THE FLAVONOID GLYCOSIDES OF THE LEAVES OF VIBURNUM URCEOLATUM SIEB. ET ZUCC.

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THE FLAVONOID GLYCOSIDES OF THE LEAVES OF *VIBURNUM URCEOLATUM* SIEB. ET ZUCC.

By

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Abstract

The flavonoid components of the leaves of *Viburnum urceolatum* Sieb. *et* Zucc. were investigated. Two flavonoid glucosides were isolated, and identified as populnin (kaempferol-7-O-β-D-glucoside) [**A**] and isoquercitrin (quercetin-3-O-β-D-glucoside) [**B**] by spectral data.

Introduction and Results

In the course of our investigation of the constituents of *Viburnum* species,[1] two flavonoid glucosides were isolated together with four bitter plinciples from *V. urceolatum* (Japanese name: Yamashigure).

We now reprot the structure elucidation of the flavonoid glucosides [**A**] and [**B**]. The Fig. 1 showed the procedure of isolation.

[**A**] was isolated as yellow needles (yield 4.6%), mp. 162–166°C and had the molecular formula $C_{21}H_{20}O_{11}$. It gave a dark green color with ferric chloride solution, reddish yellow color with magnesium and hydrochloric acid, and a positive Molish test. The IR spectrum showed absorption bands of hydroxyl groups, a conjugated carbonyl group, and phenyl groups at 3300, 1660, and 1570 and 1500 cm^{-1}, respectively. The UV spectrum exhibited the absorption maximums at 205 (ε 31,000), 264 (ε 22,000), and 348 nm (ε 18,000). From the above data, [**A**] seemed to be a flavonoid glycoside.

Acetylation of [**A**] with acetic anhydride and pyridine afforded a hepataacetate, mp 210–212°C, $C_{35}H_{34}O_{18}$. The PMR spectrum of the latter compound showed the signals at δ 1.92–2.12 (3H×4) sttributable to four alcoholic acetyl groups and at δ 2. 34–2.44 (3H×3) to three phenolic acetyl groups. An A_2B_2 system st δ 7.31 and 8.13 (2H each, d, J=10 Hz) showed the presence of a p-substituted phenyl group. Two doublets at δ 6.91 and 7.32 (1H each, J=2 Hz) were assigned to the protons at 6– and 8-positions, respectively.

On hydrolysis with 2N-sulfuric acid, [**A**] gave kaempferol and D-glucose.

The position of the glucose was determined to be located at 7-position, since in the UV spectrum of [**A**] the absorption at 264 nm suffered bathochromic shift of only 2 nm with sodium acetate.

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Therefore, [**A**] was established to be populnin.

[**B**] was crystallized as yellow prisms (yield 9.9%), mp 217–218°C with molecular formula $C_{21}H_{20}O_{12}$. It gave dark green color with ferric chloride solution, a reddish purple color on reduction with magnesium and hydrochloric acid, and a positive Molish test. The color reactions, IR spectrum [3500, 3150, 1660, 1610, 1590, 1560, 1500 cm^{-1}] and UV spectrum [207 (ε 39,000), 256 (ε 23,000), 357 nm (ε 20,000)] indicated that [**B**] was a flavonoid glycoside.

Acetyation of [**B**] with acetic anhydride and pyridine yielded a octaacetate, mp 171–172.5°C, $C_{37}H_{36}O_{20}$. The PMR spectrum of the acetate showed the presence of four alcoholic acetyl groups at δ 1.91–2.11 (3H×4) and four phenolic acetyl groups at δ 2.32–2.42 (3H×4). Signals at δ 7.38, 8.08 (1H each, d, J=8 Hz) and δ 7.97 (1H, s) were characteristic for a 3,4-disubstituted B-ring. Two doublets at δ 6.88 and 7.34 (1H each, d, J=3 Hz) were due to the protons at 6- and 8-positions, respectively.

