

Flavonoids from the Rhizomes of *Belamcanda chinensis*

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Abstract □ Two flavonoids were isolated from the rhizomes of *Belamcanda chinensis* and identified as kanzakiflavone-2 and 2R:3R-dihydrokaempferol-7-methylether, respectively.

Keywords □ *Belamcanda chinensis*, Iridaceae, flavonoids, kanzakiflavone-2, 2R:3R-dihydrokaempferol-7-methylether.

The rhizomes of *Belamcanda chinensis* (Iridaceae) have been used as a Chinese drug to treat throat trouble such as tonsillitis¹⁾. Recently, it was found that this drug contained a number of isoflavonoids by intensive phytochemical investigations²⁻⁴⁾. This paper deals with the isolation and characterization of a flavone **1** and a dihydroflavonol **2** from the drug.

Repeated column chromatography of the chloroform soluble fraction of the methanol extract gave compounds **1** and **2** in addition to previously isolated isoflavones^{2,4)}.

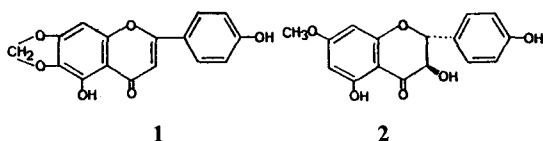
Compound **1**, mp > 310°C, gave positive FeCl₃ and Zn+HCl tests and showed the presence of a hydroxyl (3250 cm⁻¹), α, β-unsaturated ketone (1680 cm⁻¹), aromatic system (1600, 1470 cm⁻¹) and a methylenedioxy function (928 cm⁻¹) in its IR spectrum. Its UV spectrum exhibited typical absorption maxima of flavone at 287.0 and 338.5 nm. Appearance of two one proton signals at δ 6.84 and 6.93, assignable to H-3 and H-8, respectively, and a pair of two proton ortho-coupled doublets (*J*=8.8 Hz) at δ 6.92 and 7.93, accountable for 4'-substituted B ring protons and a two proton singlet at δ 6.15 indicating the presence of a methylenedioxy group in its proton NMR (DMSO-d₆) suggested that compound **1** be a 5,6,7,4'-tetraoxygenated flavone. The bathochromic shift of UV band I and II in the presence of AlCl₃ and appearance of an exchangeable proton signal at δ 13.0 indicated the presence of free 5-hydroxy group, thus compound **1** was identified as 5,4'-dihydroxy-6,7-methylenedioxyflavone (kanzakiflavone-2)⁵⁾. The ¹³C-NMR spectrum and

MS spectrum are in complete agreement with the structure of this compound.

Compound **2**, mp 187-189°C, gave positive FeCl₃, Mg+HCl, Zn+HCl tests and showed the presence of a hydroxyl (3400 cm⁻¹), α, β-unsaturated ketone (1645 cm⁻¹), aromatic system (1600, 1510, 1465 cm⁻¹) in its IR spectrum. Its UV spectrum showed an absorption maximum at 290 nm, suggesting to be a 2,3-dihydroflavonoid. Its proton NMR (DMSO-d₆) showed a two proton broad singlet at δ 6.08, assignable to H-6 and H-8 and a pair of two proton ortho-coupled doublets (*J*=8.5 Hz) at δ 6.77 and 7.31 corresponding to 4'-substitute B ring protons, all accountable for a 5,7,4'-trisubstituted flavonoid. Appearance of a doublet (*J*=11.4 Hz) at δ 5.10 and a double doublet (*J*=11.4 and 6.0 Hz) at δ 4.57, of which the latter was collapsed to a doublet by an addition of D₂O, indicating the presence of a hydroxyl group at C-3. The NMR showed clearly three hydroxyl groups at δ 11.83 (1H, s), 9.51 (1H, s) and 5.76 (1H, d, *J*=6.0 Hz), all exchangeable by D₂O and one methoxyl group at δ 3.77 (3H, s). A detailed examination of its MS spectrum, showing retro-Diels-Alder fragments at *m/z* 136 and 166, revealed the presence of one hydroxyl and one methoxyl on ring A and one hydroxyl on ring B. The bathochromic shift of the UV band in the presence of AlCl₃ or AlCl₃+HCl indicated the presence of free 5-hydroxyl group. As expected, however, its UV absorption was not changed on addition of NaOAc. Finally its ¹³C-NMR spectrum showed sixteen carbon atoms possessing multiplicity and chemical shifts in perfect agreement with the proposed struc-

