

## Isorhamnetin Glycosides from the Leaves of *Typha latifolia*

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「큰잎부들」 잎의 Isorhamnetin 배당체

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From the leaves of *Typha latifolia*, L. (Typhaceae) isorhamnetin-3-O-glucoside and isorhamnetin-3-O-neohesperidoside were isolated and characterized by chemical and spectral analysis.

Previous workers reported the occurrence of several quercetin and kaempferol glycosides in the leaves of *Typha latifolia* L. (Typhaceae).<sup>1,2)</sup> In this communication, we report the isolation of two isorhamnetin glycosides from the same source.

Column chromatography of the butanol soluble portion of the methanol extract and crystallization yielded two compounds as yellowish needles, which designated as compound I, mp 215~8° and II, mp 194~7°, in addition to 3, 3'-di-O-methylquercetin-4'-O-glycoside.<sup>2)</sup> Both compound I and II showed characteristic flavonol glycoside color reactions. The UV spectral response to shift reagents of both compounds showed the presence of three free hydroxyls at 5, 7, 4'-positions.<sup>3)</sup>

Acid hydrolysis of each compound afforded isorhamnetin(III), mp 305°, as the genin. In the hydrolysate, glucose from I and glucose and rhamnose from II, were identified, respectively. Methylation of I with CH<sub>2</sub>N<sub>2</sub> followed by acid hydrolysis afforded 5, 7, 3', 4'-tetra-O-methyl quercetin (IV), mp 193~4°, indicating that glucose is attached at C-3 in compound I. This was confirmed by direct comparison with an

authentic sample of isorhamnetin-3-O-glucoside.

Acetylation of II with Ac<sub>2</sub>O/pyridine afforded a nonaacetate (V), mp 123~6°. The signals for anomer protons of rhamnose and glucose was found at  $\delta$  5.02 and 5.73 in the PMR spectrum of II, respectively and the number of sugar protons found in the regions 4.5~5.6ppm and 3.5~4.5ppm of the spectrum of V was ratio 7:5.

This result strongly suggested that II was 3-neohesperidoside.<sup>3,4)</sup> This suggestion was confirmed by permethylation and methanolysis of II, which yielded IV and methyl glycosides of 3, 4, 6-tri-O-methyl glucopyranose and 2, 3, 4-tri-O-methyl rhamnopyranose.

This is the first report of the occurrence of isorhamnetin glycosides in this plant.

### Experimental

**Extraction and Isolation:** The MeOH extract of the leaves of *T. latifolia* was worked up as described in the previous paper.<sup>2)</sup>

**Compound I:** Crystallized from MeOH as yellowish needles, mp 215~8°,  $[\alpha]_D^{25}$  -21.7° (C=0.06, MeOH), IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup> 3360(OH),

1645(C=O), 1600, 1492(C=C), 1100-1000 (C-O); UV  $\lambda_{\max}^{\text{EtOH}}$  nm(log  $\epsilon$ ) 256(4.26), 270(sh, 4.17), 310(sh, 3.94), 361(4.20);  $\lambda_{\max}^{\text{EtONa}}$  275(4.27), 337(3.94), 426(4.33);  $\lambda_{\max}^{\text{NaOAc}}$  278(4.28), 322(4.02), 382(4.09);  $\lambda_{\max}^{\text{AlCl}_3}$  270(4.24), 304(sh, 3.86), 368(4.04), 410(4.13);  $\lambda_{\max}^{\text{AlCl}_3+\text{HCl}}$  270(4.22), 304(3.86), 362(4.03), 410(4.09);  $\lambda_{\max}^{\text{NaOAc}+\text{H}_3\text{BO}_3}$  256(sh, 4.17), 272(4.23), 324-340(4.01), 368(4.10).

