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# Chemical Constituents of Astragali Semen[1)]

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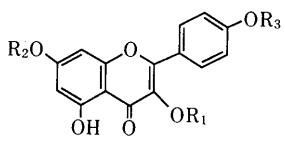
**Study on the constituents of Astragali Semen, the seeds of *Astragalus complanatus* R. BR. (Leguminosae), led to the identification of nine known flavonoids (1, 4, 6—12) and characterization of three new flavonol glycosides (2, 3, 5) as rhamnocitrin 3-*O*-*β*-D-apiofuranosyl(1→2)-*β*-D-glucopyranoside, 3-*O*-*β*-D-apiofuranosyl(1→2)-*β*-D-glucopyranosyl rhamnocitrin 4′-*O*-*β*-D-glucopyranoside and 3-*O*-*β*-D-apiofuranosyl(1→2)-*β*-D-glucopyranosyl kaempferol 4′-*O*-*β*-D-glucopyranoside, respectively. The occurrence of methyl dihydrophaseate (13), roseoside (14), blumenol C glucoside (15), (±)-3-oxo-α-ionyl glucoside (16a, 16b), tuberonic acid glucoside (17), benzylalcohol-*O*-α-L-arabiopyranosyl(1→6)-*β*-D-glucopyranoside (18), piceid (19) and deoxyrhaponticin (20) were also disclosed.**

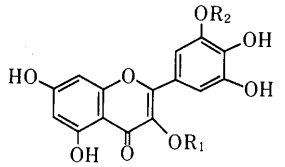
**Keywords** Astragali Semen; *Astragalus complanatus*; Leguminosae; flavonol glycoside; isoflavone; sesquiterpenoid

In previous papers, we reported the occurrence of flavonoids,[2)] six triterpene glycosides,[3)] and four new acylated flavonol glycosides[4)] from Astragali Semen, the seeds of *Astragalus complanatus* R. BR. (Leguminosae). The present paper describes the further isolation and characterization of flavonoids (**1**—**12**) and other compounds (**13**—**20**).

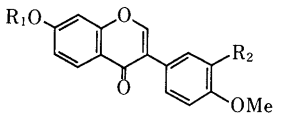
The methanol extract of Astragali Semen (4.5 kg) was partitioned between *n*-hexane and 80% MeOH, and then the MeOH layer was further shaken with 1-BuOH and water. Removal of the solvent from the organic layer gave a residue which was subjected to normal and reversed phase column chromatographies to yield compounds **1**—**20**.



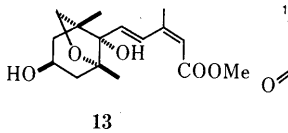
| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| **1** | -glc | -Me | -glc |
| **2** | -glc²api | -Me | -H |
| **3** | -glc²api | -Me | -glc |
| **4** | -glc | -H | -glc |
| **5** | -glc²api | -H | -glc |
| **6** | -glc²xyl | -H | -H |



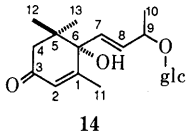
| | $R_1$ | $R_2$ |
|---|---|---|
| **7** | -glc | -H |
| **8** | -glc²xyl | -H |
| **9** | -H | -glc |



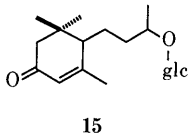
| | $R_1$ | $R_2$ |
|---|---|---|
| **10** | -glc | -H |
| **11** | -H | -OH |
| **12** | -glc | -OH |



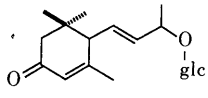
**13**



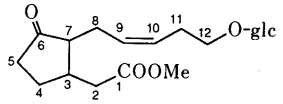
**14**



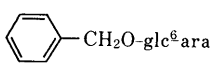
**15**



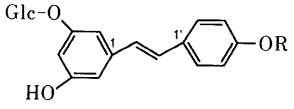
(+)-**16a**
(−)-**16b**



**17**



**18**



**19** : R=H
**20** : R=Me

Flavonoids **1**, **4** and **6**—**12** were identified as complanatuside,[5)] kaempferol 3,4′-di-*O*-*β*-D-glucopyranoside,[6)] kaempferol 3-*O*-*β*-D-xylopyranosyl(1→2)-*β*-D-glucopyranoside,[7)] myricetin 3-*O*-*β*-D-glucopyranoside,[8)] myricetin 3-*O*-*β*-D-xylopyranosyl(1→2)-*β*-D-glucopyranoside,[9)] cannabiscitrin,[7)] ononin,[10)] calycosin[7)] and calycosin 7-*O*-*β*-D-glucopyranoside,[7)] respectively.

Compound **2**, a yellow powder, $[\alpha]_D$ −125.5° (dimethylsulfoxide) (DMSO)), exhibited ultraviolet (UV) absorptions at 347 ($\log\varepsilon$, 4.39) and 266 ($\log\varepsilon$, 4.47) nm, and showed peaks due to $[M+H]^+$ at *m/z* 595, $[M-\text{pentose}+H]^+$ at *m/z* 463 and $[M-\text{pentosylhexose}+H]^+$ at *m/z* 301 in the positive fast atom bombardment mass spectrum (FAB-MS), which suggested the existence of one hexose and one pentose. The proton nuclear magnetic resonance ($^1$H-NMR) spectrum clearly displayed signals due to a *para*-disubstituted B-ring [$\delta$ 8.16 (2H, d, $J$=8.8 Hz, 2′,6′-H), 6.93 (2H, d, $J$=8.8 Hz, 3′,5′-H)] and a 5,7-disubstituted A-ring [$\delta$ 6.67 (1H, d, $J$=2.2 Hz, 8-H), 6.33 (1H, d, $J$=2.2 Hz, 6-H)] on the flavonol skeleton. The substituent at C-7 should be methoxyl group [$\delta$ 3.84 (3H, s)] which was confirmed by nuclear Overhauser Effect spectroscopy (NOESY) experiment. The carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectrum (Table I) revealed **2** to be a rhamnocitrin 3-*O*-glycoside,[2,11)] and signals due to the sugar moiety could be assigned to a *β*-D-apiofuranosyl(1→2)-*β*-D-glucopyranosyl moiety,[12)] whose configurations at the glycosidic linkages were suggested by the observation of two anomeric proton signals at $\delta$ 5.72 (1H, d, $J$=7.3 Hz) and 5.45 (1H, s) in the $^1$H-NMR spectrum. Of these two anomeric proton signals, the former was assignable to the glucosyl moiety attached to the C-3-OH of rhamnocitrin, and the latter to the apiosyl moiety linked to the C-2″-OH of the glucosyl unit, both in the *β*-form. The structure of **2** was thus constructed as rhamnocitrin 3-*O*-*β*-D-apiofuranosyl(1→2)-*β*-D-glucopyranoside as shown in the formulae.

