H, 6.68; N, 3.74. Found: C, 77.39; H, 6.55; N, 3.92. The insoluble solid in EtOH was recrystallized from CCl_4–EtOH to give 1.57 g (21%) of 2-phenyl-3-*p*-ethoxyphenyl-4-phenoxymethyloxazolidine melting at 90—92°. IR ν_{max}^{KBr} cm^{-1}: 1172, 1116, 1100 (O-C-N). *Anal.* Calcd. for $C_{24}H_{25}O_3N$: C, 76.99; H, 6.68; N, 3.74. Found: C, 77.09; H, 6.55; N, 4.02.

2-Phenyl-3-*p*-chlorophenyl-5-phenoxymethyloxazolidine——A mixture of 3.0 g (0.02 mole) of 2,3-epoxypropyl phenyl ether and 4.3 g (0.022 mole) of benzal-*p*-chloroaniline was treated with 0.3 g (0.001 mole) of $SnCl_4$ by the same procedure as described above. Recrystallization from EtOH gave 4.64 g (63.5%) of colorless needles melting at 101—103°. IR ν_{max}^{KBr} cm^{-1}: 1170, 1125, 1095 (O-C-N). *Anal.* Calcd. for $C_{22}H_{20}O_2NCl$: C, 72.60; H, 5.70; N, 3.96. Found: C, 72.31; H, 5.37; N, 3.99.

2-Phenyl-3-*p*-methoxyphenyl-5-*β*-naphthyloxymethyloxazolidine——A mixture of 4.4 g (0.02 mole) of 2,3-epoxypropyl *β*-naphthyl ether and 4.2 g (0.022 mole) of benzal-*p*-anisidine was also analogously treated with 0.3 g (0.001 mole) of $SnCl_4$. Recrystallization from EtOH gave 3.55 g (43.2%) of colorless needles melting at 107.5—109.5°. IR ν_{max}^{KBr} cm^{-1}: 1217, 1180, 1115 (O-C-N). *Anal.* Calcd. for $C_{27}H_{25}O_3N$: C, 78.81; H, 6.13; N, 3.41. Found: C, 78.89; H, 5.98; N, 3.56.

Another General Synthetic Procedure of 2-Phenyl-3-aryl-5-phenoxymethyloxazolidine——A solution of 0.03 mole of 2,3-epoxypropyl phenyl ether and 0.03 mole of arylamine in MeOH was heated for 3 hr under reflux. After removal of MeOH, 100 ml of benzene and then 0.03 mole of benzaldehyde was added to the residue and the mixture was heated under reflux until 0.03 mole of H_2O was collected in a water separator funnel. The mixture was evaporated to dryness and the residue was recrystallized from EtOH.

Acknowledgement The authors are indebted to Mrs. K. Shiraki and Yoshitomi Seiyaku Co., Ltd. for the microanalytical data and to Miss M. Sato for the measurements of IR spectra.

[Chem. Pharm. Bull. 19(11)2409—2411(1971)]

UDC 547.92.02.05 : 547.918.02.05

Steroidal Sapogenins of *Aletris spicata* (Thunb.) Franchet[1]

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(Received March 6, 1971)

The genera Aletris and Metanarthecium both belong to the family Liliaceae. Although Franchet[3] united Metanarthecium to Aletris, these two genera have commonly been considered as distinct by later botanists, some of whom[4] have ever treated the two genera as the members of widely separated subfamilies, though Hutchinson[5] classified them in the same tribe. One of main characters which has been used by botanists as a discriminating feature between the two genera is the degree of adhesion of the ovary to the perianth. Recently, Hara[6] examined some of the Asian Aletris species and observed a wide variance in the length of the part of the perianth connate with the ovary. This led him to propose the reunion of Metanarthecium with Aletris.

1) Studies on the steroidal components of domestic plants LXIV. Part LXIII: A. Akahori and F. Yasuda, *Chem. Pharm. Bull.* (Tokyo), **19**, 846 (1971).
2) Location: *Fukushima-ku, Osaka.*
3) A. Franchet, *Journ. de Bot.*, **10**, 178, 195, 197 (1896).
4) A. Engler, "Die natürliche Pflanzenfamilien," II-5, 1888; pp. 22, 85 K. Krause, "Engler-Prantl's Die natürliche Pflanzenfamilien," 2nd Ed., 15a, 1930, pp. 260, 378.
5) J. Hutchinson, "Families of Flowering Plants," 2nd Ed., Vol. 2, Oxford University Press, Oxford, 1959, p. 596.
6) H. Hara, *J. Japan. Bot.*, **42**, 312 (1967).

