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FLAVONOIDS FROM *BIDENS PILOSA* VAR. *RADIATA*

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Key Word Index—*Bidens pilosa*; Compositae; aerial parts; flavonoids; structure.

Abstract—Five new flavonoids, named (*Z*)-6-*O*-(3″,4″,6″-triacetyl-β-D-glucopyranosyl)-6,7,3′,4′-tetrahydroxyaurone, (*Z*)-6-*O*-(2″,4″,6″-triacetyl-β-D-glucopyranosyl)-6,7,3′,4′-tetrahydroxyaurone, okanin 4′-*O*-β-D-(4″,6″-diacetyl)-glucopyranoside, *iso*-okanin 7-*O*-β-D-(2″,4″,5″-triacetyl)-glucopyranoside and quercetin-3,4′-dimethyl ether-7-*O*-rutinoside, respectively, together with six known constituents (*Z*)-6-*O*-(4″,6″-diacetyl-β-D-glucopyranosyl)-6,7,3′,4′-tetrahydroxyaurone, okanin 4′-*O*-β-D-(3″,4″,6″-triacetyl)-glucopyranoside, luteolin, 4-*O*-(2-*O*-acetyl-6-*O*-*p*-coumaroyl-β-D-glucopyranosyl)-*p*-coumaric acid, butanedioic acid, and 1-phenyl-1,3,5-heptatriyne were isolated from the aerial parts of *Bidens pilosa* var. *radiata*. The structures were determined on the basis of spectroscopic methods (including 2D NMR techniques). © 1997 Elsevier Science Ltd

INTRODUCTION

Bidens pilosa L. var. *radiata* Sch. -Bip. is widely distributed in tropical, subtropical and temperate regions [1]. The whole herb has been used as a folk medicine against various diseases, such as inflammation and rheumatism. In this paper we report on the isolation and structural elucidation of five new flavonoid glycosides (**1**, **2**, **5**–**7**) together with six known constituents (*Z*)-6-*O*-(4″,6″-diacetyl-β-D-glucopyranosyl)-6,7,3′,4′-tetrahydroxyaurone (**3**) [2], okanin 4′-*O*-β-D-(3″,4″,6″-triacetyl)-glucopyranoside (**4**) [3], luteolin (**8**), 4-*O*-(2-*O*-acetyl-6-*O*-*p*-coumaroyl-β-D-glucopyranosyl)-*p*-coumaric acid (**9**) [4], butanedioic acid (**10**), and 1-phenyl-1,3,5-heptatriyne (**11**) [5] from this plant.

RESULTS AND DISCUSSION

Compound **1** had a UV spectrum typical of a naturally-occurring aurone i.e. main λ_{max} at 414.5 nm. The ^{1}H NMR spectra showed signals indicative of the presence of 2,5,6-related and *ortho*-related aromatic protons. A 28 nm bathochromic shift in its UV spectrum in the presence of NaOAc with H_3BO_3 showed the existence of a free *ortho*-dihydroxyl group in ring B. A comparison of its ^{1}H and ^{13}C NMR data with those of maritimein [6] revealed that **1** was very similar to maritimein except for the sugar moiety. The three singlets at δ_H 2.02, 2.04 and 2.07 were consistent with three acetyl groups attached to the sugar moiety [7]. The coupling constant (J = 7.8 Hz) of the doublet for H-1″ in the ^{1}H NMR spectrum indicated β-D-glucose. These data including the EI mass (*m/z* 286 [aglycone]$^+$) and positive FAB mass ([M + H]$^+$ = *m/z* 575) spectra suggested that the sugar moiety in **1** was triacetylated.

The exact positions of the acetyl groups were determined by the ^{1}H and ^{13}C NMR spectral data. The assignments of each carbon and proton signal were achieved on the basis of 2D ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY.

The three signals ascribable to H-3″, 4″ and 6″ were moved markedly further downfield at δ 5.26, 5.02, 4.31 and 4.13, respectively, and indicated that the acetyl groups in **1** were linked to the C-3″-, C-4″- and C-6″-hydroxyl positions of the glucose moiety. Furthermore, the long-range heteronuclear correlation NMR experiment (COLOC) also confirmed this conclusion. The three carbonyls (δ 172.3, 172.0 and 171.5) ascribable to three acetyl groups showed long-range correlations with H-3″, H-4″ and H-6″, respectively. Therefore, compound **1** was identified as (*Z*)-6-*O*-(3″,4″,6″-triacetyl-β-D-glucopyranosyl)-6,7,3′,4′-tetrahydroxyaurone.

