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New Flavonol Glycosides from Leaves of *Symplocarpus renifolius*

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A study was carried out to evaluate flavonol glycosides in leaves of *Symplocarpus renifolius* (Araceae). From the water fraction of the MeOH extract, three new flavonol glycosides were isolated along with three known compounds, kaempferol-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-7-*O*-β-D-glucopyranoside,quercetin-3-*O*-β-D-glucopyranosy-l-(1→2)-β-D-glucopyranoside, and caffeic acid. The structures of the new flavonol glycosides were elucidated by chemical and spectral analyses as quercetin-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-7-*O*-β-D-glucopyranoside, isorhamnetin-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-7-*O*-β-D-glucopyranoside, and quercetin-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-7-*O*-(6‴-trans-caffeoyl)-β-D-glucopyranoside.

Key words : *Symplocarpus renifolius,* Araceae, Leaves, Flavonol glycosides, Quercetin, Kaempferol, Isorhamnetin derivatives

INTRODUCTION

The Roots of *Symplocarpus renifolius* (Araceae), named Skunk cabbage, have been used as an anti-vomiting, a sedative, and a diuretic agent in the folk medicine of American Indian (Hoota, 1989). The leaves have been used as a diuretic and anti-hypertensive agent in Korea (Moon, 1973).

However, no detailed chemical investigation of *S. renifolius* has been reported. Our present study deals with the isolation and structural elucidation of three new flavonol glycosides, quercetin-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-7-*O*-β-D-glucopyranoside,isorhamnetin-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-7-*O*-β-D-glucopyranoside and quercetin-3-*O*-β-D-glucopyranosyl(1→2)-β-D-glucopyranosyl-7-*O*-(6‴-trans-caffeoyl)-β-D-glucopyranoside, and three known compounds, kaempferol-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-gluco-pyranosyl-7-*O*-β-D-glucopyranoside, quercetin-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside,and caffeic acid.

MATERIALS AND METHODS

General

Mps: uncorr.; NMR: TMS as internal standard; CC: non ionic polymer resin (Amberlite XAD-2, Sigma): ODS (Lichroprep RP-8, Merk) and gel filtration (Sephadex LH-20, Pharmacia); HPLC (Jagel ODS, Jasco Co., Ltd.). All solvent systems for chromatography were isocratic.

Plant material

Symplocarpus renifolius was collected at Mt. Kwang Duk, Korea. A voucher specimen was deposited in Department of Pharmacal Botany, College of Pharmacy, Chung-Ang University.

Extraction and isolation

The fresh leaves (4kg) of *S. renifolius* were extracted with MeOH at room temperature. After removal of the solvent by evaporation, the MeOH extract was suspended in H_2O and partitioned with ether. The water layer was concentrated and chromatographed on non ionic polymer resin with water, 20%, 40%, 60%, 80%, and 100% MeOH, successively. From 20% MeOH elute compound I, compound II and compound III were obtained by gel filtration and HPLC. The 40% MeOH eluted fraction was purified by HPLC to afford compound IV and compound V. The 60% MeOH eluted fraction was separated by HPLC to give compound VI.

Compound I: Powder, mp. 198°, $[\alpha]_D$= -80.8 (c=0.1, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1653 (C=O), 1603, 1496 (C=C), 1075 (glycosidic OH). FABMS (negative)

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m/z: 787 [M-H]$^-$, 625 [(M-glc)]$^-$, 463 [(M-2glc)]$^-$, 301 [(M-3glc)]$^-$, ^{1}H-NMR(DMSO-d_6, 500 MHz): δ 7.62 (1H, d, J=7.9Hz, H-6'), 7.58 (1H, s, H-2'), 6.90 (1H, d, J=8.3Hz, H'-5), 6.75 (1H, s, H-8), 6.43 (1H, d, J=1.1Hz, H-6), 5.67, 5.06, 4.62 (each 1H, d, J=7.3Hz, glc anomeric H). ^{13}C-NMR: (see Table I)

