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A NOVEL ACYLATED FLAVONOID GLYCOSIDE FROM *ASTRAGALUS COMPLANATUS* [1)]

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Abstract: *A novel flavonoid glycoside acylated with a sesquiterpene, dihydrophaseic acid, was obtained from the seeds of Astragalus complanatus R. BR.*

Astragali Semen, the seeds of *Astragalus complanatus* R. BR. (Leguminosae), has been used as a tonic in the traditional Chinese medicine. In the preceding paper,[2)] we reported the occurrence of the oleanene glycosides in the methanolic extract of the title plant. We now present a paper of a novel flavonoid glycoside acylated with an abscisic acid-type sesquiterpene, designated as complanatin.

Complanatin (**1**), pale yellow needles, mp 192-4°C, $[\alpha]_D$ +0.5° (MeOH), showed a peak due to $[M+1]^+$ at *m/z* 889 in the positive FAB-MS, UV absorption peaks [λmax 267 (log ε 4.88), 340 (log ε 4.39)], and IR absorptions(cm^{-1}) at 3428 (OH), 1705 (ester carbonyl), 1658 (conjugated carbonyl) and 1602 (aromatic ring). The ^1H- and ^{13}C-NMR spectra of **1**[3)] displayed that it was constituted with a flavonoid portion, glycosidic parts and a sesquiterpene moiety as listed in Table I. Since the appearance of the ester linkage was suggested, **1** was saponified with alkaline to afford a flavonoid derivative (**2**), pale yellow crystals, mp 271-3°C, $[\alpha]_D$ +28.0° (DMSO-d_6), positive FAB-MS (*m/z*): 625 $[M+1]^+$ and a sesquiterpene moiety (**3**), a resin, $[\alpha]_D$ -72.6° ($CHCl_3$), EI-MS (m/z): 296 (M^+).

The ^1H-NMR signals (in DMSO-d_6) [δ 6.38 (1H, d, J=2.2 Hz), 6.77 (1H, d, J=2.2 Hz), 7.17 (2H, d, J=8.8 Hz), 8.17 (2H, d, J=8.8 Hz), 12.56 (1H, s), 3.87 (3H, s)] of **2** could assign its structure to be a 3,5,7,4'-tetrahydroxyflavone (kaempferol) derivative. It was furthermore suggested to possess one methoxyl group at C-7 by the NOE experiment and subsequently two terminal glucosyl moieties [two anomeric proton signals at δ 5.50 (1H, d, J=7.3 Hz) and 5.04 (1H, d, J=7.3 Hz)] to attach to C-3-OH and C-4'-OH, respectively, by the ^{13}C-NMR spectrum.[4)]

