CHEMISTRY LETTERS, pp. 27-30, 1979. Published by the Chemical Society of Japan

A NEW FLAVONOID GLYCOSIDE FROM POLYGONUM NODOSUM

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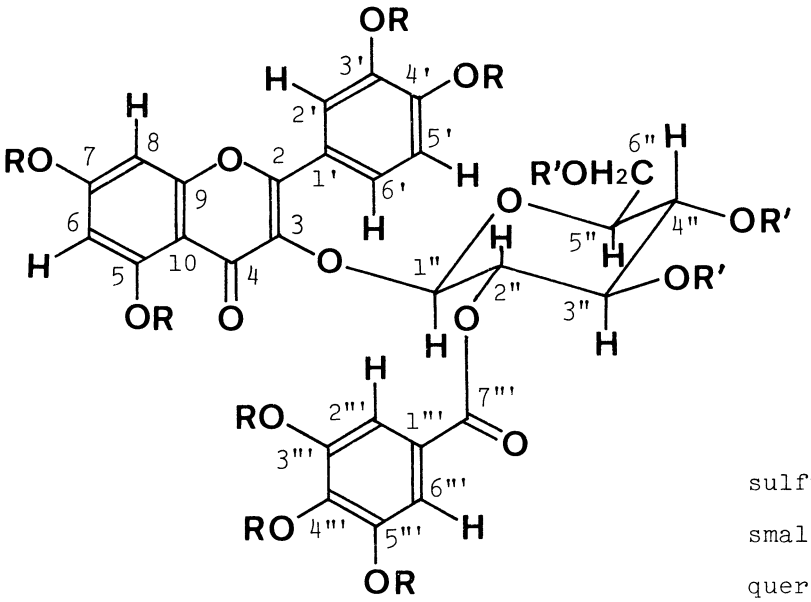
The structure of a new flavonoid glycoside with a molluscicidal activity which was isolated from Polygonum nodosum Pers. was elucidated as quercetin-3β-D-glucoside-2"-gallate by spectroscopic analysis.

Many flavonoids have been isolated from Polygonum (Polygonaceae). We now describe the isolation of a new flavonoid glycoside and a flavonol from P. nodosum Pers. (Ohinutade in Japanese).

Ethanol extract of the leaves and the stems was concentrated and divided into the soluble parts of diethyl ether, ethyl acetate, 1-butanol, and water. The precipitate which was obtained by concentration of the soluble part of ethyl acetate was recrystallized from ethanol-water or methanol-chloroform to give compound A (1) as yellowish needles. On the other hand, the filtrate was chromatographed over silica gel by use of chloroform-methanol as an eluent to give compound B (2) (19 : 1, v/v) and A (9 : 1 to 3 : 1, v/v). Compound A was also isolated from Polygonum senegalense and clarified as having a molluscicidal activity by Dr. S.F. Dossaji.[1)]

Compound B was identified as quercetin by comparison with IR spectra of the authentic sample and its acetate. Compound A (1), mp 205°C, Found : C, 50.90; H, 4.22%. Calcd for $C_{28}H_{24}O_{16}\cdot\frac{5}{2}H_2O$: C, 50.84; H, 4.42%, shows the presence of the following groups in the IR spectrum: hydroxyl (ν_{max} 3350 cm^{-1}), conjugated ester (1705 and 1230 cm^{-1}), carbonyl (1660 cm^{-1}), and aromatic group (1605 and 1565 cm^{-1}). The UV spectrum of (1) shows absorptions characteristic of flavonoid, λ_{max} (MeOH) 258 (shoulder), 268 (ε 25600), and 356 nm (ε 17800).[2)] By addition of sodium acetate and/or aluminium chloride the UV spectra of (1) show, respectively, the following absorptions, λ_{max} (MeOH + NaOAc) 271 and 362 nm, and λ_{max} (MeOH + $AlCl_3$) 276 and



(I) R = R′ = H

(5) R = CH_3 , R′ = H

(7) R = R′ = $Si(CH_3)_3$

427 nm. This basochromic shift of the UV spectrum is characteristic of the flavonol having the substituted hydroxyl group at C-3.[2)]

Acid hydrolysis of (1) with 5% sulfuric acid in water containing a small amount of methanol gave quercetin (2), gallic acid (3), and glucose (4). Quercetin was identified with an authentic sample by comparing the IR spectra, and gallic acid and glucose were identified by TLC and PPC.

