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A Flavonoid Glycoside from the Leaves of *Polygonum sachalinense* (II)

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Abstract □ Quercetin-3-O-β-D-glucofuranoside, mp 243~6°, was isolated from leaves of *Polygonum sachalinense* Fr. Schm. and characterized on the basis of its spectral data. This is the second report of its occurrence in nature.

Keywords □ *Polygonum sachalinense*, Polygonaceae, quercetin-3-O-β-D-glucofuranoside.

Previous workers reported the isolation of quercitrin[1], reynoutrin[2], quercetin and avicularin[3] from the leaves of *Polygonum sachalinense* Fr. Schm. (*Reynoutria sachalinensis* Nakai, Polygonaceae).

In this paper, we report the isolation of quercetin-3-O-β-D-glucofuranoside.

The compound, mp 243-6°, $[\alpha]_D^{20}$ −80.6°, showed positive results in $FeCl_3$, Zn+HCl, Mg+HCl, and Molisch tests and typical flavonol type in the UV spectral data and diagnostic shifts[4].

Hydrolysis of the compound gave quercetin, mp 318~9°, and glucose. Permethylation according to Brimacombe's method[5] followed by acid hydrolysis afforded 5, 7, 3′, 4′-tetra-O methyl quercetin, mp 193~5°, which indicated that the glucose was attached at C-3 of quercetin.

The IR spectrum of the compound differed from that of flavonol glucopyranosides in its finger print region.

In the region of ring and C-O vibrations of glycosidic linkage, only two sharp peaks at 1081 and 1060cm^{-1} were observed. This observation suggested that the ring size of glucose was furanose rather than pyranose[6].

This suggestion was further supported by the presence of A, B, C and D type frequencies for furanose ring at 930, 880, 865 and 790cm^{-1} respectively[6,7].

The NMR spectrum of the acetate showed that four aliphatic and four aromatic acetyl signals appeared in the regions of 1.93~2.17 ppm and of 2.37~2.47ppm, which indicated that 1 mole of glucose was linked to quercetin. Among the four aliphatic acetyl signals two signals appeared downfield from 2.05ppm unlike flavonol glucopyranoside acetate. Moreover, the chemical shifts and splitting patterns of the methine and methylene protons in the region of 3.5~5.6ppm were clearly different from those of reported α-and/or β-D-glucopyranosides[8-11].

These results coupled with IR data revealed that the ring size of glucose in the compound was clearly furanose form. Further confirmation of the configuration as well as ring size of glucose came from the coupling constant value(2Hz) of the anomeric proton appearing a doublet at 5.45ppm. Among four possible configurations of glucose, only the coupling constant of β-D-glucofuranose is 2Hz or less[12,13].

This was also supported by the $[M]_D \times K_p$ value[6] of the compound(−205.7°) which was similar to that of phenyl-β-D-glucofuranoside.

From the above results, the compound was identified as quercetin-3-O-β-D-glucofuranoside which was previously isolated only from the leaves of *Gossypium hirsutum* (Malvaceae)[14].

EXPERIMENTAL METHODS

The mps were taken on a Mitamura-Riken apparatus and are uncorrected. The UV spectra were runned on a Shimadzu model MPS-50L recording spectrophotometer and IR spectra were determined in KBr pellets on a Beckman model IR-20A spectrophotometer. The NMR spectra were recorded on a Varian model EM-360 spectrometer with TMS as internal standard. Optical rotation was obtained on a Perkin Elmer model 243 polarimeter.

Extraction and Isolation

The methanolic extracts of *P. sachalinense* leaves were shaken with $CHCl_3$, ethyl acetate and then BuOH. The ethylacetate soluble fraction was repeatedly separated by SiO_2 and Sephadex LH-20 chromatography to give the compound in addition to quercetin and avicularin[3]. The compound was crystallized from MeOH to yield yellowish needles (150mg), mp 243~6°, $[\alpha]_D^{20}$−80.6°(C=0.06, MeOH) (Lit [14]. mp 220−2°, $[\alpha]_D^{20}$−72.46°). $FeCl_3$, Mg+HCl, Zn+HCl and Molisch tests: positive.

IR ν_{max}^{KBr} cm^{-1}: 3200(OH), 1655(C=O), 1605, 1555, 1500(C=C), 1081, 1060(C-O), 1015, 994, 930, 880, 865, 825, 790; UV λ_{max}^{EtOH} nm (log ε): 259(4.27), 270(sh, 4.22), 310(4.00), 366(4.23); λ_{max}^{EtONa}: 276(4.31), 338(4.02), 420 (4.31); λ_{max}^{NaOAc}: 273(4.26), 330(4.06), 380(4.17); $\lambda_{max}^{NaOAc+H_3BO_3}$: 266(4.31), 389(4.25); $\lambda_{max}^{AlCl_3}$:276 (4.27), 301(sh, 3.95), 426(4.22); $\lambda_{max}^{AlCl_3+HCl}$:272 (4.28), 303(3.96), 411(4.19).

Acid Hydrolysis

Twenty mg of the compound was refluxed with 5%H_2SO_4(50ml) for 3hr. After cooling, the reaction mixture was filtered. The aglycone was crystallized from MeOH to give quercetin as fine needles(mp 318~9°). It was confirmed by direct comparison with authentic quercetin (mmp, TLC and UV). The filtrate was neutrallized with $BaCO_3$, filtered and concentrated in vacuo. D-Glucose was identified by TLC (precoated cellulose, pyridine-ethylacetate-HOAc-H_2O=36:36:7:21, Rf=0.46).

Permethylation followed by acid hydrolysis

A sample(30mg) was permethylated according to Brimacombe's method[5] and followed by the usual work-up. Acid hydrolysis of crude permethylether with 5% H_2SO_4 in 50% dioxane(20ml) under reflux for 3hr was followed by the usual work-up.

Crystallization of the aglycone from MeOH gave 5, 7, 3′, 4′-tetra-O-methyl quercetin, mp 193~5°, which was confirmed by direct comparison with an authentic sample(TLC, mmp and UV).

Acetylation

A sample(70mg) in pyridine and Ac_2O(1ml each) was allowed to stand at room temperature overnight. The reaction mixture was evaporated with N_2 gas to remove the solvents and subjected to NMR spectrometry. NMR ($CDCl_3$) δ: 1.93(3H, s, acetyl), 2.00(3H, s, acetyl), 2.13(3H, s, acetyl), 2.17(3H, s, acetyl), 2.37(9H, s, 3×acetyl), 2.47(3H, s, acetyl), 5.45(1H, d, J=2Hz, H-1″), 6.83(1H, d, J=2Hz, H-6), 7.32(1H, d, J=2Hz, H-8), 7.33(1H, d, J=8Hz, H-5′), 7.95(1H, d, J=2Hz, H-2′), 8.02(1H, dd, J=2 & 8Hz, H-6′).

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