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Phytochemical Study on *Prunus davidiana*

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Abstract□From the stem of *Prunus davidiana,* naringenin and its glucoside, kaempferol and its glucoside, dihydrokaempferol, kaempferide glucoside, hesperetin glucoside, quercetin glucoside, d-catechin and β-sitosterol glucoside were isolated.

Keywords□*Prunus davidiana,* Rosaceae, flavonoids, sterol glucoside.

The stem of *Prunus davidiana* has been used as folkloric medicine to treat for neuritis and rhematism in Korea. In the course of screening of Korean medicinal plants for hypolipemic and antidiabetic activities it was found that the methanol extract from this plant showed the significant activity. We here report the isolation of β-sitosterol glucoside and flavonoid components from the stem of this plant.

Silica gel and Sephadex LH-20 column chromatography of the ethylacetate soluble portion of the methanol extract yielded ten compounds (**1-10**) as shown in Chart 1. Compounds **1-4** and **7** were readily elucidated as naringenin, kaempferol, dihydrokaempferol, β-sitosterol glucoside and d-catechin respectively, by comparison of reported spectroscopic data[1-3]and finally confirmed by comparison with authentic samples. Compounds **5, 6, 8, 9** and **10** showed positive results in Molisch tests besides flavonoid color reactions and showed absorption bands for glycoside linkage (1,000 – 1,100 cm $^{-1}$) in their IR spectra. On acid hydrolysis all compounds gave glucose as the sugar and kaempferide from **5**, kaempferol from **6**, naringenin from **8**, hesperetin from **9** and quercetin from **10** as the aglycone.

The ^{1}H-NMR spectrum of each compound showed only one anomeric proton signal, indicating the presence of one mole of glucose in each compound. The band II in the UV spectra of Compound **5, 6, 8** and **10** was not affected by an addition of NaOAc, indicating that 7-hydroxyl group must be glucosylated. This was further confirmed by the inspection of the ^{13}C-NMR spectra (Table I). The configuration and conformation of sugar moiety was determined by the J value of each anomeric protein signal (See Experimental). Thus the structures of **5, 6, 8** and **10** were elucidated as kaempferide 7-O-β-D-glucopyranoside (mumenin), kaempferol 7-O-β-D-glucopyranoside (populnin), naringenin 7-O-β-D-glucopyranoside (prunin) and quercetin 7-O-β-D-glucopyranoside (guercimeritrin), respectively. However, the band II of compound **9** was shifted by an addition of NaOAc, implying the presence of free hydroxyl group at C-7 and the unchangeability by $AlCl_3$ or $AlCl_3$ and HCl in the UV spectrum, was observed, indicating that 5-hydroxyl group must be glucosylated. This was further substantiated by inspection of the ^{13}C-NMR spectrum of **9** compared with its aglycone 9a (Table I). The significant differences in the chemical shifts for C-3 (+2.3), C-4 (−6.3), C-5 (−0.4), C-6 (−2.9), C-7 (−1.9), C-8 (+2.6), C-9 (−2.3), C-10 (+3.6) were observed. Such differences clearly demonstrated that the glucose was attached at C-5. The configuration and conformation of sugar moiety was also determined by J value of the anomeric protein signal. Compound **9** was, therefore, identified as hesperetin 5-O-β-D-glucopyranoside.

EXPERIMENTAL METHODS

All melting points were determined on a Thomas Hoover 6406-H apparatus and are uncorrected. The optical rotations were measured with a Rudolph Autopol^{R} III automatic polarimeter. The IR spectra were obtained in KBr pellets on a Shimazu IR-400 spectrophotometer and the UV spectra were recorded with a CE 599 universal automatic scanning spectrophotometer. The EI-MS were measured with a

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Table I. ^{13}C-NMR spectral data of 1, 2, 5a, 5, 7, 8, 9a, 9 and 10 (DMSO-d_6)

