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Flavonoids from the Leaves of *Polygonum sachalinense* Fr. Schm. (I)

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From the leaves of *Polygonum sachalinense* Fr. Schm. (Polygonaceae) quercetin, mp 316~8°, and avicularin, mp 216~6°, $[\alpha]_{20}^{D}$-152°, were isolated and characterized by spectral data. Both are first isolation from this plant.

As a part of our chemical investigation of korean medicinal plants, we have examined *Polygonum sachalinense* Fr. Schm. =*Reynoutria sachalinensis* Nakai (Polygonaceae), a herbaceous perennial shrub which is commonly known as "Ho-Jang" in Korea and have been used for diuretic in traditional medicine. From this plant part, quercitrin[1,2], reynoutrin[2] and phenolic carboxylic acids[3] were so far isolated and identified. Further examination of this plant has led to the isolation of some flavonoids. We now describe our results on flavonoid components on this plant.

The MeOH extract of *Polygonum sachalinense* leaf was fractionated with $CHCl_3$, ethylacetate, BuOH and H_2O successively. The ethylacetate extract was subjected to chromatograph using SiO_2 and Sephadex LH-20 to yield compounds I and II in order of elution.

The compound I, mp 316~8°, showed positive $FeCl_3$, Zn+HCl and Mg+HCl tests and identified as quercetin by direct comparisons with an authentic sample (mmp, TLC, UV and NMR).

Compound II, mp 214~6°, $[\alpha]_{20}^{D}$-152°, showed positive Mg+HCl, Zn+HCl and Molisch tests.

Based on UV spectral response to the shift reagents the compound II showed typical quercetin type flavonol glycoside[4].

Acid hydrolysis of the compound II afforded quercetin, mp 315~7°, and arabinose.

Permethylation followed by acid hydrolysis gave 5, 7, 3′, 4′-tetra-0-methyl quercetin, mp 194~5°, which indicated that arabinose was attached at C-3 of quercetin.

The NMR spectrum of peracetate, mp 83~5°, showed that anomeric proton appeared as a singlet at 5.78ppm, H-2″ as a doublet at 5.47 ppm with J=2Hz, and H-3″ appeared as a doublet of doublets (J=5.5 and 2Hz) at 4.97 ppm. The signal for H-4″ appeared as a multiplet at 3.66~3.83ppm well shifted from H-5″ which appeared triplet-like at 4.08ppm[5].

In general, the coupling constant for vicinal *cis* hydrogens is in the range of 4.3 to 6.8Hz, the values for vicinal *trans* hydrogens vary from a very small value (<0.5Hz) to 7.2Hz in a five membered ring system[6~8]. In many cases where H-1″ and H-2″ are *cis* the observing coupling constant is *ca* 4.5Hz, whereas when H-1″ and

H-2″ are *trans* the observing coupling constant approches zero[5~9].

From the above results, the values of the coupling constants of the compound II ($J_{1,2}$=0, $J_{2,3}$=2Hz, $J_{3,4}$=5.5Hz) showed H-1″ and H-2″ has a *trans*, H-2″ and H-3″ has a *trans* and H-3″ and H-4″ has a *trans* relationshhip, *i.e.* L-arabinofuranose.

The coupling constant that $J_{1,2}$=0Hz indicated the α-configuration[5,6,9]. This result was supported that the $[M]_D \times K_p$ value of compound II (−343°) by Kovalev and Litvinenko[10] is similar to that of phenyl-α-L-arabinofuranose.

From the above results, the compound II is clearly quercetin-3-0-α-L-arabinofuranoside which has known as avicularin[11,12] (mp 216~7°, $[\alpha]_{25}^{D}$-164°)[11] from *Polygonum aviculare* L..

Both are hitherto unreported compounds from this plant and further examinations on this plant are in progress.

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Experimental

The mps were taken on a Mitamura-Riken apparatus and are uncorrected. The UV spectra were runned on a Shimadzu MPS-50L recording spectrophotometer and the IR spectra were determined in KBr pellets on a JASCO IR-S spectrophotometer.

The NMR spectra were recorded on a Varian EM-360 spectrometer with TMS as internal standard. Optical rotation was obtained on a Perkin Elmer 243 polarimeter.