Acid hydrolysis of [**B**] with 2N-sulfuric acid gave quercetin and D-glucose.

The UV spectra of [**B**] in methanol and methanol-sodium acetate were similar to those of rutin[2], which indicated the glucosidic linkage was located at 3-position.

These data suggested that [**B**] was isoquercitrin.

The physical properties of [**B**] and the acetate were in good agreement with those of authentic samples[3].

The structures of the four bitter principles are being determined and will be reported later.

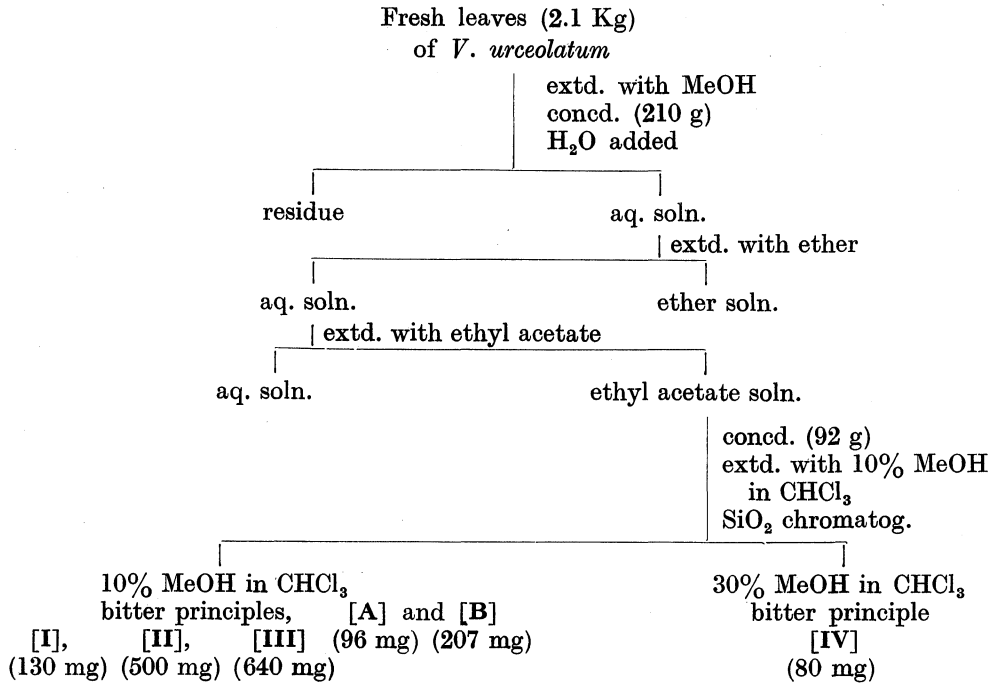

Fig. 1. isolation of the compounds

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus, and uncorrected. The IR and UV spectra were taken on a Schimadzu IR–27 and a Schimadzu UV–210 spectrophotometer, respectively. The PMR spectra were recorded on a JEOL JNM MH–100 spectrometer. Chemical shifts were given in δ values with TMS as the internal standard.

Isolation The fresh leaves of *V. urceolatum* (2.1 Kg) were extracted twice with methanol (10 $l\times2$). The combined methanol solutions were concentrated to dryness to afford a dark green residue (210 g). The residue was diluted with water, and extracted first with ether and then ethyl acetate, yielding an ether soluble porition (30 g) and an ethyl acetate soluble portion (92 g). The latter portion was further extracted three times with 10% methanol in chloroform (100 ml$\times$3) to give a dark green syrup (37g). The syrup was chromatographed on a coloum of silica gel, eluting with methanol-chloroform mixtures.