Compound Carbon No.	1[a]	2 (75 MHz)	5a[a]	5 (75 MHz)	7[b] (20 MHz)	8 (50 MHz)	9a (75 MHz)	9 (75 MHz)	10 (75 MHz)
2	78.4	144.8	146.4	147.2	80.9	78.6	78.3	77.9	147.9
3	42.0	133.7	135.8	137.0	67.0	42.0	42.2	44.6	136.1
4	196.2	174.0	175.8	176.7	27.0	197.1	196.0	189.7	176.0
5	163.6	158.8	160.6	160.5	155.7	162.9	163.6	164.0	160.4
6	95.9	96.3	98.2	99.2	94.2	96.4	95.9	98.8	98.8
7	166.7	162.0	163.9	163.1	155.8	165.3	166.7	164.8	162.7
8	95.0	91.5	93.4	94.9	95.3	95.4	95.1	97.7	94.3
9	162.9	154.3	156.2	156.1	155.3	162.7	162.8	160.5	155.8
10	101.8	101.2	103.1	105.2	99.0	103.2	101.9	105.5	104.7
1′	128.9	119.8	123.2	123.6	130.2	128.6	131.2	131.3	121.9
2′	128.2	127.5	129.0	129.8	113.8	128.3	114.1	114.0	115.6
3′	115.2	113.5	114.0	114.3	144.2	115.1	146.5	146.5	145.1
4′	157.8	157.3	160.6	160.9	144.2	157.7	147.9	147.8	147.9
5′	115.2	113.5	114.0	114.3	114.7	115.1	112.2	112.1	115.4
6′	128.2	127.5	129.0	129.8	118.4	128.3	117.7	117.5	120.1
-OMe			55.3	55.5			55.7	55.7	
1″				100.4		99.6		103.3	100.0
2″				73.3		73.0		73.4	73.2
3″				76.6		76.3		75.6	76.4
4″				69.8		69.5		69.7	69.6
5″				77.5		77.0		77.5	77.2
6″				60.7		60.5		60.8	60.7

[a]Data taken from ref. 4. [b]DMSO-d_6 + $CDCl_3$ (5:1)

Hewlett-Packard 5985 B GC/MS spectrometer operating at 70 eV. The ^{1}H- and ^{13}C-NMR spectra were recorded with Varian FT-80A, Brucker AM-200 and Brucker AM-300 spectrometer; Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. Column chromatography was carried out with Kieselgel 60 (70-230 mesh, Merck) and Sephadex LH-20 (25-100 μ, Pharmacia Co., Ltd.). TLC was performedon precoated Kieselgel 60 F_{254} plates (0.2 mm, Merck) using benzene:ether:MeOH = 8:2:1 as developing solvent for the free compounds and water saturated EtOAc for glycosides and detection was achieved by spraying 50% H_2SO_4 reagent followed by heating, or by irradiating with a UV lamp (254 nm).

Extraction, fractionation and isolation

The dried stem (2.2 kg) of commercial available *Prunus davidiana* was extracted with MeOH under reflux. The MeOH extract was partitioned with $CHCl_3$ (12g), EtOAc (59g), BuOH (35g) and H_2O (30g) successively. The EtOAc extract (59g) was chromatographed over silica gel (1 kg) using $CHCl_3$-MeOH mixture to give frs. 1-17. Frs 2-3, 12-13 and 14-15 were further chromatographed to afford compound **1-10** as shown in Chart 1.

Compound 1 (naringenin)

Colorless needles from MeOH, mp. 254-6°C, $[\alpha]_D^{20}$ - 19.8° (c = 0.116, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3300-3000 (br., -OH), 1590 (br., α, β-unsaturated C=O), 1490, 1460, 1415, 1380, 1335, 1305, 1245, 1175, 1155, 1075, 1060, 827. UV λ_{max}^{MeOH}nm (log ε): 290 (4.33), 330 (sh., 3.74); $\lambda_{max}^{MeOH+NaOMe}$nm: 246 (4.38), 325 (4.57); $\lambda_{max}^{MeOH+NaOAc}$nm: 285 (sh., 3.94), 325 (4.51); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$nm: 290 (4.34), 330 (sh., 3.91) $\lambda_{max}^{MeOH+AlCl_3}$nm: 313 (4.51), 380 (3.73); $\lambda_{max}^{MeOH+AlCl_3+HCl}$: 310 (4.48), 375 (3.73). MS (*m/z*, rel. int.): 272 (M^+, 100), 254 ($M^+ - H_2O$, 9.9), 179 (M^+ - B ring, 32.4), 153 (RDA + H, A ring, 69), 152 (RDA,

