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HOMOISOFLAVANONES FROM *BELLEVALIA ROMANA*

MATTEO ADINOLFI, TULLIA AQUILA, GASPARE BARONE, ROSA LANZETTA* and MICHELANGELO PARRILLI*

Dipartimento di Chimica Organica e Biologica, Università di Napoli, Via Mezzocannone 16, 80134 Napoli, Italy; *Istituto di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy

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Key Word Index—*Bellevalia romana*; Liliaceae; homoisoflavanones.

Abstract—From the bulbs of *Bellevalia romana*, a novel 3-benzyl-4-chromanone and a novel 3-benzylidene-4-chromanone were isolated, besides known homoisoflavanones. Their structures were elucidated by spectral analysis (^{13}C and ^{1}H NMR, MS, CD).

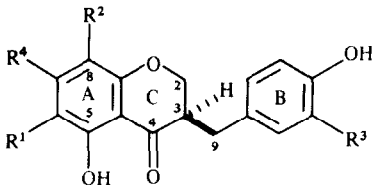
INTRODUCTION

The isolation and the structure elucidation of a number of homoisoflavanones of both the 3-benzyl-4-chromanone type and the scillascillin type from bulbs of *Muscari* species has been recently described [1, 2]. This study has been extended to other Liliaceae genera. We now report on the isolation of a novel 3-benzyl-4-chromanone (**1**) and a novel 3-benzylidene-4-chromanone (**2**), in addition to known [3] homoisoflavanones (**3** and **4**), from the bulbs of *Bellevalia romana* L.

RESULTS

The molecular formula $C_{18}H_{18}O_8$ was deduced for compound **1** from its HR mass spectrum. The 3-benzyl-4-chromanone structure was indicated by the presence in the ^{1}H NMR spectra (Table 1) of the signals of the –(2)CH_2–(3)CH–(9)CH_2– grouping at δ4.14(*dd*) and 4.29(*dd*) (CH_2-2), 2.83(*m*), (CH – 3), 2.63(*dd*) and 3.04(*dd*) (CH_2-9). Ring B bears two oxygenated functions (base peak in the mass spectrum at *m/z* 123, due to the dihydroxytropylium fragment) at C-3′ and C-4′ (NMR signals of H-2′ at δ 6.67*d*, J_{meta} = 1.8 Hz, of H-5′ at δ6.70*d*, J_{ortho} = 7.7 Hz, and of H-6′ at δ 6.55*dd*, J_{meta} = 1.8 Hz, J_{ortho} = 7.7 Hz). Accordingly, the ring-B carbon NMR signals (Table 2) were very similar to those of known 3′,4′-dihydroxyhomoisoflavanones [4]. The ^{1}H NMR spectrum lacks signals for protons directly attached to ring A. The peak in the mass spectrum at *m/z* 213, due to hydrogen shift and retro-Diels–Alder cleavage of the chromone fragment [5], indicated that ring A is fully substituted with two hydroxyl and two methoxyl groups. The NMR signal of the hydroxyl proton at δ11.74 [chelated with the (4) C=O group] and the measurement of a NOE between the two methoxyl groups revealed that one hydroxyl group is at C-5 and one methoxyl group is at C-7. The chemical shift of ring-A carbons were different from those of known **5**. Therefore, the second methoxyl group is at C-8 and the second hydroxyl group is at C-6. Finally, the CD curve of 3-benzyl-4-chromanone **1** exhibits a negative Cotton effect ($[\theta]_{294} - 2300$, $[\theta]_{260} + 560$), that may be taken as indicative of *R* configuration at C-3 [1].