An elute with 10% methanol in chloroforom was purified by repeated silica gel chromatography to give bitter principles [**I**] (130 mg,), [**II**] (500 mg), [**III**] (640 mg), and yellow needles [**A**] (96 mg), mp. 162–166°C, from methanol. λ_{max}^{MeOH} nm: 205 (ε 31,000), 264 (ε 21,000), 348 (ε 18,000); $\lambda_{max}^{MeOH\text{-}AcONa}$ nm: 205, 266, 352. ν_{max}^{nujol} cm^{-1}: 3300, 1660, 1570, 1500.

Found: C, 52.37; H, 4.7%. Calcd for $C_{21}H_{20}O_{11}2H_2O$: C, 52.07; H, 5.0%.

Further elution with 10% methanol in chloroform and recrystallization from methanol gave yellow prisms [**B**] (20.7 mg), mp 217–218°C. λ_{max}^{MeOH} nm: 207 (ε 39,000), 256 (ε 23,000), 357 (ε 20,000); $\lambda_{max}^{MeOH\text{-}AcONa}$ nm; 207, 266, 363. ν_{max}^{nujol} cm^{-1}; 3500, 3150, 1660, 1610, 1590, 1560, 1500.

Found: C, 50.21; H, 4.60%. Calcd for $C_{21}H_{20}O_{12}2H_2O$: C, 50.40; H, 4.83%.

Elute with 30% methanol in chloroform afforded bitter principle [**IV**] (80 mg).

Acetylation of [**A**] [**A**] (45 mg) was acetylated with acetic anhydride (0.5 ml) and pyridine (0.5 ml). The crude product was chromatographed of a coloum of silica gel (1.5 g). Elution with 1% methanol in chloroform and recrystallization from ethanol gave colorless needles, mp 210–212°C. ν_{max}^{nujol} cm^{-1}: 1770, 1660, 1630, 1590, 1510. PMR ($CDCl_3$): δ 1.92, 1.99, 2.00, 2.12, 2.44 (3H each, s), 2.34 (3H$\times$2, s), 5.60 (1H, d, J=7 Hz), 6.91, 7.32 (1H each, d, J=2 Hz), 7.37, 8.13 (2H, d, J=10 Hz).

Found: C, 56.35; H, 4.64%. Calcd for $C_{35}H_{34}O_{18}$: C, 56.60; H, 4.61%.

Acid hydrolysis of [**A**] [**A**] (39 mg) was refluxed with 2N-sulfuric acid (5 ml) for 2 hr. The resulting precipitate was filtered and recrystallized from aqueous alcohol to give yellow needles (18 mg), mp 276–278°C. ν_{max}^{nujol} cm^{-1}: 3300, 1660, 1620, 1600, 1570, 1550. The IR spectrum was identical with that of kaempherol.

The aqueous solution was treated with excess of barium carbonate, the precipitate was filtered off, and the filtrate was evaporated to dryness in *vacuo*. The presence of D-glucose in the residue was confirmed by paper chromatography.

Acetylation of [**B**] [**B**] (45 mg) was treated as described above to give yellow needles (35 mg), mp 171–172.5°C from ethanol. ν_{max}^{nujol} cm^{-1}: 1785, 1770, 1630, 1220. PMR ($CDCl_3$): δ 1.91, 1.92, 2.01, 2.11, 2.45 (3H each, s), 2.32 (3H×3, s), 5.64 (1H, d, J=6 Hz), 6.88, 7.34 (1H each, d, J=3 Hz), 7.97 (1H, s), 7.38, 8.08 (1H each, d, J=8 Hz).

Found: C, 55.51; H, 4.51%. Calcd for C, 55.50; H, 4.53%.

Acid hydrolysis of [**B**] [**B**] (50 mg) in 2N-sulfufic acid (5 ml) was worked up in a similar way to [**A**] to give yellow needles (20 mg), mp>300°C from aqueous alcohol. ν_{max}^{nujol} cm^{-1}: 3200, 1665, 1600, 1570, 1500. The compound was identified as quercetin by comparing its IR spectrum with that of an authentic sample.

The sugar from the aqueous solution was identified as D-glucose by paper chromatography.

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