Compound **2** exhibited a major UV absorption band at λ_{max} 405.0 nm and a bathochromic shift of 36.5 nm on addition of NaOAc with H_3BO_3. The ^{1}H NMR spectrum showed the typical signal pattern of a 6,7-disubstituted and 3′,4′-disubstituted aurone, three singlets (δ 2.02, 2.10 and 2.14) ascribable to three acetyl groups and a doublet at δ 5.28 (J = 7.9 Hz)

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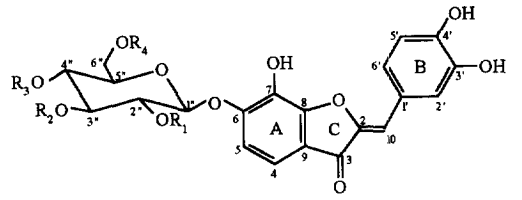

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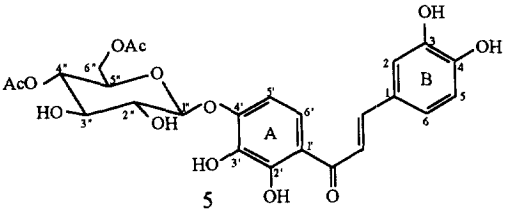

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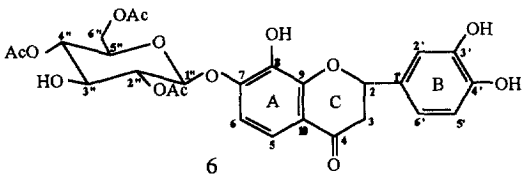

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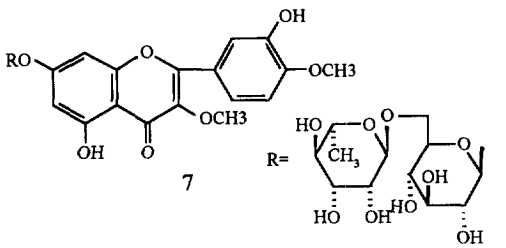

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assignable to the β-anomeric proton of the β-D-glucopyranose.

Comparison of the ^{1}H and ^{13}C NMR data revealed an identical substitution pattern for compounds **1** and **2**. The EI mass (*m/z* 286 [aglycone]$^+$) and positive FAB mass ([M+H]$^+$ = *m/z* 575) spectra confirmed that both of them had the same molecular formula. Indeed, compounds **1** and **2** only differed in the acylation positions of sugar moiety. The assignments of the ^{1}H and ^{13}C NMR signals were completed by 2D ^{1}H-^{1}H and ^{1}H-^{13}C COSY. The characteristic downfield shifts of the signals for H-2″ (δ 5.14), H-4″ (δ 4.99) and H-6″ (δ 4.27 and 4.10) were only consistent with acetylation at the C-2″-, C-4′- and C-6″-OH positions. Accordingly, compound **2** was elucidated as (*Z*)-6-*O*-(2″,4″,6″-triacetyl-β-D-glucopyranosyl)-6,7,3′,4′-tetrahydroxyaurone.

Compound **5** exhibited a major UV absorption band at λ_{max} 376.0 nm typical of a chalcone. A bathochromic shift of 46 nm after the addition of aluminium chloride and hydrochloric acid indicated the presence of a free 2′-hydroxyl group.

The ^{1}H NMR spectrum indicated a chalcone with a 3,4-disubstituted B-ring and two *ortho*-H atoms in the A-ring. The coupling constant of the doublet for H-1″ in the ^{1}H NMR spectrum (J = 7.7 Hz) indicated β-D-glucose. Two signals at δ_H 2.05 and 2.10 were consistent with two acetyl groups attached to the sugar moiety. These data including the EI mass (*m/z* 288 [aglycone]$^+$) and negative FAB mass ([M−H]$^-$ = *m/z* 533) spectra suggested okanin as the aglycone and okanin diacetylated β-D-glucoside as the parent compound. Comparison of ^{13}C NMR data of **5** with those of okanin 4′-*O*-β-D-glucoside [8] confirmed that **5** was an acetylated okanin 4′-glucoside. The exact positions of the acetyl groups were determined from the ^{13}C NMR and ^{1}H NMR spectral data. 2D ^{1}H-^{1}H and ^{1}H-^{13}C COSY spectra were utilized to assign the carbon and proton signals.

