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鬼针草中一个新的查耳酮甙

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摘要：从鬼针草 *Bidens pilosa* L. 地上部分的丙酮提取物中，分离鉴定了18个化合物，其中包括一个新的查耳酮甙类化合物（α，3，2′，4′-tetrahydroxy-2′-O-β-D-glucopyranosylchalcone，**2**）。其它化合物分别鉴定为 butein（**1**），okanin 4-methyl ether-3′-O-β-glucoside（**3**），sulfuretin（**4**），6，7，3′，4′-tetrahydroxyaurone（**5**），海生菊苷（maritimein，**6**），（*Z*）-6-O-(6″-acetyl-β-D-glucopyranosyl)-6，7，3′，4′-tetrahydroxy-aurone（**7**），（*Z*）-6-O-(4″，6″-diacetyl-β-D-glucopyranosyl)-6，7，3′，4′-tetrahydroxy-aurone（**8**），（*Z*）-6-O-(3″，4″，6″-triacetyl-β-D-glucopyranosyl)-6，7，3′，4′-tetrahydroxy-aurone（**9**），木犀草素（luteolin，**10**），槲皮素（quercetin，**11**），异槲皮苷（isoquercitrin，**12**），芦丁（rutin，**13**），黄芪苷（astragalin，**14**），quercetin-3，4′-dimethyl ether-7-O-rutinoside（**15**），反式丁烯二酸（**16**），2-β-D-glucopyranosyloxy-1-hydroxy-trideca-3，5，7，9，11-pentayne（**17**）和 3-β-D-glucopyranosyloxy-1-hydroxy-6（*E*）-tetradecene-8，10，12-triyne（**18**）。

关键词：鬼针草；菊科；查耳酮；黄酮
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A New Chalcone Glycoside from *Bidens pilosa*

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Abstract：Eighteen compounds，including a new chalcone glycoside（**2**），were isolated from the aerial parts of *Bidens pilosa* L. Their structures were elucidated as butein（**1**），α，3，2′，4′-tetrahydroxy-2′-O-β-D-glucopyranosylchalcone（**2**），okanin 4-methyl ether-3′-O-β-glucoside（**3**），sulfuretin（**4**），6，7，3′，4′-tetrahydroxyaurone（**5**），maritimein（**6**），（*Z*）-6-O-(6″-acetyl-β-D-glucopyranosyl)-6，7，3′，4′-tetrahydroxy-aurone（**7**），（*Z*）-6-O-(4″，6″-diacetyl-β-D-glucopyranosyl)-6，7，3′，4′-tetrahydroxy-aurone（**8**），（*Z*）-6-O-(3″，4″，6″-triacetyl-β-D-glucopyranosyl)-6，7，3′，4′-tetrahydroxy-aurone（**9**），luteolin（**10**），quercetin（**11**），isoquercitrin（**12**），rutin（**13**），astragalin（**14**），querce-

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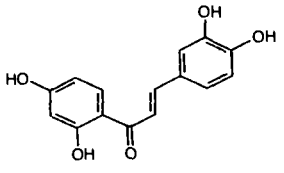
tin-3, 4′-dimethyl ether-7-O-rutinoside (**15**), *E*-butenedioic acid (**16**), 2-β-D-glucopyranosyloxy-1-hydroxy-trideca-3, 5, 7, 9, 11-pentayne (**17**), 3-β-D-glucopyran osyloxy-1-hydroxy-6 (*E*)-tetradecene-8, 10, 12-triyne (**18**), respectively, based on the spectral analysis.

Key words: *Bidens pilosa*; Compositae; Chalcone; Flavonoids

Bidens pilosa is a famous medicinal herb in China which could be used for the treatment of various diseases, especially for anti-hypertension (Zhou *et al*, 1989). Phytochemical analysis on this plant led to the isolation of eighteen compounds (**1-18**), including a new chalcone glycoside (**2**). This paper presents the structure elucidation of the new compound.



