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Studies on the Constituents of *Pueraria lobata*. IV.[1] Chemical Constituents in the Flowers and the Leaves

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A new triterpenoidal saponin, 3-*O*-[α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranosyl(1→2)-β-D-glucuronopyranosyl]sophoradiol (I), was isolated from the flowers of *Pueraria lobata* (WILLD.) OHWI (Leguminosae). Its structure was elucidated on the basis of chemical and physicochemical evidence. In addition, a known oligoglycoside kaikasaponin III (II) was isolated from both flowers and leaves of this plant, together with several known aromatic compounds.

Keywords——*Pueraria lobata*; Leguminosae; oleanene-saponin; sophoradiol; ^{13}C-NMR spectrum

In the course of our systematic studies on the constituents of *Pueraria lobata* (WILLD.) OHWI (Leguminosae), we found a series of triterpenoidal saponins in Pueraiae Radix, the roots of *P. lobata*, and elucidated the structures of their aglycones.[2] Furthermore, we isolated two novel aromatic glycosides, puerosides A and B,[3] besides fifteen isoflavonoids and related compounds,[1] from this crude drug. Meanwhile, Puerariae Flos, the flowers of this plant, is also an important oriental crude drug used to ameliorate crapulence. Its extract has a promotive action on alcholic metabolism.[4] As regards the constituents, many isoflavonoids have been reported.[5] We were interested in surveying the constituents of the flowers and leaves of this plant, which is abundant in nature. This paper deals with the chemical constituents in the flowers and the leaves of the title plant.

The methanolic extract of the dried flowers of *P. lobata* was partitioned between *n*-BuOH and water. Evaporation of the organic solvent provided a residue, from which by a combination of MCI gel CHP 20P and silica gel column chromatographies and some other means, a new oleanene-saponin (Ia) was obtained together with a known saponin (IIa)[6] and a phenolic (III). In a similar manner, the extract from the leaves of *P. lobata* gave II and compounds IV—VIII. Compounds III—VIII were identified as kakkalide,[5b] daidzin,[7] genistin,[8] rutin,[9] robinin (kaempferol 3-*O*-rhamnosyl (1→6)galactosyl-7-*O*-rhamnoside)[10] and nicotiflorin(kaempferol 3-*O*-rutinoside),[11] respectively, by comparison of their physical and spectral data with the reported values.

The infrared (IR) spectrum of Ia showed ester carbonyl (1746 cm^{-1}) and hydroxy (3400 cm^{-1}) absorptions. Methanolysis of Ia furnished a sapogenol identical with sophoradiol (Ib). The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectral data (Table I) of Ia showed thirty signals which were superimposable on those of Ib[2] except for that of C-3,

TABLE I. ^{13}C-NMR Spectral Data for the Aglycone Moieties of Ib, Ia and II (Pyridine-d_5)

	Ib	Ia	II
C-1	39.2	38.9	38.8
C-2	28.2	26.6	26.5
C-3	78.1	89.3	89.9
C-4	39.4	39.5	39.6
C-5	55.9	55.8	55.8
C-6	18.9	18.5	18.5
C-7	33.3	33.2	33.2
C-8	40.1	40.0	39.9
C-9	48.1	47.9	47.9
C-10	37.3	36.9	36.8
C-11	23.9	23.8	23.7
C-12	122.5	122.5	122.5
C-13	144.9	144.8	144.7
C-14	42.5	42.3	42.3
C-15	26.5	26.5	26.4
C-16	28.7	28.7	28.6
C-17	38.0	38.0	37.9
C-18	45.4	45.3	45.3
C-19	46.9	46.8	46.7
C-20	30.9	30.9	30.8
C-21	42.3	42.4	42.2
C-22	75.6	75.6	75.5
C-23	28.8	28.7	28.6
C-24	15.9	15.7	15.6
C-25	16.6	16.9	16.7
C-26	17.3	17.1	17.1
C-27	25.8	25.8	25.7
C-28	28.8	28.2	28.3
C-29	33.3	33.3	33.2
C-30	21.2	21.2	21.1

TABLE II. ^{13}C-NMR Spectral Data for the Sugar Moieties of Ia, II and IXa (Pyridine-d_5)