Compound **3**, a yellow powder, $[\alpha]_D$ −132.7° (DMSO), showed UV absorptions at 342 ($\log\varepsilon$, 4.39), 316 ($\log\varepsilon$, 4.38) and 267 ($\log\varepsilon$, 4.59) nm. The $^1$H-NMR spectrum and NOESY displayed the characteristic signals for rhamno-

citrin glycoside at $\delta$ 12.60 (1H, s, 5-OH), 8.21 (2H, d, $J$=8.8 Hz, 2',6'-H), 7.17 (2H, d, $J$=8.8 Hz, 3',5'-H), 6.76 (1H, d, $J$=2.2 Hz, 8-H), 6.38 (1H, d, $J$=2.2 Hz, 6-H), 3.86 (3H, s, 7-OMe) and three anomeric proton signals at $\delta$ 5.64 (1H, d, $J$=7.3 Hz), 5.37 (1H, s) and 5.05 (1H, d, $J$=7.3 Hz). Furthermore, the $^{13}$C-NMR spectrum (Table I) also indicated that **3** was a rhamnocitrin triglycoside (anomeric carbons: $\delta$ 108.8, 100.0, 98.6) and that the C-3-OH and C-4'-OH of rhamnocitrin were connected with a $\beta$-D-apiofuranosyl(1→2)-$\beta$-D-glucopyranosyl moiety and a $\beta$-D-glucopyranosyl unit, respectively, by comparing chemical shifts with those of **2** in terms of the glycosylation shifts.[2,12] The peaks at $m/z$ 757 $[M+H]^+$, 625 $[M-apiose+H]^+$, 595 $[M-glucose+H]^+$. 463 $[M-glucose-apiose+H]^+$ and 301 $[aglycone+H]^+$ in the positive FAB-MS spectrum of **2** were also in good agreement with the above deduced structure.

Meanwhile, enzymatic hydrolysis of **3** provided a product **3a** as a yellow powder, $[\alpha]_D$ −124.7° (DMSO), which could be estimated as the deglucosyl product at C-4'-OH of **3** by the UV, positive FAB-MS, $^1$H- and $^{13}$C-NMR spectra. Therefore, **3a** was characterized as rhamnocitrin 3-$O$-$\beta$-D-apiofuranosyl(1→2)-$\beta$-D-glucopyranoside identical with **2**. Based on the above data, the full structure of **3** was characterized as 3-$O$-$\beta$-D-apiofuranosyl(1→2)-$\beta$-D-glucopyranosyl rhamnocitrin 4'-$O$-$\beta$-D-glucopyranoside as shown in the formulae.

Compound **5** was obtained as a yellow powder, $[\alpha]_D$ −92.0° (DMSO), which showed UV absorptions at 343 (log $\varepsilon$, 4.35), 304 (log $\varepsilon$, 4.35) and 267 (log $\varepsilon$, 4.57) nm, and the peaks at $m/z$ 743 $[M+H]^+$, 611 $[M-pentose+H]^+$, 581 $[M-hexose+H]^+$, 449 $[M-pentose-hexose+H]^+$ and 287 $[aglycone+H]^+$ in the positive FAB-MS spectrum. The $^1$H-NMR signals appeared at $\delta$ 12.60 (1H, s, 5-OH), 10.31 (1H, s, 7-OH), 8.15 (2H, d, $J$=8.8 Hz, 2',6'-H), 7.14 (2H, d, $J$=8.8 Hz, 3',5'-H), 6.48 (1H, br s, 8-H), 6.23 (1H, br s, 6-H) and anomeric proton signals at $\delta$ 5.61 (1H, d, $J$=7.3 Hz, glc 1''-H), 5.34 (1H, s, api 1'''-H), 5.03 (1H, d, $J$=7.3 Hz, glc 1''''-H), suggesting that **5** was a kaempferol triglycoside, which was also verified by the $^{13}$C-NMR spectrum (Table I). Moreover, the location of glycosidic linkages was determined at the C-3-OH and C-4'-OH of kaempferol by comparing chemical shifts with those of kaempferol-3-$O$-glycoside [C-1', 123.7 (+2.7); C-3', 5', 115.8 (+0.8); C-4', 159.2 (−0.6)].[12] Furthermore, signals originated from the sugar moiety were identical with those of **3**, suggesting the presence of a apiosyl(1→2)glucosyl group at C-3-OH and a terminal glucosyl group at C-4'-OH, the same as that of **3**. Therefore, the full structure of **5** could be represented as 3-$O$-$\beta$-D-apiofuranosyl(1→2)-$\beta$-D-gluco-

TABLE I. $^{13}$C-NMR Spectral Data for **1**—**9** (in DMSO-$d_6$)