The signals for H-4″ and H_2-6″ appeared further downfield (δ 4.91, 4.25 and 4.09). Hence, the acetyl groups were located at C-4″- and C-6″-OH. Thus, compound **5** was identified as okanin 4′-*O*-β-D-(4″-6″-diacetyl)-glucopyranoside.

Compound **6** was assigned the molecular formula $C_{27}H_{28}O_{14}$ (FAB mass: [M+H]$^+$ = *m/z* 577; ^{13}C NMR as well as DEPT). The ^{1}H NMR spectrum showed a flavone with 3,4-disubstituted B-ring and two *ortho*-H atoms in the A-ring. In the UV spectrum of **6**, the major absorption appeared at λ_{max} 281.0 nm. These data closely resembled to those of *iso*-okanin 7-*O*-β-D-glucopyranoside [9]. Examination of the NMR data of these two compounds revealed that **6** as a triacetylated derivative of *iso*-okanin-7-*O*-β-D-glucopyranoside. The sites of acylation were readily inferred from the downfield shift of the H-2″, 4″ and 6″ signals (δ 5.39, 5.08, 4.26 and 4.09).

Thus, compound **6** was determined as *iso*-okanin 7-*O*-β-D-(2″,4″,6″-triacetyl)-glucopyranoside. The configuration of C-2 is still under investigation.

Compound **7** showed a UV bathochromic shift of 48.5 nm after the addition of aluminum chloride and hydrochloric acid. This indicated the presence of free 5-hydroxyl group. This was also confirmed by the singlet at δ 12.64 characterized for 5-OH. Examination of the UV spectrum recorded after the addition of shift reagents such as sodium acetate (and boric acid) or sodium methoxide revealed that there was no free hydroxyl group at the C-3, 7 or 4′ positions.

The ^{1}H NMR spectrum showed **7** was a derivative of flavonol with a 3,4-disubsituted B-ring and two *meta*-H atoms in the A-ring. Since the presence of a 5-OH group was known from UV and ^{1}H NMR spectra, ring A could be further deduced to have a 5,7-disubstituted pattern. The ^{1}H and ^{13}C NMR data (δ 100.5 and 99.9; two anomeric carbons) showed the presence of two sugar units. The two sugar units were determined as glucose and rhamnose, respectively, and the rhamnose was attached to the C-6″-OH of glucose judging from the downfield shift of the C″-6 signal. These facts together with EI mass (*m/z* 330 [aglycone]$^+$) and positive FAB mass ([M+H]$^+$ = *m/z* 639) spectra indicated that **7** was a flavonol *O*-diglycoside, the substituents of which were two hydroxyls,

two methoxyls and a rutionse. The molecular formula was established as $C_{29}H_{34}O_6$.

The fragment ion at m/z 151(B_2^+) suggested there was one hydroxyl and one methoxyl in the B-ring. Since the UV data indicated that the free hydroxyl group was not located at C-4′, the hydroxyl had to be situated at C-3′ and the methoxyl at C-4′.

The location of rutinose and another methoxyl were determined by a COLOC experiment which revealed the long range couplings of the anomeric proton of glucose with C-7 and the proton of one methoxyl with C-3. The coupling between the proton of another methoxyl and C-4′ was also observed. Hence, compound **7** was elucidated as quercetin-3,4′-dimethyl ether-7-*O*-rutinoside.

EXPERIMENTAL

General. Mp: uncorr; MS: VG Autospec-3000 spectrometer. NMR: chemical shifts (δ) expressed in ppm with reference to the solvent signals.

Plant material. The plant was collected in Kunming, Yunnan, Peoples Republic of China, in 1994 and identified by Prof. X. X. Zhuang. A voucher specimen is deposited in the herbarium of Kunming Institute of Botany.