	Ia	II	IXa
3-Glucuronic acid C-1′	105.7	105.2	105.3
C-2′	79.0	79.0	77.9
C-3′	74.9	76.1	76.3
C-4′	72.9	73.4	72.5
C-5′	77.3	77.2	76.8
C-6′	170.1	172.6	170.0
6′-COOMe	52.0		52.0
2′-Arabinose C-1″	100.7		
C-2″	76.8		
C-3″	66.6		
C-4″	71.7		
C-5″	62.9		
2′-Galactose C-1″		101.9	101.7
C-2″		78.5	77.5
C-3″		76.0	74.3
C-4″		70.3	71.0
C-5″		76.5	76.8
C-6″		61.8	61.7
2″-Rhamnose C-1‴	102.3	102.6	102.0
C-2‴	72.4	72.2	72.1
C-3‴	72.6	72.5	72.5
C-4‴	74.0	74.2	73.3
C-5‴	70.3	69.3	69.2
C-6‴	18.8	18.5	18.7

where a glycosylation shift[12] was observed. In addition, Ia exhibited eighteen signals in the sugar region (Table II), including three anomeric carbons and one methyl carbon of the ester moiety. Furthermore, the peracetyl derivative (Ic) of Ia gave fragment ion peaks at *m/z* 273 (terminal peracetylated methylpentosyl cation)[13a] and *m/z* 489 (terminal peracetylated methylpentosyl pentosyl cation)[13a] in the electron impacting-mass spectrum (EI-MS). These peaks suggested that *Ia* possessed a terminal methylpentosyl-pentosyl moiety in the carbohydrate residue.

In order to clarify the structure of Ia, chemical modification of Ia was conducted. Methylation of Ia with methyl iodide and dimsyl carbanion[14] furnished the nona-*O*-methyl derivative (Id). The IR spectrum of Id showed no hydroxy absorption but gave an ester carbonyl absorption. The ^{1}H-NMR spectrum of Id also gave nine singlet signals at lower field ascribable to eight methoxy and one methyl ester cabons. $NaBH_4$ reduction of Id afforded the product Ie, which showed no ester carbonyl absorption but gave a weak hydroxy absorption in the IR spectrum. Its ^{1}H-NMR spectrum showed eight methoxy signals.

Methanolic acid hydrolysis of Ie liberated 22-*O*-methyl-sophoradiol (If) together with sugar components a and b. The EI-MS of If showed the prominent fragment ion peak (D/E ring) at *m/z* 248 which was derived from the characteristic *retro* Diels–Alder type fragmentation at ring C.[13b] Compounds a and b were shown to be identical with authentic samples of

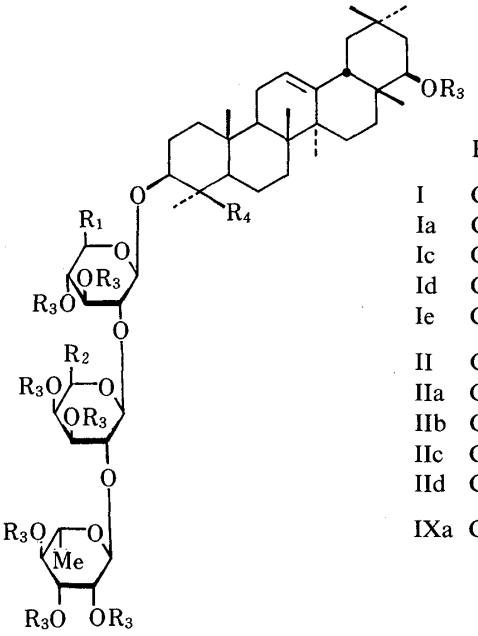
methyl 2,3,4-tri-*O*-methyl rhamnopyranoside and methyl 3,4-di-*O*-methylglucopyranoside, respectively, by means of thin layer chromatographic (TLC) analysis. Based on the evidence described above, the structure of I was assumed to be 3-*O*-[rhamnopyranosyl-pentosyl (1→2)glucuronopyranosyl]sophoradiol.

By comparison with the ^{13}C-NMR spectral data reported by Tori *et al.*,[15] those of Ia suggested the occurrence of an α-L-arabinopyranosyl residue and the 1→2 linkage between arabinose and rhamnose in the molecule. They also supported the presence of α-L-rhamnopyranosyl and β-D-glucuronopyranosyl moieties. In addition, glycosylation shifts at C-1—3 of glucuronic acid were observed. The accumulated evidence described above has led us to conclude that the structure of I is as illustrated.

