easily interpreted, and at the same time, the type of sugar, its configuration, and conformation could be assigned (Table 2). The isolated ^{1}H NMR signals, which resonated at uncrowded regions of the spectrum between δ 4.30 and 5.40, were the starting point for the 1D-TOCSY experiments.[10] Because of the selectivity of multistep coherence transfer, the 1D-TOCSY subspectrum of a single monosaccharide unit could be extracted from the crowded overlapping region between δ 3.10 and 4.20. Each subspectrum could be attributed to one set of coupled protons such as H-1 to H-5 or H-6 of a sugar moiety. Moreover, the 1D-TOCSY subspectra obtained by irradiating at δ 5.18, 5.00, or 4.75 recognized these protons as belonging to hexopyranose units. Irradiation of the anomeric signals at δ 5.00 and 4.75 allowed the identification of two deoxyhexose units. Irradiation of the signal at δ 4.60 showed connectivities to three methines and one methylene, allowing the identification of one pentose unit.

A HSQC[11] experiment correlated all proton resonances in **1** with those of the corresponding carbons (Tables 1 and 2). Data from the above experiments determined the position of the interglycosidic linkages by comparison of the carbon chemical shift observed with those of the corresponding methyl pyranoside and taking in account the known effects of glycosidation.[12] Unambiguous determination of the interglycosidic linkages and sugar sequences was obtained from the long-range CH correlations (HMBC spectrum).[13] The HMBC spectrum of **1** was also useful in the determination of the linkages of the sugar moieties. Diagnostic long-range correlations were observed between H-1glc and C-7, H-1xyl and C-2glc, H-1rha′ and C-6glc, H-1rha″ and C-2rha′ (Table 3). Thus, compound **1** was assigned as quercetin 3-methyl ether-7-*O*-β-D-glucopyranosyl-[(1→6)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl]-(1→2)-β-D-xylopyranoside.

The FABMS of **2** showed the [M − H]⁻ ion at *m/z* 755 with prominent fragments at *m/z* 609 [(M − H) − 146]⁻ and *m/z* 315 [(M − H) − (146 + 132 + 162)]⁻, due to the sequential loss of one deoxyhexose unit, one pentose unit, and one hexose unit. Analysis of the NMR data of compound **2** and comparison with those of **1** indicated that **2** differs from **1** only in the absence of the second rhamnopyranosyl unit (Tables 1 and 2). Therefore, the structure quercetin 3-methyl ether-7-*O*-β-D-glucopyranosyl-[(1→6)-α-L-rhamnopyranosyl]-(1→2)-β-D-xylopyranoside was assigned to **2**.

Acid methanolysis of **3** gave glucose, rhamnose, and xylose in a ratio of 2:1:1. The FABMS of **3** showed the [M − H]⁻ ion at *m/z* 917 with prominent fragments at *m/z* 771 [(M − H) − 146]⁻ and 609 [(M − H) − (146 + 162)]⁻, due to the subsequent loss of one hexose unit and one deoxyhexose unit. Intense fragments were also observed at *m/z* 477 [(M − H) − (162 + 132 + 146)]⁻ and *m/z* 315 [(M − H) − (162 + 132 + 146 + 162)]⁻. The ^{13}C and DEPT ^{13}C NMR spectra showed 39 signals, of which 23 were assigned to the saccharide portion and 16 to the flavonol moiety. The oligosaccharide structure was determined by 2D NMR. Even at high field (600 MHz), the 1D sugar spectral region of **3** was complex as most of the shifts were found between δ 5.40 and 3.00 and were overlapped by the aglycon signals. 1D and 2D TOCSY spectroscopy[10] experiments allowed resolution of the overlapped spectra of the oligosaccharides into a subset of individual monosaccharide spectra. In the 1D and 2D TOCSY spectra of **3**, the anomeric proton signal ascribable to one of the β-D-glucopyranose moieties (H-1, δ 5.12, J = 7.0 Hz) showed connectivities to four methines (δ 3.54, 3.40, 3.45, and 3.31). This, together with the 2D DQF-COSY spectrum, established the proton sequence within this sugar fragment as H-1 (δ 5.12), H-2 (δ 3.54), H-3 (δ 3.40), H-4 (δ 3.45), H-5 (δ 3.31), H-6a (δ 3.69), and H-6b (δ 3.95) (Table 2). Similar observations from the TOCSY and COSY experiments for all the other sugar residues (Tables 1 and 2) allowed complete sequential assignments for all proton resonances starting from the anomeric proton signals. HSQC (Tables 1 and 2) permitted assignments of the interglycosidic linkages by comparison of the ^{13}C NMR shifts observed with those of the corresponding methyl

