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Flavonol Glycosides from the Leaves of *Kalopanax pictum*

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Abstract—Quercitrin and hyperin were isolated from the leaves of *Kalopanax pictum* and these structures were characterized on the basis of chemical and spectral data.

Keywords—*Kalopanax pictum* · Araliaceae · flavonol glycoside · quercitrin · hyperin

Kalopanax pictum Nakai(Araliaceae) is a deciduous tree, which has been used as folkloric medicine for the treatment of rheumatic arthritis caused by the wind and dampness, pains in the loin and knee, scabies, antidiabetes and nutritious tonic.[1] The previous authors reported on the isolation of various triterpenoidal saponins from *Kalopanax* species.[2] The present paper describes isolation and structural characterization of two flavonol glycosides(**1** and **2**) from the leaves of *K. pictum*.

Experimental

General procedure—The mps were taken on a Yanaco micro-melting point apparatus and are uncorrected. The IR spectra were determined in KBr tablets on a Perkin-Elmer 841 spectrophotometer and the UV spectra were run with a Varian DMS 200 UV-Vis spectrophotometer. The MS spectrum was recorded on a Kratos MS 25 RFA mass spectrometer. The ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AM-300 spectrometer with TMS as an internal standard and chemical shifts are given as ppm. TLC chromatography was performed on precoated Kieselgel 60 F_{254} plates(Merck, 5715).

Plant Material—The leaves of *K. pictum* were collected in Kyung Bug province of Korea in the summer season of 1991, and authenticated by Prof. Song Jong Suk, Department of Biology, Andong National University, Korea. A voucher specimen is deposited in College of Pharmacy, Yeungnam University.

Extraction, Fractionation and Isolation—The dried chopped leaves of *K. pictum* (1 kg) were extracted with MeOH under reflux(3 times, 12 h each) and evaporated in vacuo to give a residue(297 g). The MeOH extract was partitioned with n-hexane (80.19 g), $CHCl_3$ (29.7 g), EtOAc (8.91 g) and n-BuOH (65.34 g), successively. The EtOAc extract was subjected to column chromatography over silica gel using $CHCl_3$-MeOH-H_2O(7 : 3 : 1, lower layer) elution to give crude **1** and **2**. Each compound was rechromatographed over Sephadex LH-20 eluted with MeOH to yield pure **1** and **2**, respectively.

Quercitrin(1)—A yellow amorphous powder from MeOH, mp 178~180°, $FeCl_3$, Mg/HCl, Molisch tests: positive. IR, ν_{max}^{KBr} 3264(OH), 1660 (α,β-unsaturated ketone), 1599, 1557, 1517 (aromatic C=C), 1050(glycosidic C—O) cm^{-1}; UV, λ_{max}^{MeOH} nm(log ε) 268(4.3), 296(4.1), 350(4.3);

$\lambda_{max}^{MeOH+NaOMe}$ nm (log ε) 274(4.5), 328(4.1), 398 (4.4); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε) 275(4.5), 305(sh, 3.7), 435(4.4); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ε) 272 (4.4), 305(sh, 3.8), 356(4.1), 398(4.1); $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε) 273(4.5), 325(sh, 3.9), 374(4.3); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm (log ε) 266 (4.3), 300(sh, 3.8), 368(4.2); ^{1}H-NMR (DMSO-d_6) δ: 12.6(1H, brs, C_5-OH), 7.32 (1H, d, J=1.6 Hz, H-2′), 7.27 (1H, dd, J=1.6 and 8.3 Hz, H-6′), 6.88(1H, d, J=8.3 Hz, H-5′), 6.39 (1H, d, J=1.7 Hz, H-8), 6.21(1H, d, J=1.7 Hz, H-6), 5.28(1H, s, anomeric H), 0.84(3H, d, J=5.9 Hz, Me of Rha); ^{13}C-NMR: see Table I.

Hyperin (2)—A yellow amorphous powder from MeOH, mp 253~254°, $FeCl_3$, Mg/HCl, Molisch tests: positive. IR, ν_{max}^{KBr} 3348(OH), 1653 (α, β-unsaturated ketone), 1606, 1558, 1507 (aromatic C=C), 1021(glycosidic C—O) cm^{-1}; UV, λ_{max}^{MeOH} nm (log ε) 256(4.3), 268(sh, 4.2), 295(sh, 3.9), 350(4.2); $\lambda_{max}^{MeOH+NaOMe}$ nm (log ε) 274(4.2), 328(3.9), 412(4.3); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε) 276(4.2), 302(3.6), 339(3.5), 441 (4.3); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ε) 269(4.0), 301 (3.7), 368(4.0), 408(4.1); $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε) 275(4.2), 328(3.9), 368(4.1); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm (log ε) 260(4.2), 309(3.7), 378(4.2); ^{1}H-NMR (DMSO-d_6) δ: 12.6(1H, brs, C_5-OH), 7.66(1H, dd, J=2.3 and 8.5 Hz, H-6′), 7.54 (1H, d, J=2.3 Hz, H-2′), 6.82(1H, d, J=8.5 Hz, H-5′), 6.40(1H, d, J=1.9 Hz, H-8), 6.20(1H, d, J=1.9 Hz, H-6), 5.36(1H, d, J=7.7 Hz, anomeric H); ^{13}C-NMR: see Table I.

