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Decursin from the Rhizome of *Belamcanda chinensis*

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Abstract – Six components were isolated from the CH_2Cl_2 fraction of *Belamcanda chinensis* rhizome by open column chromatography. Their structures were elucidated as β-sitosterol (**1**), apocynin (**2**), decursin (**3**), iristectorigenin A (**4**), irigenin (**5**) and tectorigenin (**6**) by spectral analysis. Among these compounds, decursin (**3**) was isolated for the first time from a plant of the family Iridaceae.
Keywords – *Belamcanda chinensis*, Iridaceae, decursin

Introduction

Belamcanda chinensis (Iridaceae) is a perennial shrub growing on the hillside in East Asia including the Korean peninsula, and have been used as Chinese traditional medicine for the treatment of throat ailment such as asthma and tonsillitis (Perry, 1980). However, a great portion of the drug is imported from China because of shortage of domestic drug supply.

Investigations on the components from *B. chinensis* have revealed the presence of belamcanidin (Yamaki *et al.*, 1990), kanzakiflavone-2 and 2*R*:3*R*-dihydrokaempferol-7-methylether (Chung and Woo, 1991), belamcandal (Abe *et al.*, 1991), belamcandols A and B (Fukuyama *et al.*, 1991), belamcandaquinones A and B (Fukuyama *et al.*, 1993), noririsflorentin (Woo and Woo, 1993), belamcandones A-D (Seki *et al.*, 1995), isoflavonoids (Eu *et al.*, 1991; Ito *et al.*, 2001; Lee *et al.*, 1989; Yamaki *et al.*, 1990), iridal-type triterpenoids (Ito *et al.*, 1999), *etc.* But there is no report on the isolation of coumarins from this plant.

In this paper, we report the isolation and structure elucidation of a coumarin from *B. chinensis* rhizome.

Experimental

Instruments and reagents – EI-MS spectra were measured with a Jeol JMS-AX505WA mass spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AVANCE 400 NMR spectrometer in $CDCl_3$ or DMSO using TMS as an internal standard. Other reagents were commercial grade without purification.

Plant material – The rhizome of *Belamcanda chinensis* DC. was collected in the vicinity of Seoul, Korea and the voucher specimen was deposited at the Herbarium of College of Pharmacy, Seoul National University, Korea.

Extraction and isolation – The dried rhizome was extracted four times with methanol by refluxing for 5 hr. After removal of the solvent *in vacuo*, the residue was suspended in water and then extracted with *n*-hexane, CH_2Cl_2, EtOAc and *n*-BuOH.

A portion of the CH_2Cl_2 fraction was chromatographed on silica gel column (7×60 cm) eluting with a gradient of $CHCl_3$ and MeOH to afford compounds **1** (7 mg, 95:5), **2** (5 mg, 90:10), **4** (57 mg, 80:20), **5** (57 mg, 80:20) and **6** (142 mg, 78:22). Among the sub-fractions, No. 3 sub-fraction was done over preparative TLC using *n*-hexane-EtOAc (8:2) to afford compounds **2** (3 mg, R_f 0.45) and **3** (5 mg, R_f 0.50).

Compound **1**; EI-MS (70 eV, rel. int., %): *m/z* 414 $[M]^+$ (100), 396 (43.1), 329 (36.7), 303 (35.0), 273 (31.8), 255 (60.2), 213 (37.4), 199 (15.2), 159 (37.7), 145 (37.9); ^{1}H-NMR (400 MHz, $CDCl_3$-*d*): δ 5.35 (1H, br d, *J* = 5.1 Hz, H-6), 3.53 (2H, m, H-3), 1.03 (3H, s, 19-Me), 0.94 (3H, d, *J* = 6.6 Hz, 21-Me), 0.85 (3H, t, *J* = 7.6 Hz, 29-Me), 0.83 (3H, d, *J* = 7.3 Hz, 26-Me), 0.79 (3H, d, *J* = 6.8 Hz, 27-Me) 0.68 (3H, s, 18-Me); ^{13}C-NMR (100 MHz, $CDCl_3$-*d*): δ 140.7 (C-5), 121.7 (C-6), 71.8 (C-3), 56.8 (C-14), 56.0 (C-17), 50.1 (C-9), 45.8 (C-24), 42.3 (C-13), 40.5 (C-12), 39.7 (C-4), 37.2 (C-1), 36.5 (C-10), 36.1 (C-20), 33.9 (C-22), 31.8 (C-7), 31.6 (C-8), 29.7 (C-2), 29.1 (C-25), 28.3 (C-16), 26.0 (C-23), 24.3 (C-15), 23.1 (C-28), 21.1 (C-

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11), 19.8 (C-26), 19.4 (C-27), 19.0 (C-19), 18.8 (C-21), 12.2 (C-29), 12.0 (C-18).