Table 2. ^{1}H NMR Data of the Oligosaccharide Moieties of Compounds **1**–**3** and **6** in $CD_3OD^{a,b}$

	1 δ_H	2 δ_H	3 δ_H		6 δ_H
Glc I 1	5.18 d (7.5)	5.12 d (7.5)	5.12 d (7.0)	Glu1″	5.10 d (7.6)
2	3.55 dd (7.5, 9.0)	3.56 dd (7.5, 9.0)	3.54 dd (7.0, 9.0)	2″	4.32 dd (7.6, 9.5)
3	3.43 t (9.0)	3.44 t (9.0)	3.40 t (9.0)	3″	3.50 t (9.5)
4	3.47 dd (9.0, 10.0)	3.47 dd (9.0, 10.0)	3.45 dd (9.0, 10.0)	4″	3.57 t (9.5)
5	3.33 m	3.32 m	3.31 m	5″	3.64 m
6a	3.65 dd (12.0, 5.0)	3.70 dd (12.0, 5.0)	3.69dd (12.0, 5.0)	6a″	4.28 dd (12.0, 2.5)
6b	4.00 dd (12.0, 3.0)	3.98 dd (12.0, 3.0)	3.95 dd (12.0, 3.0)	6b″	4.70 dd (12.0, 4.5)
Rha I 1	4.75 d (1.5)	5.00 d (1.5)	5.03 d (1.5)	Cinn 1‴	
2	3.87 dd (1.5, 9.0)	3.91 dd (1.5, 9.0)	3.90 dd (1.5, 9.0)	2‴	6.68 d (16.0)
3	3.76 dd (3.0, 9.0)	3.74 dd (3.0, 9.0)	3.78 dd (3.0, 9.0)	3‴	7.80 d (16.0)
4	3.55 t (9.0)	3.55 t (9.0)	3.58 t (9.0)	4‴	
5	4.05 m	4.00 m	4.03 m	5‴	7.40 dd (7.5, 1.4)
6	1.28 d (6.5)	1.30 d (6.5)	1.28 d (6.5)	6‴	7.62 m
				7‴	7.62 m
Rha I I1	5.00 d (1.5)			8‴	7.62 m
2	3.90 dd (1.5, 9.0)			9‴	7.40 dd (7.5, 1.4)
3	3.76 dd (3.0, 9.0)			*CH*$_3$CO	1.92 s
4	3.56 t (9.0)				
5	4.05 m				
6	1.28 d (6.5)				
Xyl 1	4.60 d (7.6)	4.58 d (7.6)	4.62 d (7.5)		
2	3.20 dd (7.6, 9.0)	3.24 dd (7.6, 9.0)	3.20 dd (7.5, 9.0)		
3	3.30 t (9.0)	3.35 t (9.0)	3.30 t (9.5)		
4	3.50 ddd (10,9.0,5.0)	3.53 ddd (10,9.0,5.0)	3.55 ddd (10, 9.5, 5)		
5a	3.85 dd (10.0, 12.0)	3.86 dd (10.0, 12.0)	3.89 dd (10.0, 12.0)		
5b	3.15 dd (4.5, 12.0)	3.20 dd (4.5, 12.0)	3.12 dd (5.0, 12.0)		
Glc II 1			4.72 d (7.5)		
2			3.28 dd (9.0, 7.5)		
3			3.40 t (9.0)		
4			3.38 t (9.0)		
5			3.42 m		
6a			3.81 dd (12.0, 2.5)		
6b			3.66 dd (12.0, 6.0)		

[a] Assignments were confirmed by a combination of COSY-DQF and 1D-TOCSY data. [b] Coupling constants (*J* values) are given in Hz in parentheses.

