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A METHYLATED CHALCONE GLUCOSIDE FROM *BIDENS PILOSA*

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Key Word Index—*Bidens pilosa*, Asteraceae, chalcones, okanin 4-methyl ether 3′-glucoside

Abstract—A methylated chalcone glucoside has been isolated from the leaves of *Bidens pilosa*. Its structure has been elucidated by spectroscopic methods.

INTRODUCTION

Bidens pilosa L. (Heliantheae, Coreopsidinae) is a widely distributed pantropical weed. Members of the genus *Bidens* are known to contain chalcones based on okanin (3,4,2′,3′,4′-pentahydroxychalcone) [1] and in previous papers we reported on the isolation and structure elucidation of acylated okanin glucosides from the leaves of *B. pilosa* [2, 3]. The present communication deals with another chalcone glucoside, okanin 4-methyl ether 3′-*O*-*β*-D-glucoside, a new natural compound, which was characterized previously by UV spectroscopy [4].

RESULTS AND DISCUSSION

On TLC compound **1** appeared dark in UV and bright yellow in visible light. It didn't change colour immediately when sprayed with Naturstoffreagenz, but after some days it became pink in visible light. The UV spectrum exhibited a major absorbance at 376 nm, which is typical of a chalcone. The large bathochromic shift after the addition of aluminium chloride and hydrochloric acid revealed the presence of an unsubstituted 2′-hydroxyl group. Acid hydrolysis yielded glucose, and the coupling constant of the doublet for the anomeric proton in the ^{1}H NMR spectrum (8 Hz) indicated *β*-D-glucose. The ^{1}H NMR spectrum exhibited a chalcone with two *ortho*-H atoms in the A-ring and a 3,4-disubstituted B-ring. The singlet at 3.89 ppm was consistent with an aromatic methoxyl group. The ^{1}H and ^{13}C NMR spectral data for the A-ring were in good agreement with those of okanin 3′-*O*-*β*-D-glucoside (**2**) [2] (Table 1), whereas the signals for the B-ring protons shifted downfield and agreed well with those given for okanin 4-methyl ether 4′-glucoside [5].

These results, including the FD mass spectrum ([M + H]$^+$ at 465), suggested that **1** is okanin 4-methyl ether 3′-*O*-*β*-D-glucoside.

The position of the methoxyl group was proved by ^{13}C NMR spectroscopy (gated-decoupling method, assignments according to [6]). Methylation of a phenolic hydroxyl group with an *ortho* and unsaturated *para*-substituent causes a strong upfield shift (about 4.5 ppm) of the signal for the unsubstituted *ortho*-carbon (C-5), whereas the signals for C-1, C-3 and C-4 move downfield by *ca* 1 ppm [7]. In comparison with the data for compound **2** (Table 1), the spectra of **1** revealed a marked upfield shift of the C-5 signal to 112.50 ppm. The signals for C-1, C-3 and C-4 shifted downfield by 0.8, 1.0 and 1.1 ppm, respectively. Thus, compound **1** was confirmed as okanin 4-methyl ether 3′-*O*-*β*-D-glucoside.

EXPERIMENTAL

Plant material. Leaves were collected from plants cultivated in the Botanical Garden, Universität Marburg. A voucher specimen is deposited in the Botanical Garden Herbarium Nr. 72-880.

Table 1. ^{13}C NMR spectral data of compounds **1** and **2** (CD_3OD, 100 MHz, solvent as int. standard, *δ*-values, ppm)

C	1	2
1	129.42 *t*	128.28
2	115.30 *dt*	115.87
3	148.02 *m*	146.81
4	151.86 *m*	150.09
5	112.50 *d*	116.60
6	123.69 *dt*	123.83
OMe	56.39 *q*	
C=O	193.73 *d*	193.80
α	119.12 *d*	118.08
β	146.09 *d*	146.63
1′	115.40 *d*	115.45
2′	158.85*d*	158.53†
3′	133.66 *d*	133.61
4′	159.12*d*	159.06†
5′	109.43 *d*	109.29
6′	128.84 *d*	128.72
1″	106.60 *dd*	106.57
2″	75.34 *dd*	75.32
3″	78.34 *d*	78.30
4″	70.66 *d*	70.65
5″	77.64 *d*	77.60
6″	61.95 *t*	61.94

*,†Interchangeable in the vertical columns.