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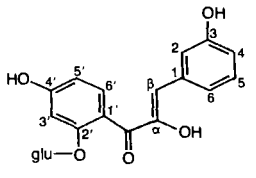

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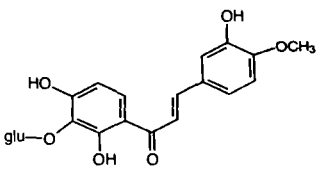

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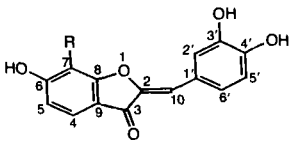
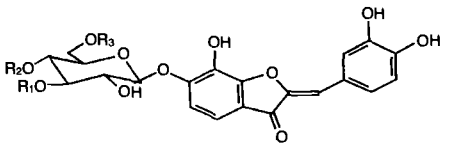
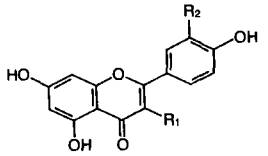


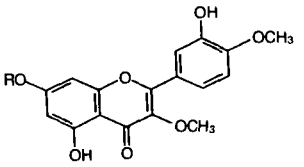
4 R=H
5 R=OH



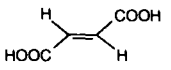
6 $R_1=R_2=R_3=H$
7 $R_1=R_2=H, R_3=Ac$
8 $R_1=H, R_2=R_3=Ac$
9 $R_1=R_2=R_3=Ac$



10 $R_1=H, R_2=OH$
11 $R_1=OH, R_2=OH$
12 $R_1=O$-glu, $R_2=OH$
13 $R_1=O$-rutinose, $R_2=OH$
14 $R_1=O$-glu, $R_2=H$



15 R=rutinose



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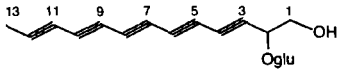
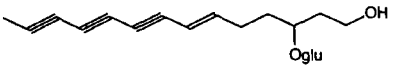


17



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Results and Discussion

Compound **2** gave the molecular formula $C_{21}H_{22}O_{10}$ by positive FAB-HRMS (obsd. 435.2320, calcd. 435.2380). In the DEPT spectrum of **2**, apart from six signals due to a glucopyranosyl moiety, fifteen carbons including a characteristic carbonyl group at δ_C 192.3 (s) were composed of a chalcone skeleton, which had four hydroxyl groups according to the molecular weight. Inspection of ^1H NMR spectrum of **2**, a singlet rather than the two AB type protons attributable to α- and β- positions was displayed, suggesting that one hydroxyl group located at α- or β- position. Further analysis of the correlations in its HMBC, H-2 [δ_H 8.13 (1H, br s)] and H-6 [δ_H 7.23 (1H, br d, J=8.9 Hz)]

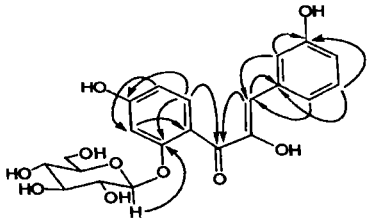

Fig. 1 The key HMBC correlations of **2**. (H→C)

with C－β [δ_C 145.9 (d)] led to the conclusion that the hydroxyl group was located at α- position. Moreover, HMBC correlations of H－5 and H－2 with C－3 (s), and H－6′ with C－2′ (s), C－4′ (s) and carbonyl carbon also revealed that others three hydroxyl groups were located at C－3, C－2′ and C－3′. In addition, the anomeric proton of glucopyranosyl at δ_H 5.44 (1H, d, J＝7.2 Hz) coupling to the C－2′ at δ_C 163.8 (s) confirmed the sugar moiety connected to C－2′. Therefore, compound **2** was elucidated as α, 3, 2′, 4′-tetrahydroxy-2′-O-β-D-glucopyranosylchalcone.

