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A FLAVONOL GLUCOSIDE FROM *TYPHA LATIFOLIA*

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Key Word Index—*Typha latifolia*; Typhaceae; flavonoid glycoside; 3,3′-di-*O*-methylquercetin 4′-*O*-glucoside.

Abstract—Chromatographic separation of the butanol-soluble part of the methanol extract of *Typha latifolia* leaves resulted in the isolation of a new flavonoid, 3,3′-di-*O*-methylquercetin 4′-*O*-glucoside, together with the known isorhamnetin 3-*O*-glucoside and 3-*O*-neohesperidoside.

Typha latifolia is a perennial herbaceous plant, which has been used in traditional Chinese medicine as an anti-inflammatory agent and diuretic. Previous workers have reported that the leaves of this plant contain quercetin and kaempferol 3-*O*-glucosides, quercetin and kaempferol 3-*O*-galactosides and quercetin 3-*O*-neohesperidoside [1]. In this communication, we deal with the isolation of a new compound, 3,3′-di-*O*-methylquercetin 4′-*O*-glucoside (**1**). In addition, isorhamnetin 3-*O*-glucoside and 3-*O*-neohesperidoside are also reported for the first time from this plant.

Column chromatography of the butanol-soluble part of the methanol extract of the leaves and crystallization yielded yellowish needles (**1**), $C_{23}H_{24}O_{12}$, mp 216–218°, $[\alpha]_D^{26}$ −47.2°, which gave characteristic flavonol glycoside colour reactions, pink with Zn + HCl and Mg + HCl, dark blue with $FeCl_3$ and a positive Molisch test. The IR spectrum of **1** showed a broad hydroxyl and α,β-unsaturated carbonyl absorptions at 3300 and 1640 cm^{-1}, respectively, and C–O stretching bands at 1010, 1020 and 1060 cm^{-1}, indicating its glycosidic nature. The UV maxima at 253, 271 and 350 nm were very similar to those reported for a number of 3-hydroxyl substituted flavonols [2]. It showed a bathochromic shift with $AlCl_3$ and $AlCl_3$ + HCl in band I and with NaOAc in band II which indicated the presence of free 5-hydroxyl and 7-hydroxyl groups. Acid hydrolysis of **1** gave an aglycone (**2**), mp 255°, and glucose. The aglycone (**2**) showed UV maxima at 256, 270 and 360 nm. A bathochromic shift of the UV with NaOEt, with an increase in intensity of band I, indicated the presence of a free 4′-hydroxyl group in **2**.

The ^1H NMR spectrum of **2** in DMSO-d_6 showed two methoxy singlets at δ3.87 and 3.92, two *meta*-coupled doublets of one proton each at 6.20 (J = 2 Hz, H-6) and 6.46 (J = 2 Hz, H-8), one *ortho*-coupled doublet of one proton at 6.95 (J = 8 Hz, H-5′), a double-doublet of one proton at 7.55 (J = 8 and 2 Hz, H-6′), a *meta*-coupled doublet of one proton at 7.63 (J = 2 Hz, H-2′) and a singlet of one proton at 12.65 (5-OH). These data indicated that **2** was a 3,5,7,3′,4′-oxygenated flavonoid derivative. The appearance of the H-2′ signal at lower field than the H-6′ signal suggested the presence of a 3′-methoxy-4′-hydroxy moiety in the B-ring [2]. This suggestion was confirmed by vanillic acid formation on alkali degradation of **2**.

The mass spectrum of **2** showed the molecular ion peak at m/z 330 (100%) and the retro-Diels–Alder fragments at m/z 153 (A ring, 21.3) and 151 (B ring, 32.7). The presence of intense peaks at m/z 329 ($[M-H]^+$, 62.2), 315 ($[M-Me]^+$, 38.5), 312 ($[M-H_2O]^+$, 7.6), 301 ($[M-HCO]^+$, 11.9), 299 ($[M-MeO]^+$, 14.1), 287 ($[M-MeCO]^+$, 50.8) suggested that one of the methoxy groups was located at C-3 [3]. The physico-chemical and spectral data of **2** were identical with those of 3,3′-di-*O*-methylquercetin [4–6]. The position of sugar attachment in **2** was established by the formation of 3,5,7,3′-tetra-*O*-methylquercetin, mp 198–200°, on hydrolysis of the methylated glycoside with Me_2SO_4 and K_2CO_3.

Acetylation of **1** gave the hexaacetate (**3**). The ^1H NMR spectrum of **3** showed four sugar acetoxyls at δ2.08 (6H) and 2.04 (6H), confirming the presence of 1 mol of glucose unit. β-Orientation of the glucosidic linkage was supported not only by the J value (8 Hz) of the anomeric proton signal, but also by the molecular rotation difference (−232°) between **1** and **2** ($[M]_D$ of phenyl-β-D-glucopyranoside −182°) [7].

On the basis of these results, the structure of **1** was established as 3,3′-di-*O*-methylquercetin 4′-*O*-β-D-glucopyranoside. This is the first report of its occurrence in nature to our best knowledge.

EXPERIMENTAL

Plant material. Fresh leaves of *Typha latifolia* were collected near Seoul in autumn, 1980. A voucher specimen has been deposited in the Herbarium of the Royal Botanical Gardens in Kew.