Compound II: Powder, mp. 196°, $[\alpha]_D$= -83.3 (c=0.1, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3444 (OH), 1653 (C=O), 1077 (glycosidic OH). FABMS(negative) *m/z*: 771 [M-H]$^-$, 609 [(M-glc)]$^-$,447[(M-2glc)]$^-$,285 [(M-3glc)]$^-$, ^{1}H-NMR(DMSO-d_6, 500 MHz): δ 8.06 (2H, d, J=8.3Hz, H-2',6'), 6.92 (2H, d, J=8.3Hz, H-3', 5'), 6.79 (1H, s, H-8), 6.42 (1H, s, H-6), 5.71, 5.04, 4.61 (each 1H, d, J=6.8Hz, glc anomeric H) ^{13}C-NMR: (see Table I)

Compound III: Powder, mp. 198-200°, $[\alpha]_D$=-162.8(c=0.1, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3398 (OH), 1655 (C=O), 1600, 1517, 1499 (C=C), 1072 (glycosidic OH). FABMS(negative) *m/z*: 949 [M-H]$^-$, 787 [(M-caffeoyl)]$^-$, 625 [(M-caffeoyl-glc)]$^-$, 463 [(M-caffeoyl-2glc)]$^-$, 301 [(M-caffeoyl-3glc)]$^-$, ^{1}H-NMR(DMSO-d_6, 500 MHz): δ 7.63 (1H, d, J=7.6Hz, H-6'), 7.59 (1H, s, H-2'), 7.46 (1H, d, J=15.9Hz, caffeoyl trans -H), 6.97, 6.72 (each 1H, d, J=7.0Hz, caffeoyl H-5, 6), 6.89 (1H, d, J=8.3Hz, H'-5), 6.75 (1H, s, H-8), 6.50 (1H, d, J=1.8Hz, H-6), 6.26 (1H, d, J=15.9Hz, caffeoyl trans -H), 5.72, 5.18, 4.62 (each 1H, d, J=7.3Hz, glc anomeric H). ^{13}C-NMR:(see Table I)

Compound IV: Powder, mp. 205°, $[\alpha]_D$=-90.8° (c=0.1, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1653 (C=O), 1603, 1496 (C=C), 1075 (glycosidic OH), 806 (aromatic ring) FABMS(negative) *m/z*: 801 [M-H]$^-$, 639 [(M-glc)]$^-$, 477 [(M-2glc)]$^-$, 315[(M-3glc)]$^-$, ^{1}H-NMR(DMSO-d_6, 500 MHz) : δ 7.79 (1H, d, J=1.86Hz, H-2'), 7.68 (1H, d, J=8.4Hz, H-6'),6.92 (1H, d, J=8.4Hz, H-5'), 6.81 (1H, d, J=1.8Hz, H-8), 6.43 (1H, d, J=1.9Hz, H-6), 5.77, 5.41, 4.63 (each 1H, d, J=7.2Hz, glc anomeric H), 3.84 (3H, s, OCH_3). ^{13}C-NMR: (see Table I)

Compound V: Powder, mp. 200°, $[\alpha]_D$= -30.8° (c=0.1, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3402 (OH), 1663 (C=O), 1608, 1499(C=C), 1066 (glycosidic OH). FABMS (negative) *m/z*: 625[M-H]$^-$, 463[(M-glc)]$^-$,301[(M-2glc)]$^-$,^{1}H-NMR(DMSO-d_6, 500 MHz) : δ 7.61 (1H, d, J=8.7Hz, H-6'), 7.55 (1H, s,H-2'), 6.88 (1H, d, J=8.4Hz, H-5'), 6.39 (1H, d, J=1.6Hz, H-8), 6.18 (1H, s, H-6), 5.67, 4.61 (each 1H, d, J=7.4Hz, glc anomeric H). ^{13}C-NMR: (see Table I)

Compound VI: Powder, mp. 224-226°,$[\alpha]_D$=-162.8° (c=0.1, MeOH)). IR ν_{max}^{KBr} cm^{-1}: 3414 (OH), 1710 (C=O), 1606 (C=C), 1516, 981 (aromatic ring), EIMS *m/z*: 180 [M$^+$], 163 [M$^+$-OH], 135 [M$^+$-COOH], ^{1}H-NMR(DMSO-d_6, 500 MHz): δ 6.16 (1H, d, J=15.9Hz, -H), 6.77 (1H, d, J=8.0Hz, H-5), 6.98 (1H, dd, J=2.0, 8.0Hz, H-6), 7.02 (1H, s, H-2), 7.41 (1H, d, J=15.9Hz, -H), ^{13}C-NMR: (see Table I)