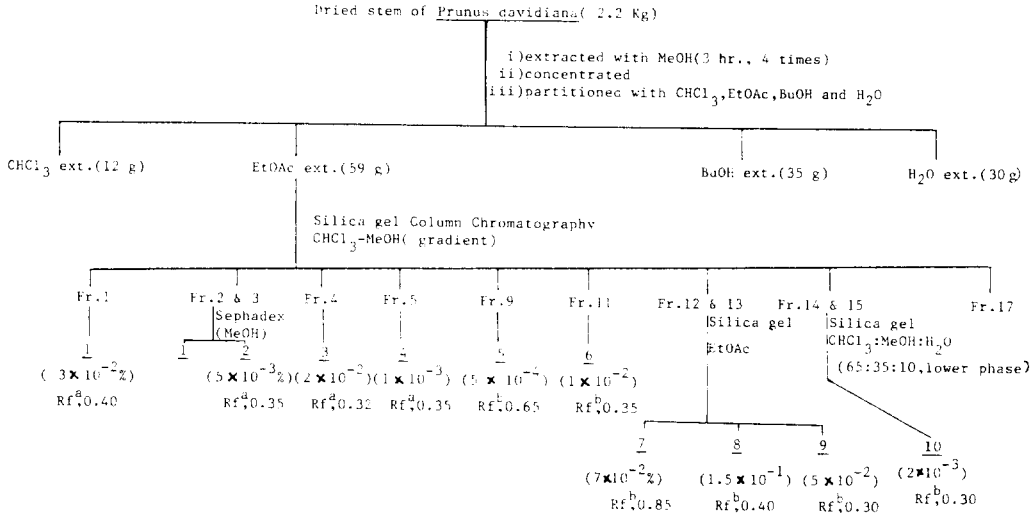


Chart 1. Extraction, fractionation and separation of *Prunus davidiana*
[a]TLC solvent system (Benzene:ether :MeOH = 8:2:1) [b]TLC solvent system (water saturated EtOAc)

A ring, 12.5), 124 (152-CO, 6), 120 (RDA, B ring, 31). ^{1}H-NMR (DMSO-d_6, 300 MHz, TMS): 12.1 (1H, s, C_5-OH), 7.31 (2H, d, J = 8.5 Hz, H-2′ and 6′), 6.79 (2H, d, J = 8.5 Hz, H-3′ and 5′), 5.88 (2H, s, H-6 and 8), 5.43 (1H, dd, J = 3.0 & 12.7 Hz, H-2), 3.24 (1H, dd, J = 12.9 & 17.2 Hz, H-3$_{trans}$), 2.69 (1H, dd, J = 3.0 & 17.2 Hz, H-3$_{cis}$).

Compound 2 (kaempherol)

Yellowish needles from MeOH, mp. 275-8°, IR ν_{max}^{KBr}cm^{-1}: 3350 (OH), 1660 (α, β-unsaturated C=O), 1614, 1570, 1508 (C=C). UV λ_{max}^{MeOH}nm (log ε): 257 (sh., 364), 269 (3.72), 300 (sh., 3.47), 330 (3.50), 370 (3.78); $\lambda_{max}^{MeOH+NaOMe}$nm: 280 (3.80), 320 (3.54), 420 (3.84); $\lambda_{max}^{MeOH+AlCl_3}$nm: 270 (3.80), 308 (3.30), 350 (3.42), 428 (3.85); $\lambda_{max}^{MeOH+AlCl_3+HCl}$nm: 258 (sh., 3.72), 270 (3.77), 308 (3.31), 350 (3.47), 427 (3.83); $\lambda_{max}^{MeOH+NaOAc}$nm: 274 (3.79), 310 (3.55), 380 (3.74); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$nm: 270 (3.73), 298 (3.46), 324 (3.51), 370 (3.79). MS (*m/z*, rel. int.): 286 (M^+, 100), 285 (M^+-H, 30.1), 258 (M^+-CO, 9.8), 257 (M^+-HCO, 9.8), 229 (257-CO, 10.4), 153 (AH^+, 5.9), 121 (B_2^+, 18.6), 93 (B_2^+-CO, 5.8). ^{1}H-NMR (DMSO-d_6, 300 MHz, TMS) δ : 12.45 (1H, brs., H-5), 8.05 (2H, d, J = 8.89 Hz, H-2′ & 6′), 6.92 (2H, d, J = 8.89 Hz, H-3′ & 5′), 6.44 (1H, d, J = 2 Hz, H-8), 6.19 (1H, d, J = 2 Hz, H-6).

