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Isolation and Identification of Swertisin from the Leaves of *Desmodium caudatum* A.P. de CANDOLLE

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Desmodium caudatum A. P. de CANDOLLE ("Misonaoshi" in Japanese) is a small tree of Leguminosae distributed in western part of Japan. According to Makino,[2] its leaves and stems are used to kill the maggots hatched in miso (bean paste). To our knowledge, no report has appeared so far on the flavonoid constituents of this plant.

A flavonoid C-glycoside (I), $C_{21}H_{19}O_9(OCH_3)\cdot 2.5\ H_2O$, mp 241° (decomp.), $[\alpha]_D^8$ −9.6° (pyridine), was isolated from its leaves and identified as swertisin, a constituent of whole herbs of *Swertia japonica* MAKINO,[3] which has been isolated in pure state and formulated as 6–C–β–D–glucopyranosyl–genkwanin by Komatsu, *et al.*[4]

I gave pentaacetate II, $C_{32}H_{32}O_{15}\cdot \frac{1}{2}H_2O$, mp 191—192°, and dimethyl ether (III), $C_{21}H_{17}O_7(OCH_3)_3$, mp 304—305° (decomp.) (dimethyl ether tetraacetate (IV), mp 127—129°). 6–C–β–D–Glucopyranosyl–genkwanin was presumed as the structure of I from the results of scission with hydroiodic acid[5] giving apigenin and oxidation with ferric chloride[6] to afford glucose and arabinose, and on the basis of the ultraviolet (UV)[7] as well as nuclear magnetic resonance[8] (NMR) spectral data.

Identity with swertisin was unequivocally established by direct comparison of I, II and III with authentic specimens.

Experimental

Isolation and Properties of the Compound I——The air–dried leaves of *D. caudatum* A.P. de CANDOLLE were extracted with boiling MeOH. After removal of the solvent, the residue was digested with hot H_2O. On leaving stand overnight, a resulting brown gum was removed by decantation and the supernatant was shaken successively with benzene (5 times), ether (5 times) and EtOAc (10 times). The aqueous layer was allowed to stand for several days in a refrigerator. An yellow deposite was collected by filtration, dissolved in MeOH, and treated with a saturated solution of $(AcO)_2Pb$ in MeOH. The precipitates were filtered off, and the filtrate was bubbled with H_2S. After removal of PbS, the clear MeOH solution was concentrated to a small volume and allowed to stand overnight to give crude I.

A pure sample of I was obtained by repeated recrystallization from dilute MeOH as yellow needles, mp 241° (decomp.), $[\alpha]_D^8$ −9.6° (c=1.05, l=1/5, pyridine), undepressed on admixture with authentic swertisin, mp 243° (decomp.) (reported[4] $[\alpha]_D^{20}$ −10° (pyridine)). Color test: $FeCl_3$, brown; Mg–HCl, yellow; Zn–HCl, pink. Its *Rf* values on paper, 0.54 (BuOH–AcOH–H_2O (4: 2: 1)), 0.87 (60% AcOH), and 0.64 (15% AcOH) and the infrared (IR) spectrum were identical with those of an authentic specimen. UV λ_{max}^{EtOH} mμ (log ε): 272 (4.34), 340 (4.36). UV $\lambda_{max}^{EtOH-AlCl_3}$ mμ (log ε): 281 (4.32), 302 (4.28), 345 (4.40). UV $\lambda_{max}^{EtOH-AcONa}$ mμ (log ε):

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[1] Location: *a*) *Kurokami–machi, Kumamoto*; *b*) *Katakasu, Fukuoka.*

[2] T. Makino, "Makino's New Illustrated Flora of Japan," Hokuryu–kan Publishing Co., Ltd., Tokyo, 1961, p. 308.

[3] T. Nakaoki, *Yakugaku Zasshi*, 47, 144 (1927).

[4] M. Komatsu, T. Tomimori and M. Ito, *Chem. Pharm. Bull.* (Tokyo), **15**, 263 (1967).

[5] S. Iseda, *Bull. Chem. Soc. Japan*, 30, 625 (1957).

[6] J.E. Hay and L.J. Haynes, *J. Chem. Soc.*, **1956**, 3141.

[7] L. Jurd, "The Chemistry of Flavonoid Compounds," ed. by T.A. Geissman, Pergamon Press, Oxford, 1962, p. 107.

[8] W.E. Hillis and D.H.S. Horn, *Australian J. Chem.*, **18**, 531 (1965).