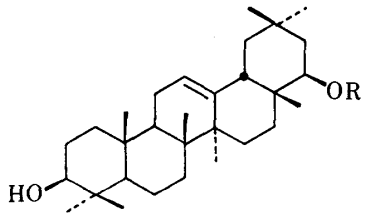
Compound II, colorless fine needles, mp 170—172 °C, $[\alpha]_D$ −8.1° (pyridine), showed strong hydroxy and carboxylic absorptions in the IR spectrum. Acid methanolysis of II provided sophoradiol (Ib) as in the case of Ia. The EI-MS of the acetylated derivative (IIb) exhibited two peaks at *m/z* 273 (terminal peracetylated methylpentosyl cation) and 561 (terminal peracetylated methylpentosyl hexosyl cation).

Complete methylation with methyl iodide and dimsyl carbanion furnished the daca-*O*-methyl derivative (IIc), which shows no hydroxy absorption in the IR spectrum. $NaBH_4$ reduction followed by methanolysis of IIc liberated methyl 2,3,4-tri-*O*-methylrhamnopyranoside (a), methyl 3,4-di-*O*-methylglucopyranoside (b) and methyl 3,4,6-tri-*O*-methylgalactopyranoside (d) from the carbohydrate moiety and 22-*O*-methylsophoradiol (If) as the sapogenol.

The structure of II was supported by its ^{13}C-NMR spectral data (Tables I and II) in comparison with those of soyasaponin I methyl ester (IXa).[16] Based on these data, the structure of II was concluded to be 3-*O*-[α-L-rhamnopyranosyl(1→2)β-D-garactopyranosyl(1→2)β-D-glucuronopyranosyl]sophoradiol, *i.e.*, kaikasaponin III.[6]



	R_1	R_2	R_3	R_4	
I	COOH	H	H	CH_3	
Ia	COOMe	H	H	CH_3	
Ic	COOMe	H	Ac	CH_3	
Id	COOMe	H	Me	CH_3	
Ie	CH_2OH	H	Me	CH_3	
II	COOH	CH_2OH	H	CH_3	(kaikasaponin III)
IIa	COOMe	CH_2OH	H	CH_3	
IIb	COOH	CH_2OAc	Ac	CH_3	
IIc	COOMe	CH_2OMe	Me	CH_3	
IId	CH_2OH	CH_2OMe	Me	CH_3	
IXa	COOMe	CH_2OH	H	CH_2OH	(soyasaponin I methyl ester)



	R	
Ib	H	(sophoradiol)
If	Me	

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-360 digital polarimeter (cell length: 0.5 dm). EI-MS were recorded with a JEOL JMS-01SG spectrometer. ^{1}H (400 MHz)- and ^{13}C (67.5 MHz)-NMR spectra were taken with JEOL GX-400 and GX-270 spectrometers, respectively. IR spectra were obtained with a Hitachi 215 IR-spectrometer. Column chromatography was carried out with Sephadex LH-20 (25—100 μm, Pharmacia Fine Chem. Co., Ltd.), MCI gel CHP 20P (75—100 μm, Mitsubishi Chem. Ind. Co., Ltd.) and Kieselgel 60 (70—230 mesh, Merck). TLC was conducted on precoated Kieselgel 60 F_{254} plates (0.2 mm, Merck) with $CHCl_3$–MeOH–H_2O (7 : 3 : 0.5) and *n*-hexane–acetone (3 : 1); spots were located by ultraviolet illumination and by the use of 10% H_2SO_4 sprays. For gas-liquid chromatography (GLC), a Shimadzu GC-3BF apparatus was used.

Extraction and Isolation——The flowers of *Pueraria lobata* (1.85 kg) were powdered, then extracted with refluxing MeOH. Removal of the solvent under reduced pressure gave the MeOH extract (340 g). The MeOH extract was partitioned into *n*-BuOH–water and removal of the solvent from the organic phase provided the *n*-BuOH extract (115 g). Separation of the *n*-BuOH extract by MCI gel CHP 20P column chromatography (H_2O–MeOH (1 : 1→0 : 1)) furnished crude saponin fraction (6 g) and kakkalide (III, 30 g). A solution of the crude saponin fraction in MeOH was treated with excess ethereal diazomethane and the reaction mixture was allowed to stand overnight. The product obtained after removal of the solvent under reduced pressure was purified by MCI gel CHP 20P (H_2O–MeOH (1 : 1→0 : 1)) and silica gel ($CHCl_3$–MeOH–H_2O (8 : 2 : 0.2)) column chromatographies to give compounds Ia (100 mg) and IIa (60 mg). In a similar manner, the leaves of *P. lobata* (1 kg) gave kaikasaponin III (II, 200 mg), daidzin (IV, 400 mg), genistin (V, 20 mg), rutin (VI, 350 mg), robinin (VII, 500 mg) and nicotiflorin (VIII, 350 mg).