Compound 3 (dihydrokaempherol)

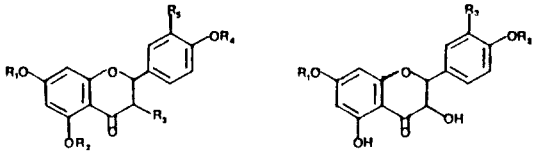
Colorless needles from MeOH, mp. 225-226°C, $[\alpha]_D^{20}$ + 18.3° (c = 0.115, MeOH). IR ν_{max}^{KBr}cm^{-1}: 3520, 3500-3000 (br., -OH), 1600 (α, β-unsaturated C=O), 1510, 1460, 1365, 1275, 1240, 1190, 1160, 1135, 1070, 1015, 995, 825; UV λ_{max}^{MeOH}nm (log ε): 292 (4.59), 329 (sh., 4.03); $\lambda_{max}^{MeOH+NaOMe}$nm: 248 (4.65), 325 (4.79); $\lambda_{max}^{MeOH+NaOAc}$nm: 255 (sh., 4.09), 280 (sh., 4.06), 328 (4.73); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$nm: 295 (4.54), 327 (sh, 4.22); $\lambda_{max}^{MeOH+AlCl_3}$ nm; 318 (4.72), 380 (4.00); $\lambda_{max}^{MeOH+AlCl_3+HCl}$nm; 313 (4.54), 380 (3.90). MS (*m/z*, rel. int.): 288 (M^+, 21.2), 259 (M^+-CHO, 43.0), 165 (259-PhOH, 22.1), 153 (RDA + H, A ring, 100), 136 (RDA, B ring, 23.2), 107 (136-CHO, 43.2). ^{1}H-NMR (DMSO-d_6, 80 MHz, TMS) δ : 11.88 (1H, brs., C_5-OH), 7.31 (2H, d, J = 8.5 Hz, H-2′ & 6′), 6.78 (2H, d, J = 8.5 Hz, H-3′ & 5′), 5.91 (1H, d, J = 2.1 Hz, H-8), 5.85 (1H, d, J = 2.1 Hz, H-6), 5.05 (1H, d, J = 11.4 Hz, H-2), 4.53 (1H, dd, J = 5.7 & 11.4 Hz, H-3).

Compound 4 (β-sitosterol glucoside)

Colorless amorphous powder, mp. 298-300°. LB and Molisch tests: positive. IR ν_{max}^{KBr}cm^{-1}: 3400 (br., OH), 2960, 2930, 2860 (CH), 1630 (C=C), 1460, 1365, 1380 (CH_2), 1100-1000 (glycoside). MS (*m/z*): 414 (M^+-glucose). Acid hydrolysis (10% H_2SO_4) of compound 4 yielded β-sitosterol, mp 138-9° and glucose which were identified with an authentic sample (TLC, MS).

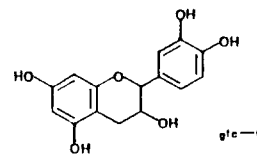
Compound 5 (kaempferide 7-O-glucoside)

Yellow amorphous powder, mp 296-7°. Mg/HCl and Molisch test: positive. IR ν_{max}^{KBr}cm^{-1}: 3360 (br., -OH), 1640 (α, β-unsaturated CO), 1620, 1590, 1500 (C=C), 1080 (C-O). UV λ_{max}^{MeOH}nm (log ε): 257 (4.39),



1: $R_1=R_3=R_5=R_6=R_8=H$
3: $R_1=R_3=R_6=R_8=H$, $R_5=OH$
8: $R_1=glc$, $R_3=R_5=R_6=R_8=H$
9: $R_1=R_8=H$, $R_3=glc$, $R_6=CH_3$, $R_5=OH$