The known compounds were determined as butein **1** (Shimokoriyama *et al.*), okanin 4-methyl ether-3′-O-β-glucoside **3** (Bernhard *et al.*), sulfuretin **4** (Julian *et al.*), 6, 7, 3′, 4′-tetrahydroxyaurone **5** (Sashida *et al.*), maritimein **6** (Sashida *et al.*), (*Z*)-6-O-(6″-acetyl-β-D-glucopyranosyl)-6, 7, 3′, 4′-tetrahydroxy-aurone **7** (Sashida *et al.*), (*Z*)-6-O-(4″, 6″-diacetyl-β-D-glucopyranosyl)-6, 7, 3′, 4′-tetrahydroxy-aurone **8** (Wang *et al.*), (*Z*)-6-O-(3″, 4″, 6″-triacetyl-β-D-glucopyranosyl)-6, 7, 3′, 4′-tetrahydroxy-aurone **9** (Wang *et al.*), luteolin **10**, quercetin **11**, isoquercitrin **12**, rutin **13** (Ines *et al.*), astragalin **14**, quercetin-3, 4′-dimethyl ether-7-O-rutinoside **15**, *E*-butenedioic acid **16** (Nunziatina *et al.*), 2-β-D-glucopyranosyloxy-1-hydroxyl-trideca-3, 5, 7, 9, 11-pentayne **17** (Rücker *et al.*), 3-β-D-glucopyranosyloxy-1-hydroxy-6 (*E*)-tetradecene-8, 10, 12-triyne **18** (Rücker *et al.*) based on comparison their spectra data, and the values of R_f with those of literatures or authentic samples.

Experimental

General Optical rotation was recorded on a SEPA-300 polarimetre. UV spectra were obtained on a Shimadzu double-beam 210A spectrometer in MeOH. The MS spectra were performed on a VG Autospec-3000 spectrometer with 70 eV. ^{1}H, ^{13}C NMR and 2D NMR were recorded on a Bruker AM-400 and DRX-500 spectrometer with TMS as internal standard. The silica gel for TLC and column chromatography were obtained from Qingdao Marine Chemical Inc., China.

Plant Material The aerial parts of *Bidens pilosa* were collected in Kunming, Yunnan Province, in November 2001, and were identified by Professor Lin Zhong-Wen. The voucher specimen (11－2001-Lin) is deposited in Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation The dried and powdered aerial plants (8.7 kg) were extracted with 70% aq. acetone at room temperature for 4×24 h. The extract was concentrated *in vacuo* and filtered to remove pigment, the filtrate was then partitioned between EtOAc and H_2O. The EtOAc extract (135 g) was subjected to column chromatograph over MCI and eluted with H_2O and 90% MeOH/H_2O to give eluting fraction. Then the 90% MeOH/H_2O eluate (110 g) was submitted to silica gel CC with $CHCl_3$/MeOH/H_2O (7:2:0.2) as eluent to divide into three fractions. Compounds **1** (36 mg), **4** (18 mg), **5** (42 mg), **10** (53 mg) and **11** (810 mg) were purified from fraction Ⅰ, **2** (14 mg), **3** (26 mg), **6** (215 mg), **7** (28 mg) and **8** (19 mg) were obtained from fraction Ⅱ, and **9** (18 mg), **12** (700 mg), **13** (65 mg), **14** (64 mg), **15** (23 mg), **16** (1.2 g), **17** (140 mg), **18** (29 mg) were achieved from fraction Ⅲ, respectively, after repeatedly column chromatography including reversed-phase column (RP-18) and Sephadex LH-20.

Butein (1): yellow crystals; $C_{15}H_{12}O_5$; ^{1}H NMR (DMSO-d_6): 7.87 (1H, d, J＝8.4 Hz, H－6′), 7.65 (1H, d, J＝15.4 Hz, H－β), 7.47 (1H, d, J＝15.4 Hz, H－α), 7.11 (1H, d, J＝1.8 Hz, H－3′), 7.03

(1H, dd, J=8.5, 2.2 Hz, H-6), 6.75 (1H, d, J=8.4 Hz, H-5'), 6.34 (1H, br d, J=8.5 Hz, H-5), 6.22 (1H, d, J=2.2 Hz, H-2); EI MS *m/z*: 272 $[M]^+$ (100), 163 (15), 150 (14), 137 (53).

α, 3, 2', 4'-Tetrahydroxy-2'-O-β-D-glucopyranosylchalone (2): yellow powder; $C_{21}H_{22}O_{10}$; $[\alpha]_D^{20}$ -89.2 (*c* 0.24 MeOH); UV λ_{max}^{MeOH} (log ε): 313 (4.2), 382 (3.4) nm; IR ν_{max}^{KBr}: 3400, 1737, 1628, 1548, 1500, 1436, 1269, 1218, 1028 cm^{-1}; ^1H and ^{13}C NMR (DMSO-d_6) data see Table 1; FAB-MS (positive) *m/z*: 435 $[M+H]^+$ (100); HR-FAB (positive) *m/z*: 435.2320 (calcd. 435.2380).