On the other hand, *M. Luteo-viride* Maxim. contains some novel sapogenins; metagenin (25D, 5β-spirostane-2β,3β, 11α-triol),[7] nogiragenin (25D, 5β-spirostane-3β,11α-diol),[8] neonogiragenin (25L isomer of nogiragenin), narthogenin (25L-spirost-5-ene-3β,27-diol) and isonarthogenin (25D-isomer of narthogenin).[9] These sapogenins have not yet been found in other plants,[10] which led us to search for steroidal components of Aletris species.

Steroidal components isolated from the dried powder of *Aletris spicata* (Thunb.) Franchet collected in Mie Pref. were three sapogenins and a mixture of two sterols. The three sapogenins were isolated as crystals and identified as diosgenin (25D-spirost-5-en-3β-ol), isonarthogenin and bethogenin (16α-methoxy-25D-spirost-5-en-3β-ol) by comparison of their physical properties with those of authentic substances. In the mass spectra of sapogenins having no substitution group in their E and F rings, peaks i (*m/e* 115), j (139), k(168) and n (126) are assigned to the fragments derived from side chains.[11] Peaks i, k and n were absent in the spectrum of bethogenin. Instead a prominent peak (198) and two moderate peaks (180 and 165) were found in the spectrum of thissapogenin. The two sterols were identified as β-sitosterol and stigmasterol by gas liquid chromatography.

Although 11-hydroxysapogenins were not found in this plant, another sapogenin peculiar to *M. luteo-viride*, isonarthogenin, was isolated from *A. spicata*. This resemblance of the chemical components may suggest that these two species are fairly closely related to each other and supports Hara's proposal to unite Metanarthecium with Aletris.

Experimental

Aletris spicata was collected at Shimagahara, Mie Pref. during its flowering period, in June. The whole plants were air-dried and powdered and the powder (260 g) was extracted twice with methanol (total 1 liter The methanol solution was concentrated, HCl was added to a concentration of 5%, and the solution was refluxed for 4 hr. The reaction mixture was evaporated to dryness under reduced pressure and the residue was saponified in 90% methanol (20 ml) containing KOH (1 g) for 1 hr on a water bath. The reaction mixture was poured into water and extracted with ether to yield a dark brownish tar (867 mg). This was chromatographed on Al_2O_3 (30 g, neutral, Woelm, containing 3% water). The benzene and benzene–chloroform (9: 1—5: 5) eluate (541 mg, brownish yellow tar) was dissolved in pyridine (2 ml), acetic anhydride (1 ml) was added and the mixture was allowed to stand overnight at room temperature. The reaction mixture was poured into water and extracted with ether. The acetylation product (559 mg, yellowish orange tar) was again chromatographed on Al_2O_3 (20 g). The petroleum ether–benzene (9: 1) eluate (41 mg, colorless crystals) was recrystallized from methanol to yield colorless needles, mp 124—131° (9 mg). This product was identified as a mixture of stigmasterol acetate and β-sitosterol acetate by gas liquid chromatography (Barber–Coleman Model 10, 3% QF-1, 210°, carrier gas Ar, flow rate 100 ml/min) and thin-layer chromatography (Kieselgel G plate, 250 mμ, developed with benzene–acetone–acetic acid; 14: 6: 0.5). The petroleum ether–benzene (8: 2—5: 5) eluate (84 mg, colorless crystals) was recrystallized from methanol to yield colorless needles (mp 198—201°, 46 mg). *Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.27; H, 9.71. Found: C, 76.54; H, 9.75. This was identified with authentic diosgenin acetate by mixed melting point and comparison of infrared (IR) spectrum. The benzene and benzene–chloroform (9: 1) eluate (yellowish tar, 46 mg) was refluxed in 90% methanol containing 5% KOH for 1 hr to yield a brownish tar (46 mg), which was further chromatographed on Al_2O_3 (3 g). The benzene–methylene chloride (7: 3—2: 8) eluate (yellowish crystals, 22 mg) was recrystallized from methanol to yield colorless platelets, mp 238—240° (11 mg). *Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.31; H, 9.83. Found: C, 75.11; H, 9.85. This was identified with isonarthogenin by mixed melting point and IR and mass spectra. Crystals recovered from the crystallization mother liquor of diosgenin acetate were further chromatographed on Al_2O_3 after saponification in KOH–

