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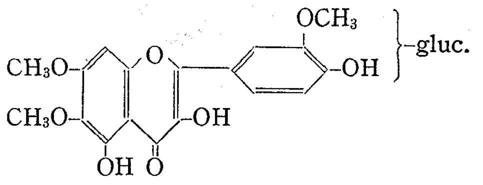
The Constituents of Chrysosplenium Plants in Japan
Structure of "Chrysosplenin"

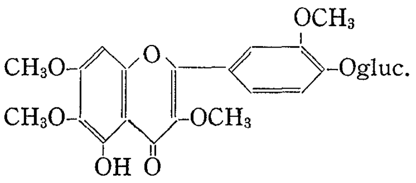
Previously, Nakaoki and Morita proposed the structure of "chrysosplenin,"[1] a new flavonoid glycoside of *Chrysosplenium japonicum* Makino, as 3,5,4'-trihydroxy-6,7,3'-trimethoxyflavone (chrysosplenetin)-monoglucoside.

For the purpose of obtaining "chrysosplenin," the whole plant of *C. japonicum* was extracted with methanol and separated a crystaline substance (A), mp 203°, by lead salt method. Its infrared (IR) spectrum was found to be superimposable with that of "chrysosplenin". Paper partition chromatography of A gave two spots, *Rf* 0.585 (I), 0.50 (II) (15% AcOH). The aglycone also afforded two spots, *Rf* 0.87 (III), 0.80 (IV) (60% AcOH), but only one spot with any other solvents (15% AcOH, BuOH-AcOH-H_2O=4:1:2) tried. Therefore, "chrysosplenin" are clearly a mixture of I and II.

A was separated by silica gel chromatography into two components, I and II, with 68 and 32% yield, respectively.

I, mp 226—228°, $C_{25}H_{28}O_{13}\cdot 2H_2O$, UV $^{\mathrm{EtOH}}_{\mathrm{max}}$ mμ: 254, 274, 341, was identified as chrysosplenoside-B[2] (5,4'-dihydroxy-3,6,7,3'-tetramethoxyflavone-4'-monoglucoside).


"Chrysosplenin" by T. Nakaoki and N. Morita


Chrysosplenoside-B

II, mp 163—165°, $C_{24}H_{26}O_{13}$, UV $^{\mathrm{EtOH}}_{\mathrm{max}}$ mμ: 255, 273, 342, exhibited a positive reduction test for flavonoids and gave brownish green color with ferric chloride. Hydrolysis of II with 10% H_2SO_4 yielded one mole each of D-glucose and aglycone (IV), yellow needles, $C_{18}H_{16}O_8$, mp 236—238°, which afforded green color with ferric chloride and a negative Zircone–citric

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1) T. Nakaoki and N. Morita, *Yakugaku Zasshi*, **76**, 320 (1956).
2) M. Shimizu and N. Morita, *Yakugaku Zasshi*, **88**, 1349 (1968).

acid test[3] for 3-hydroxyl group. IV formed a triacetate (V), colorless needles, mp 165—167°, whose IR spectrum showed the absence of hydroxyl group.

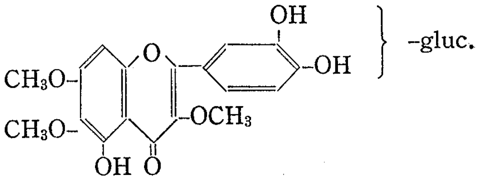
In the nuclear magnetic resonance (NMR) spectrum of V taken in deuterochloroform, exhibited 3H singlet at 2.50 and 6H singlet at 2.33 ppm, attributed to three acetoxyl groups, three 3H singlets at 3.97, 3.85, 3.83 ppm, attributed to three methoxyl groups, and 1H singlet at 6.84 ppm due to an aromatic proton, which is assigned to the C_8 proton. The other three aromatic proton signals were observed as a 1H doubelt (J=9.0 cps) at 7.33, a 1H quartet (J_1=9.0 cps, J_2=3.0 cps) at 7.97 and a 1H doubelt (J=3.0 cps) at 7.91 ppm. These are assigned to C-5′, 6′, 2′ protons on B ring.

Methylation of IV with dimethyl sulfate gave a trimethyl ether, colorless needles, mp 145°, which gave no color with ferric chloride and was found to be identical with quercetagetin hexamethyl ether by direct comparison with an authentic specimen.

Alkaline decomposition of IV furnished 4,5-dimethoxyresorcinol and protocathecuic acid.

II formed a complex with aluminum chloride and resulted in considerable bathochromic shifts of Band I and II in its ultraviolet (UV) spectrum. Therefore II has a free hydroxyl group at C_5 position.

Based on these facts above mentioned, IV is concluded to be 5,3′,4′-trihydroxy-3,6,7-trimethoxyflavone and II is consequently the 3′ or 4′-monoglucoside of IV. Since II is novel natural product, we proposed the names chrysosplenoside-D and chrysosplenol-D for the glucoside (II) and its aglycone (IV), respectively.



Chrysosplenoside-D (Chrysosplenol-D-monoglucoside)

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[3] L. Härhammer and R. Hansel, *Arch. Pharm.*, **286**, 425 (1953).