**Compound II:** Crystallized from MeOH as yellowish needles, mp 194~7°,  $[\alpha]_D^{23} -104^\circ$  (C=0.1, MeOH), IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup> 3300(OH), 1650 (C=O), 1595, 1490(C=C), 1100~1000(C-O); UV  $\lambda_{\max}^{\text{EtOH}}$  nm(log  $\epsilon$ ) 254(4.40), 270(sh, 4.30), 300(sh, 4.07), 356(4.33);  $\lambda_{\max}^{\text{EtONa}}$  272(4.39), 334(4.09), 415(4.43);  $\lambda_{\max}^{\text{NaOAc}}$  276(4.41), 321(4.16), 371(4.23);  $\lambda_{\max}^{\text{AlCl}_3}$  271(4.40), 304(4.00), 368(4.21), 410(4.27);  $\lambda_{\max}^{\text{AlCl}_3+\text{HCl}}$  271(4.36), 304(4.00), 362(4.21), 403(4.22);  $\lambda_{\max}^{\text{NaOAc}+\text{H}_3\text{BO}_3}$  258(4.38), 267(4.33), 358(4.30); NMR(DMSO-d<sub>6</sub>, TMS)  $\delta$  0.65(3H, d, J=6, Rha-CH<sub>3</sub>), 3.86(3H, s, OCH<sub>3</sub>), 5.02(1H, s, Rha H-1), 5.73(1H, bs, Glu H-1), 6.21(1H, d, J=2, H-6), 6.44(1H, d, J=2, H-8), 6.91(1H, d, J=8, H-5'), 7.51(1H, dd, J=8 & 2, H-6'), 7.96(1H, d, J=2, H-2'), 12.62(1H, s, 5-OH).

**Hydrolysis of I:** A solution of I(8mg) in 5% H<sub>2</sub>SO<sub>4</sub>(10ml, H<sub>2</sub>O+dioxane=1:1) was refluxed for 3hr. After removing the solvent, the precipitate was filtered and crystallized from MeOH to give III, mp 305°, as yellowish needles, which was identical with an authentic sample of isorhamnetin.

The filtrate was neutralized with BaCO<sub>3</sub>, filtered and concentrated in vacuo. D-Glucose was identified by TLC (Precoated cellulose, pyridine:ethylacetate:HOAc:H<sub>2</sub>O=5:5:1:3, Rf 0.40).

**Methylation and hydrolysis of I:** To a solution of I(15mg) in MeOH, ethereal CH<sub>2</sub>N<sub>2</sub>

was added to stand in the cold room for 2 days. The reaction mixture was concentrated, dissolved in 5% H<sub>2</sub>SO<sub>4</sub>(dioxane-H<sub>2</sub>O=1:1, 10ml) and refluxed for 2hr. The aglycone, after the usual work-up, was identified as 5, 7, 3', 4'-tetra-O-methyl quercetin, mp 193~4°, by direct comparison with an authentic sample.

**Hydrolysis of II:** A sample (10mg) of II was hydrolyzed as described of I to give III and glucose and rhamnose.

**Acetylation of II:** A sample (15mg) of II was acetylated with Ac<sub>2</sub>O/pyridine(1ml each) at room temperature overnight. The reaction mixture was poured onto water and filtered. The filtrate was crystallized from acetone-water to yield whitish amorphous powder, mp 123~6°, IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup> 1745, 1200(acetate); NMR (CDCl<sub>3</sub>, TMS)  $\delta$  0.94(3H, d, J=6, Rha-CH<sub>3</sub>), 1.89(3H, s, acetoxy), 2.00(6H, s, 2×acetoxy), 2.04(3H, s, acetoxy), 2.10(3H, s, acetoxy), 2.13(3H, s, acetoxy), 2.34(6H, s, 2×acetoxy), 2.49(3H, s, acetoxy), 3.90(3H, s, OCH<sub>3</sub>), 4.91(1H, s, Rha H-1), 5.60(1H, d, J=8, Glu H-1), 6.81(1H, d, J=2, H-6), 7.09(1H, d, J=8, H-5'), 7.25(1H, d, J=2, H-8), 7.55(1H, dd, J=8 & 2, H-6'), 7.63(1H, d, J=2, H-2').

**Permethylation followed by methanolysis of II:** A sample (30mg) of II was methylated with CH<sub>2</sub>N<sub>2</sub> and the solution was evaporated to dryness to give a residue, to which MF(2ml), CH<sub>3</sub>I(1ml) and NaH(50mg) were added (Brimacombe's method<sup>5</sup>) and the mixture was allowed to stand at room temperature overnight. After the usual work-up, the resulting permethylether was hydrolyzed with 2% HCl-MeOH(100ml) for 5hr on a steam bath. 5, 7, 3', 4'-Tetra-O-methyl quercetin(IV), mp 193~4°, was identified by direct comparison with an authentic sample (mmp, TLC and UV) and methylglycosides of 3, 4, 6-tri-O-methyl gluco-

pyranose(Rf 0.13; Rt 4.7 and 5.4) and 2,3,4-tri-O-methyl rhamnose(Rf 0.57; Rt 0.8) were detected (GLC: column 5% NPGS on Gas chrom Q, 2.2m×4mm, column temp 175°, FID temp 200°, chart speed 1cm/min, N<sub>2</sub> gas 45ml/min; TLC: hexane-ethylacetate=2:3).

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