7) K. Takeda, T. Okanishi, K. Hamamoto, A. Shimaoka and N. Maezono, *Yakugaku Zasshi*, **77**, 175 (1957); K. Takeda and K. Hamamoto, *Tetrahedron Letters*, **3**, 1 (1960); *idem*, *Chem. Pharm. Bull.* (Tokyo), **8**, 1004 (1960); K. Hamamoto, *ibid.*, **8**, 1099 (1960); **9**, 32 (1961).

8) K. Takeda, T. Okanishi, H. Osaka, A. Shimaoka and N. Maezono, *Chem. Pharm. Bull.* (Tokyo), **9**, 388 (1961).

9) H. Minato and A. Shimaoka, *Chem. Pharm. Bull.* (Tokyo), **11**, 876 (1963).

10) Recently, isonarthogenin was isolated also from *Dioscorea quinqueloba* Thunb. of the family Dioscoreaceae.[1]

11) H. Budzikiewicz, K. Takeda and K. Schreiber, *Monatsh. Chem.*, **101**, 1003 (1970).

methanol. From the benzene and benzene–chloroform (9: 1) eluate, diosgenin, mp 200—202° (5 mg) was recovered after recrystallization from methanol. The benzene-chloroform (9: 1—7: 3) eluate (14 mg) was saponified in methanol containing 5% KOH and recrystallized from methanol containing 2% KOH to yield colorless needles, mp 181—183° (2 mg). This was identified with bethogenin by comparison of its mobilities on thin-layer plates and IR, mass spectra and nuclear magnetic resonance (NMR) spectra with those of an authentic sample.

[Chem. Pharm. Bull. 19(11)2411—2413(1971)]

UDC 581.192 : 547.45.02.05 : 547.466.02.05

Water-soluble Constituents of Rehmanniae Radix. II.[1] On the Constituents of Roots of *Rehmannia glutinosa* var. *purpurea*

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(Received April 24, 1971)

In the previous paper,[1] the presences of fifteen amino acids, phosphoric acid, five monosaccharides and five oligosaccharides in the water extract obtained from the fresh roots of *Rehmannia glutinosa* Libos. forma *hueichingensis* Hsiao were described. We have now described on the water-soluble constituents of roots of *Rehmannia glutinosa* Libos. var *purpurea* Makino in the present paper. And for the purpose of comparison, data on Chinese dry roots of *Rehmannia glutinosa* Libos. forma *hueichingensis* Hsiao are also presented here.

The extraction and fractionation of the water-soluble constituents by ion-exchange chromatography were carried out as described in the previous report.[1] The yields of fractions from the dry weight of materials are shown in Table I.

Table I. Yields of Fractions

	R. glu. v. *purpurea*		Dry material of *R. glu.* f. *hueichingensis* (%)
	Fresh material (%)	Dry material (%)	
Neutral frac.	50.1	67.9	67.4
Basic frac.	2.0	3.1	3.2
Acidic frac.	2.7	3.2	6.2

The neutral fractions were analyzed by cellulose thin-layer chromatography and gas-liquid chromatography of trimethylsilyl derivatives. D-Glucose, D-galactose, D-fructose, D-mannitol, sucrose, raffinose, manninotriose, stachyose and verbascose were found in each sample. For the quantitative analyses of them, the fraction was separated into several parts by the use of paper chromatography. Monosaccharides were determined by gas liquid chromatography of trimethylsilyl derivatives, and oligosaccharides were estimated colorimetrically. The contents of them in the neutral fractions are shown in Table II.

The basic fractions were examined by two dimensional cellulose thin-layer chromatography and determined by the use of an amino acid analyzer. For the analysis of D-glucosamine,

1) Part I: M. Tomoda, S. Katō and M. Ōnuma, *Chem. Pharm. Bull.* (Tokyo), **19**, 1455 (1971).
2) Location: *6-3, Shibakōen, Minato-ku, Tokyo.*