Acid hydrolysis of compound I, II, III and IV

Each solution of compound I, II, III and IV (each 10mg) in 1N-HCl (3 ml) was heated at 100°C for 5 h. After cooling, the reaction mixture was extracted with EtOAc. The organic layers were washed with H_2O and concentrated to dryness to yield a yellow powder, which was identified as quercetin, kaempferol and isorhametin, on the basis of the ^{1}H-NMR and EIMS in comparison with those of authentic samples. All water layers were neutralized with Dowex (CO_3^{2-}) and concentrated to obtain glucose which were identified by TLC in comparison with an authentic sample.

Aglycone of compound I and compound III. mp. 313°, EIMS *m/z*: 302[M]$^+$, 153, 137,^{1}H-NMR(DMSO-d_6, 500 MHz) : δ 7.67(1H, s, H-2'), 7.57(1H, d, J=8.0Hz, H-6'),6.92 (1H, d, J=8.0Hz, H'-5), 6.47 (1H, d, J=1.8Hz, H-8), 6.23 (1H, d, J=1.8Hz, H-6).

Aglycone of compound II. Powder, mp. 276°,EIMS) *m/z*: 286[M]$^+$, ^{1}H-NMR(DMSO-d_6, 500 MHz) : δ 8.10 (2H, d, J=8.6Hz, H-2',6'), 6.98 (2H, d, J=8.6Hz, H-3', 5'), 6.45 (1H, d, J=1.6Hz, H-8), 6.20 (1H, d, J=1.6Hz, H-6).

Aglycone of compound IV. mp. 304-305°, EIMS *m/z*: 316[M$^+$] ^{1}H-NMR(DMSO-d_6, 500 MHz) : δ 7.80 (1H, d, J=1.6Hz, H-2'), 7.65 (1H, d, J=8.2Hz, H-6'), 6.94 (1H, d, J=8.2Hz, H-5'), 6.81 (1H, d, J=1.8Hz, H-8), 6.42 (1H, d, J=1.8Hz, H-6), 3.90 (3H, s, OCH_3).

Alkaline Hydrolysis of compound III.

A solution of Compound III (30mg) in 1% KOH(1ml) was kept at room temperature overnight. After neutralization with Amberlite MB-3, the reaction mixture was extracted with ether. The water layer was chromatographed on Sephadex LH-20 with 20% MeOH to yield compound I (15mg) as a yellow amorphous powder, which was identified on the basis of diagnostic shifts in the ^{1}H-NMR, ^{13}C-NMR and FABMS. The organic layer was concen-trated, to yield colorless needles, which were identified as caffeic acid by comparison of TLC and HPLC chroma-togram with the authentic sample.

Alkaline hydrolyzed compound III. Powder, mp. 199-198°, FABMS (negative) *m/z*: 787 [M-H]$^-$, 625 [(M-glc)]$^-$,463 [(M-2glc)]$^-$, 301 [(M-3glc)]$^-$, ^{1}H-NMR(DMSO-d_6, 500 MHz) : δ 7.62 (1H, d, J=7.8Hz, H-6'), 7.56 (1H, s, H-2'), 6.90 (1H, d, J=7.9Hz, H'-5), 6.77 (1H, s, H-8), 6.41 (1H, d, J=1.1Hz, H-6), 5.68, 5.06, 4.61 (each 1H, d, J=7.4Hz, glc anomeric H). ^{13}C-NMR: (see Table I)

Partial acid hydrolysis of compound III.