The 3-benzylidene-4-chromanone structure of compound **2** was inferred from the absence of H-3 and of H_2-9 signals in the ^{1}H NMR spectrum. The H_2-2 signal (δ5.36, *d*, $J_{2,9}$ = 1.6 Hz) was at much lower field than in 3-benzyl-4-chromanones [4, 5], and a signal, attributable to one benzylidene 9-proton, appeared at δ7.69, *t*, $J_{2,9}$ = 1.6 Hz. The *Z*-geometry of the 3(9)-double bond was indicated by the long-range coupling between the protons at C-2 and C-9 and by the downfield location of their signals (*E*-isomers display both these signals as singlets at much



	R¹	R²	R³	R⁴
1	OH	OMe	OH	OMe
3	H	H	OH	H
4	H	OH	OH	OMe
5	OMe	OH	H	OMe

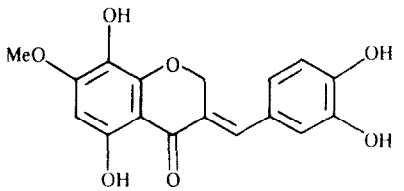


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Table 1. ^{1}H NMR data of homisoflavanones **1** and **2** in CD_3OD*

Compound	H_2-2	H-3	H-5	H-6	H-7	H-8	H_2-9/H-9	H-2′	H-3′	H-4′	H-5′	H-6′
1	4.14 *dd* (7.4, 11.5) 4.29 *dd* (4.4, 11.5)	2.83 *m*	11.74	8.65 *s*[a]	3.75 *s*[b]	3.99 *s*[b]	2.63 *dd* (10.3, 13.8) 3.04 *dd* (5.0, 13.8)	6.67 *d* (1.8)	8.87 *s*[a]	8.87 *s*[a]	6.70 *d* (7.7)	6.55 *dd* (1.8, 7.7)
2	5.36 *d* (1.6)	—	12.54	6.16 *s*	3.88 *s*	§	7.69 *t* (1.6)	6.83 *d* (1.8)	§	§	6.86 *d* (8.1)	6.80 *dd* (1.8, 8.1)

*Chemical shifts are given in δ (ppm) relative to TMS. Coupling constants (in parentheses) are given in Hz. The signals of the hydroxyl protons, which were not detected in CD_3OD owing to deuteron-proton exchange, are reported for solutions in DMSO-d_6.

[a,b] Interchangeable values.

§A very broad signal in the δ 7–8 zone of the spectrum in DMSO-d_6 solution may be due to the 7-, 3′- and 4′-OH protons.

higher field [5]). In accordance with the additional unsaturation introduced with the double bond, the molecular formula $C_{17}H_{14}O_7$ was deduced from the high resolution mass spectrum. In latter, the peak at *m/z* 148, due to the (2) CH_2=(3)C=(9)CH-ring B fragment [5], indicated the presence of two hydroxyl groups attached at ring-B carbons. Their location at C-3′ and C-4′ was revealed by the usual appearance of the signals of the 2′-, 5′-, and 6′-protons. The two hydroxyl groups and the methoxyl group revealed by the *m/z* 183 peak due to the ring-A fragment in the mass spectrum are located at C-5, C-8, and C-7, respectively. In fact, the NMR signals of the hydroxyl proton at δ12.54 and of the ring-A methine proton at $\delta > 6.00$ [4] show that one hydroxyl group is at C-5 and the methoxyl group is at C-7, respectively. Accordingly, a NOE was measured for the ring-A proton at δ6.16 by irradiation of the methoxyl signal at δ3.88. The close similarity of the chemical shifts of the ring-A carbons with those of compound **4** indicated that the remaining hydroxyl group is linked at C-8. The full assignment of the ^{13}C signals of **2**, based on the comparison with known compounds [4, 5] and on carbon–proton long-range correlation 2D-spectra are shown in Table 2.

The known compounds **3** and **4** were identified by comparison of their physical properties with those of authentical samples [3].

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded at 30° and 400/75 (^{1}H/^{13}C) MHz. One-dimensional spectra were typically obtained with 500 Hz (^{1}H) and 15000 Hz (^{13}C) spectral widths. Long-range 2D carbon–proton shift correlation experiments were performed with the Bruker XHCORR program using delay $D_3 = 71.4$ msec, corresponding to $J_{C,H} = 7$ Hz. CD curves were measured with a Jasco J-500 dichrograph.