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
|---|---|---|---|---|---|---|---|---|---|
| Flavonol moiety | | | | | | | | | |
| C- 2 | 156.4 | 156.1 | 156.3 | 156.5 | 156.4 | 156.6 | 156.3 | 155.8[a] | 146.4[a] |
| C- 3 | 134.0 | 133.2 | 133.9 | 133.6 | 133.5 | 133.2 | 133.6 | 133.4 | 136.1 |
| C- 4 | 177.8 | 177.5 | 177.7 | 177.6 | 177.5 | 177.8 | 177.5 | 177.6 | 175.9 |
| C- 5 | 161.0 | 160.9 | 161.0 | 161.4 | 161.2 | 161.6 | 161.3 | 161.7 | 160.7 |
| C- 6 | 98.0 | 97.7 | 98.0 | 98.5 | 98.7 | 98.9 | 98.7 | 99.3 | 98.3 |
| C- 7 | 165.2 | 164.9 | 165.5 | 164.5 | 164.4 | 164.5 | 164.2 | 165.4 | 164.0 |
| C- 8 | 92.4 | 92.0 | 92.4 | 93.8 | 93.7 | 93.9 | 93.4 | 93.8 | 93.6 |
| C- 9 | 156.0 | 155.9 | 155.4 | 155.5 | 155.4 | 155.6 | 156.3 | 155.7[a] | 156.2 |
| C-10 | 105.2 | 104.9 | 105.2 | 104.2 | 104.0 | 104.3 | 104.0 | 104.0 | 103.1 |
| C- 1' | 123.7 | 120.9 | 123.7 | 124.0 | 123.7 | 121.2 | 120.1 | 120.3 | 121.1 |
| C- 2' | 130.7 | 130.9 | 130.7 | 130.5 | 130.5 | 130.9 | 108.6 | 109.0 | 107.5 |
| C- 3' | 115.8 | 115.1 | 115.9 | 115.8 | 115.8 | 115.5 | 145.5 | 145.9 | 145.6[a] |
| C- 4' | 159.4 | 160.0 | 159.4 | 159.1 | 159.2 | 160.3 | 136.7 | 137.4 | 137.4 |
| C- 5' | 115.8 | 115.1 | 115.9 | 115.8 | 115.8 | 115.5 | 145.5 | 145.9 | 146.0[a] |
| C- 6' | 130.7 | 130.9 | 130.7 | 130.5 | 130.5 | 130.9 | 108.6 | 109.0 | 110.8 |
| OMe | 56.2 | 55.9 | 56.2 | | | | | | |
| 3-$O$-Glc | | | | | | | | | |
| 1 | 100.9 | 98.4 | 98.6 | 101.2 | 98.5 | 98.2 | 101.0 | 98.4 | |
| 2 | 74.2 | 77.0[a] | 77.1[a] | 74.3 | 77.1[a] | 82.1 | 74.0 | 82.3 | |
| 3 | 76.6[a] | 76.1 | 76.2 | 76.6 | 76.5 | 76.5 | 76.6 | 76.4 | |
| 4 | 69.9 | 70.1 | 70.3 | 69.9[a] | 70.2 | 69.9[a] | 69.9 | 69.9[b] | |
| 5 | 77.1 | 77.3[a] | 77.3[a] | 77.1[b] | 77.2[a] | 77.2 | 77.7 | 77.2 | |
| 6 | 60.9[b] | 60.6 | 60.8[b] | 60.9[c] | 60.6[b] | 60.8 | 61.1 | 61.2 | |
| 2''-$O$-Api or Xyl | | | | | | | | | |
| 1 | | 108.7 | 108.8 | | 108.7 | 104.9 | | 104.9 | |
| 2 | | 77.1[a] | 77.2[a] | | 77.1[a] | 74.2 | | 74.3 | |
| 3 | | 79.3 | 79.3 | | 79.2 | 77.9 | | 78.0 | |
| 4 | | 73.9 | 73.9 | | 73.9 | 69.8[a] | | 69.8[b] | |
| 5 | | 64.2 | 64.2 | | 64.1 | 66.1 | | 65.8 | |
| 4' or 3'-$O$-Glc | | | | | | | | | |
| 1 | 99.9 | | 100.0 | 100.0 | 100.0 | | | | 102.9 |
| 2 | 73.3 | | 73.3 | 73.3 | 73.3 | | | | 73.4 |
| 3 | 76.5[a] | | 76.6 | 76.6 | 76.5 | | | | 75.9 |
| 4 | 69.6 | | 69.7 | 69.6[a] | 69.6 | | | | 69.6 |
| 5 | 77.6 | | 77.6[a] | 77.5[b] | 77.5[a] | | | | 77.3 |
| 6 | 60.7[b] | | 60.7[b] | 60.7[c] | 60.7[b] | | | | 60.7 |

*a*—c) In each vertical column may be interchanged.

TABLE II. $^{13}$C-NMR Spectral Data for **14**, **15**, **16a** and **16b** (in Pyridine-$d_5$).

| | **14** | **15** | **16a** | **16b** |
|---|---|---|---|---|
| Aglycone moiety | | | | |
| C- 1 | 163.9 | 165.1 | 161.2 | 161.5 |
| C- 2 | 126.6 | 125.0 | 135.5 | 135.8 |
| C- 3 | 197.9 | 198.3 | 198.3 | 198.2 |
| C- 4 | 50.2 | 47.5 | 47.8 | 48.1 |
| C- 5 | 41.6 | 36.1 | 35.9 | 36.2 |
| C- 6 | 79.0 | 51.0 | 55.4 | 55.7 |
| C- 7 | 132.5[a] | 25.4 | 125.5 | 125.9 |
| C- 8 | 132.6[a] | 36.4 | 129.2 | 129.6 |
| C- 9 | 73.2 | 75.7 | 73.1 | 73.5 |
| C-10 | 22.3 | 21.8 | 22.1 | 22.4 |
| C-11 | 24.5 | 26.9 | 26.8 | 27.1 |
| C-12 | 23.5 | 28.5 | 27.4 | 27.7 |
| C-13 | 19.1 | 24.2 | 22.9 | 23.2 |
| Glcose moiety | | | | |
| 1′ | 101.7 | 103.9 | 101.6 | 101.9 |
| 2′ | 75.0 | 74.8 | 74.9 | 75.1 |
| 3′ | 78.5 | 78.4[a] | 78.4 | 78.7 |
| 4′ | 71.4 | 71.3 | 71.4 | 71.6 |
| 5′ | 78.5 | 78.1[a] | 78.4 | 78.7 |
| 6′ | 62.6 | 62.4 | 62.5 | 62.8 |

*a*) In each vertical column may be interchanged.

pyranosyl kaempferol-4′-*O*-*β*-D-glucopyranoside as shown in the formulae.