A solution of compound III (30mg) in 1% H_2SO_4 (2ml) were heated at 100°C for 50min. After cooling, the reaction mixture was extracted with EtOAc. The organic layer was chromatographed on Sephadex LH-20 with EtOH to yield 7-*O*-β-D-glucosylquercetin from Compound III, and caffeic acid. 7-*O*-β-D-gluco-sylquercetinfrom Compound III, which was identified on the basis of diagnostic shifts in the UV spectrum, the ^{1}H-NMR, ^{13}C-NMR and FABMS. The water layer were neutralized with Dowex (CO_3^{-2}) and concentrated to obtain glucose which was

Table I. ^{13}C-NMR spectral data of Compound I,II,III,IV,V, VI, III-A and III-E (125MHz) in DMSO-d_6

	I	II	III	IV	V	VI	III-A*	III-P*	III-E*
C-2	156.5	56.2	156.4	156.7	156.5		156.5	147.9	156.3
C-3	133.9	133.3	133.5	133.1	133.2		133.7	135.9	133.2
C-4	177.9	177.8	177.8	177.6	177.6		177.9	175.9	177.7
C-5	163.0	162.9	162.8	163.0	161.5		163.1	160.3	162.0
C-6	99.6	99.5	99.2	99.5	98.8		99.7	98.9	98.6
C-7	161.2	161.0	161.3	161.0	164.3		161.3	162.8	164.1
C-8	94.6	94.6	94.8	94.7	93.7		94.5	94.5	93.9
C-9	156.2	156.1	156.0	156.0	155.8		156.4	155.7	155.7
C-10	105.8	105.8	105.9	105.8	104.1		105.4	104.7	104.9
C'-1	121.3	120.9	121.5	120.3	121.3		121.3	121.9	120.8
C'-2	115.7	131.2	115.6	115.8	115.6		115.7	115.5	115.5
C'-3	145.1	115.5	145.1	151.0	145.0		145.0	145.0	145.0
C'-4	149.0	160.3	149.0	147.5	148.7		149.1	147.8	148.7
C'-5	116.6	115.5	116.6	113.3	116.3		116.5	115.5	116.5
C'-6	122.6	131.2	122.2	123.3	122.0		122.7	120.1	122.2
OCH_3				56.0					
3-O-Glc									
1	98.2	98.1	98.2	98.3	98.2		98.2		98.2
2	83.0	82.7	83.1	82.3	82.9		83.1		82.8
3	76.8	76.8	76.8	76.7	76.7		76.9		76.7
4	69.8	69.8	69.8	70.0	69.8		69.8		69.7
5	77.8	77.7	77.8	77.6	76.7		77.8		76.8
6	60.9	60.8	60.9	60.8	60.9		60.9		60.8
Glc									
1	104.5	104.5	104.5	103.8	104.4		104.4		104.2
2	74.7	74.6	74.7	74.5	74.6		74.6		74.6
3	77.0	76.8	77.0	77.0	77.7		77.0		78.0
4	69.8	69.8	69.8	70.0	69.8		69.7		69.9
5	76.7	76.7	76.8	76.7	77.0		76.7		77.1
6	60.9	60.8	60.9	61.0	60.9		60.6		60.8
7-O-Glc									
1	100.0	99.9	100.0	100.1			100.0	100.3	
2	73.4	73.3	73.3	73.3			73.4	73.2	
3	76.8	76.8	76.4	76.7			76.7	77.2	
4	69.8	69.8	69.8	70.0			69.9	69.9	
5	77.4	77.2	77.8	77.6			77.5	76.5	
6	60.9	60.8	63.4	60.8			61.0	60.9	
CH=CH-			145.8			144.9			
CH=CH-			116.0			116.0			
-COO			166.7			168.2			
1			125.7			126.0			
2			115.2			115.4			
3			145.6			145.8			
4			148.7			148.4			
5			113.9			114.9			
6			121.5			121.4			

* III-A: akaline hydrolyzed compound III
* III-P: partial hydrolyzed compound III
* III-E: enzymatic hydrolyzed compound III

identified by TLC comparison with the authentic sample.

Partial acid hydrolyzed compound III. FABMS(negative) *m/z*: 463 [M-H]$^-$, 301 [(M-Glc)]$^-$, ^{1}H-NMR(DMSO-d_6, 500 MHz) : δ 7.66 (1H, dd, J=7.8, 1.6Hz, H-6'), 7.60 (1H, s, H-2'), 6.89 (1H, d, J=7.8Hz, H-5'), 6.74 (1H, s, H-8), 6.51 (1H, d, J=1.6Hz, H-6), 5.18(1H, d, J=7.4Hz, glc anomeric H). ^{13}C-NMR: (see Table I)

Enzymatic hydrolysis of compound III.