Isolation of homoisoflavanones. Fresh bulbs (500 g) of *Bellevalia romana* L. (collected in May 1987 near Potenza, Italy, and authenticated by the staff of the Botanical Garden of the University of Naples) where homogenized, freeze-dried and extracted in a Soxhlet with petrol (12 hr), with Et_2O (12 hr) and then with MeOH (12 hr). The Et_2O extract was evapd (0.8 g) and chromatographed on a silica gel (50 g) column to yield fractions a (310 mg), b (42 mg), c (27 mg), d (16 mg) and e (17 mg) by elution with $CHCl_3$ containing increasing amounts of Me_2CO.

Fraction a yielded compound **4** (220 mg) on PLC [silica gel, C_6H_6–MeOH (9:1), two runs]. PLC [silica gel, C_6H_6–MeOH (9:1), three runs] of fraction b afforded compound **1** (17 mg). EIMS, 70 e/V, *m/z* (rel. int.): 362.0990 ($[M]^+$: calc. for $C_{18}H_{18}O_8$ 362.0996) (30), 213 (100). CD (MeOH): see text. PLC [silica gel $CHCl_3$–MeOH (19:1), two runs] of fraction c gave compound **2** (7 mg). EIMS, 70 eV, *m/z* (rel. int.): 330.0727 $[M]^+$; calc. for $C_{17}H_{14}O_7$ 330.0735) (45), 183 (100), 148 (40). Fraction d gave compound **3** (7 mg) on PLC [silica gel $CHCl_3$–MeOH (9:1), two runs].

Table 2. ^{13}C NMR data homisoflavanones **1**, **2**, **4** and **5** in CD_3OD*

C	1	5	2	4	C	1	5	2	4
2	70.5	70.6	69.0	70.5	1′	130.7	130.0	127.8	131.0
3	†	48.5	128.6	†	2′	117.2	131.1	118.6	117.2
4	201.4	200.9	187.3	200.1	3′	146.4	116.4	148.5[d]	146.4
4a	104.9	104.8	107.7	103.2	4′	145.1	157.0	146.7[d]	145.1
5	148.6[a]	149.2	158.9	158.2	5′	116.5	116.4	116.8	116.5
6	134.4[b]	135.1	93.9	93.5	6′	121.5	131.1	124.9	121.5
7	151.3	151.2	158.3	158.0	6-OMe	—	61.4	—	—
8	132.7[b]	131.4	127.7	127.6	7-OMe	61.6[c]	61.6	56.6	56.7
8a	147.6[a]	146.4	149.1	149.3	8-OMe	61.9[c]	—	—	—
9	33.2	32.6	139.0	33.0					

*Chemical shifts are given in δ (ppm) relative to TMS.
†Buried in solvent signals.
[a–d]Interchangeable values.

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CYANIDIN 3-MALONYLGLUCOSIDE IN TWO *ECHINACEA* SPECIES

A. CHEMINAT, R. BROUILLARD, P. GUERNE,* P. BERGMANN* and B. RETHER*

Laboratoire de Chimie des Pigments des Plantes, associé au CNRS (UA 31) Institut de Chimie, 1, rue Blaise Pascal, 67008 - Strasbourg Cedex, France; *Laboratoire de Recherches Technologiques, Département de Biologie Appliquée, IUT Louis Pasteur, 3, rue de l'Argonne-67000 Strasbourg, France

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Key Word Index—*Echinacea*; Compositae; malonated anthocyanins.

Abstract—The major anthocyanins of two *Echinacea* species, *E. purpurea* and *E. pallida* have been identified as cyanidin 3-*O*-(β-D-glucopyranoside) and cyanidin 3-*O*-(6-*O*-malonyl-β-D-glucopyranoside) by NMR.

INTRODUCTION

Recently, the occurrence of several malonylated anthocyanins has been reported in numerous plants, especially in Compositae [1]. Our interest in *Echinacea* species [2] was an opportunity to isolate and identify the major anthocyanins from two of them, *E. pallida* Nutt and *E. purpurea* (L.) Moensch, 3-*O*-(β-D-glucopyranosyl) and 3-*O*-(6-*O*-malonyl-β-D-glucopyranosyl) cyanidin were detected in these two plants.

RESULTS AND DISCUSSION

Anthocyanins were extracted from dry *Echinacea* flowers by mild extraction with acetic acid–methanol–water