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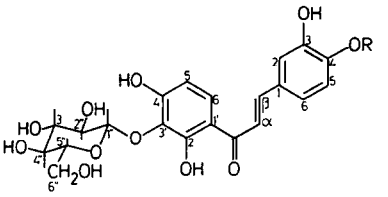

1 R = Me
2 R = H

Isolation. The extract of the dried leaves (1 kg) with aqueous methanol was successively partitioned between H_2O, trichloroethylene and EtOAc The residue obtained after evapn of the EtOAc extract (20 g) was chromatographed over Sephadex® LH-20 with MeOH–H_2O (1 4) and increasing amounts of MeOH, 13 fractions were collected Fraction 8 (3300 mg) was separated by RLCC using the system $CHCl_3$–MeOH–*iso*-PrOH–H_2O (8 7 1 6) in the descending mode and finally purified over LH-20 with *iso*-PrOH as eluent to yield 46 mg of **1**. R_f s **1** on TLC silica gel $60F_{254}$ were 0.16 in $CHCl_3$–MeOH–H_2O (13 7.4, lower phase) 0.56 in EtOAc–MeOH–H_2O (100:17 13) and 0 77 in EtOAc–HCOOH–H_2O (15·3:4).

Mp. (uncorr) 196°, UV λ_{max}^{MeOH} 376, 311 (sh), 260, +$AlCl_3$ 433, 330 (sh), 270, +$AlCl_3$+HCl 433, 323 (sh), 269, 240 (sh); +NaOAc 397, 275 (sh), 262, +NaOAc+H_3BO_3 482 (sh), 447, 429, 398 (sh), 293 (sh), 263, ^{1}H NMR (CD_3OD, solvent int standard, 400 MHz, δ-values, ppm) 7 80 (1H, *d*, 9 Hz, H-6′), 7.74 (1H, *d*, 15 Hz, H-β), 7 56 (1H, *d*, 15 Hz, H-α), 7.22 (1H, *d*, 2 Hz, H-2), 7.18 (1H, *dd*, 8 Hz, 2 Hz, H-6), 6 95 (1H, *d*, 8 Hz, H-5), 6 50 (1H, *d*, 9 Hz, H-5′), 4.80 (1H, *d*, 8 Hz, H-1″), 3 89 (3H, *s*, –OMe), 3.81 (1H, *dd*, 12 Hz, 2 Hz, H-6″), 3 74 (1H, *dd*, 12 Hz, 4 Hz, H-6″), 3.42–3 55 (3H, *m*, H-2″, H-3″, H-4″), 3 28–3 30 (1H, *m*, H-5″)

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CYANIDIN 3-ACETYLRUTINOSIDE IN *EURYA JAPONICA* BERRIES

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Key Word Index—*Eurya japonica*; Theaceae; berries; acylated anthocyanin; acetic acid; cyanidin 3-acetylrutinoside

Abstract—The major anthocyanin in the berries of *Eurya japonica* was identified as cyanidin 3-acetylrutinoside, from chromatographic and spectral methods.

INTRODUCTION

The pigment in the black berries of *Eurya japonica* Thunberg was earlier identified as cyanidin 3-glucoside (Cy 3-G) by Shibata *et al.*[1] In the course of an acylated anthocyanin survey, however, the major pigment from the same plant was observed to have different R_f values on TLC from authentic Cy 3-G. This prompted us to re-examine the anthocyanin. This paper deals with the elucidation of the major anthocyanin in the *Eurya japonica* berries.