Ia——A white amorphous powder, $[\alpha]_D^{22}$ −4.3° (c=0.5, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1746 (COOMe). ^{13}C-NMR: Tables I and II.

Methanolysis of Ia——A solution of Ia (5 mg) in 1 N HCl–MeOH (3 ml) was heated under reflux for 2 h. After neutralization with 1 N NaOH–MeOH solution, the reaction mixture was filtered to remove the inorganic material. Removal of the solvent from the filtrate gave the product, which was identified as sophoradiol (Ib) by TLC comparisons (*Rf* 0.40, *n*-hexane–acetone (3 : 1); *Rf* 0.54, $CHCl_3$–MeOH (49 : 1)) with an authentic sample.

Acetylation of Ia——A solution of Ia (10 mg) in Ac_2O–pyridine (1 : 1, 1 ml) was allowed to stand at room temperature (20 °C) for 12 h. The reaction mixture was evaporated under an N_2 atmosphere to give Ic. Ic, a white amorphous powder, EI-MS (*m/z*): 273 (terminal peracetylated methylpentosyl cation), 489 (terminal peracetylated methylpentosyl pentosyl cation).

Methylation of Ia——A solution of Ia (80 mg) in dimethyl sulfoxide (DMSO) (4 ml) was treated with dimsyl carbanion solution (3 ml) and the whole mixture was stirred under an N_2 atmosphere at 50°C for 1 h. The reaction mixture was cooled, then treated with methyl iodide (5 ml) and the whole was stirred at room temperature (20 °C) for 15 h, then poured into ice-water and extracted with diethyl ether. The diethyl ether extract was washed with 10% aqueous $Na_2S_2O_3$ and water, and then dried over Na_2SO_4. The product obtained by evaporation of the solvent under reduced pressure was purified by silica gel column chromatography (*n*-hexane–acetone (9 : 1→4 : 1)) to furnish the nona-*O*-methyl derivative (Id, 15 mg). Id, a white amorphous powder, $[\alpha]_D^{23}$ −4.8° (c=1.3, pyridine). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1748 (COOMe), no OH. ^{1}H-NMR ($CDCl_3$) δ: 0.85 (6H), 0.90, 0.92, 0.95, 1.00, 1.05, 1.10 (3H each, all s, *tert*-Me×8), 1.22 (3H, d, J=6 Hz, rhamnose 6-Me), 3.28, 3.36, 3.44, 3.46, 3.47, 3.49, 3.52, 3.68, 3.80 (3H each, all s, OMe×8 and COOMe×1), 4.31, 4.63 (1H each, both d, J=8 Hz, glucuronic acid and arabinose 1-H), 5.21 (2H, br s, 12-H and rhamnose 1-H).

$NaBH_4$ Reduction of Id——A solution of Id (10 mg) in MeOH was treated with a mixture of $NaBH_4$ (50 mg) in MeOH at room temperature for 24 h. The reaction mixture was then neutralized with AcOH. After filtration to remove the inorganic precipitate, the filtrate was concentrated. The concentrate was subjected to silica gel column chromatography (*n*-hexane–acetone (3 : 1)) to furnish the reduction product (Ie, 3 mg). Ie, a white amorphous powder. $[\alpha]_D^{20}$ −10.4° (c=0.25, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3688 (OH), no COOMe. ^{1}H-NMR ($CDCl_3$) δ: 0.86, 0.88, 0.90, 0.90, 1.00, 1.09, 1.10 (each 3H, all s, *tert*-Me×8), 3.28, 3.36, 3.44, 3.46, 3.47, 3.52, 3.55, 3.69 (each 3H, all s, OMe×8).