Table 1 ^{13}C and ^1H NMR data of compound **2** (in DMSO-d_6, J in Hz)

No.	δ_C	δ_H	No.	δ_C	δ_H
1	126.5 s		3'	103.8 d	6.99 (1H, br s)
2	116.3 d	8.13 (1H, s)	4'	165.4 s	
3	146.0 s		5'	108.6 d	7.03 (1H, d, J=9.0)
4	117.6 d	7.65 (1H, d, J=8.3)	6'	132.8 d	8.67 (1H, d, J=9.0)
5	116.1 d	7.88 (1H, dd, J=8.3, 8.9)	glu		
6	123.0 d	7.23 (1H, d, J=8.9)	1''	100.0 d	5.44 (1H, d, J=7.2)
β	145.9 d	8.12 (1H, s)	2''	73.5 d	3.70 (1H, t, J=8.6)
α	149.5 s		3''	77.5 d	3.86 (1H, overlap)
C=O	192.3 s		4''	69.9 d	3.60 (1H, t, J=8.6)
1'	115.2 s		5''	76.8 d	3.81 (1H, m)
2'	163.8 s		6''	60.9 t	4.11 (1H, br d, J=11.6)
					3.88 (1H, dd, J=11.6, 5.5)

Okanin 4-methyl ether 3'-O-β-glucoside (3): yellow powder; $C_{22}H_{24}O_{11}$; ^1H NMR (DMSO-d_6): 7.83 (1H, d, J=7.2 Hz, H-6'), 7.76 (1H, d, J=12.2 Hz, H-β), 7.58 (1H, d, J=12.2 Hz, H-α), 7.23 (1H, d, J=1.3 Hz, H-2), 7.19 (1H, dd, J=6.7, 1.3 Hz, H-6), 6.97 (1H, d, J=6.7 Hz, H-5), 6.52 (1H, d, J=7.2 Hz, H-5'), 4.81 (1H, d, J=6.2 Hz, H-1''), 3.91 (3H, s, -OMe); ^{13}C NMR (DMSO-d_6): 129.8 (s, C-1), 115.3 (d, C-2), 148.0 (s, C-3), 151.9 (s, C-4), 112.5 (d, C-5), 123.7 (d, C-6), 193.8 (s, C=O), 146.2 (d, C-β), 119.2 (d, C-α), 115.5 (s, C-1'), 158.6 (s, C-2'), 133.6 (s, C-3'), 159.1 (s, C-4'), 109.3 (d, C-5'), 128.9 (d, C-6'), 106.6 (d, C-1''), 75.3 (d, C-2''), 78.4 (d, C-3''), 70.7 (d, C-4''), 77.6 (d, C-5''), 62.0 (t, C-6''); FAB-MS (negative) *m/z*: 463 $[M-H]^+$ (100).

Sulfuretin (4): yellow crystals; $C_{15}H_{10}O_5$; ^1H NMR (DMSO-d_6): 7.50 (1H, d, J=8.3 Hz, H-5'), 7.41 (1H, d, J=2.0 Hz, H-2'), 7.14 (1H, dd, J=8.3, 2.0 Hz, H-5), 6.74 (1H, d, J=8.0 Hz, H-4), 6.61 (1H, d, J=1.7 Hz, H-7), 6.60 (1H, dd, J=8.3, 2.0 Hz, H-6'), 6.59 (1H, s, H-10); ^{13}C NMR (DMSO-d_6): 145.6 (s, C-2), 180.9 (s, C-3), 125.3 (d, C-4), 115.9 (d, C-5), 167.3 (s, C-6), 98.2 (d, C-7), 165.9 (s, C-8), 113.7 (s, C-9), 112.6 (d, C-10), 123.3 (s, C-1'), 111.5 (d, C-2'), 145.3 (s, C-3'), 147.7 (s, C-4'), 117.9 (d, C-5'), 124.2 (d, C-6'); EI-MS *m/z*: 270 $[M]^+$ (100), 253 (13), 213 (12), 137 (29), 112 (11).