2: $R_1=R_3=R_5=H$
5: $R_1=glc$, $R_3=CH_3$, $R_5=H$
6: $R_1=glc$, $R_3=R_5=H$
10: $R_1=glc$, $R_3=H$, $R_5=OH$



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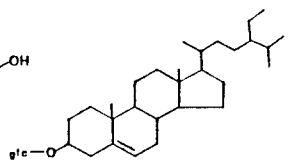

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273 (4.46), 291 (4.33), 327 (4.24), 370 (4.41); $\lambda_{max}^{MeOH+NaOMe}$nm: 260 (4.47), 278 (4.46), 330 (3.99), 412 (4.38); $\lambda_{max}^{MeOH+NaOAc}$nm: 257 (4.39), 271 (4.45), 290 (4.31), 325 (4.21), 370 (4.37); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$: 257 (4.39), 273 (4.46), 291 (4.31), 327 (4.24), 370 (4.41); $\lambda_{max}^{MeOH+AlCl_3}$nm: 258 (sh., 4.47), 272 (4.53), 298 (sh., 4.23), 358 (4.18), 428 (4.50); $\lambda_{max}^{MeOH+AlCl_3+HCl}$nm: 258 (sh., 4.48), 270 (4.52), 305 (sh., 4.27), 354 (4.24), 428 (4.44). ^{1}H-NMR (DMSO-d_6, 300 MHz, TMS) δ : 12.36 (1H, brs., C_5-OH, D_2O exchanged), 8.17 (2H, d, J = 9.0 Hz, H-2′ & 6′), 7.11 (2H, d, J = 9.1 Hz, H-3′ & 5′), 6.80 (1H, d, J = 2.1 Hz, H-8), 6.44 (1H, d, J = 2.1 Hz, H-6), 5.06 (1H, d, J = 7.15 Hz, H-1″), 3.85 (3H, s, $-OCH_3$).

Acid hydrolysis of 5

Ten mg of **5** was refluxed with 10% H_2SO_4 (20 m*l*) for 5 hr. After cooling, the reaction mixture was filtered. The aglycone was crystallized from MeOH to give kaempferide as yellow needles, mp 226-8°. It was confirmed by direct comparison with an authentic sample (TLC, mmp and MS). The filtrate was neutralized with $BaCO_3$, filtered and concentrated in vacuo. D-glucose was identified by TLC.

Compound 6 (kaempferol 7-O-glucoside, populnin)

Yellowish needles from MeOH. Mg/HCl and Molisch tests: positive, mp 243-4°. IR ν_{max}^{KBr}cm^{-1}: 3400 (OH), 1650 (α, β-unsaturated C = O), 1600, 1550, 1493 (C = C), 1070 (C-O). UV λ_{max}^{MeOH} (log ε): 258 (4.14), 274 (sh., 4.11), 295 (sh., 4.02), 328 (sh., 3.83), 374 (3.94); $\lambda_{max}^{MeOH+NaOMe}$nm: 252 (4.14), 274 (4.21), 440 (4.23); $\lambda_{max}^{MeOH+NaOAc}$nm: 255 (4.17), 274 (sh., 4.08), 295 (sh., 3.98), 328 (sh., 3.87), 372 (4.00); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$nm: 260 (4.16), 271 (4.17), 295 (4.01), 325 (sh., 3.89), 372 (4.00); $\lambda_{max}^{MeOH+AlCl_3}$nm: 272 (4.28), 300 (3.96), 326 (3.86), 350 (3.79), 428 (4.06); $\lambda_{max}^{MeOH+AlCl_3+HCl}$nm: 270 (4.20), 300 (3.98), 324 (3.83), 355 (3.79), 428 (3.98); MS (*m/z*, rel. int.); 286 (M^+-glucose, base peak). ^{1}H-NMR (DMSO-d_6 + D_2O, 300 MHz, TMS) δ : 8.28 (2H, d, J = 8.6 Hz, H-2′ & 6′), 6.87 (2H, d, J = 8.9 Hz, H-3′ & 5′), 6.63 (1H, brs., H-8), 6.29 (1H, brs., H-6), 5.01 (1H, d, J = 7.25 Hz, H-1″), 3.70-3.10 (6H, m, H-2″-6″). ^{13}C-NMR (DMSO-d_6, 75 MHz, TMS) δ : sugar, 99.9 (C-1″), 77.1 (C-3″), 76.5 (C-5″), 73.1 (C-2″), 69.7 (C-4″), 60.7 (C-6″).