Methanolysis of Ie——A solution of Ie (2 mg) in 3 N HCl–MeOH was heated under reflux for 5 h. The reaction mixture was neutralized with 1 N NaOH–MeOH and filtered. After evaporation of the solvent from the filtrate under reduced pressure, the residue was subjected to silica gel column chromatography (*n*-hexane–acetone (4 : 1)) to give 22-*O*-methylsophoradiol (If) and compounds a, b and c. If, colorless needles, mp 171—173 °C. $[\alpha]_D^{22}$ +26.7° (c=0.1, $CHCl_3$) EI-MS *m/z*: 456 (M^+), 248. Compounds a and b were shown to be identical with authentic samples of methyl 2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside and methyl 3,4-di-*O*-methyl-α-D-glycopyranoside, respectively by means of TLC [solv. EtOAc–MeOH (25 : 1); *Rf*, a 0.25, b 0.73] analysis. Compound c could not be definitively identified owing to the lack of an authentic specimen of methyl 3,4-di-*O*-methylarabinopyranoside.

Kaikasaponin III(II)——Colorless fine needles, mp 170—172 °C. $[\alpha]_D^{22}$ −8.1° (c=1.0, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3400(OH), 1720 (COOH). ^{13}C-NMR: Tables I and II.

Methanolysis of II——A solution of II (5 mg) in 1N HCl–MeOH was heated under reflux for 2 h. The reaction mixture was worked up as described in the case of Ia and the filtrate was shown to be identical with sophoradiol (Ib)

by TLC analysis (as above) in comparison with the authentic sample.

Acetylation of II——A solution of II (10 mg) in Ac_2O–pyridine (1 : 1, 1 ml) was allowed to stand at room temperature (20 °C) for 12 h. The reaction mixture was worked-up as described above to give IIb. IIb, a white amorphous powder, EI-MS *m/z*: 273 (terminal peracetylated methylpentosyl cation), 561 (terminal peracetylated methylpentosyl hexosyl cation).

Complete Methylation of II——A solution of II (40 mg) in DMSO (2 ml) was methylated with dimsyl carbanion (2 ml) and methyl iodide (5 ml) as described in the case of Ia. The purification of the product by silica gel column chromatography (*n*-hexane–acetone (9 : 1→4 : 1)) furnished the deca-*O*-methyl derivative (IIc, 13 mg). IIc, a white amorphous powder. $[\alpha]_D^{20}$ −5.0° (*c* = 1.0, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750 (COOMe), no OH. ^{1}H-NMR ($CDCl_3$) *δ*: 0.82, 0.85, 0.90, 0.93, 0.96, 1.00, 1.04, 1.10 (3H each, all s, *tert*-Me × 8); 1.22 (3H, d, *J* = 6 Hz, rhamnose 6-Me), 3.28, 3.37, 3.45, 3,46, 3.48, 3.485, 3.492, 3.52, 3.67, 3.80 (each 3H, all s, OMe × 9 and COOMe × 1), 4.92, 4.62 (each 1H, d, *J* = 8 Hz, glucuronic acid 1-H and galactose 1-H), 5.21, 5.25 (each 1H, br s, 12-H and rhamnose 6-H).

$NaBH_4$ Reduction of IIc——A solution of IIc (10 mg) in MeOH was treated with a mixture of $NaBH_4$ (100 mg) in MeOH at room temperature for 24 h. Work-up as described above yielded the reduction product (IId, 6 mg). IId, a white amorphous powder. $[\alpha]_D^{22}$ +7.1° (*c* = 0.24, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}:3692 (OH), ^{1}H-NMR ($CDCl_3$) *δ*: 0.84, 0.85, 0.90. 0.92, 0.98, 1.00, 1.07, 1.10 (3H each, all s, *tert*-Me × 8), 3.28, 3.37, 3.45, 3.46, 3.48, 3.50, 3.52, 3.54, 3.67 (each 3H, all s, OMe × 9).

Methanolysis of IId——A solution of IId (6 mg) in 3 N HCl–MeOH was heated under reflux for 5 h. The reaction mixture was worked up as described above for the methanolysis of Ie and the resulting product was examined by TLC (as above) and GLC to identify 22-*O*-methylsophoradiol (If), methyl 2,3,4-tri-*O*-methyl-α-L-rhamnopyranoside (a), methyl 3,4-di-*O*-methyl-α-D-glucopyranoside (b) and methyl 3,4,6-tri-*O*-methyl-α-D-galactopyranoside (d). GLC: 3% 1,4-butanediol succinate; 3 mm × 2 m glass column; column temperature 160°C; carrier gas N_2; t_R, d 8.6 min.