Other compounds, **13**—**15**, **16a**, **16b** and **17**—**20** were identical with (−)methyl dihydrophaseate,[13] roseoside,[14] blumenol C-*O*-*β*-D-glycopyranoside,[15] (+)-3-oxo-α-ionyl-*O*-*β*-D-glycopyranoside,[16] (−)-3-oxo-α-ionyl-*O*-*β*-D-glycopyranoside,[16] tuberonic acid 13-*O*-*β*-D-glucopyranoside,[17] benzylalcohol-*O*-α-L-arabinopyranosyl(1→6)-*β*-D-glucopyranoside, piceid[18] and deoxyrhaponticin,[19] respectively, with respect to the electron impact (EI-MS), positve FAB-MS, $^1$H- and $^{13}$C-NMR spectra.

## Experimental

Optical rotations were measured on a JASCO DIP-360 automatic digital polarimeter. The IR spectra were recorded with a Hitachi IR spectrometer, model 270-30. The $^1$H- and $^{13}$C-NMR spectra were measured with a JEOL JNM-GX 400 NMR spectrometer and chemical shifts are given on a $\delta$ (ppm) scale with tetramethylsilane (TMS) as an internal standard. The FAB- and EI-MS were recorded with a JEOL DX-303 HF specrometer and taken in a glycerol matrix containing NaI. Thin layer chromatography (TLC) was performed on a precoated Kieselgel 60 $F_{254}$ plate (0.2 mm Merck) and detection was achieved by spraying 10% $H_2SO_4$ followed by heating. Column chromatography was carried out with Sephadex LH-20 (Pharmacia Co., Ltd.), Bondapak $C_{18}$ (Waters Associates) and Kieselgel 60 (70—230 and 230—400 mesh, Merck).

**Extraction and Separation** The dried seeds (4.5 kg) of *Astragalus complanatus* were extracted with MeOH, and then the extract (371 g) was partitioned between *n*-hexane and 80% MeOH. The 80% MeOH extract was further shaken with 1-BuOH and water. The 1-BuOH soluble portion (90 g) was subjected to Sephadex LH-20 column chromatography with MeOH. The aromatic fractions (28 g) were collected and chromatographed over MCI gel CHP 20P column eluting with water and 10% MeOH→MeOH, gradiently, to afford fourteen fractions based upon the TLC monitoring, which were further separated by column chromatographies on Bondapak $C_{18}$ and silica gel to provide compounds **1** (724 mg), **2** (140 mg), **3** (79 mg), **4** (32 mg), **5** (28 mg), **6** (62 mg), **7** (230 mg), **8** (60 mg), **9** (32 mg), **10** (72 mg), **11** (150 mg), **12** (38 mg), **13** (24 mg), **14** (72 mg), **15** (22 mg), **16a** (17 mg), **16b** (24 mg), **17** (12 mg), **18** (64 mg), **19** (28 mg) and **20** (85 mg).