Extraction and isolation: The dried leaf of *P. sachalinense* (360g) was refluxed with MeOH for 3hr (3times) and concentrated in vacuo (62g). The concentrate was fractionated to yield $CHCl_3$ (20g), ethylacetate (5.2g), *n*-BuOH (10.85g) and H_2O (24.96g) soluble portions successively. The ethylacetate soluble portion was subjected to chromatograph using SiO_2 ($CHCl_3$-MeOH-H_2O =13:7:2, lower phase) and Sephadex LH-20 (MeOH) columns to give compounds I and II in order of elution.

Compound I was crystallized from MeOH to yield yellowish fine needles (80mg). It showed positive results in $FeCl_3$, Mg+HCl and Zn+HCl tests. mp 316~8°.

It was confirmed by comparisons with an authentic quercetin. (mmp, TLC, UV and NMR).

Compound II was crystallized from MeOH to give yellowish fine needles (120mg). It showed positive results in $FeCl_3$, Mg+HCl, Zn+HCl and Molisch tests. mp 214~6°, $[\alpha]_{20}^{D}$-152° (C =0.05, MeOH) (Lit.[11] mp 216~7°, $[\alpha]_{25}^{D}$ -164°)

IRν: $^{KBr}_{max}$ cm^{-1} 3400~3200 (OH), 1644 (C=O), 1594 (C=C), 1000~1100 (C—O).

UV: λ_{max}^{EtOH} nm (log ε) 259 (4.23), 270 (sh, 4.19), 304 (sh, 3.95), 363 (4.18); λ_{max}^{EtONa} 274 (4.29), 336 (3.99), 412 (4.26); λ_{max}^{NaOAc} 275 (4.25), 323 (4.02), 381 (4.13); $\lambda_{max}^{NaOAc+H_3BO_3}$ 265 (4.29), 387 (4.23); $\lambda_{max}^{AlCl_3}$ 278 (4.26), 304 (sh, 3.93), 430 (4.20); $\lambda_{max}^{AlCl_3+HCl}$ 272 (4.21), 300 (sh, 3.94), 365 (4.08), 407 (4.12).

Acid hydrolysis of compound II: 10mg of compound II was refluxed with 5% H_2SO_4 (50ml) for 4hr. After cooling, the reaction mixture was filtered. The aglycone was crystallized from MeOH to afford quercetin as fine needles. mp 315~7°.

It was confirmed by direct comparisons with an authentic sample (TLC, mmp and UV). The filtrate was neutralized with $BaCO_3$, filtered and concentrated. L-arabinose was identified by TLC (precoated cellulose, pyridine-ethyl acetate-HOAc-H_2O=36:36:7:21, Rf 0.52).

Permethylation followed by acid hydrolysis: 30mg of sample was permethylated using Brimacombe's method[13] and followed by the usual work-up. Acid hydrolysis of the crude permethylether with 5 % H_2SO_4 in 50% dioxane under reflux for 3hr was followed by the usual work-up.

Crystallization of the aglycone from MeOH gave 5, 7, 3′, 4′-tetra-0-methyl quercetin, mp 194~5, which was confirmed by direct comparisons with an authentic sample(TLC, mmp and UV).

Acetylation of compound II: A sample(25 mg) in pyridine and Ac_2O(0.5ml each) was allowed to stand at room temperature overnight. The reaction mixture was poured into crushed ice and filtered. The precipitate was crystallized from $CHCl_3$-hexane to give amorphous white powder(27mg). mp 83~5°.

IR: ν_{max}^{KBr} cm^{-1} 1765, 1745, 1203(acetate).

NMR($CDCl_3$) δ 2.00(3H, s, acetyl); 2.10(6H, s, 2×acetyl); 2.33(9H, s, 3×acetyl); 2.42(3H, s, acetyl); 3.66~3.83(1H, m, H-4″); 4.08(2H, *t*-like, H-5″); 4.97(1H, dd, J=2 and 5.5Hz, H-3″); 5.47(1H, d, J=2Hz, H-2″); 5.78(1H, s, H-1″); 6.83(1H, d, J=2Hz, H-6); 7.30(1H, d, J=2Hz, H-8); 7.33(1H, d, J=7.5Hz, H-5′); 7.77(1H, d, J=2Hz, H-2′); 7.88(1H, dd, J=2 and 7.5Hz, H-6′).

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