Kakkalide (III)——Colorless needles, mp 250—252 °C. $[\alpha]_D^{23}$ −58.4° (*c* = 0.51, DMSO). ^{13}C-NMR (DMSO-d_6) *δ*: 154.1, 122.1, 179.8, 152.1, 131.8, 155.7, 93.8, 151.7, 106.0, 121.1, 129.5, 113.1, 158.4 (C-2-8, 8a, 4a, 1′—4′), 60.0 (6-OMe), 54.8 (4′-OMe) 99.6, 72.6, 76.1, 69.0, 75.4, 68.2 (glc C-1-6), 103.6, 73.0, 76.2, 69.3, 65.2 (xyl C-1-5).

Daidzin (IV)——Colorless needles, mp 238—240 °C $[\alpha]_D^{20}$ −23.1° (*c* = 0.54, DMSO). ^{1}H-NMR (DMSO-d_6) *δ*: (2H, d, *J* = 9 Hz, 3′, 5′-H), 7.22 (1H, d, *J* = 2 Hz, 8-H), 7.31 (1H, dd, *J* = 9,2 Hz, 6-H), 7.40 (2H, d, *J* = 9 Hz, 2′, 6′-H), 8.05 (1H, d, *J* = 9Hz, 5-H), 8.36 (1H, s, 2-H).

Genistin (V)——Colorless needles, mp 254—256°C. $[\alpha]_D^{24}$ −36.6° (*c* = 0.5, DMSO). ^{1}H-NMR (DMSO-d_6) *δ*: 6.48 (1H, d, *J* = 2 Hz, 6-H), 6.72 (1H, d, *J* = 2 Hz, 8-H), 6.84 (2H, d, *J* = 9 Hz, 3′, 5′-H), 7.40 (2H, d, *J* = 9 Hz, 2′, 6′-H), 8.42 (1H, s, 2-H). ^{13}C-NMR (DMSO-d_6) *δ*: 153.7, 121.9, 179.6, 160.8, 99.0, 162.1, 94.0, 156.7, 105.5, 120.3, 129.4, 114.5, 156.4 (C-2-8, 8a, 4a, 1′—4′), 99.3, 72.6, 76.0, 69.2, 76.7, 60.6 (glc C-1-6).

Rutin (VI)——Pale yellow needles, mp 181—186 °C. $[\alpha]_D^{22}$ −26.5° (*c* = 0.5, DMSO). ^{1}H-NMR (DMSO-d_6) *δ*: 6.21 (1H, d, *J* = 2 Hz, 6-H), 6.40 (1H, d, *J* = 2 Hz, 8-H), 6.85 (1H, d, *J* = 9 Hz, 5′-H), 7.54 (1H, dd, *J* = 9,2 Hz, 6′-H), 7.55 (1H, s, *J* = 9 Hz, 2′-H). ^{13}C-NMR (DMSO-d_6) *δ*: 155.6, 132.6, 176.4, 160.3, 98.1, 163.2, 93.1, 155.8, 103.4, 120.5, 114.6, 144.0, 147.6, 115.6, 120.9 (C-2-8, 8a, 4a, 1′—6′), 100.2, 73.6, 76.0, 69.6, 75.5, 66.6(glc C-1-6), 100.7, 70.1, 69.9, 71.4, 67.8 (rha C-1-5).

Robinin (VII)——Pale yellow needles, mp 196—199 °C. $[\alpha]_D^{23}$ −114.3° (*c* = 0.5, pyridine). ^{13}C-NMR (DMSO-d_6) *δ*: 156.0, 133.5, 177.6, 160.8, 98.3, 161.5, 94.6, 157.1, 105.5, 131.0, 115.1, 160.1 (C-2-8, 8a, 4a, 1′—4′), 101.8, 71.0, 72.9, 67.9, 73.6, 65.2 (gal C-1-6), 100.0, 70.2, 70.5, 71.8, 68.2, 17.8 (rha C-1-6), 99.3, 70.0, 70.3, 71.5, 69.8, 17.8 (rha C-1′—6′).

Nicotiflorin (VIII)——Pale yellow needles, mp 181—186 °C. $[\alpha]_D^{25}$ −33.5° (*c* = 0.5, DMSO). ^{13}C-NMR (DMSO-d_6) *δ*: 156.4, 133.1, 177.3, 161.1, 98.6, 164.0, 93.7, 156.8, 103.9, 120.8, 130.8 115.0, 159.8 (C-2-8, 8a, 4a, 1′–4′), 100.7, 74.1, 76.3, 69.9, 75.7, 66.8 (glc C-1-6) 101.2, 70.5, 70.3, 71.7, 68.1, 17.6 (rha C-1-6).

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