**Rhamnocitrin 3, 4′-Di-*O*-*β*-D-glucopyranoside (Complanatuside) (1)** A yellow powder, $[\alpha]_D^{25}$ −65.4° (DMSO). UV $\lambda_{max}^{MeOH}$ nm (log ε): 343 (4.34), 267 (4.85). Positive FAB-MS (*m/z*): 625 $[M+H]^+$, 463 $[M-glucose+H]^+$, 301 $[M-2\times glucose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.56 (1H, s, 5-OH), 8.16 (2H, d, $J$=8.8 Hz, 2′,6′-H), 7.18 (2H, d, $J$=8.8 Hz, 3′,5′-H), 6.76 (1H, d, $J$=2.2 Hz, 8-H), 6.38 (1H, d, $J$=2.2 Hz, 6-H), 5.50 (1H, d, $J$=7.3 Hz, glc 1″-H), 5.04 (1H, d, $J$=7.3 Hz, glc 1‴-H), 3.86 (3H, s, 7-OMe). The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**Rhamnocitrin 3-*O*-*β*-D-Apiofuranosyl(1→2)-*β*-D-glucopyranoside (2)** A yellow powder, $[\alpha]_D^{24}$ −125.5° (DMSO). UV $\lambda_{max}^{MeOH}$ nm (log ε): 347 (4.39), 266 (4.47). *Anal.* Calcd for $C_{27}H_{30}O_{15}\cdot 3/2H_2O$: C, 52.17; H, 5.31. Found: C, 52.16; H, 5.26. Positive FAB-MS (*m/z*): 595 $[M+H]^+$, 463 $[M-apiose+H]^+$, 301 $[M-apiose-glucose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.67 (1H, s, 5-OH), 10.26 (1H, s, 4′-OH), 8.16 (2H, d, $J$=8.8 Hz, 2′,6′-H), 6.93 (2H, d, $J$=8.8 Hz, 3′,5′-H), 6.67 (1H, d, $J$=2.2 Hz, 8-H), 6.33 (1H, d, $J$=2.2 Hz, 6-H), 5.72 (1H, d, $J$=7.3 Hz, glc 1″-H), 5.45 (1H, s, api 1‴-H), 3.84 (3H, s, 7-OMe) and NOESY. The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**3-*O*-*β*-D-Apiofuranosyl(1→2)-*β*-D-glucopyranosyl Rhamnocitrin 4′-*O*-*β*-D-Glucopyranoside (3)** A yellow powder, $[\alpha]_D^{24}$ −132.7° (DMSO). UV $\lambda_{max}^{MeOH}$ nm (log ε): 342 (4.39), 316 (4.38), 267 (4.59). *Anal.* Calcd for $C_{33}H_{40}O_{20}\cdot 2H_2O$: C, 50.00; H, 5.56. Found: C, 49.71; H, 5.47. Positive FAB-MS (*m/z*): 757 $[M+H]^+$, 625 $[M-apiose+H]^+$, 595 $[M-glucose+H]^+$, 463 $[M-glucose-apiose+H]^+$, 301 $[M-2\times glucose-apiose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.60 (1H, s, 5-OH), 8.21 (2H, d, $J$=8.8 Hz, 2′,6′-H), 7.17 (2H, d, $J$=8.8 Hz, 3′,5′-H), 6.76 (1H, d, $J$=2.2 Hz, 8-H), 6.38 (1H, d, $J$=2.2 Hz, 6-H), 5.64 (1H, d, $J$=7.3 Hz, glc 1″-H), 5.37 (1H, s, api 1‴-H), 5.05 (1H, d, $J$=7.3 Hz, glc 1⁗-H), 3.86 (3H, s, 7-OMe) and NOESY. The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**Enzymatic Hydrolysis of 3** A solution of **3** (52 mg) in acetate buffer (pH=4.2, 12 ml) was incubated with glucosidase at 37 °C for 34 h and the hydrolysate was extracted with EtOAc. The organic layer was evaporated to dryness and chromatographed over silica gel column [$CHCl_3$–MeOH–$H_2O$ (9:1:0.1→8:2:0.2)] to provide **3a** (18 mg), a yellow amorphous powder, $[\alpha]_D^{24}$ −123.7° (DMSO). UV $\lambda_{max}^{MeOH}$ nm (log ε): 348 (4.39), 267 (4.46). Positive FAB-MS (*m/z*): 595 $[M+H]^+$, 301 $[M-glucose-apiose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.64 (1H, s, 5-OH), 10.24 (1H, s, 4′-OH), 8.14 (2H, d, $J$=8.8 Hz, 2′,6′-H), 6.91 (2H, d, $J$=8.8 Hz, 3′,5′-H), 6.72 (1H, d, $J$=1.83 Hz, 8-H), 6.35 (1H, d, $J$=2.2 Hz, 6-H), 5.67 (1H, d, $J$=7.3 Hz, glc 1″-H), 5.39 (1H, s, api 1‴-H), 3.86 (3H, s, 7-OMe) and NOESY. The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**Kaempferol 3, 4′-Di-*O*-*β*-D-glucopyranoside (4)** A yellow powder, $[\alpha]_D^{26}$ −48.8° (DMSO). Positive FAB-MS (*m/z*): 611 $[M+H]^+$, 449 $[M-glucose+H]^+$, 287 $[M-2\times glucose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.48 (1H, s, 5-OH), 10.30 (1H, s, 7-OH), 8.10 (2H, d, $J$=8.8 Hz, 2′,6′-H), 7.14 (2H, d, $J$=8.8 Hz, 3′,5′-H), 6.38 (1H, s, 8-H), 6.17 (1H, s, 6-H), 5.44 (1H, d, $J$=7.3 Hz, glc 1″-H), 5.02 (1H, d, $J$=7.3 Hz, glc 1‴-H). The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**3-*O*-*β*-D-Apiofuranosyl(1→2)-*β*-D-glucopyranosyl Kaempferol 4′-*O*-*β*-D-Glucopyranoside (5)** A yellow powder, $[\alpha]_D^{24}$ −92.0° (DMSO). UV $\lambda_{max}^{MeOH}$ nm (log ε): 343 (4.35), 304 (4.35), 267 (4.57). *Anal.* Calcd for $C_{32}H_{38}O_{20}\cdot 3/2H_2O$: C, 49.93; H, 5.33. Found: C, 49.75; H, 5.19. Positive FAB-MS (*m/z*): 743 $[M+H]^+$, 611 $[M-apiose+H]^+$, 581 $[M-glucose+H]^+$, 449 $[M-glucose-apiose+H]^+$, 287 $[M-2\times glucose-apiose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.60 (1H, s, 5-OH), 10.31 (1H, s, 7-OH), 8.15 (2H, d, $J$=8.8 Hz, 2′,6′-H), 7.14 (2H, d, $J$=8.8 Hz, 3′,5′-H), 6.48 (1H, s, 8-H), 6.23 (1H, s, 6-H), 5.61 (1H, d, $J$=7.3 Hz, glc 1″-H), 5.34 (1H, s, api 1‴-H), 5.03 (1H, d, $J$=7.3 Hz, glc 1⁗-H). The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**Kaempferol 3-*O*-*β*-D-Xylopyranosyl(1→2)-*β*-D-glucopyranoside (6)** A yellow powder, $[\alpha]_D^{26}$ −69.5° (MeOH). Positive FAB-MS (*m/z*): 581 $[M+H]^+$, 287 $[M-xylose-glucose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.67 (1H, s, 5-OH), 10.38 (2H, br s, 7,4′-OH), 8.11 (2H, d, $J$=8.8 Hz, 2′,6′-H), 6.91 (2H, d, $J$=8.8 Hz, 3′,5′-H), 6.46 (1H, s, 8-H), 6.21 (1H, s, 6-H), 5.73 (1H, d, $J$=7.3 Hz, glc 1″-H), 4.62 (1H, d, $J$=6.6 Hz, xyl 1‴-H). The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**Myricetin 3-*O*-*β*-D-Glucopyranoside (7)** A yellow powder, $[\alpha]_D^{26}$ −25.3° (DMSO). Positive FAB-MS (*m/z*): 481 $[M+H]^+$, 319 $[M-glucose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 7.21 (2H, s, 2′,6′-H), 6.39 (1H, d, $J$=1.8 Hz, 8-H), 6.21 (1H, d, $J$=1.8 Hz, 6-H), 5.48 (1H, d, $J$=7.7 Hz, glc 1″-H). The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**Myricetin 3-*O*-*β*-D-Xylopyranosyl(1→2)-*β*-D-glucopyranoside (8)** A yellow powder, $[\alpha]_D^{24}$ −58.8° (MeOH), Positive FAB-MS (*m/z*): 613 $[M+H]^+$, 595 $[M-H_2O+H]^+$, 481 $[M-xylose+H]^+$, 319 $[M-xylose-glucose+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.70 (1H, s, 5-OH), 7.23 (2H, s, 2′,6′-H), 6.36 (1H, d, $J$=1.5 Hz, 8-H), 6.17 (1H, d, $J$=1.5 Hz, 6-H), 5.76 (1H, d, $J$=7.3 Hz, glc 1″-H), 4.62 (1H, d, $J$=7.3 Hz, xyl 1‴-H). The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**Myricetin 3′-*O*-*β*-D-Glucopyranoside (Cannabiscitrin) (9)** A yellow powder, $[\alpha]_D^{24}$ −37.3° (MeOH). Positive FAB-MS (*m/z*): 481 $[M+H]^+$, 319 $[M-\text{glucose}+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 12.47 (1H, s, 5-OH), 10.82 (1H, s, 7-OH), 9.43 (1H, s, 4′-OH), 9.34 (1H, s, 5′-OH), 8.87 (1H, s, 3-OH), 7.56 (2H, s, 2′,6′-H), 6.48 (1H, d, $J$=2.2 Hz, 8-H), 6.21 (1H, d, $J$=2.2 Hz, 6-H), 4.75 (1H, d, $J$=6.6 Hz, glc 1″-H). The $^{13}$C-NMR spectrum (in DMSO-$d_6$) is listed in Table I.

