Notes

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Masakazu Aritomi, Ikuko Kiyota, and Tatsuji Mazaki : Flavonoid Constituents in Leaves of *Rumex acetosa* LINNAEUS and *R. japonicus* HOUTTUYN.

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Rumex acetosa LINNAEUS and *R. japonicus* HOUTTUYN are the perennial herbs of Polygonaceae, which are distributed throughout Japan.

In 1955, Hörhammer, *et al.*[1] reported the isolation of hyperin from *R. acetosa* LINNAEUS.

As described in the experimental part, a flavonoid compound, $C_{21}H_{20}O_{10}$, m.p. 253~254° (decomp.), (I), was isolated in pure form from the leaves of *R. acetosa* LINNAEUS, and identified as vitexin, furnishing an additional example of its occurrence in Polygonaceae.

A flavonoid glycoside, $C_{21}H_{20}O_{11}\cdot 1\frac{2}{3}H_2O$, m.p. 180~181° (decomp.), (II), was isolated in pure form from the leaves of *R. japonicus* HOUTTUYN, and identified as quercitrin.

Experimental

Paper chromatography : Flavonoid compounds were run in the solvent systems of (1) BuOH–AcOH–H_2O (4:1:5 by volume, upper layer), (2) 60% AcOH, (3) 15% AcOH, and detected by spraying with 5% Na_2CO_3 solution. Sugars were run in the solvent system of BuOH–pyridine–H_2O (3:2:1 by volume) by the double ascending method, and detected by spraying with 0.5% *p*-anisidine·HCl in MeOH.

Spectrophotometry : The UV spectra were measured in EtOH using a self-recording ultraviolet spectrophotometer (Hitachi EPS 2 Type), and the IR spectra in KBr discs using a self-recording infrared spectrophotometer (Nihon Koken DS-301 Type).

Isolation of Vitexin (I)——The air-dried leaves of *R. acetosa* LINNAEUS were refluxed twice with MeOH. After removal of the solvent, the residue was digested with boiling H_2O. Next day, a brown gum that separated was removed by decantation, and the supernatant was successively shaken with benzene (3 times), ether (3 times), and then with EtOAc (20 times). The EtOAc extract was treated with $(AcO)_2Pb$ in MeOH, giving the precipitable and non-precipitable fractions.

The latter fraction was bubbled with H_2S and filtered. The yellow filtrate was concentrated to a small volume and allowed to stand overnight. The yellow deposit was collected and recrystallized several times from dioxane–H_2O (1:1). After liquid chromatography on a column of Nylon powder, I was obtained as yellow, lustrous plates, m.p. 253~254°(decomp.), undepressed on admixture with authentic vitexin.

I gave an orange color with Mg–HCl, a red color with Zn–HCl, and a brown color with $FeCl_3$. Its Rf values in the three solvent systems tried as well as IR and UV spectra were found to be the same as those of authentic specimen. *Anal.* Calcd. for $C_{21}H_{20}O_{10}$: C, 58.33; H, 4.66. Found : C, 58.22; H, 4.63.

Treatment of I with conc. HCl. A solution of I (10 mg.) in 2 ml. of conc. HCl was heated on a water-bath for 10 min. The reaction mixture was diluted with 2 volumes of H_2O and allowed to stand overnight. The yellow deposit was centrifuged, washed with H_2O, and chromatographed on paper in three solvent systems. In each case, two spots were revealed on paper chromatograms of two flavonoid compounds, the Rf values of which were found to be the same as those of vitexin and saponaretin, respectively.

No sugar was detected in the supernatant.

Treatment of I with HI. A mixture of I (10 mg.), 100 mg. of phenol, 2 ml. of HI (d. 1.7) and 100 mg. of red phosphorus was refluxed for 1 hr. After being cooled, the reaction mixture was poured into 20 ml. of 1% $NaHSO_3$ solution and allowed to stand overnight. The deposit was centrifuged, washed with H_2O, and chromatographed on paper in three solvent systems. In each case, only one spot was revealed

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1) L. Hörhammer, E. Volz : Arch. Pharm., 288, 58 (1955).

on paper chromatograms of a flavonoid compound, the Rf value of which was found to be the same as that of apigenin.

Isolation of Quercitrin (II)——The air-dried leaves of *R. japonicus* HOUTTUYN were worked up in the same manner as in the case of *R. acetosa* LINNAEUS. The non-precipitable fraction obtained by treating the EtOAc extract with $(AcO)_2Pb$ was bubbled with H_2S and filtered. The yellow filtrate was concentrated to a small volume and chromatographed on a column of Nylon powder using MeOH as eluant. The fractions indicating only one spot on the paper chromatograms were collected, concentrated to a small volume, and diluted with H_2O. After standing overnight, the needles separated were collected and purified by recrystallization from MeOH-H_2O and by subsequent column chromatography on Nylon powder.

II was obtained as yellow needles, m.p. 180~181°(decomp.), undepressed on admixture with authentic quercitrin. II gave a red color with Mg-HCl, a red color with Zn-HCl, and a brown color with $FeCl_3$. The Rf values in the three solvent systems as well as IR and UV spectra were found to be the same as those of authentic specimen. *Anal.* Calcd. for $C_{21}H_{20}O_{11}\cdot 1\frac{2}{3}H_2O$: C, 52.86; H, 4.91; H_2O, 6.2. Found : C, 52.74; H, 4.81; H_2O, 6.4.

Acid Hydrolysis of II——A solution of II in 5% H_2SO_4 was refluxed for 1 hr. The reaction mixture was allowed to stand overnight, and the aglycone separated was collected, washed with H_2O, and recrystallized from MeOH-H_2O. It crystallized as yellow needles, m.p. 300°(decomp.), undepressed on admixture with authentic quercetin.

Acetylation of the aglycone with Ac_2O and AcONa in the usual manner gave colorless needles, m.p. 194~195°, undepressed on admixture with authentic quercetin penta-O-acetate.

The acid filtrate freed of the aglycone was neutralized with $BaCO_3$, filtered, concentrated to a syrup *in vacuo*, and chromatographed on parer. The running distance of the spot on the paper chromatogram of a sugar was found to be the same as that of L-rhamnose.

Infrared spectra were kindly measured by Mrs. Yukiko Tanaka, Faculty of Pharmaceutical Sciences of this University, and ultraviolet spectra by Mr. Masanori Ishii, Faculty of Engeneering of this University. Elemental analyses were also kindly carried out by Dr. Ken'ichi Saruwatari, Director of the Laboratory of Yoshitomi Factory, Yoshitomi Pharmaceutical Ltd.

Summary

A flavonoid compound, $C_{21}H_{20}O_{10}$, m.p. 253~254° (decomp.), was isolated from the leaves of *Rumex acetosa* LINNAEUS and identified as vitexin. Quercitrin was isolated as yellow needles, $C_{21}H_{20}O_{11}\cdot 1\frac{2}{3}H_2O$, m.p. 180~181° (decomp.), from the leaves of *R. japonicus* HOUTTUYN, and identified as such.

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