A solution of Compound III (20 mg) and β-glucosidase (20 mg, Sigma) in pH 5.0 Mcallvaine buffer (20 ml) was incubated at 37°C for 10 h. Afetr cooling, reaction mixture was extracted with BuOH. The organic layer was washed with water and concentrated to dryness to yield quercetin-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside (compound V), caffeic acid (compound VI) and D-glucose which was identified on the basis of diagnostic shifts in the UV spectrum, the ^{1}H-NMR, ^{13}C-NMR and FAB-MS. The water layer was concentrated to obtain D-glucose which was identified by TLC in comparison with the authentic sample.

Enzymatic hydrolyzed compound III. FABMS(negative) *m/z*: 625 [M-H]$^-$, 463 [(M-glc)]$^-$, 301 [(M-2glc)]$^-$, ^{1}H-NMR(DMSO-d_6, 500 MHz) : δ 7.61 (1H, dd, J=8.4, 1.8Hz, H-6'), 7.55 (1H, d, J=1.8Hz, H-2'), 6.86 (1H, d, J=8.4Hz, H-5'), 6.39 (1H, d, J=1.2Hz, H-8), 6.18 (1H, d, J=1.2Hz, H-6), 5.67, 4.63 (each 1H, d, J=7.6Hz, glc anomeric H). ^{13}C-NMR: (see Table I)

RESULTS AND DISCUSSION

The water soluble part of the methanolic extract of the eaves of *Symplocarpus renifolius* was chromato-gaphed successively on a column of Amberlite XAD-2(non ionic polymer resin), RP-8, SephadexLH-20, and HPLC to obtain three new flavonol glycosides (compound **I**, **III**, and **IV**) together with three known compounds (**II**, **V** and **VI**).

Compound I was initially identified as a flavonol glycoside based upon its UV absorption bands (λ_{max} 256, and 357nm). The FABMS(negative) spectrum of **I** showed an [M-H]$^-$ peak at *m/z* 787 and fragment ions at *m/z* 625, 463, and 301.

The three anomeric protons arising from the sugar moieties appeared at 5.67, 5.06 and 4.62 ppm in the ^{1}H-NMR spectrum and three anomeric carbons were observed at 104.5, 100.0, and 98.2 ppm in the ^{13}C-NMR spectra, as shown in the Table I.

In the ^{13}C-NMR spectra of **I**, as shown in Table I, the signals due to C-3 and C-7 have shifted upfield from those of quercetin.

On acid hydrolysis, **I** produced quercetin and D-glucose (3 mole). Partial hydrolysis of **I** gave D-glucose (2 mol) and quercetin-7-*O*-β-D-glucoside (Harbone and Mabry, 1982).

The linkage between the anomeric carbons and protons of glucose was determined from ^{1}H-^{1}H COSY, HMQC and HMBC spectra. From the HMBC spectrum of **I**, the linkage between a glucose anomeric proton (δ 5.67 ppm) as an inner sugar and C-3 (δ 133.9 ppm), and C-2" of inner glucose (δ 83.0 ppm) and another glucose anomeric proton (δ 4.62 ppm), and the other glucose anomeric proton (δ 5.06 ppm) and C-7 (δ 161.2 ppm) was determined.

On the basis of the above results, the structure of **I** was established as quercetin-3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-7-*O*-β-D-glucopyranoside (Yoshida *et al*, 1987).

Compound II was identified as a flavonol glycoside based upon its UV absorption bands (λ_{max} 266, and 349 nm). The FABMS(negative) spectrum of **II** showed an [M-H]$^-$ peak at *m/z* 771 and fragment ions at *m/z* 609, 447, and 285.

The ^{1}H-NMR and ^{13}C-NMR spectra of **II** exhibited signals which can be ascribed to the kaempferol moieties along with those of three anomeric protons of glucose (3 mole) linked to C-2", C-3 and C-7 at δ 5.71, 5.04, and 4.61 ppm, respectively.

From the^{1}H-NMR and ^{13}C-NMR spectral data, **II** was founded to contain a D-glucose(1→2)-D-glucose and a D-glucose moiety attached to kaempferol which was the same as the sugar moiety of **I**. In order to confirm this assumption, acid hydrolysis of **II** was carried out. On acid hydrolysis, **II** gave quercetin and glucose (3 mole)

These results established compound II as kaempferol-3-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl-7-*O*-β-D-glucopyranoside (Markham *et al*, 1978).