**Formononetin 7-*O*-*β*-D-Glucopyranoside (Ononin) (10)** A white powder, $[\alpha]_D^{26}$ −20.2° (DMSO). Positive FAB-MS (*m/z*): 431 $[M+H]^+$, 269 $[M-\text{glucose}+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 8.43 (1H, s, 2-H), 8.07 (1H, d, $J$=8.8 Hz, 5-H), 7.53 (1H, d, $J$=2.2 Hz, 2′,6′-H), 7.25 (1H, d, $J$=2.2 Hz, 8-H), 7.16 (1H, dd, $J$=8.8, 2.2 Hz, 6-H), 7.00 (2H, d, $J$=8.8 Hz, 3′,5′-H), 5.11 (1H, d, $J$=7.3 Hz, glc 1″-H), 3.79 (3H, s, 4′-OMe) and NOESY. $^{13}$C-NMR (in DMSO-$d_6$) $\delta$: 174.6 (C-4), 161.4 (C-7), 158.9 (C-4′), 157.0 (C-9), 153.5 (C-2), 130.0 (C-2′,6′), 126.9 (C-5), 123.9 (C-1′), 123.3 (C-3), 118.4 (C-10), 115.5 (C-6), 113.5 (C-3′,5′), 103.3 (C-8), 99.9 (C-1″), 77.1 (C-5″), 76.4 (C-3″), 73.0 (C-2″), 69.5 (C-4″), 60.5 (C-6″), 55.0 (3′-OMe).

**Calycosin (11)** Colorless plates (MeOH), Gibb's test (+), mp 236—237 °C, $[\alpha]_D^{24}$ +3.75° (MeOH). EI-MS (*m/z*): 284 $[M]^+$, 269 $[M-CH_3]^+$, 255, 241 $[M-CO-CH_3]^+$, 213 $[M-2\times CO-CH_3]^+$, 137. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 9.05 (1H, s, 3′-OH), 8.28 (1H, s, 2-H), 8.00 (1H, d, $J$=8.8 Hz, 5-H), 7.08 (1H, t, $J$=1.1 Hz, 6′-H), 6.96 (2H, d, $J$=1.1 Hz, 2′,5′-H), 6.95 (1H, dd, $J$=8.8, 2.2 Hz, 6-H), 6.88 (1H, d, $J$=2.2 Hz, 8-H), 3.81 (3H, s, 4′-OMe) and NOESY. $^{13}$C-NMR (in DMSO-$d_6$) $\delta$: 174.5 (C-4), 162.4 (C-7), 157.3 (C-9), 152.9 (C-2), 147.4 (C-4′), 146.0 (C-3′), 127.2 (C-5), 124.7 (C-3), 123.3 (C-1′), 119.6 (C-6′), 116.6 (C-10), 116.4 (C-5′), 115.0 (C-6), 111.8 (C-2′), 102.0 (C-8), 55.6 (3′-OMe).

**Calycosin 7-*O*-*β*-D-Glucopyranoside (12)** A white powder, Gibb's test (+), $[\alpha]_D^{26}$ −42.3° (DMSO). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 285 (4.25), 260 (4.44), 219 (4.59), 203 (4.63). Positive FAB-MS (*m/z*): 447 $[M+H]^+$, 285 $[M-\text{glucose}+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 9.04 (1H, s, 3′-OH), 8.39 (1H, s, 2-H), 8.06 (1H, d, $J$=8.8 Hz, 5-H), 7.24 (1H, d, $J$=2.2 Hz, 8-H), 7.15 (1H, dd, $J$=8.8, 2.2 Hz, 6-H), 7.08 (1H, br s, 6′-H), 6.97 (2H, br s, 2′,5′-H), 5.11 (1H, d, $J$=7.3 Hz, glc 1″-H), 3.80 (3H, s, 4′-OMe) and NOESY. $^{13}$C-NMR (in DMSO-$d_6$) $\delta$: 174.5 (C-4), 161.3 (C-7), 156.9 (C-9), 153. 4 (C-2), 147.5 (C-4′), 145.9 (C-3′), 126.9 (C—5), 124.3 (C-3), 123.5 (C-1′), 119.6 (C-6′), 118.4 (C-10), 116.3 (C-5′), 115.5 (C-6), 111.8 (C-2′), 103.3 (C-8), 99.9 (C-1″), 77.1 (C-5″), 76.4 (C-3″), 73.0 (C-2″), 69.5 (C-4″), 60.6 (C-6″), 55.6 (3′-OMe).