Acid hydrolysis of 6

Twenty mg of **6** was refluxed with 10% H_2SO_4 (50 m*l*) for 5 hr. After cooling, the reaction mixture was filtered. The aglycone was crystallized from MeOH to give kaempferol as yellow needles, mp 275-7°. It was confirmed by direct comparison with an authentic sample (TLC, mmp and UV). The filtrate was neutralized with $BaCO_3$, filtered and concentrated in vacuo. D-glucose was identified by TLC.

Compound 7 ((+)-catechin)

Colorless needles from aq.-MeOH, mp. 174-5°, $[\alpha]_D^{20}$ + 10° (c = 0.123, MeOH). IR ν_{max}^{KBr}cm^{-1}; 3350, 1630, 1525, 1470, 1290, 1150, 1080, 1030. UV λ_{max}^{MeOH}nm (log ε): 282 (3.50). MS (*m/z*, rel. int.): 290 (M^+, 21.1), 152 (RDA fragment with B ring, 43.4), 139 (RDA fragment with A ring + H, 100), 123 (152-CHO, 69.7), 109 (123-CO, 8.0). ^{1}H-NMR (DMSO-d_6, 80 MHz, TMS) δ : 6.74 (1H, d, J = 2 HZ, H-2′), 6.68 (1H, d, J = 8 Hz, H-5′), 6.62 (1H, dd, J = 8 & 2 Hz, H-6′), 5.91 (1H, d, J = 2.0 Hz, H-8), 5.72 (1H, d, J = 2.0 Hz, H-6), 4.51 (1H, d, J = 7 Hz, H-2), 3.85-3.75 (1H, m, H-3), 2.50 (2H, ddd, J = 5.4, 8.1 and 16.0, H_2-H).

Compound 8 (naringenin-7-O-glucoside, prunin)

Colorless needles from MeOH, mp. 220-3°, $[\alpha]_D^{20}$ -66.6 (c = 0.3, MeOH), Mg/HCl and Molisch tests; positive. IR ν_{max}^{KBr}cm^{-1}: 3300 (br., -OH), 1615 (α, β-unsaturated C = O), 1570, 1520 (C = C), 1100-1000 (br., glycoside). UV λ_{max}^{MeOH}nm (log ε): 228 (4.61), 285 (4.36), 330 (3.51); $\lambda_{max}^{MeOH+NaOMe}$nm: 246 (4.57), 286 (4.31), 370 (3.91), 420 (3.84); $\lambda_{max}^{MeOH+NaOAc}$nm: 285 (4.42), 330 (3.51); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$nm: 285 (4.42), 330 (3.51); $\lambda_{max}^{MeOH+AlCl_3}$nm: 226 (4.76), 312 (4.55), 360 (3.94); $\lambda_{max}^{MeOH+AlCl_3+HCl}$nm: 226 (4.72), 309 (4.47), 360 (3.91). ^{1}H-NMR (DMSO-d_6, 200 MHz, TMS) δ : 12.16 (1H, br s, C_5-OH), 7.44 (2H, d, J = 8.5 Hz, H-2′ & 6′), 6.90 (2H, d, J = 8.5 Hz, H-3′

& 5′), 6.26 (1H, d, J = 2.2 Hz, H-8), 6.23 (1H, d, J = 2.2 Hz, H-6), 5.61 (1H, dd, J = 2.5 & 12.6 Hz, H-2), 5.06 (1H, d, J = 7.0 Hz, H-1″), 3.30 (1H, dd, J = 12.6 & 17.2 Hz, H-3_B), 2.84 (1H, dd, J = 2.9 & 17.2 Hz, H-3_A).

Acid hydrolysis of 8

Fifty mg of **8** was refluxed with 10% H_2SO_4 (50 m*l*) for 5 hr. After cooling. The reaction mixture was filtered. The aglycone was crystallized from MeOH to give naringenin as colorless needles, mp 254-5°. It was confirmed by direct comparison with an authentic sample (TLC, mmp, and MS). The filtrate was neutralized with $BaCO_3$, filtered and concentrated in vacuo. D-glucose was identified by TLC.