Extraction and isolation. Air-dried, powdered aerial parts of *Bidens pilosa* L. var. *radiata* Sch. -Bip. (5.5 kg) were extracted with EtOH (4 × 30 l) at room temp. for three weeks. After solvent evapn, the concentrate (450 g) was successively extracted with petrol; EtOAc and *n*-BuOH. The residue (59 g) after removal of EtOAc was chromatographed on silica gel (600 g, 200–300 mesh), eluting with petrol containing increasing amounts of EtOAc. Five frs were collected. Each fr. was submitted to Sephadex LH-20 with MeOH–H_2O as eluent. Final purification was achieved by reversed-phase silica gel (RP-18) CC and over Sephadex LH-20 CC repeatedly to yield 10 compounds: **1** (17 mg), **2** (47 mg), **3** (100 mg), **4** (15 mg), **5** (50 mg), **6** (55 mg), **7** (40 mg), **8** (15 mg), **9** (30 mg) and **10** (100 mg). Additionally, polyacetylene **11** (70 mg) was isolated from the petrol part.

(Z)-6-O-(3″,4″,6″-*Triacetyl-β*-D-*glucopyranosyl*)-6,7,3′,4′-*tetrahydroxyaurone* (**1**). $C_{27}H_{26}O_{14}$, yellow powder, mp 145.5–147.5°, $[\alpha]_D^{27}$ −38.1° (CH_3OH, *c* 0.335); IR ν_{max}^{KBr} cm^{-1}: 3380, 1730, 1630, 1593, 1500, 1433, 1360, 1240, 1160, 1110, 1070 and 1030; UV λ_{max}^{MeOH} nm (log ε): 267.0 (4.01), 329.5 (4.07), 414.5 (4.28); +NaOMe: 262.0, 287.0 (sh), 347.5, 492.0; +$AlCl_3$: 247.0, 287.5, 457.5; +AlCl+HCl_3: 276.0, 324.0, 415.5; +NaOAc: 261.5, 338.0, 462.0; +NaOAc+H_3BO_3: 284.0, 325.5, 442.5; EIMS 70 eV m/z (rel. int.): 286 [aglycone]$^+$ (100), 258 [agl-CO]$^+$ (18), 247 [acetyglucosyl]$^+$ (5), 229 (21), 169 (13), 153 (79), 152 (71), 134 (29), 115 (48) and 81 (25); FABMS (positive ion mode) m/z (rel. int.): 575 [M+H]$^+$ (19) and 287 [agl+H]$^+$ (100); HR FABMS (positive ion mode) m/z: found: 574.1350 [M]$^-$ ($C_{27}H_{26}O_{14}$, calcd 574.1323; ^{13}C NMR (CD_3OD) δ: 147.6 (C-2), 185.4 (C-3), 115.8 (C-4), 113.8 (C-5), 153.2 (C-6), 134.7 (C-7), 156.4 (C-8), 119.6 (C-9), 115.8 (C-10), 125.5 (C-1′), 119.5 (C-2′), 146.7 (C-3′), 149.7 (C-4′), 116.8 (C-5′), 126.9 (C-6′), 102.8 (C-1″), 72.9 (C-2″), 75.9 (C-3″), 70.1 (C-4″), 73.3 (C-5″), 63.3 (C-6″), 172.3, 172.0, 171.5 (C=O, OAc), 20.8, 20.6 and 20.6 (CH_3, OAc); ^1H NMR (CD_3OD) δ: 7.23 (*d*, *J* = 8.6 Hz, H-4), 7.06 (*d*, *J* = 8.6 Hz, H-5), 6.75 (*s*, H-10), 7.53 (*d*, *J* = 2.3 Hz, H-2′), 6.85 (*d*, *J* = 8.3 Hz, H-6′), 5.18 (*d*, *J* = 7.8 Hz, H-1″), 3.85 (*dd*, *J* = 7.8 and 9.4 Hz, H-2″), 5.26 (*dd*, *J* = 9.4 and 9.4 Hz, H-3″), 5.02 (*dd*, *J* = 9.4 and 9.6 Hz, H-4″), 4.05 (*m*, H-5″), 4.31 (*dd*, *J* = 5.4 and 12.3 Hz, H-6″a), 4.13 (*dd*, *J* = 2.2 and 12.3 Hz, H-6″b), 2.07, 2.04 and 2.02 (each 3H, *s*, CH_3, OAc).