6, 7, 3', 4'-Tetrahydroxy-aurone (5): red powder; $C_{15}H_{10}O_6$; ^1H NMR (C_5D_5N): 7.60 (1H, br s, H-2'), 7.56 (1H, d, J=6.5 Hz, H-6'), 7.51 (1H, d, J=6.6 Hz, H-4), 7.18 (1H, s, H-10), 7.12 (1H, d, J=6.5 Hz, H-5'), 7.06 (1H, d, J=6.6 Hz, H-5); ^{13}C NMR (C_5D_5N): 147.5 (s, C-2), 183.4 (s, C-3), 116.9 (d, C-4), 112.6 (d, C-5), 156.8 (s, C-6), 132.3 (s, C-7), 156.4 (s, C-8), 116.0 (s, C-9), 113.5 (d, C-10), 125.0 (s, C-1'), 119.3 (d, C-2'), 147.4 (s, C-3'), 149.7 (s, C-4'), 116.9 (d, C-5'), 125.2 (d, C-6'); EI-MS *m/z*: 286 $[M]^+$ (100), 152 (34), 115 (20).

Maritimein (6): orange powder; $C_{21}H_{20}O_{11}$; ^1H NMR (DMSO-d_6): 7.54 (1H, d, J=2.0 Hz, H-2'), 7.34 (1H, dd, J=8.2, 2.0 Hz, H-6'), 7.24 (1H, d, J=8.5 Hz, H-4), 7.12 (1H, d, J=8.5 Hz, H-5), 6.85 (1H, d, J=8.2 Hz, H-5'), 6.75 (1H, s, H-10), 5.00 (1H, d, J=7.6 Hz, H-1''), 3.92

(1H, dd, J=12.0, 2.1 Hz, H-6a), 3.73 (1H, dd, J=12.0, 5.4 Hz, H-6b), 3.60-3.41 (3H, overlap, H-2′, 3′, 4′), 3.52 (1H, m, H-5′); ^{13}C NMR (DMSO-d_6): 147.6 (s, C-2), 185.5 (s, C-3), 115.9 (d, C-4), 114.0 (d, C-5), 153.7 (s, C-6), 134.4 (s, C-7), 156.3 (s, C-8), 119.4 (s, C-9), 115.6 (d, C-10), 125.5 (s, C-1′), 119.3 (d, C-2′), 146.7 (s, C-3′), 149.7 (s, C-4′), 116.9 (d, C-5′), 126.6 (d, C-6′), 103.5 (d, C-1″), 74.9 (d, C-2″), 78.6 (d, C-3″), 71.3 (d, C-4″), 77.7 (d, C-5″), 62.4 (t, C-6″); FAB-MS (negative) m/z: 447 $[M-H]^+$.

(Z)-6-O-(6′-O-Acetyl-β-D-glucopyranosyl)-6, 7, 3′, 4′-tetrahydroxyaurone (7): orange powder; $C_{23}H_{22}O_{12}$; ^{1}H NMR (C_5D_5N): 7.60 (1H, d, J=6.6 Hz, H-6′), 7.58 (1H, br s, H-2′), 7.50 (1H, d, J=6.7 Hz, H-4), 7.41 (1H, d, J=6.7 Hz, H-5), 7.18 (1H, s, H-10), 7.15 (1H, d, J=6.6 Hz, H-5′), 5.68 (1H, d, J=6.2 Hz, H-1″), 1.96 (3H, s, OAc); ^{13}C NMR (C_5D_5N): 147.6 (s, C-2), 183.9 (s, C-3), 114.7 (d, C-4), 113.5 (d, C-5), 153.5 (s, C-6), 135.2 (s, C-7), 156.2 (s, C-8), 119.0 (s, C-9), 114.0 (d, C-10), 124.8 (s, C-1′), 119.5 (d, C-2′), 147.0 (s, C-3′), 149.7 (s, C-4′), 116.8 (d, C-5′), 125.8 (d, C-6′), 171.0 (s, -OAc), 20.7 (q, -OAc), 103.3 (d, C-1″), 74.7 (d, C-2″), 78.2 (d, C-3″), 71.3 (d, C-4″), 75.7 (d, C-5″), 64.6 (t, C-6″); FAB-MS (negative) m/z: 489 $[M-H]^+$ (75).