Compound 9 (hesperetin-5-O-glucoside)

Colorless from MeOH, mp 212-6°, Mg/HCl and Molisch tests: positive, $[\alpha]_D^{20}$-106.4° (c = 0.125, MeOH). IR ν_{max}^{KBr}cm^{-1}: 3350 (OH), 1640 (α, β-unsaturated C = O), 1612, 1580, 1534, 1512 (C = C), 1070 (C-O). UV λ_{max}^{MeOH}nm (log ε): 229 (4.39), 288 (4.29), 320 (sh., 3.79); $\lambda_{max}^{MeOH+NaOMe}$nm: 253 (4.19), 329 (4.43); $\lambda_{max}^{MeOH+NaOAc}$nm: 257 (sh., 3.97), 292 (sh., 3.96), 330 (4.38); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$nm: 285 (4.26), 324 (sh., 3.84); $\lambda_{max}^{MeOH+AlCl_3}$nm: 228 (4.39), 285 (4.28); $\lambda_{max}^{MeOH+AlCl_3+HCl}$: 229 (4.38), 285 (4.26). ^{1}H-NMR (DMSO-d_6, 300 MHz, TMS) δ: 6.93 (1H, d, J = 8 Hz, H-5′), 6.92 (1H, d, J = 2 Hz, H-2′), 6.85 (1H, dd, J = 2 & 8 Hz, H-6′), 6.35 (1H, d, J = 2.1 Hz, H-8), 6.08 (1H, d, J = 2.1 Hz, H-6), 5.32 (1H, dd, J = 3 & 12.2 Hz, H-2), 4.72 (1H, d, J = 7.2 Hz, H-1″), 3.74 (3H, s, -OCH_3), 2.97 (1H, dd, J = 12.2 & 17.0 Hz, H-3_B) 2.65 (1H, dd, J = 3.0 & 17.0 Hz, H-3_A).

Enzymatic hydrolysis of 9

Fifty mg of **9** was standed with cellulase (Sigma) at room temp. overnight and extracted with EtOAc, concentrated in vacuo and crystallized with MeOH to give hesperetin (**9a**) mp 224°. The mother liquor was concentrated in vacuo and D-glucose was identified by TLC.

Compound 10 (quercetin 7-O-glucoside, quercimeritrin)

Yellowish needles from MeOH, mp 250° Mg/HCl and Molisch test; positive. UV λ_{max}^{MeOH} (log ε): 258 (4.77), 263 (sh., 4.56), 375 (4.73); $\lambda_{max}^{MeOH+NaOMe}$ nm: 249 (4.71), 268 (4.58), 423 (4.64); $\lambda_{max}^{MeOH+NaOAc}$ nm: 259 (4.75), 383 (4.67), 420 (4.34); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$nm: 261 (4.81), 387 (4.76); $\lambda_{max}^{MeOH+AlCl_3}$nm: 258 (sh., 4.70), 272 (4.80), 345 (sh., 3.97), 460 (4.82); $\lambda_{max}^{MeOH+AlCl_3+HCl}$nm: 269 (4.80), 360 (sh., 4.29), 430 (4.77). ^{1}H-NMR (DMSO-d_6, 300 MHz, TMS) δ: 12.5 (1H, s, C_5-OH), 7.74 (1H, d, J = 2.0 Hz, H-2′), 7.59 (1H, dd, J = 8.5 and 2.0 Hz, H-6′), 6.92 (1H, d, J = 8.5 Hz, H-5′), 6.78 (1H, d, J = 2.2 Hz, H-8), 6.45 (1H, d, J = 2.2 Hz, H-6), 5.09 (1H, d, J = 7.2 Hz, H-1″).

Acid hydrolysis of 10

Ten mg of **10** was refluxed with 10% H_2SO_4 (30 m*l*) for 5 hr. After cooling, the reaction mixture was filtered. The aglycone was crystallized from MeOH to give quercetin as yellow needles, mp 314-5°. It was confirmed by direct comparison with an authentic sample (TLC, mmp and MS). The filtrate was neutralized with $BaCO_3$, filtered and concentrated in vacuo. D-glucose was identified by TLC.

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