Table I ^{13}C-NMR Spectral Data for **1**, **2**, **3**, **4** and **5**

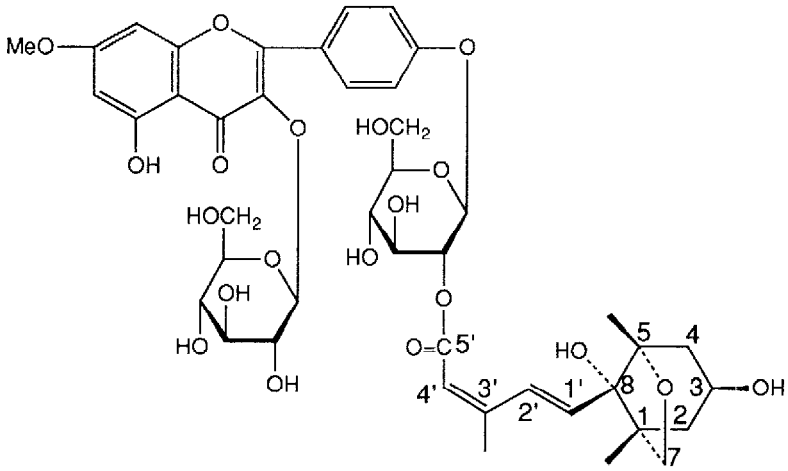
	1	**2**	**3**	**4**	**5**
Flavone moiety					
C-2	156.3	156.4			146.1
3	133.9	134.0			136.6
4	177.6	177.7			176.2
5	160.8	160.9			160.3
6	97.5	98.0			97.4
7	165.1	165.2			165.0
8	92.2	92.4			92.0
9	155.6	155.9			156.1
10	105.0	105.1			104.0
1'	124.0	123.6			124.7
2'	130.6	130.7			129.2
3'	116.5	115.8			116.1
4'	158.6	159.3			157.9
5'	116.5	115.8			116.1
6'	130.6	130.7			129.2
MeO-7	56.0	56.2			56.0
3-O-glc					
C-1	100.7	100.8			
2	74.1	74.2			
3	76.3	76.5			
4	69.8	69.9			
5	77.5	77.6			
6	60.8	60.9			
4'-O-glc					
C-1	97.8	99.9			97.6
2	74.0	73.2			74.0
3	72.6	76.4			72.6
4	69.7	69.6			69.8
5	77.1	77.1			77.2
6	60.3	60.7			60.3
Terpene moiety					
C-1	48.1		48.4	48.3	48.1
2	43.8		43.5	52.5	43.7
3	63.8		65.3	208.1	63.8
4	45.4		45.0	52.8	45.4
5	81.5		82.4	82.3	81.5
7	75.3		76.3	77.6	75.2
8	85.7		86.0	85.8	85.7
1'	136.1		133.3	131.8	136.1
2'	116.5		116.5	118.8	116.5
3'	151.2		149.9	149.0	151.2
4'	129.3		130.5	131.2	129.2
5'	163.9		166.6	166.5	163.9
Me-1	16.1		16.0	15.7	16.1
Me-5	19.4		19.1	18.9	19.4
Me-3'	20.7		21.2	21.1	20.7
MeO-5'			51.2	51.3	

These assignments were made by ^{1}H-^{13}C COSY experiment.
1, **2** and **5** were measured in DMSO-d_6; **3** and **4** were in $CDCl_3$.

On the other hand, the ^{1}H-NMR spectrum (in $CDCl_3$) of **3** showed signals due to two methyl groups (δ 0.89, 1.11, each s), one vinyl methyl (δ1.99, d, J=1.5 Hz), one methoxyl group (δ 3.65, s), three olefinic protons [δ 5.69 (1H, s), 6.36 (1H, d, J=16.1 Hz), 7.95 (1H, d, J=16.1 Hz)], a methylene group bearing oxygen atom [δ 3.69 (1H, d, J=7.7 Hz), 3.74 (1H, dd, J=7.7, 2.2 Hz)], methine group adjacent to the hydroxyl group [δ 4.22 (1H, dddd, J=10.6, 10.3, 7.0, 7.0 Hz), and other methylene signals [δ 1.60 (1H, dd, J=13.6, 10.6 Hz), 1.67 (1H, dd, J=13.6, 10.3 Hz), 1.84 (1H, ddd, J=13.6, 7.0, 1.5 Hz), 2.10 (1H, ddd, J=13.6, 7.0, 1.5 Hz)] attributable to a sesquiterpene moiety, methyl dihydrophaseate,[5] which was derived from (-)-methyl phaseate[6,7] by reduction with $NaBH_4$. Oxidation of **3** with chromic acid yielded a product (**4**),[8] $[\alpha]_D$ -26.7° ($CHCl_3$), being identical with (-)-methyl phaseate in respects with specific rotation, ^{1}H- and ^{13}C-NMR spectra.