(Z)-6-O-(2″,4″,6″-*Triacetyl-β*-D-*glucopyranosyl*)-6,7,3′,4′-*tetrahydroxyaurone* (**2**). $C_{27}H_{26}O_{14}$, yellow powder, mp 143.0–145.0°, $[\alpha]_D^{27}$ −44.1° (CH_3OH, *c* 0.329); IR ν_{max}^{KBr} cm^{-1}: 3375, 1728, 1626, 1590, 1500, 1430, 1360, 1230, 1160, 1120 and 1030; UV λ_{max}^{MeOH} nm (log ε): 255.0 (4.01), 315.0 (4.11), 405.0 (4.27); +NaOMe: 264.5, 354.0, 488.5; +$AlCl_3$: 298.0 (sh), 312.5, 451.0; +$AlCl_3$+HCl: 238.0 (inf), 274.0, 323.0, 416.0; +NaOAc: 263.5, 305.5 (sh), 362.5, 473.5; +NaOAc+H_3BO_3: 284.0, 327.0, 441.5; EIMS 70 eV m/z (rel. int.): 286 [Aglycone]$^+$ (100), 258 [agl-CO]$^+$ (6), 229 (22), 169 (19), 153 (84), 152 (97), 127 (30) and 115 (59); FABMS (positive ion mode) m/z (rel. int.): 575 [M+H]$^+$ (10) and 287 [agl+H]$^+$ (97); HR FABMS (positive ion mode) m/z: found 574.1292 [M]$^+$ ($C_{27}H_{26}O_{14}$), calcd 574.1322; ^{13}C NMR (CD_3OD) δ: 147.5 (C-2), 185.4 (C-3), 115.9 (C-4), 114.1 (C-5), 153.1 (C-6), 134.8 (C-7), 156.6 (C-8), 119.5 (C-9), 115.9 (C-10), 125.4 (C-1′), 119.5 (C-2′), 146.7 (C-3′), 149.7 (C-4′), 116.8 (C-5′), 126.9 (C-6′), 101.1 (C-1″), 74.9 (C-2″), 73.5 (C-3″), 71.8 (C-4″), 73.6 (C-5″), 63.4 (C-6″), 172.4, 172.1, 171.8 (C=O, OAc). 21.0, 20.8 and 20.6 (CH_3, OAc); ^1H NMR (CD_3OD) δ: 7.23 (*d*, *J* = 8.4 Hz, H-4), 6.99 (*d*, *J* = 8.4 Hz, H-5), 6.75 (*s*, H-10), 7.51 (*d*, *J* = 1.5 Hz, H-2′), 6.85 (*d*, *J* = 8.2 Hz, H-5′), 7.37 (*dd*, *J* = 1.5 and 8.2 Hz, H-6′), 5.28 (*d*, *J* = 7.9 Hz, H-1″), 5.14 (*dd*, *J* = 7.9 and 9.3 Hz, H-2″), 3.88 (*m*, H-3″), 4.99 (*dd*, *J* = 9.4 and 9.6 Hz, H-4″), 3.88 (*m*, H-5″), 4.27 (*dd*, *J* = 5.5 and 12.3 Hz, H-6″a), 4.10 (*dd*, *J* = 2.0 and 12.3 Hz, H-6″b), 2.14, 2.10 and 2.02 (each 3H, *s*, CH_3, OAc).

Okanin 4′-O-*β*-D-(4″,6″-*diacetyl*)-*glucopyranoside* (**5**). $C_{25}H_{26}O_{13}$, orange crystals (from MeOH–H_2O), mp 190.0–192.5°, $[\alpha]_D^{23}$ −104.7° (CH_3OH, *c* 0.344); IR ν_{max}^{Kbr} cm^{-1}: 3400, 1730, 1620, 1550, 1500, 1430, 1355, 1270, 1225, 1100 and 1028; UV λ_{max}^{MeOH} nm (log ε): 265.0 (3.92), 313.0 (4.70, sh), 376.0 (4.45); +NaOMe: 259.0, 439.0; +$AlCl_3$: 333.0, 512.0; +$AlCl_3$+HCl: 243.0 (sh). 273.5, 327.0, 422.0; +NaOAc: 256.0 (sh), 384.5, 453.0; +NaOAc+H_3BO_3: 272.0, 312.5, 387.0; EIMS 70 eV m/z (rel. int.): 288 [aglycone]$^+$ (85), 247 [acetyglucosyl]$^+$ (9), 229 (14), 187 (18), 169 (21), 153 (100), 152 (95), 136 (70), 115 (51) and 73 (55); FABMS (negative ion mode) m/z: 533 [M−H]$^-$; HR FABMS (negative ion mode) m/z: found: 534.1409 [M]$^+$ ($C_{25}H_{26}O_{13}$), calcd 534.1373; ^{13}C NMR (CD_3OD) δ:

128.4 (C-1), 116.1 (C-2), 146.9 (C-3), 150.2 (C-4), 116.7 (C-5), 123.9 (C-6), 194.7 (C=O), 118.4 (C-α), 147.0 (C-β), 117.7 (C-1′), 153.9 (C-2′)*, 136.2 (C-3′), 151.3 (C-4′)*, 108.3 (C-5′), 122.4 (C-6′), 102.5 (C-1″), 74.8 (C-2″), 75.1 (C-3″), 72.1 (C-4″), 73.5 (C-5″), 63.7 (C-6″), 172.5, 172.0 (C=O, OAc), 20.9 and 20.7 (CH_3, OAc); ^{1}H NMR (CD_3OD) δ: 7.19 (*d*, *J* = 2.1 Hz, H-2), 6.82 (*d*, *J* = 8.2 Hz, H-3), 7.11 (*dd*, *J* = 2.1 and 8.2 Hz, H-6), 7.53 (*d*, *J* = 15.4 Hz, H-α), 7.75 (*d*, *J* = 15.4 Hz, H-β), 6.75 (*d*, *J* = 9.2 Hz, H-5′), 7.58 (*d*, *J* = 9.2 Hz, H-6′), 5.04 (*d*, *J* = 9.2 Hz, H-1″), 3.63 (*dd*, *J* = 7.7 and 9.3 Hz, H-2″), 3.71 (*dd*, *J* = 9.3 and 9.2 Hz, H-3″), 4.91 (*dd*, *J* = 9.2 and 9.4 Hz, H-4″), 3.88 (*m*, H-5″), 4.25 (*dd*, *J* = 5.4 and 12.3 Hz, H-6″a), 4.09 (*dd*, *J* = 2.4 and 12.3 Hz, H-6″b), 2.10 and 2.05 (each 3H, *s*, CH_3, OAc).

iso-*Okanin* 7-O-β-D-(2″,4″,6″-*triacetyl*)-*glucopyranoside* (**6**). $C_{27}H_{28}O_{14}$, white powder, mp 153.0–155.5°, $[\alpha]_D^{27}$ −49.1 (CH_3OH, *c* 0.570); IR ν_{max}^{KBr} cm^{-1}: 3600, 3420, 1732, 1655, 1600, 1444, 1360, 1310, 1230, 1075, 1055 and 1043; UV λ_{max}^{MeOH} nm (log ε): 217.0 (4.47, sh), 226.5 (4.38 sh), 281.0 (4.22), 318.5 (sh); +NaOMe: 250.0, 297.0, 378.5, 413.5 (inf); +$AlCl_3$: 232.5 (sh), 289.0, 318.0 (sh); +$AlCl_3$+HCl: 229.0 (inf), 280.0, 324.0, 420.5; +NaOAc: 250.0 (sh), 289.0; +NaOAc+H_3BO_3: 283.5; EIMS 70 eV *m/z* (rel. int.): 288 [aglycone]$^+$ (54), 229 (7), 187 (8), 179 (4), 169 (19), 153 (100), 152 (81), 136 (32), 127 (21), 115 (41) and 73 (40); FABMS (positive ion mode) *m/z*: 577 $[M+H]^+$, 289 $[agl+H]^+$; HR FABMS (positive ion mode) *m/z*: 576.1525 $[M]^+$ ($C_{27}H_{28}O_{14}$), calcd 576.1479; ^{13}C NMR (CD_3OD) δ: 81.6 (C-2), 44.9 (C-3), 193.9 (C-4), 118.2 (C-5), 112.0 (C-6), 151.7 (C-7), 137.5 (C-8), 152.7 (C-9), 118.6 (C-10), 131.7 (C-1′), 115.1 (C-2′), 147.0 (C-3′), 146.5 (C-4′), 146.5 (C-5′), 119.6 (C-6′), 100.9 (C-1″), 74.9 (C-2″), 73.5 (C-3″), 71.9 (C-4″), 73.5 (C-5″), 63.5 (C-6″), 172.4, 172.0, 171.3 (C=O, OAc), 20.9, 20.8 and 20.6 (CH_3, OAc); ^{1}H NMR (CD_3OD) δ: 4.95 (*dd*, *J* = 3.0 and 12.2 Hz, H-2), 3.09 (*dd*, *J* = 12.2 and 17.0 Hz, H-3), 2.78 (*dd*, *J* = 3.0 and 17.0 Hz, H-4), 7.31 (*d*, *J* = 9.0 Hz, H-5), 6.81 (*d*, *J* = 9.0 Hz, H-6), 6.97 (*d*, *J* = 2.0 Hz, H-2′), 6.76 (*d*, *J* = 8.1 Hz, H-5′), 6.83 (*dd*, *J* = 2.0 and 8.1 Hz, H-6′), 5.20 (*d*, *J* = 8.0 Hz, H-1″), 5.39 (*dd*, *J* = 8.0 and 9.4 Hz, H-2″), 3.87 (*m*, H-3″), 5.08 (*dd*, *J* = 9.5 and 9.5 Hz, H-4″), 3.87 (*m*, H-5″), 4.26 (*dd*, *J* = 5.5 and 12.3 Hz, H-6″a), 4.09 (*dd*, *J* = 2.3 and 12.3 Hz, H-6″b), 2.09 and 2.05 (each 3H, *s*, CH_3, OAc).

