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## 地黄の水溶性成分 (第1報) カイケイジオウの糖質と酸類

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Water-soluble Constituents of *Rehmanniae Radix*. I. Carbohydrates and Acids of *Rehmannia glutinosa* f. *hueichingensis*\*.

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The roots of *Rehmannia glutinosa* LIBOS. have long been used in Chinese medicine for the purpose of blood-making, analeptic and antipyretic. On the constituents of this crude drug, a few substances, that is,  $\beta$ -sitosterol<sup>1)</sup>, mannitol, sucrose and catalpol<sup>2)</sup> have been reported until present time.

We have now obtained the water extract from the roots of *Rehmannia glutinosa* LIBOS. forma *hueichingensis* HSIAO, and fractionated into three fractions by the chromatographies on Dowex 50W and Dowex 2. The yields from the dried weight of the material were 74.4% in neutral fraction, 3.3% in basic fraction, and 7.2% in acidic fraction. These procedures are shown in Chart 1.

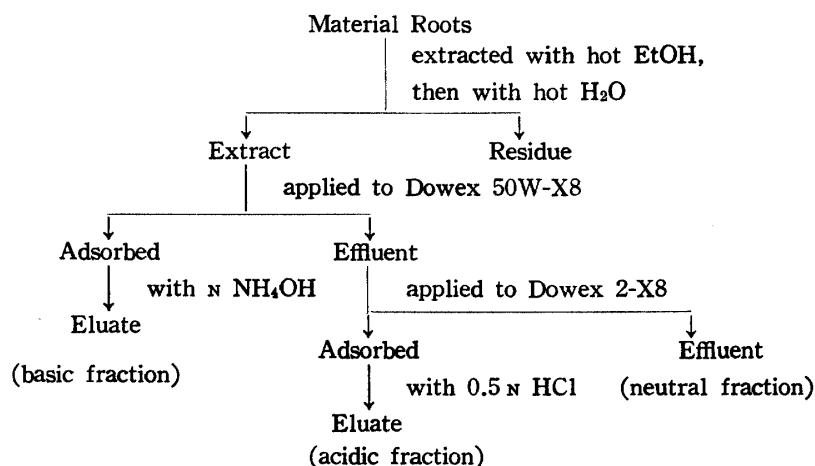


Chart 1. Fractionation of Water-soluble Constituents.

The neutral fraction was applied to a column of active charcoal, and several fractions were eluted with water and further stepwise increments of ethanol. Each fraction was examined by cellulose thin-layer chromatography, and component sugars were purified by repeated charcoal column chromatography and paper chromatography. D-Glucose, D-galactose, D-fructose, sucrose, raffinose and stachyose were identified. In addition to these monosaccharides and oligosaccharides, the presences of manninotriose and verbascose were proved by determination of their component sugars, analyses of methylation products, periodate oxidation and enzymic transformation. From the results of gas-

\* 本報告は *Chem. Pharm. Bull.* (Tokyo), **19**, 1455 (1971) に発表.1) Z. Sakura, *Toyama, Yakusen Kiho*, **2**, 125 (1936).2) I. Kitagawa, T. Nishimura, A. Kobayashi and I. Yosioka, *Yakugaku Zasshi*, **91**, 593 (1971).

TABLE I. Contents of Carbohydrates in the Neutral Fraction

Carbohydrates	Contents (%)	Carbohydrates	Contents (%)
D-Glucose	3.1	Raffinose	4.9
D-Galactose	0.7	Manninotriose	4.4
D-Fructose	1.7	Stachyose	64.9
D-Mannitol	1.8	Verbascose	4.2
Sucrose	5.2		

TABLE II. Contents of Amino Acids and Sugar in the Basic Fraction

Components	Contents (%)	Components	Contents (%)
L-Lysine	0.3	L-Alanine	0.9
L-Histidine	0.4	L-Valine	0.7
L-Arginine	8.7	L-Isoleucine	0.9
L-Aspartic acid	3.9	L-Leucine	0.5
L-Glutamic acid	5.3	L-Tyrosine	0.3
L-Threonine	1.1	L-Phenylalanine	0.6
L-Serine	0.9	$\gamma$ -Amino butyric acid	0.4
Glycine	0.1	D-Glucosamine	1.4

liquid chromatography of trimethylsilyl derivatives, D-mannitol was also detected and determined. The contents of them in the neutral fraction are shown in Table I. Analytical data by chromatographies showed the presences of several unknown carbohydrates in the neutral fraction, but they must be minor components.

The basic fraction was examined by two dimensional cellulose thin-layer chromatography and fifteen amino acids were detected. The analyses and determinations of amino acids were also performed by the use of an amino acid analyzer. In addition to these amino acids, D-glucosamine was detected by thin-layer chromatography and by gas chromatography of its trimethylsilyl derivative, and it was estimated colorimetrically. The results are shown in Table II.

The acidic fraction was examined by cellulose thin-layer chromatography and phosphoric acid was detected. The result of colorimetric determination of this acid showed the content in the fraction is only 1.30%.

In conclusion, it was revealed that stachyose is the chief element of the material, and the other several oligosaccharides belonging to "raffinose family" and monosaccharides composing those oligosaccharides were also found as secondary main components. Although stachyose has been isolated from different plant species more than forty<sup>3)</sup>, the root of *Rehmannia glutinosa* f. *hueichingensis* must be one of the richest source of the tetrasaccharide.

3) a) D. French, *Adv. Carbohydr. Chem.*, **9**, 149 (1954); b) M. L. Wolfrom and A. Thompson, "*Methods in Carbohydr. Chem.*", **1**, 368 (Academic Press, New York and London, 1962); c) J. H. Pazur, "*The Carbohydrates, Chemistry and Biochemistry*" (ed. by W. Pigman and D. Horton), **IIA**, 69 (Academic Press, New York and London, 1970).