Heptamethyl ether (5) of (1) which was obtained by methylation of (1) with diazomethane, mp 153-155°C shows molecular ion peak m/e 714 by FDMS, which corresponds to molecular formula $C_{35}H_{38}O_{16}$, and shows the presence of seven phenolic hydroxyl groups in (1). Among the fragment ion peaks, the signal of m/e 520 is assignable to M^+- trimethylgalloyl, that is, tetramethylquercetin glucoside and the signal of m/e 358 is tetramethylquercetin. On the other hand, the fragment ions of (1) by FDMS are assignable as galloyl glucose (m/e 314), quercetin (m/e 302), and gallic acid (m/e 170).

Acid hydrolysis of (5) with 3% sulfuric acid in 50% aqueous methanol gave (6), mp 194-195°C, which was identified with 5,7,3′,4′-tetramethylquercetin by IR spectrum. These results indicate that glucose may be linked at C-3 of quercetin.

The structure of compound A was assignable to be (1) from CMR spectrum (DMSO-d_6) as shown in Table 1. The signal of the C-1 of glucose in the flavonol glucoside generally appears at ca. δ 101 ppm, however the corresponding signal of (1) is slightly upfield by 2.5 ppm. Although the downfield shift of the C-2" is not observed, the upfield shift of the adjacent C-3" is 2.5 ppm. This result indicates that gallic acid is esterified with the hydroxyl group of C-2 of glucose.

Table 1. The CMR spectrum of compound A (1).

Carbon	δ	Carbon	δ	Carbon	δ	Carbon	δ
2	156.3	9	156.3	6'	122.1	1"'	119.8
3	132.8	10	104.1	1"	98.5	2"'	109.1
4	177.1	1'	121.1	2"	74.3	3"'	145.5
5	161.3	2'	115.3	3"	74.3	4"'	138.4
6	98.8	3'	145.0	4"	70.3	5"'	145.5
7	165.2	4'	148.6	5"	77.8	6"'	109.1
8	93.6	5'	116.1	6"	60.9	7"'	164.1

Chemical shifts are expressed in ppm from TMS in DMSO-d_6.