Isolation of flavonoids. The dried leaves (2.5 kg) were extracted with MeOH and concd to a dark residue, which was partitioned between hexane and H_2O. The aq. layer was extracted with $CHCl_3$ followed by BuOH. The BuOH extract (80 g) was then subjected to silica gel CC, using $CHCl_3$–MeOH–H_2O (13:7:2, lower phase) as eluant, to yield **1** (400 mg), mp 216–218°, $[\alpha]_D^{26}$ −47.2° (*c* 0.036; MeOH); isorhamnetin 3-*O*-glucoside (50 mg), mp 215–218°, $[\alpha]_D^{23}$ −21.7° (*c* 0.06; MeOH); isorhamnetin 3-*O*-neohesperidoside (90 mg), mp 194–197°, $[\alpha]_D^{23}$ −104° (*c* 0.1; MeOH).

Compound **1**: UV λ_{max}^{EtOH} nm (log ε): 253 (4.23), 271 (4.31), 350 (4.21); with NaOEt 280 (4.48), 308 (sh, 4.14), 382 (4.11); with $AlCl_3$ 262 (4.21), 280 (4.28), 298 (sh, 4.11), 352 (4.20), 402 (4.09); with

$AlCl_3$ + HCl 259 (4.21), 281 (4.27), 350 (4.19), 402 (4.02); with NaOAc 279 (4.46), 311 (4.12), 375 (4.11); with NaOAc + H_3BO_3 272 (4.34), 318 (4.13), 352 (4.15); ^{1}H NMR (DMSO-d_6, TMS): δ3.87 (3H, *s*, OMe), 3.92 (3H, *s*, OMe), 6.20 (1H, *d*, J = 2 Hz, H-6), 6.48 (1H, *d*, J = 2 Hz, H-8), 7.28 (1H, *d*, J = 8 Hz, H-5'), 7.63 (1H, *dd*, J = 8 and 2 Hz, H-6'), 7.67 (1H, *d*, J = 2 Hz, H-2'), 5.10 (1H, *br s*, $W_{1/2}$ = 10 Hz, anomer H), 12.60 (1H, *br s*, 5-OH).

Hydrolysis of **1**. A soln of **1** (100 mg) in 5% H_2SO_4 (20 ml) was refluxed for 4 hr. The solid, after cooling and separating, was crystallized from MeOH to give yellowish needles (**2**) (35 mg), mp 255° (lit. [4], mp 257–260°); IR ν_{max}^{KBr} cm^{-1}: 3480, 3100 (OH), 1645 (C=O), 1610 (C=C); UV λ_{max}^{EtOH} nm (log ε): 256 (4.24), 270 (4.21), 360 (4.24); with NaOEt 277 (4.30), 334 (3.98), 416 (4.43); with $AlCl_3$ 268 (4.25), 277 (4.22), 301 (3.85), 367 (4.12), 406 (4.17); with $AlCl_3$ + HCl 268 (4.16), 278 (4.18), 299 (3.87), 357 (4.11), 4.02 (4.08); with NaOAc 279 (4.32), 321 (4.03), 389 (4.14); with NaOAc + H_3BO_3 257 (4.21), 270 (4.24), 360 (4.30). The aq. layer was concd *in vacuo*. D-Glucose was identified by TLC (precoated cellulose, pyridine–EtOAc–HOAc–H_2O, 5:5:1:3, R_f 0.40).

Acetate of **1**. This was obtained from EtOAc as an amorphous white powder (**3**), mp 209–211°; IR ν_{max}^{KBr} cm^{-1}: 1750, 1215 (acetate); ^{1}H NMR ($CDCl_3$, TMS): δ2.04 (6H, *s*, 2 × MeCO), 2.08 (6H, *s*, 2 × MeCO), 2.33 (3H, *s*, MeCO), 2.46 (3H, *s*, MeCO), 3.83 (3H, *s*, OMe), 3.92 (3H, *s*, OMe), 4.25 (2H, *br s*, $W_{1/2}$ = 7 Hz, H-6''), 5.23 (1H, *d*, J = 8 Hz, β-anomer H), 4.90–5.50 (3H, *m*, H-2'', 3'', 4''), 6.82 (1H, *d*, J = 2 Hz, H-6), 7.25 (1H, *d*, J = 8.5 Hz, H-5'), 7.30 (1H, *d*, J = 2 Hz, H-8), 7.60 (1H, *dd*, J = 8.5 and 2 Hz, H-6'), 7.63 (1H, *d*, J = 2 Hz, H-2').

Methylation of **1** *followed by hydrolysis*. The product crystallized from MeOH to yield 3,5,7,3'-tetra-*O*-methylquercetin, mp 198–200° (lit. [8], mp 199–201°), identified by direct comparison with an authentic sample (mmp, UV, TLC).

Degradation of **2** *with alkali*. A mixture of **2** (2 mg) and 2 M NaOH in 50% EtOH (30 ml) was heated at 120° until the soln was evapd. After cooling and dilution with H_2O, the reaction mixture was acidified with dilute HCl and extracted with Et_2O. Vanillic acid was identified by TLC ($CHCl_3$–MeOH–H_2O, 13:7:2, lower phase, R_f = 0.49).

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