Table 3. HMBC Correlations Observed for Compounds **1** and **3**

1 (C-carbon)	1 (H-proton)	3 (C-carbon)	3 (H-proton)
165.2 (C-7)	5.18 (H-1 Glc)	165.0 (C-7)	5.12 (H-1 Glc I)
83.0 (C-2 GlcI)	4.60 (H-1 Xyl)	82.8 (C-2 GlcI)	4.62 (H-1 Xyl)
69.0 (C-6 Glc I)	4.75 (H-1 Rha I)	68.8 (C-6 Glc I)	4.72 (H-1 Glc II)
102.0 (C-1 Rha I)	4.00 (H-6b Glc I)	104.1 (C-1 Glc II)	3.95 (H-6b Glc I)
	3.65 (H-6a Glc I)		3.69 (H-6a Glc I)
104.3 (C-1 Rha II)	3.87 (H-2 Rha I)	104.8 (C-1 Rha)	3.54 (H-2 Glc I)

pyranosides and taking into account the known effects of glycosidation.[12] The absence of any ^{13}C NMR glycosidation shifts for the xylopyranosyl and rhamnopyranosyl residues suggested that these sugars were terminal units, while glycosidation shifts for C-2 (~+9 ppm) and C-6 (~+7 ppm) of the glucopyranosyl unit linked at C-7 indicated that one of the glucopyranosyl residues was disubstituted. Glycosidation shifts at C-2 (~+8 ppm) of the second glucopyranosyl unit allowed us to define the structure of the saccharide chain linked to C-7. The position of each sugar unit was deduced from a HMBC experiment. The ^{1}H NMR and ^{13}C NMR data indicated the β configuration at the anomeric position for the glucopyranosyl and xylopyranosyl units and the α configuration at the anomeric positions for the rhamnopyranosyl unit (Tables 1 and 2). Therefore, the structure quercetin 3-methyl ether-7-*O*-β-D-glucopyranosyl-[(1→6)-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranosyl]-(1→2)-β-D-xylopyranoside was assigned to **3**.

The FABMS of **4** showed a [M − H]$^-$ ion at *m*/*z* 887 with prominent fragments at *m*/*z* 741 [(M − H) − 142]$^-$, 609 [(M − H) − 146 + 132]$^-$, 463 [(M − H) − (132 + 146 + 146]$^-$, and 301 [(M − H) − (132 + 162 + 146 + 146)]$^-$, due to the subsequent loss of two deoxyhexose units, one hexose unit, and one pentose unit. The ^{13}C and DEPT ^{13}C NMR spectra showed 38 signals, of which 23 were assigned to the saccharide portion and 15 to the flavonol moiety. Analysis of the NMR data of compound **4** and comparison with those of **1** showed **4** to differ from **1** only in the absence of methoxyl group at C-3 (Tables 1 and 2; Experimental Section). Therefore, the structure quercetin 7-*O*-β-D-glucopyranosyl-[(1→6)-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranosyl]-(1→2)-β-D-xylopyranoside was assigned to **4**.

The FABMS of compound **5** displayed a molecular ion peak at *m*/*z* 741 [(M − H)]$^-$ and prominent fragments at *m*/*z* 595 [(M − H) − 146]$^-$, 463 [(M − H) − 146 + 132]$^-$, and 301 [(M − H) − 146 + 132 + 162]$^-$, corresponding to the subsequential losses of a pentose unit, a deoxyhexose unit, and a hexose unit. The ^{13}C NMR signals for the flavonoid portion were similar to those of **4**, allowing identification of the aglycon of **5** as

quercetin. Analysis of the spectral data of **5** revealed that this compound had the same glycosidic chain as compound **2**. Therefore, compound **5** was determined as quercetin 7-*O*-β-D-glucopyranosyl-[(1→6)-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranosyl]-(1→2)-β-D-xylopyranoside.