(Z)-6-O-(4″, 6″-Diacetyl-β-D-glucopyranosyl)-6, 7, 3′, 4′-tetrahydroxyaurone (8): yellow powder; $C_{25}H_{24}O_{13}$; ^{1}H NMR (CD_3OD): 7.54 (1H, br s, H-2′), 7.33 (1H, d, J=8.5 Hz, H-6′), 7.20 (1H, d, J=7.7 Hz, H-4), 7.02 (1H, d, J=7.7 Hz, H-5), 6.85 (1H, d, J=8.5 Hz, H-5′), 6.74 (1H, s, H-10), 5.03 (1H, d, J=7.7 Hz, H-1″), 2.15, 2.04 (each 3H, s, OAc); ^{13}C NMR (CD_3OD): 147.5 (s, C-2), 185.5 (s, C-3), 115.9 (d, C-4), 113.5 (d, C-5), 153.4 (s, C-6), 134.5 (s, C-7), 156.3 (s, C-8), 119.3 (s, C-9), 115.6 (d, C-10), 125.4 (s, C-1′), 119.4 (d, C-2′), 146.7 (s, C-3′), 149.7 (s, C-4′), 116.8 (d, C-5′), 127.0 (d, C-6′), 172.4, 172.0 (each s, OAc), 20.9, 20.7 (each q, OAc), 102.9 (d, C-1″), 74.7 (d, C-2″), 75.0 (d, C-3″), 72.0 (d, C-4″), 73.5 (d, C-5″), 63.6 (t, C-6″); FAB-MS (negative) m/z: 531 $[M-H]^+$ (54).

(Z)-6-O-(3″, 4″, 6″-Triacetyl-β-D-glucopyranosyl)-6, 7, 3′, 4′-tetrahydroxyaurone (9): yellow powder; $C_{27}H_{26}O_{14}$; ^{1}H NMR (CD_3OD): 7.49 (1H, br s, H-2′), 7.29 (1H, d, J=7.0 Hz, H-6′), 7.13 (1H, d, J=7.9 Hz, H-4), 6.94 (1H, d, J=7.9 Hz, H-5), 6.84 (1H, d, J=7.0 Hz, H-5′), 6.68 (1H, s, H-10), 5.08 (1H, d, J=7.4 Hz, H-1″), 2.16, 2.12, 2.02 (each 3H, s, OAc); ^{13}C NMR (CD_3OD): 147.4 (s, C-2), 185.4 (s, C-3), 115.8 (d, C-4), 113.3 (d, C-5), 153.1 (s, C-6), 134.5 (s, C-7), 156.1 (s, C-8), 119.4 (s, C-9), 115.6 (d, C-10), 125.4 (s, C-1′), 119.3 (d, C-2′), 146.6 (s, C-3′), 149.6 (s, C-4′), 116.8 (d, C-5′), 127.0 (d, C-6′), 172.4, 172.2, 171.6 (each s, 3×OAc), 20.8, 20.7, 20.6 (each q, 3×OAc), 102.5 (d, C-1″), 72.7 (d, C-2″), 75.7 (d, C-3″), 70.0 (d, C-4″), 73.1 (d, C-5″), 63.3 (t, C-6″); FAB-MS (negative) m/z: 573 $[M+H]^+$ (36).

Luteolin (10): yellow needles; $C_{15}H_{10}O_6$; EI-MS m/z: 286 $[M]^+$ (100); The value of R_f is consistent with that of authentic sample on TLC.

Quercetin (11): yellow crystals; $C_{15}H_{10}O_7$; EI-MS m/z: 302 $[M]^+$ (100); The value of R_f is consistent with that of authentic sample on TLC.

Isoquercetrin (12): yellow powder; $C_{21}H_{20}O_{12}$; FAB-MS (positive) m/z: 465 $[M+H]^+$ (100), 303 $[M-glu+H]^+$ (75); The value of R_f is consistent with that of authentic sample on TLC.

Rutin (13): yellow powder; $C_{27}H_{30}O_{16}$; FAB-MS (positive) m/z: 611 $[M+H]^+$ (100), 465 (10), 303 (89); The value of R_f is consistent with that of authentic sample on TLC.

Astragalin (14): yellow powder; $C_{21}H_{20}O_{11}$; FAB-MS (negative) *m/z*: 447 $[M-H]^+$ (100), 286 (46); The value of R_f is consistent with that of authentic sample on TLC.