Table I. ^{13}C -NMR chemical shifts of compounds **1** and **2** (DMSO- d_6 , 20 MHz)

Carbon No.	1	2	Carbon No.	1	2
2	163.9	83.4	1'	121.0	127.7
3	106.6	71.8	2',6'	128.3	129.9
4	182.3	198.6	3',5'	115.9	115.3
5	153.6	163.3	4'	161.1	158.0
6	129.4	95.3			
7	141.1	168.0			
8	89.3	94.2	O		
			CH ₂	102.6	
9	152.3	162.9	O		
10	106.6	101.7	OCH ₃		56.3



ture. All the spectral data together with its optical value led to the conclusion that compound **2** was 2R:3R-dihydrokaempferol-7-methylether⁶⁾. This is the first record on the occurrence of dihydroflavonol in this family.

EXPERIMENTAL

Isolation of compounds

The CHCl_3 soluble fraction of the MeOH extract from the dried rhizomes of *B. chinensis* purchased in a drug market, was chromatographed over an SiO_2 column and eluted with CHCl_3 -MeOH (gradient) and then the fractions containing compounds **1** and **2** subjected to SiO_2 column chromatography using hexane-EtOAc (gradient) to give each compound.

Compound **1** (kanzakiflavone-2)-crystallized from MeOH as pale yellow needles, mp >310°C, UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 287.0 (4.38), 338.5 (4.57); $\lambda_{\text{max}}^{\text{MeOH}+\text{MeONa}}$ 294.0 (4.25), 305.0 (4.25), 361.5 (4.58); $\lambda_{\text{max}}^{\text{MeOH}+\text{NaOAc}}$ 284.0 (4.34), 336.5 (4.57); $\lambda_{\text{max}}^{\text{MeOH}+\text{NaOAc}+\text{H}_3\text{BO}_3}$

284.0 (4.34), 336.5 (4.57); $\lambda_{\text{max}}^{\text{MeOH}+\text{AlCl}_3}$ 304.0 (4.43), 368.0 (4.62); $\lambda_{\text{max}}^{\text{MeOH}+\text{AlCl}_3+\text{HCl}}$ 302.5 (4.43), 360.5 (4.58); MS m/z (rel. int.): 298 (M^+ , 100), 180 (RDA with A ring, 25.5), 118 (RDA with B ring, 19.4); IR, ^1H -NMR: see text; ^{13}C -NMR: see Table I.

Compound **2** (2R:3R-dihydrokaempferol-7-methylether)-crystallized from CHCl_3 as yellow needles, mp 180-182°C, $[\alpha]_D^{25} + 30.9^\circ\text{C}$ ($c=0.11$, MeOH); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 290.0 (4.37); $\lambda_{\text{max}}^{\text{MeOH}+\text{MeONa}}$ 289.5 (4.34), 359.0 (3.96), $\lambda_{\text{max}}^{\text{MeOH}+\text{NaOAc}}$ 290.5 (4.44); $\lambda_{\text{max}}^{\text{MeOH}+\text{NaOAc}+\text{H}_3\text{BO}_3}$ 290.5 (4.44); $\lambda_{\text{max}}^{\text{MeOH}+\text{AlCl}_3}$ 314.5 (4.48); $\lambda_{\text{max}}^{\text{MeOH}+\text{AlCl}_3+\text{HCl}}$ 312.0 (4.40); MS m/z (rel. int.): 302 (M^+ , 2.7), 167 (RDA with A ring + H^+ , 100), 166 (RDA with A ring 4.5), 136 (RDA with B ring, 22.8), 134 (167- CH_3 - H_2O , 53.3); IR, ^1H -NMR: see text; ^{13}C -NMR: see Table I.

ACKNOWLEDGEMENT

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