Compound **2**; EI-MS (70 eV, rel. int., %): *m/z* 166 $[M]^+$ (51.2), 151 (100), 123 (24.6), 108 (6.4); ^{1}H-NMR (400 MHz, $CHCl_3$-*d*): δ 7.54 (1H, dd, *J* = 1.9, 8.7 Hz, H-6), 7.52 (1H, d, *J* = 1.9 Hz, H-2), 6.94 (1H, d, *J* = 8.7 Hz, H-5), 6.06 (1H, s, -OH), 3.96 (3H, s, -OMe), 2.56 (3H, s, -Me); ^{13}C-NMR (100 MHz, $CHCl_3$-*d*): δ 196.8 (C=O), 150.4 (C-3), 146.6 (C-4), 130.3 (C-1), 124.0 (C-6), 113.8 (C-5), 109.7 (C-2), 56.1 (-OMe), 26.2 (-Me).

Compound **3**; EI-MS (70 eV, rel. int., %): *m/z* 328 $[M]^+$ (14.7), 228 (77.6), 213 (100), 147 (3.4). 83 (40.5), 55 (12.5); ^{1}H-NMR (400 MHz, $CHCl_3$-*d*): δ 7.58 (1H, d, *J* = 9.4 Hz, H-4), 7.14 (1H, s, H-5), 6.79 (1H, s, H-8), 6.23 (1H, d, *J* = 9.4 Hz, H-3), 5.65 (1H, s, H-2"), 5.07 (1H, t, *J* = 4.8 Hz, H-3'), 3.18 (1H, dd, *J* = 4.8, 18.1 Hz, H-4'$_a$), 2.85 (1H, dd, *J* = 4.8, 18.1 Hz, H-4'$_b$), 2.14 (3H, d, *J* = 1.2 Hz, 3"-CH_3), 1.87 (3H, d, *J* = 1.2 Hz, H-4"), 1.38 (3H, s, gem-Me), 1.36 (3H, s, gem-Me); ^{13}C-NMR (100 MHz, $CHCl_3$-*d*): δ 165.8 (C-1"), 161.4 (C-2), 158.5 (C-3"), 156.4 (C-7), 154.1 (C-9), 143.2 (C-4), 128.6 (C-5), 115.9 (C-6), 115.5 (C-2"), 113.2 (C-3), 112.8 (C-10), 104.7 (C-8), 76.7 (C-2'), 69.1 (C-3'), 27.8 (C-4'), 27.5 (C-4"), 24.9 (gem-Me), 23.2 (gem-Me), 20.3 (3"-Me).

Compound **4**; EI-MS (70 eV, rel. int., %): *m/z* 330 $[M]^+$ (61.1), 315 (24.0), 312 (34.1), 301 (3.0), 287 (40.1), 272 (8.1), 182 (1.0), 149 (13.0), 118 (3.0), 69.1 (100); ^{1}H-NMR (400 MHz, DMSO-d_6): see Table 1; ^{13}C-NMR (100 MHz, DMSO-d_6): see Table 2.

Compound **5**; EI-MS (70 eV, rel. int., %): *m/z* 360 $[M]^+$ (20.1), 345 (10.1), 330 (13.0), 317 (13.0), 312 (10.1), 287 (12.1), 182 (3.1), 149 (7.0), 105 (21.2), 69.1 (100); ^{1}H-NMR (400 MHz, DMSO-d_6): see Table 1; ^{13}C-NMR (100 MHz, DMSO-d_6): see Table 2.

Compound **6**; EI-MS (70 eV, rel. int., %): *m/z* 300 $[M]^+$ (44.2), 282 (26.5), 257 (30.1), 182 (1.0), 149 (0.9), 118 (9.0); ^{1}H-NMR (400 MHz, DMSO-d_6): see Table 1; ^{13}C-NMR (100 MHz, DMSO-d_6): see Table 2.