**(−) Methyl Dihydrophaseate (13)** A white powder, $[\alpha]_D^{25}$ −71.8° ($CHCl_3$). EI-MS (*m/z*): 296 $[M]^+$, 278 $[M-H_2O]^+$, 264, 246, 220, 188, 154, 122, 109, 94. $^1$H-NMR (in pyridine-$d_5$) $\delta$: 8.79 (1H, d, $J$=15.8 Hz, 1′-H), 6.95 (1H, d, $J$=15.8 Hz, 2′-H), 5.83 (1H, s, 4′-H), 4.70—4.77 (1H, m, 3-H), 4.21 (1H, d, $J$=7.3, 1.5 Hz, 7-$H_a$), 3.94 (1H, d, $J$=7.3 Hz, 7-$H_b$), 2.55 (1H, dd, $J$=13.2, 7.3 Hz, 4-$H_a$), 2.30 (1H, dd, $J$=13.6, 10.3 Hz, 2-$H_a$), 2.21 (1H, dd, $J$=13.2, 6.6 Hz, 4-$H_b$), 2.20 (1H, m, overlapped, 2-$H_b$), 1.92 (3H, s, 3′-Me), 1.52 (3H, s, 5-Me), 1.18 (3H, s, 1-Me). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: 166.3 (C-5′), 150.8 (C-3′), 136.6 (C-1′), 130.4 (C-4′), 117.4 (C-2′), 86.8 (C-8), 82.8 (C-5), 76.7 (C-7), 65.0 (C-3), 50.7 (COOMe), 49.1 (C-1), 46.7 (C-4), 45.1 (C-2), 20.8 (3′-Me), 20.2 (5-Me), 16.6 (1-Me).

**Roseoside (14)** A white powder, $[\alpha]_D^{26}$ +64.0° (MeOH). Positive FAB-MS (*m/z*): 387 $[M+H]^+$, 225 $[M-\text{glucose}+H]^+$. $^1$H-NMR (in pyridine-$d_5$) $\delta$: 6.55 (1H, d, $J$=15.4 Hz, 7-H), 6.19 (1H, dd, $J$=15.4, 6.2 Hz, 8-H), 6.00 (1H, s, 2-H), 4.97 (1H, d, $J$=8.1 Hz, glc 1′-H), 4.86 (1H, m, 9-H), 3.10 (1H, d, $J$=16.5 Hz, 4-$H_a$), 2.49 (1H, d, $J$=16.9 Hz, 4-$H_b$), 2.03 (3H, s, 13-H), 1.36 (3H, d, $J$=6.2 Hz, 10-H), 1.28 (3H, s, 11-H), 1.22 (3H, s, 12-H). The $^{13}$C-NMR spectrum (in pyridine-$d_5$) is listed in Table II.

**Blumenol C-*O*-*β*-D-Glucopyranoside (15)** A white powder, $[\alpha]_D^{26}$ +47.3° (MeOH). Positive FAB-MS (*m/z*): 395 $[M+Na]^+$, 373 $[M+H]^+$, 211 $[M-\text{glucose}+H]^+$. $^1$H-NMR (in pyridine-$d_5$) $\delta$: 5.89 (1H, s, 2-H), 4.87 (1H, d, $J$=7.7 Hz, glc 1′-H), 4.02 (1H, m, 9-H), 2.48 (1H, d, $J$=16.9 Hz, 4-$H_a$), 2.07 (1H, d, $J$=16.9 Hz, 4-$H_b$), 1.86 (3H, s, 13-H), 1.66—1.78 (5H, m, 6, 7, 8-H), 1.35 (3H, d, $J$=6.2 Hz, 10-H), 0.97 (3H, s, 11-H), 0.93 (3H, s, 12-H). The $^{13}$C-NMR spectrum (in pyridine-$d_5$) is listed in Table II.

**(+)-3-Oxo-α-ionyl-*O*-*β*-D-Glucopyranoside (16a)** A white powder, $[\alpha]_D^{26}$ +96.8° (MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 237 (4.21). Positive FAB-MS (*m/z*): 371 $[M+H]^+$, 209 $[M-\text{glucose}+H]^+$. $^1$H-NMR (in pyridine-$d_5$) $\delta$: 5.95 (1H, dd, $J$=9.5, 15.4 Hz, 7-H), 5.94 (1H, s, 2-H), 5.66 (1H, dd, $J$=15.4, 6.6 Hz, 8-H), 4.90 (1H, d, $J$=8.1 Hz, glc 1′-H), 4.72 (1H, m, 9-H), 2.67 (1H, d, $J$=16.5 Hz, 4-$H_a$), 2.49 (1H, d, $J$=9.5 Hz, 6-H), 2.17 (1H, d, $J$=16.5 Hz, 4-$H_b$), 1.81 (3H, s, 13-H), 1.36 (3H, d, $J$=6.2 Hz, 10-H), 0.95 (3H, s, 11-H), 0.93 (3H, s, 12-H). The $^{13}$C-NMR spectrum (in pyridine-$d_5$) is listed in Table II.