Meanwhile, enzymatic hydrolysis of **1** provided a sole product (**5**),[9] which was estimated as a deglucosyl compound of **1** by the FAB-MS {$[M+1]^+$ at *m/z* 727} and ^{13}C-NMR spectrum. Moreover, the ^{13}C-NMR spectrum revealed that the acylated glucosyl moiety attached to the C-4'-OH and furthermore the sesquiterpene residue linked to the C-2 hydroxyl group of glucosyl moiety [acylation shifts (ppm): C-1, δ 97.6(-2.3); C-2, δ 74.0(+0.8); C-3, δ 72.6 (-3.8)],[10] whose ^{1}H-NMR spectrum also supported by the fact that signals due to H-1 and H-2 appeared at δ5.83 (1H, d, J=8.1 Hz) and 5.94 (1H, dd, J=8.1, 9.5 Hz), respectively, being substantiated by the ^{1}H-^{1}H COSY.

Consequently, the structure of complanatin (**1**) was determined as shown in the formula. A novel flavonoid glycoside acylated with sesquiterpene is firstly reported.



Structure of **1**

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3. The ^{1}H-NMR spectrum of **1** (δ ppm, in DMSO-d_6): flavone moiety, 3.86 (3H, s, MeO-7), 6.37 (1H, d, J=2.2 Hz, H-6), 6.73 (1H, d, J=2.2 Hz, H-8), 7.12(2H, d, J=8.8 Hz, H-3', 5'), 8.15 (2H, d, J=8.8 Hz, H-2', 6'), 12.54 (1H, s, HO-5); sugar anomeric protons, 5.52 (1H, d, J=7.7 Hz, 3-*O*-glc H-1), 5.35 (1H, d, J=7.3 Hz, 4'-*O*-glc H-1); terpene moiety, 0.87 (3H, s, Me-1), 1.03 (3H, s, Me-5), 1.57 (1H, br t, Ha-2), 1.64 (1H, br t, Ha-4), 1.74 (1H, dd, J=13.2, 6.6 Hz, Hb-2), 1.90 (1H, dd, J=13.2, 6.2 Hz, Hb-4), 2.07 (3H, s, Me-3'), 3.55 (1H, d, J=8.1 Hz, Ha-7), 3.77 (1H, d, J=8.1 Hz, Hb-7), 3.93 (1H, m, H-3), 5.78 (1H, s, H-4'), 6.53 (1H, d, J=15.8 Hz, H-2'), 7.98 (1H, d, J=15.4 Hz, H-1').
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9. The ^{1}H-NMR spectrum of **5** (δ ppm, in pyridine-d_6): flavone moiety, 3.80 (3H, s, MeO-7), 6.60 (1H, d, J=2.2 Hz, H-6), 6.70 (1H, d, J=2.2 Hz, H-8), 7.47 (2H, d, J=9.2 Hz, H-3',5'), 8.43 (2H, d, J=9.2 Hz, H-2',6'); sugar moiety, 4.23 (1H, overlapped with other signal, H-5), 4.37 (1H, dd, J=8.8, 9.2 Hz, H-4), 4.38 (1H, d, J=12.1 Hz, Hb-6), 4.48 (1H, dd, J=8.8, 9.5 Hz, H-3), 4.59 (1H, br d, J=12.1 Hz, Ha-6), 5.83 (1H, d, J=8.1 Hz, H-1), 5.94 (1H, dd, J=8.1, 9.5 Hz, H-2); terpene moiety, 1.22 (3H, s, Me-1), 1.51 (3H, s, Me-5), 1.88 (3H, d, J=1.1 Hz, Me-3'), 2.19 (1H, br t, Ha-4), 2.20 (1H, dd, J=13.2, 7.3 Hz, Ha-2), 2.27 (1H, dd J=13.6, 10.3 Hz, Hb-4), 2.53 (1H, ddd, J=13.2, 7.0, 1.8 Hz, Hb-2), 3.94 (1H, d, J=7.3 Hz, Ha-7), 4.24 (1H, d, J=7.3 Hz, Hb-7), 4.71 (1H, tdd, J=10.3, 7.3, 7.0 Hz, H-3), 5.92 (1H, s, H-4'), 6.93 (1H, d, J=15.8 Hz, H-2'), 8.86 (1H, d, J=15.8 Hz, H-1').
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