Table I. ^{13}C-NMR Spectral data for **1**, **2** and **3** in DMSO-d_6

Carbon No.	1	2	3
C-2	157.3	156.2[a]	146.7
C-3	134.3	133.5	135.6
C-4	177.8	177.4	175.7
C-5	161.3	161.2	160.6
C-6	98.7	98.6	98.1
C-7	164.3	164.2	163.8
C-8	93.7	93.5	93.3
C-9	156.5	156.3[a]	156.1
C-10	104.1	103.8	102.9
C-1′	120.8	121.1	121.9
C-2′	115.5	115.1	115.0
C-3′	145.2	144.8	145.0
C-4′	148.5	148.4	147.6
C-5′	115.7	115.9	115.5
C-6′	121.1	121.9	119.9
C-1″	101.7	101.9	
C-2″	70.1[a]	71.2	
C-3″	70.4[a]	73.2	
C-4″	71.2	67.9	
C-5″	70.6[a]	75.8	
C-6″	17.5	60.1	

[a]Assignments may be reversed in the vertical column.

Acid hydrolysis of 1 and 2—Solutions of each glycoside(30 mg each) in 4% methanolic H_2SO_4(5 ml) was refluxed for 1h, and each reaction mixture was diluted with ice water. The precipitates were collected by filtration and purified by recrystallization from MeOH to afford the same aglycone, quercetin(**3**).

Quercetin (3)—Yellow amorphous powder from MeOH, mp> 300°, $FeCl_3$, Mg/HCl tests: positive. IR, ν_{max}^{KBr} 3380(OH), 1669(α, β-unsaturated ketone), 1614, 1512(aromatic C=C) cm^{-1}; UV, λ_{max}^{MeOH} nm (log ε) 267(4.3), 371(4.5); $\lambda_{max}^{MeOH+NaOMe}$ nm (log ε) 251(4.5), 332(4.5); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε) 273(4.5), 337(3.7), 368 (3.7), 459(4.6); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ε) 269 (4.4), 362(4.0), 427(4.5); $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε) 267(4.3), 275(4.4), 325(4.2), 392(4.3); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm (log ε) 252(4.5), 266(4.3), 388(4.4); EI-MS, m/z (rel. int.) 302 [M]$^+$ (100.0), 301 [M-H]$^+$ (16.9), 274 [M-CO]$^+$ (7.0), 273 [M-HCO]$^+$ (8.6), 245 [273-CO]$^+$ (5.4), 153 [RDA fragment with A ring+H]$^+$ (10.7), 137 [RDA fragment with B ring]$^+$

(19.2), 109 [137-CO]$^+$ (14.4); ^{1}H-NMR (DMSO-d_6) δ : 12.5 (1H, brs, C_5-OH), 7.67 (1H, d, J=2.1 Hz, H-2′), 7.54 (1H, dd, J= 2.1 and 8.5 Hz, H-6′), 6.89(1H, d, J=8.5 Hz, H-5′), 6.40 (1H, d, J=1.9Hz, H-8), 6.18 (1H, d, J=1.9 Hz, H-6); ^{13}C-NMR: see Table I.

Results and Discussion

After repeated chromatography of the EtOAc-soluble portion of a methanolic extract, two compounds(1 and 2) were obtained as yellow amorphous powder.

Compounds 1 and 2 gave positive $FeCl_3$, Mg/HCl and Molisch tests and showed absorption bands for glycosidic linkage in their IR spectra, indicating to be flavonoid glycosides. Acid hydrolysis of each compound yielded the common aglycone(3) along with rhamnose from 1 and galactose from 2. Compound 3 was identified as quercetin on the basis of spectroscopic evidence (see Experimental). The ^{1}H-NMR spectrum of each compound showed only one anomeric proton signal, suggesting the presence of one mole of sugar in each compound. The UV spectra in both compounds exhibited typical absorption maxima(band I) of 3-hydroxyl substituted flavonol at 350~360nm. A bathochromic shift of band I in the presence of $AlCl_3$ or $AlCl_3$+HCl and of band II in the presence of NaOAc relative to MeOH spectrum indicated the presence of free 5- and 7-hydroxyl groups. A bathochromic shift of band I in the NaOAc +H_3BO_3 spectrum relative to MeOH spectrum and a hypsochromic shift observed in band I of the $AlCl_3$+HCl spectrum relative to $AlCl_3$ spectrum showed the presence of an *ortho*-dihydroxyl groups in the B ring.[3] Thus, it was suggested that the sugar might be attached to 3-hydroxyl group. On the comparison of the ^{13}C-NMR data of 1 and 2 with that of quercetin(3), the signals due to C-2, C-3 and C-4 of each compound revealed significant glycosidation shift, which was further confirmed the glycosidic position at C-3 in both compounds. The configuration of sugar moiety was determined by J value of the anomeric signal. In the light of the above evidence, the structures of 1 and 2 were identified as quercetin 3-O-α-L-rhamnopyranoside (quercitrin) and quercetin 3-O-β-D-galactopyranoside(hyperin), respectively.

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