**(−)-3-Oxo-α-ionyl-*O*-*β*-D-Glucopyranoside (16b)** A white powder, $[\alpha]_D^{26}$ −225.2° (MeOH). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 236 (4.22). Positive FAB-MS (*m/z*): 393 $[M+Na]^+$, 209 $[M-\text{glucose}+H]^+$. $^1$H-NMR (in pyridine-$d_5$) $\delta$: 6.01 (1H, s, 2-H), 5.83 (1H, dd, $J$=9.5, 15.4 Hz, 7-H), 5.66 (1H, dd, $J$=15.4, 6.6 Hz, 8-H), 4.95 (1H, d, $J$=7.7 Hz, glc 1′-H), 4.73 (1H, m, 9-H), 2.50 (1H, d, $J$=9.5 Hz, 6-H), 2.47 (1H, d, $J$=16.1 Hz, 4-$H_a$), 2.14 (1H, d, $J$=16.5 Hz, 4-$H_b$), 1.78 (3H, s, 13-H), 1.36 (3H, d, $J$=6.2 Hz, 10-H), 0.95 (3H, s, 11-H), 0.93 (3H, s, 12-H). The $^{13}$C-NMR spectrum (in pyridine-$d_5$) is listed in Table II.

**Tuberonic Acid 13-*O*-*β*-D-Glucopyranoside (17)** A white powder, $[\alpha]_D^{26}$ +96.8° (MeOH). Positive FAB-MS (*m/z*): 371 $[M+H]^+$, 209 $[M-\text{glucose}+H]^+$. $^1$H-NMR (in pyridine-$d_5$) $\delta$: 5.59 (1H, dt, $J$=10.6, 7.3 Hz, 10-H), 5.48 (1H, ddd, $J$=10.6, 7.7, 7.3 Hz 9-H), 4.87 (1H, d, $J$=7.7 Hz, glc 1′-H), 4.13 (1H, dd, $J$=16.5, 7.3 Hz, 12-$H_a$), 3.74 (1H, dd, $J$=16.5, 7.3 Hz, 12-$H_b$), 2.73 (1H, dd, $J$=14.3, 3.7 Hz, 5-$H_a$), 2.54 (2H, dd, $J$=14.3, 7.0 Hz, 11-H), 2.40—2.45 (2H, m, 8-H), 2.33—2.39 (2H, m, 7-H, 5-$H_b$), 2.24—2.31 (1H, m, 2-$H_a$), 2.10—2.17 (1H, m, 3-H), 2.05 (1H, m, 2-$H_b$), 1.96 (1H, m, 4-$H_a$), 1.44 (1H, m, 4-$H_b$). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: 218.1 (C-6), 172.6 (C-1), 128.3 (C-9), 128.2 (C-10), 104.7 (C-1′), 78.5 (C-3′,5′), 75.1 (C-2′), 71.6 (C-4′), 69.1 (C-12), 62.8 (C-6′), 53.9 (C-7), 51.4 (COOMe), 38.8 (C-5), 38.1 (C-3), 37.7 (C-2), 28.2 (C-11), 27.3 (C-4), 25.8 (C-8). $^1$H–$^1$H correlation spectroscopy (COSY), $^1$H–$^{13}$C COSY and $^1$H–$^{13}$C long range COSY.

**Benzylalcohol *O*-α-L-Arabinopyranosyl(1→6)-*β*-D-glucopyranoside (18)** A white powder, $[\alpha]_D^{27}$ −39.8° (MeOH). Positive FAB-MS (*m/z*): 425 $[M+Na]^+$, 403 $[M+H]^+$. $^1$H-NMR (in pyridine-$d_5$) $\delta$: 7.22—7.57 (5H, m), 5.20, 4.82 (2H, ABq, $J$=12.1 Hz), 4.96 (1H, d, $J$=7.0 Hz), 4.89 (1H, d, $J$=7.7 Hz). $^{13}$C-NMR (in DMSO-$d_6$) $\delta$: 138 (s), 128.2×2 (d), 127.8×2 (d), 127.4 (d), 103.6 (d), 102.0 (d), 76.7 (d), 75.8 (d), 73.4 (d), 72.6 (d), 70.6 (d), 70.3 (d), 69.6 (t), 68.2 (t), 67.4 (d), 64.9 (t).

**Piceid (19)** A white powder, $[\alpha]_D^{27}$ −77.7° (MeOH). Positive FAB-MS (*m/z*): 391 $[M+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 7.40 (2H, d, $J$=8.4 Hz), 7.03 (1H, d, $J$=16.1 Hz), 6.86 (1H, d, $J$=16.1 Hz), 6.76 (2H, d, $J$=8.4 Hz), 6.73 (1H, s), 6.57 (1H, s), 6.34 (1H, s), 4.80 (1H, d, $J$=7.3 Hz). $^{13}$C-NMR (in DMSO-$d_6$) $\delta$: 158.8 (s), 158.2 (s), 157.2 (s), 139.2 (s), 128.4 (d), 127.9 (s), 127.8×2 (d), 125.1 (d), 115.4×2 (d), 107.1 (d), 104.6 (d), 102.6 (d), 100.6 (d), 77.0 (d), 76.6 (d), 73.2 (d), 69.6 (d), 60.6 (t).

**Deoxyrhaponticin (20)** A white powder, $[\alpha]_D^{27}$ −63.9° (MeOH). Positive FAB-MS (*m/z*): 405 $[M+H]^+$, 243 $[M-\text{glcose}+H]^+$. $^1$H-NMR (in DMSO-$d_6$) $\delta$: 7.53 (2H, d, $J$=8.4 Hz), 7.09 (1H, d, $J$=16.1 Hz), 6.95 (1H, d, $J$=16.1 Hz), 6.93 (2H, d, $J$=8.4 Hz), 6.76 (1H, s), 6.59 (1H, s), 6.36 (1H, s), 4.81 (1H, d, $J$=7.3 Hz), 3.77 (3H, s) and NOESY. $^{13}$C-NMR (in DMSO-$d_6$) $\delta$: 158.9 (s), 158.8(s), 158.3 (s), 139.1 (s), 129.5 (s), 128.1 (d), 127.7×2 (d), 126.2 (d), 114.1×2 (d), 107.3 (d), 104.8 (d), 102.9 (d), 100.6 (d), 77.0 (d), 76.6 (d), 73.2 (d), 69.7 (d), 60.7 (t), 55.5 (q).

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**References and Notes**

1) Part XXXV in the series of studies on the constituents of leguminous plants.
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