Compound III was identified as a flavonol glycoside based uponits UV absorption bands (λ_{max} 254, and 338 nm). The FABMS (negative) spectrum of **III** showed an [M-H]$^-$ peak at *m/z* 949, and fragment ions at *m/z* 787, 625, 463, and 301.

The ^{1}H-NMR and ^{13}C-NMR spectra of **III** exhibited signals which were assigned to quercetin and caffeoyl moieties along with those of three anomeric protons of glucose (3 mole) linked to C-2", C-3, and C-7 at δ 5.72, 5.18, and 4.62 ppm, respectively.

From the^{1}H-NMR and ^{13}C-NMR spectral data, **III** was found to contain a D-glucose(1→2)-D-glucose and a D-glucose moiety attached to quercetin which was the same as those of **I**. In order to confirm this assumption, acid and akaline hydrolysis of **III** was carried out.

On acid hydrolysis, **III** gave quercetin, glucose (3 mole) and caffeic acid. On alkaline hydrolysis, **III** afforded caffeic acid and **I**. In the ^{13}C-NMR spectrum of **III**, the signals due to C-6"" were shifted downfield when compared with those for **I** while other signals remained almost unaffected. These data indicated that the caffeoyl group was linked to C-6"".

On the basis of the above results and comparison with

I, the structure of **III** was established as quercetin-3-O- β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl-7-*O*-(6'''-trans-caffeoyl)-β-D-glucopyranoside (Victoire *et al*, 1988) Compound IV was found to be a flavonol glycoside from its UV absorption bands(λ_{max} 256, and 350 nm). The negative FABMS spectrum of **IV** gave the $[M-H]^-$ peak at *m/z* 801 and fragment ions at *m/z* 639, 477, and 315.

The ^{1}H-NMR and ^{13}C-NMR spectra of **IV** exhibited signals ascribable to isorhamnetin along with those of three anomeric protons of D-glucose (3 mole) linked to C-2", C-3 and C-7 at δ 5.77, 5.41 and 4.63 ppm, respectively.

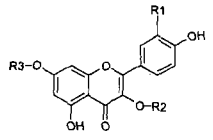
From the^{1}H-NMR and ^{13}C-NMR spectral data, **IV** was found to contain a D-glucose(1→2)-D-glucose and a D-glucose moiety attached to isorhamnetin.

In order to confirm this assumption, acid hydrolysis of **IV** was carried out. On acid hydrolysis, **IV** gave isorhamnetin and glucose (3 mole). These results established **IV** as isorhamnetin-3-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucopyranosyl-7-*O*-*β*-D-glucopyranoside (Mulinacci et a*l*, 1995). Compound V was identified as a flavonol glycoside based upon its UV absorption bands (λ_{max} 256, and 357 nm). The negative FABMS spectrum of **V** showed an $[M-H]^-$ peak at *m/z* 625 and fragment ions at *m/z* 463 and 301

The ^{1}H-NMR and ^{13}C-NMR spectra of **V** exhibited signals ascribable to quercetin along with those anomeric protons of glucose linked to C-2" and C-3 respectively, and led to the identification of a D-glucose(1 →2)-D-glucose moiety attached to quercetin. In order to confirm this assumption, acid hydrolysis of **V** was performed.

V was hydrolyzed on acid to give quercetin and D-glucose (2 mol). On the basis of the results and comparison with **I**, the structure of Compound V established as quercetin-3-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-glucopyranoside (Wang *et al*, 1985).

Compound VI was identified as caffeic acid by direct comparison of its physical and spectral data with those of purchased authentic samples (Whang *et al*, 1995).



	R1	R2	R3
Compound I	OH	Glc^{2}—Glc	Glc
Compound II	H	Glc^{2}—Glc	Glc
Compound III	OH	Glc^{2}—Glc	Glc^{6}—Caffeic acid
Compound IV	O-CH$_3$	Glc^{2}—Glc	Glc
Compound V	OH	Glc^{2}—Glc	H

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