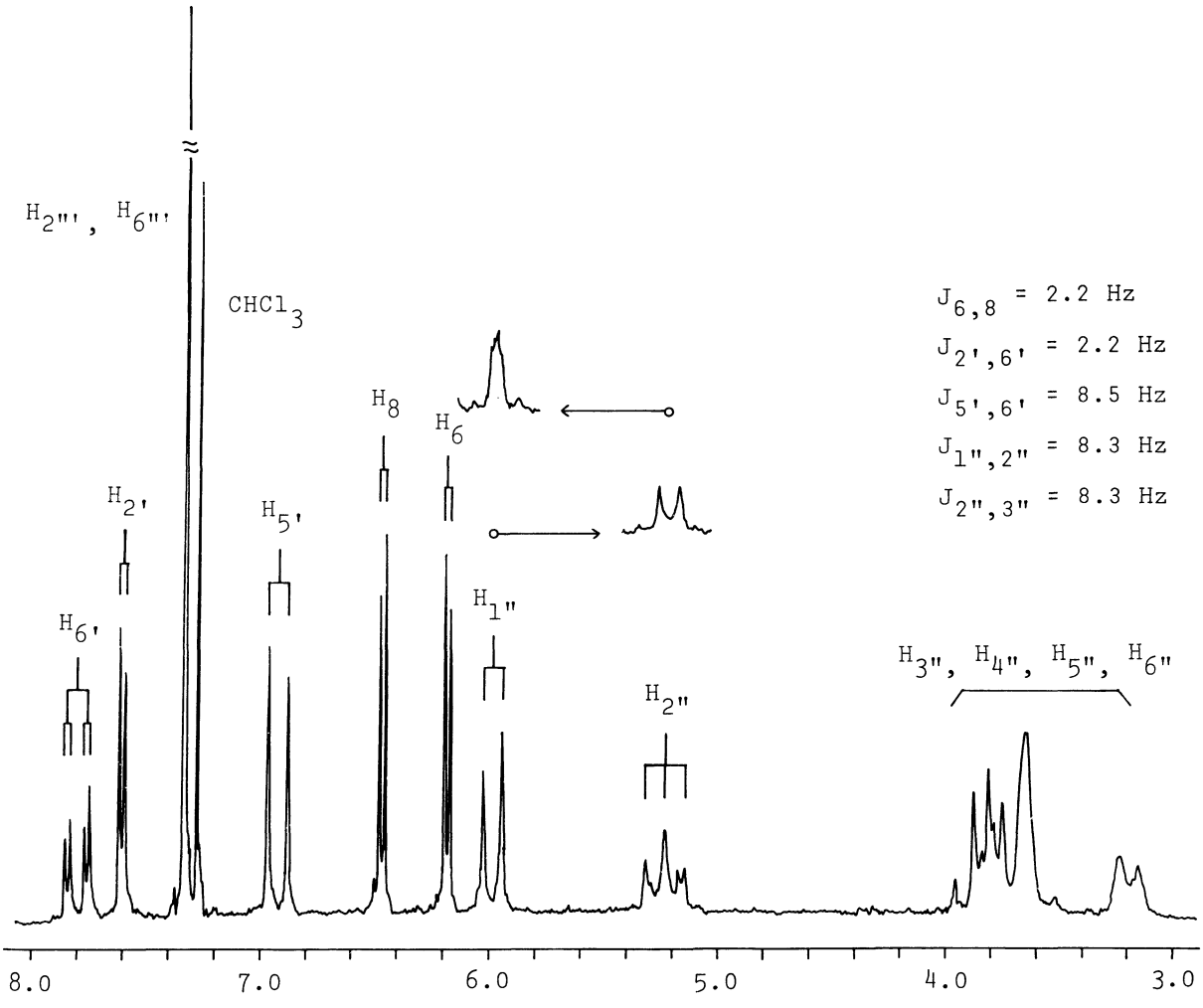


Fig. 1. The PMR spectrum of trimethylsilylate of compound A (1) in CCl_4-$CDCl_3$.

The PMR spectrum of trimethylsilyl ether (7) of (1) (CCl_4-$CDCl_3$) shows the characteristic signals of trimethylsilyl ether of quercetin as shown in Fig. 1. The signal of δ 5.98 ppm (d, J = 8.3 Hz) is assigned to the proton attached to C-1" of glucose part. The magnitude of the coupling constant appears reasonable for β-glucosidic linkage. The multiplet at 5.22 ppm (J = 8.3 Hz), which is coupled with the signal at δ 5.98 ppm (confirmed by decoupling experiment), is attributed to the proton attached to the carbon bearing a galloyl group. This fact elucidates that the galloyl group is attached to C-2" of glucose.[3)]

From these experimental results, the structure of compound A was determined as quercetin-3β-D-glucopyranoside-2"-gallate. The isolation of this compound is the first case although quercetin-3β-D-galactopyranoside-2"-gallate[4)] and quercetin-3β-D-glucopyranoside-6"-gallate[5)] were isolated.

We are grateful to Dr. Mamoru Endo, Suntory Co., LTD. for the measurement of FDMS, and Dr. Takamasa Kinoshita and Mr. Kozo Shibata, Osaka City University for the measurement of PMR and CMR.

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(Received October 24, 1978)