Quercetin-3,4′-*dimethyl ether*-7-O-*rutinoside* (**7**). $C_{29}H_{34}O_{16}$, white powder, mp: 240.5–242.0°, $[\alpha]_D^{25}$ −93.6° (CH_3OH, *c* 0.359); IR ν_{max}^{KBr} cm^{-1}: 3380, 2910, 1645, 1590, 1480, 1430, 1345, 1300, 1275, 1250, 1210, 1175, 1120 and 1060; UV λ_{max}^{MeOH} nm (log ε): 255.0 (4.40), 264.5 (4.32, sh), 354.5 (4.31); +NaOMe: 267.0, 383.5; +$AlCl_3$: 269.0, 295.5 (sh), 361.0 (sh), 405.0; +$AlCl_3$+HCl: 272.0, 292.0 (sh), 357.5, 403.0; +NaOAc: 266.0, 358.5; +NaOAc+H_3BO_3: 253.0 (sh), 264.5 (inf), 355.0; EIMS 70 eV *m/z* (rel. int.): 330 [aglycone]$^+$ (7), 238 (5), 152 (4), 143 (14), 122 (26), 105 (43), 91 (27) and 79 (100); FABMS (positive ion mode) *m/z*: 639 $[M+H]^+$ and 331 $[agl+H]^+$, HR FABMS (positive ion mode) *m/z*: found 638.1900 $[M]^+$ ($C_{29}H_{34}O_{16}$), calc. 638.1847; ^{13}C NMR (CD_3OD) δ: 156.0 (C-2), 138.2 (C-3), 178.1 (C-4), 160.9 (C-5), 99.2 (C-6), 162.9 (C-7), 94.5 (C-8), 156.0 (C-9), 105.9 (C-10), 122.1 (C-1′), 115.2 (C-2′), 146.3 (C-3′), 150.3 (C-4′), 112.1 (C-5′), 120.4 (C-6′), 100.5 (C-1″), 73.1 (C-2″), 76.2 (C-3″), 70.7 (C-4″), 75.6 (C-5″), 66.0 (C-6″), 99.9 (C-1‴), 70.3 (C-2‴), 69.6 (C-3‴), 72.0 (C-4‴), 68.3 (C-5‴), 17.7 (C-6‴), 59.8 (3-OCH_3) and 55.7 (4′-OCH_3); ^{1}H NMR (CD_3OD) δ: 6.44 (1H, *d*, *J* = 2.0 Hz, H-6), 6.72 (1H, *d*, *J* = 2.0 Hz, H-8), 7.53 (1H, *s*, H-2′), 7.14 (1H, *d*, *J* = 8.0 Hz, H-5′), 7.54 (1H, *d*, *J* = 8.0 Hz, H-6′), 12.64 (1H, *br s*, OH-5), 5.07 (1H, *d*, *J* = 7.2 Hz, H-1″), 3.85 and 3.79 (each 3H, *s*, 2×OCH_3).

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* Interchangeable.

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