The molecular formula $C_{32}H_{30}O_{12}$ of compound **6** was determined by FABMS and ^{13}C and DEPT ^{13}C NMR analysis. Its negative FABMS spectrum showed a quasimolecular ion at *m/z* 605 and peaks at *m/z* 475 $[(M - H) - 130]^-$, due to the loss of a cinnamoyl moiety, and at *m/z* 433 $[(M - H) - 130 + 42]^-$ and 271 $[(M - H) - (162 + 130 + 42]^-$, ascribable to the loss of cinnamoyl, acetyl, and glucopyranosyl moieties. The ^1H NMR spectrum exhibited the characteristic pattern of a chalcone with a hydroxyl group at position C-4 of the B-ring and a 2,3,4-trioxygenated A-ring. Two ortho-coupled ($J = 8$ Hz) doublet signals, each integrating for two H, at δ 6.98 and 7.05, were ascribable to H-2 and H-6, respectively, while two ortho-coupled H signals at δ 6.80 and 7.55 (each d, $J = 8$ Hz) were attributed to H-5′ and H-6′. The doublet ($J = 7.5$ Hz) signal at δ 5.10 was assignable to the anomeric proton of a β-D-glucopyranose unit. A signal at δ 4.40 (1H, t, $J = 9.0$ Hz) and two signals at δ 4.28 and 4.70 (ABX system: $J_{AB} = 12.5$, $J_{AX} = 2.5$, $J_{BX} = 4.5$ Hz) indicated esterification of the glucose.[14] Analysis of the DQF-COSY spectrum allowed complete sequential assignments for all proton resonances of the glucose unit starting from the anomeric proton signal and showed that the hydroxyl groups at C-2″ and C-6″ were acetylated.[14] These results were consistent with the typical downfield shift of the C-6″ signal (+2 ppm) and C-2″ (+2 ppm) and the upfield shift (−1.5 ppm) of C-5″, C-3″, and C-1″ of the glucose moiety in the ^{13}C NMR spectrum of compound **6** (Table 2), with respect to homologous carbons of unsubstituted glucose.[5] The ester groups linked at C-6″ and C-2″ were cinnamoyl and acetyl residues, as deduced by ^1H and ^{13}C NMR spectra, which were in agreement with the published data.[15] The 4′-O-glycosylation was deduced by superimposition of the A-ring signals with those of okanin-4′-*O*-glucoside[5] and its known ester derivatives.[6,16,17]

It only remained to establish the relative disposition of the cinnamoyl and acetyl residues at C-2″ and C-6″ of the β-D-glucopyranosyl moiety in **6**. To confirm the position of the ester linkages, a HMBC experiment was carried out. Since the carbonyl carbon of the cinnamoyl moiety showed correlations with H-2‴, H-3‴, H-6″a and H-6″b, it was concluded that this cinnamic acid residue esterified the hydroxyl group at C-6″. Consequently, the acetyl group was at C-2″. Accordingly, the structure of **6** was established as 4′-*O*-β-D-(2″-acetyl-6″-cinnamoyl)-glucopyranosyl-4,2′,3′-tetrahydroxychalcone.

Several known compounds were also isolated. The structures of the five known compounds, okanin 4′-*O*-β-D-(4″-acetyl-6″-*p*-coumaroyl)glucopyranoside, okanin 4′-*O*-β-D-(6″-acetyl)glucopyranoside, okanin 4′-*O*-β-D-(3″,6″-diacetyl)glucopyranoside, okanin 4′-*O*-β-D-(3″,4″,6″-triacetyl)glucopyranoside, and okanin 4′-*O*-β-D-(3″,4″-diacetyl)glucopyranoside, were determined by spectral data comparison with those previously reported for these compounds.[6,16−18]