Table 1. ^{1}H-NMR data of compounds **4-6**

No.	**4**	**5**	**6**
2	8.38 (s)	8.37 (s)	8.32 (s)
8	6.51 (s)	6.50 (s)	6.50 (s)
2'	7.13 (d 1.8)	6.71 (d 1.9)	7.37 (dd 1.8, 8.7)
3'	–	–	6.83 (dd 1.8, 8.7)
5'	6.82 (d 8.1)	–	6.83 (dd 1.8, 8.7)
6'	6.99 (dd 1.8, 8.1)	6.66 (d 1.9)	7.37 (dd 1.8, 8.7)
5-OH	13.07 (s)	13.07 (s)	13.06 (s)
-OMe	3.75 (s)	3.69 (s)	3.75 (s)
	3.80 (s)	3.75 (s)	
		3.78 (s)	

Table 2. ^{13}C-NMR data of compounds **4-6**

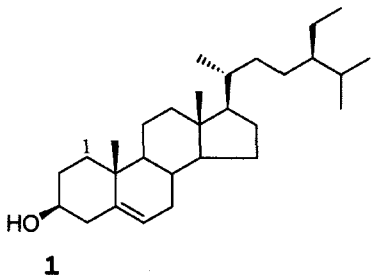
No.	**4**	**5**	**6**
2	154.4	154.8	154.1
3	121.6	121.7	121.8
4	180.6	180.3	180.6
5	152.7	152.9	152.8
6	131.4	131.5	131.4
7	153.3	153.3	153.3
8	93.9	94.0	93.9
9	157.5	157.7	157.6
10	104.8	104.8	104.9
1'	121.8	126.1	121.3
2'	115.3	110.4	130.2
3'	146.7	150.3	115.1
4'	147.3	136.4	157.4
5'	113.2	152.7	115.1
6'	121.7	104.5	130.2
-OMe	55.7	55.8	59.9
	59.9	59.9	
		60.1	

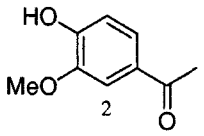
Results and Discussion

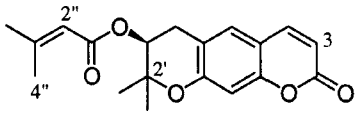
A chromatographic separation of the CH_2Cl_2 fraction from *B. chinensis* led to the isolation of compounds **1-6**. Among them, compounds **1**, **2** and **4-6** were already reported (Lee *et al.*, 1989; Eu *et al.*, 1991; Jung *et al.*, 2002). Their structures were elucidated as β-sitosterol (**1**), apocynin (**2**), iristectorigenin A (**4**), irigenin (**5**) and tectorigenin (**6**) by spectral analysis. The structures of these compounds were shown in Fig. 1.

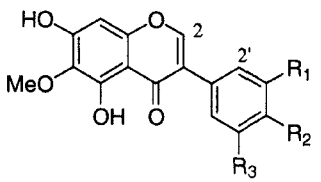
Compound **3** was obtained as white crystals from MeOH. The EI-MS of **3** showed an $[M]^+$ ion at *m/z* 328. In the ^{1}H-NMR spectrum of **3**, the typical signals of linear pyranocoumarin were observed. The H-3 and -4 signals were observed at δ 6.23 (d, *J* = 9.4 Hz) and 7.58 (d, *J* = 9.4 Hz), respectively. The singlet signals at δ 7.14 and 6.79 were shown aromatic H-5 and -8 signals, respectively. The triplet at δ 5.07 (*J* = 4.8 Hz) and two doublet of doublets at δ 3.18 (*J* = 4.8, 18.1 Hz) and 2.85 (*J* = 4.8, 18.1 Hz) assigned as the pyran signals of H-3' and -4', respectively. Two germinal CH_3 signals were assigned at δ 1.38 and 1.36. Two CH_3 signals of side chain were observed at δ 2.14 (*J* = 1.2 Hz) and 1.87 (*J* = 1.2 Hz). Its ^{13}C-NMR spectrum of **3** showed C=O signal at δ 161.4 and four CH_3 at δ 27.5, 24.9, 23.2 and 20.3. Accordingly, the structure of **3** was elucidated as decursin.

Decursin has previously been isolated from *Angelica gigas* (Konoshima *et al.*, 1968), *A. decursiva* form. *albiflora* (Yook, 1973), *A. flaccida* (Seong *et al.*, 1988), *Peucedanum terebinthaceum* (Yook *et al.*, 1986) and *Polygonum cuspidatum* (Rho *et al.*, 2001). To our knowledge, this is the first report of the isolation of decursin from a plant of









4 R_1: OH, R_2: OMe, R_3: H

5 R_1: OMe, R_2: OMe, R_3: OH

6 R_1: H, R_2: OH, R_3: H

Fig. 1. Structures of compounds **1-6**.

the family Iridaceae.

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