Quercetin-3, 4'-dimethyl ether-7-O-rutinoside (15): yellow powder; $C_{29}H_{34}O_{16}$; ^1H NMR (DMSO-d_6): 7.86 (1H, br s, H-8), 7.77 (1H, d, J=8.6 Hz, H-6'), 7.75 (1H, br s, H-2'), 7.12 (1H, d, J=8.6 Hz, H-5'), 6.65 (1H, br s, H-6), 5.20 (1H, d, J=7.4 Hz, H-1''), 5.21 (1H, br s, H-1'''), 4.08, 3.97 (each 3H, s, OMe), 1.30 (3H, d, J=6.1 Hz, H-6'''); FAB-MS (positive) *m/z*: 637 $[M-H]^+$.

(*E*)-2-Butenedioic acid (16): $C_4H_4O_4$; ^1H NMR (D_2O): 6.59 (2H, d, J=11.8 Hz, H-2 and H-3); ^{13}C NMR (D_2O): 137.8 (d, C-2 and C-3), 174.8 (s, C-1 and C-4); EI-MS *m/z*: 116 $[M]^+$ (31), 98 (100), 88 (16), 81 (14), 72 (29), 55 (19), 53 (39).

2-β-D-Glucopyranosyloxy-1-hydroxy-trideca-3, 5, 7, 9, 11-pentayne (17): brown powder; $C_{19}H_{18}O_7$; ^1H NMR (DMSO-d_6): 4.70 (1H, t, J=5.7 Hz, H-2), 4.34 (1H, d, J=6.2 Hz, H-1'), 3.64 (1H, m, H-1a), 3.56 (2H, m, H-6'a/b), 3.36 (1H, m, H-1b), 3.19 (1H, t, J=8.9 Hz, H-3'), 3.13 (1H, m, H-5'), 3.05 (1H, t, J=8.9 Hz, H-4'), 3.00 (1H, t, J=8.9 Hz, H-2'), 2.08 (3H, s, Me-13); ^{13}C NMR (DMSO-d_6): 61.1 (t, C-1), 68.5 (d, C-2), 69.8 (s, C-3)*, 60.5 (s, C-4)*, 61.1 (s, C-5)*, 62.7 (s, C-6)*, 62.9 (s, C-7)*, 63.6 (s, C-8)*, 63.8 (s, C-9)*, 78.9 (s, C-10)*, 58.6 (s, C-11), 81.1 (s, C-12), 4.3 (q, C-13), 100.4 (d, C-1'), 73.3 (d, C-2'), 77.2 (d, C-3'), 70.1 (d, C-4'), 76.6 (d, C-5'), 63.4 (t, C-6'); FAB-MS (positive) *m/z*: 359 $[M+H]^+$ (164), 179 (100). * could be interchanged.

3-β-D-Glucopyranosyloxy-1-hydroxy-6 (*E*)-tetradecene-8, 10, 12-triyne (18): yellow crystals; $C_{20}H_{26}O_7$; ^1H NMR (CD_3OD): 6.73 (1H, dt, J=16.1, 7.0 Hz, H-6), 5.89 (1H, d, J=16.1 Hz, H-7), 4.67 (1H, d, J=7.8 Hz, H-1'), 4.18 (1H, dd, J=11.8, 2.7 Hz, H-6a'), 3.70 (1H, m, H-3), 2.95-3.35 (5H, m, H-2'-H-5', H-6b'), 2.58-2.62 (2H, m, H-5), 2.28 (3H, s, H-14); ^{13}C NMR (CD_3OD): 59.5 (t, C-1), 38.2 (t, C-2), 77.8 (d, C-3), 35.2 (t, C-4)*, 30.2 (t, C-5)*, 152.2 (d, C-6), 109.1 (d, C-7), 59.7 (s, C-8)*, 65.2 (s, C-9)*, 66.9 (s, C-10)*, 73.4 (s, C-11)*, 75.8 (s, C-12)*, 78.9 (s, C-13)*, 3.9 (s, C-14), 99.4 (d, C-1'), 73.9 (d, C-2'), 76.8 (d, C-3'), 70.9 (d, C-4'), 76.0 (d, C-5'), 63.8 (t, C-6'); FAB-MS (positive) *m/z*: 379 $[M+H]^+$ (30), 217 [aglycone+H]$^+$ (56). * could be interchanged.

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