Experimental Section

General Experimental Procedures. A Bruker DRX-600 NMR spectrometer, operating at 599.19 MHz for ^1H and 150.86 MHz for ^{13}C, using the UXNMR software package was used for NMR experiments in CD_3OD. DEPT (distortionless enhancement by polarization transfer) experiments were performed using a transfer pulse of 135° to obtain positive signals for CH and CH_3 and negative ones for CH_2. Polarization transfer delays were adjusted to an average CH coupling of 135 Hz. $^1H-^1H$ DQF-COSY (double quantum-filtered COSY),[19] $^1H-^{13}C$ HSQC, and HMBC[11,13] experiments were carried out using the conventional pulse sequences as described in the literature, and 1D TOCSY[10] spectra were acquired using a waveform generator-based GAUSS-shaped pulse at mixing times ranging from 80 to 100 ms and a MLEV-17 spin-lock field of 10 kHz preceded by a 2.5 ms trim pulse. UV spectra were obtained from a Beckman DU 670 spectrophotometer. HPLC separations were performed on a Waters 590 series pumping system equipped with a Waters R401 refractive index detector and with a Waters μ-Bondapak C_{18} column and a U6K injector. GC were run using a Hewlett-Packard 5890 gas chromatograph equipped with mass-selective detector MSD 5970 MS, a split/splitness injector, and a Hewlett-Packard HP-5 fused-silica column (25 m × 0.2 mm; i.d. 0.33 μm film, Wilmington, DE).

Plant Material. *B. andicola* H.B.K. was collected at Sierra Centrale, Peru, in March 1994 and identified by R. Ferrera. A voucher specimen is deposited in the Herbarium of the Museo De Historia Natural, Universidad de San Marcos, Lima, Peru.

Extraction and Isolation. The air-dried, powdered aerial parts (700 g) of *B. andicola* were defatted with petroleum ether and then with chloroform and extracted with MeOH (23.0 g). Chromatography of the methanol extract (8 g) over a Sephadex LH-20 column eluting with MeOH (100 × 5 cm) gave fractions (8 mL each) that were combined into three main pools (A−C). Pool A from the Sephadex LH-20 column was further chromatographed by RP-HPLC on a C_{18} μ-Bondapak column (30 cm × 7.8 mm, flow rate 2.0 mL/min) with MeOH−H_2O (45:55) to yield compounds **1** ($t_R = 9.5$ min, 26 mg), **2** ($t_R = 15$ min, 31 mg), **3** ($t_R = 7$ min, 29 mg), **4** ($t_R = 12$ min, 32.5 mg), and **5** ($t_R = 16.5$ min, 10 mg). Pool B was separated by RP-HPLC with MeOH−H_2O (9:1) to yield compounds **6** ($t_R = 9$ min, 14 mg) and okanin 4′-*O*-β-D-(4″-acetyl-6″-*p*-coumaroyl)glucopyranoside ($t_R = 11$ min, 5 mg). Pool C under the same conditions yielded okanin 4′-*O*-β-D-6″-acetylglucopyranoside ($t_R = 9$ min, 8 mg), okanin 4′-*O*-β-D-3″,6″-diacetylglucopyranoside ($t_R = 11$ min, 19 mg), okanin 4′-*O*-β-D-3″,4″,6″-triacetylglucopyranoside ($t_R = 5$ min, 20 mg), and okanin 4′-*O*-β-D-3″,4″-diacetylglucopyranoside ($t_R = 6$ min, 32.5 mg).[6,16−18]

Compound 1: mp 210−218 °C; $[\alpha]^{25}_D$ +9.0° (*c* 1, MeOH); UV (MeOH) λ_{max} 251, 270, 305, 333 nm; ^1H NMR for aglycon (CD_3OD, 600 MHz) δ 3.82 (3H, s, OMe), 6.51 (1H, d, $J = 2.0$ Hz, H-6), 6.71 (1H, d, $J = 2.0$ Hz, H-8), 6.90 (1H, d, $J = 2.0$ Hz H-5′), 7.62 (1H, dd, $J = 8.0$, 1.6 Hz, H-6′), 7.68 (1H, d, $J = 1.5$ Hz, H-2′); ^{13}C NMR for aglycon (CD_3OD, 600 MHz) δ 96.0 (C-8), 101.8 (C-6), 107.0 (C-10), 116.2 (C-2′), 117.5 (C-5′), 123.5

(C-6′), 124.0 (C-1′), 140.5 (C-3), 145.0 (C-3′), 150.0 (C-4′), 158.1 (C-2), 158.5 (C-9), 164.5 (C-5), 165.2 (C-7), 181.0 (C-4); for NMR data of sugar moiety, see Tables 1 and 2; negative FABMS *m*/*z* $[M - H]^-$ 901, $[(M - H) - 146]^-$ 755, $[(M - H) - (146 + 132)]^-$ 623, $[(M - H) - (132 + 146 + 146)]^-$ 477, $[(M - H) - (132 + 146 + 146 + 162)]^-$ 315.