272 (4.34), 340 (4.36). UV $\lambda_{\max}^{\text{EtOH-EtONa}}$ mμ (log ε): 271 (4.28), 401 (4.62). *Anal.* Calcd. for $C_{21}H_{19}O_9$–$(OCH_3)\cdot 2.5\ H_2O$: C, 53.78; H, 5.50; OCH_3, 6.31; H_2O, 9.2. Found: C, 53.42; H, 5.21; OCH_3, 6.10; H_2O, 8.8.

On refluxing with HI after the procedure of Iseda,[5] I gave apigenin, mp 340—341° (decomp.), which was identified by mixed melting point determination and the comparison of its IR spectrum with that of authentic specimen.

Ferric chloride oxidation of I was carried out after the procedure of Hay, *et al.*[6] to afford glucose and arabinose, which were identified on paper chromatogram (BuOH–pyridine–H_2O (3: 2: 1), double ascending method).

Penta-O-acetylswertisin (II)——Acetylation of I with Ac_2O and pyridine in the usual manner yielded II as colorless needles, mp 191—192° (from MeOH), which gave a reddish brown color with $FeCl_3$. The same treatment of authentic swertisin gave colorless needles, mp 186—187°. Mixed melting point determination showed the identity of two specimens. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 252 (4.38), 273 (4.61), 317 (4.26). NMR ($CDCl_3$, δ): 7.82 (2H, d, J=9 cps) (2′, 6′–H), 7.22 (2H, d, J=9 cps) (3′, 5′–H), 6.57 (H, s) (8–H), 6.42 (H, s) (3–H), 3.92 (3H) (OCH_3), 2.34 (3H) (4′–OAc), 2.06 (6H) (3″, 4″–OAc), 2.01 (3H) (6″–OAc), 1.77 (3H) (2″–OAc). *Anal.* Calcd. for $C_{32}H_{32}O_{15}\cdot \frac{1}{2}\ H_2O$: C, 57.74; H, 4.96; H_2O, 1.4. Found: C, 57.63; H, 5.01; H_2O, 1.0.

Di-O-methylswertisin (III)——To a solution of I (0.5 g) in MeOH (30 ml) was added an etheral solution of CH_2N_2 prepared from 3 g of nitrosomethylurea. The reaction mixture was allowed to stand overnight and the product separated out as colorless crystals was collected by filtration, washed with MeOH, and recrystallized from dioxane–H_2O to yield III as colorless needles, mp 304—305° (decomp.), undepressed on admixture with authentic di–O–methylswertisin.[9] Its IR and UV spectra were also identical with those of an authentic specimen. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 264 (4.34), 322 (4.39). *Anal.* Calcd. for $C_{21}H_{17}O_7\ (OCH_3)_3$: C, 60.75; H, 5.52; OCH_3, 19.62. Found: C, 60.30; H, 5.58; OCH_3, 19.44.

Di-O-methylswertisin Tetraacetate (IV)——Acetylation of III with Ac_2O and pyridine in the usual manner yielded IV as colorless needles, mp 127—129° (from MeOH) (reported[4] mp 150—155° (from $CHCl_3$–hexane)). Its IR and NMR spectra were identical with those of authentic di–O–methylswertisin tetraacetate. NMR ($CDCl_3$, δ): 7.75 (2H, d, J=9 cps) (2′, 6′–H), 6.93 (2H, d, J=9 cps) (3′, 5′–H), 6.71 (H, s) (8–H), 6.52 (H, s) (3–H), 3.99, 3.92, 3.88 (9H) (OCH_3), 2.06, 2.04, 2.02 (9H) (3″, 4″, 6″–OAc), 1.75 (3H) (2″–OAc).

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The Oxidation of p-Toluidine with Potassium Ferricyanide in Liquid Ammonia

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In a previous paper,[2] it was shown that oxidation of p–cresol with potassium ferricyanide in liquid ammonia in the presence of sodium amide afforded the Pummerer's ketone in better yield than that of Haynes' method.[3] In order to continue our investigation regarding the

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[1] Location: *No. 85, Kita–4–bancho, Sendai.*

[2] T. Kametani and K. Ogasawara, *Chem. Pharm. Bull.* (Tokyo), **16**, 1138 (1968).

[3] C.G. Haynes, A.H. Turner, and W.A. Waters, *J. Chem. Soc.*, **1956**, 2823.