Compound 2: mp 201−208 °C; $[\alpha]^{25}_D$ +11° (*c* 1, MeOH); UV (MeOH) λ_{max} 253, 272, 333 nm; NMR data for the aglycon moiety were superimposable on those presented for compound **1**, for NMR data of the sugar moiety, see Tables 1 and 2; negative FABMS *m*/*z* $[M - H]^-$ 755, $[(M - H) - 146]^-$ 609, $[(M - H) - (146 + 132 + 162)]^-$ 315.

Compound 3: mp 220−227 °C; $[\alpha]^{25}_D$ +9.5° (*c* 1, MeOH); UV (MeOH) λ_{max} 251, 269, 302, 334 nm; NMR data for the aglycon moiety were superimposable on those reported for compound **1**, for NMR data of sugar moiety, see Tables 1 and 2; negative FABMS *m*/*z* $[M - H]^-$ 917, $[(M - H) - 146]^-$ 771, $[(M - H) - (146 + 162)]^-$ 609, $[(M - H) - (146 + 162 + 132)]^-$ 477, $[(M - H) - (146 + 162 + 162 + 132)]^-$ 315.

Compound 4: mp 234−232 °C; $[\alpha]^{25}_D$ +16° (*c* 1, MeOH); UV (MeOH) λ_{max} 269, 324, 363 nm; ^{1}H NMR for aglycon (CD_3OD, 600 MHz) δ 6.58 (1H, d, $J = 2.0$ Hz, H-6), 6.72 (1H, d, $J = 2.0$ Hz, H-8), 6.80 (1H, d, $J = 2.0$ Hz, H-5′), 7.57 (1H, dd, $J = 8.0$, 1.6 Hz, H-6′), 7.63 (1H, d, $J = 1.5$ Hz, H-2′); ^{13}C NMR for aglycon (CD_3-OD, 600 MHz) δ 94.5 (C-8), 100.0 (C-6), 103.5 (C-10), 116.5 (C-2′), 117.0 (C-5′), 122.5 (C-6′), 122.0 (C-1′), 136.5 (C-3), 144.8 (C-3′), 148.0 (C-4′), 148.1 (C-2), 160.0 (C-9), 157.7 (C-5), 165.0 (C-7), 177.0 (C-4); NMR data of the sugar moiety were superimposable on those presented for compound **1**; negative FABMS *m*/*z* $[M - H]^-$ 887, $[(M - H) - 146]^-$ 741, $[(M - H) - (146 + 132)]^-$ 609, $[(M - H) - (132 + 146 + 146)]^-$ 463, $[(M - H) - (132 + 146 + 146 + 162)]^-$ 301.

Compound 5: mp 190−194 °C; $[\alpha]^{25}_D$ +10.5° (*c* 1, MeOH); UV (MeOH) λ_{max} 271, 323, 370 nm; NMR data for the aglycon moiety were identical to those for compound **4**, and the sugar moiety signals were superimposable on those presented for compond **2**; negative FABMS *m*/*z* $[M - H]^-$ 741, $[(M - H) - 146)]^-$ 595, $[(M - H) - (132 + 146)]^-$ 463, $[(M - H) - (132 + 146 + 162)]^-$ 301.

Compound 6: mp >170 °C; $[\alpha]^{25}_D$ +90.5° (*c* 1, MeOH); UV (MeOH) λ_{max} 298, 319, 385; NMR data for the aglycon moiety were identical to those for 4,2′,3′,4′-tetrahydroxychalcone;[18] for NMR data of the sugar moiety and esterified residues, see Tables 1 and 2; negative FABMS *m*/*z* $[M - H]^-$ 605, $[(M - H) - 130)]^-$ 475, $[(M - H) - (42)]^-$ 560, $[(M - H) - (130 + 42)]^-$ 433, $[(M - H) - (130 + 42 + 162)]^-$ 271.

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