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ISOCOUMARINS FROM *XYRIS INDICA*

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Key Word Index—*Xyris indica*; Xyridaceae; isocoumarins; xyridin A; xyridin B; 3-*n*-propyl-6,7-(methylenedioxy)-1H-2-benzopyran-1-one; 3-(1′-oxopropyl)-6,7-(methylenedioxy)-1H-2-benzopyran-1-one.

Abstract—Two new isocoumarins named xyridin A and B were isolated from the chloroform extract of the flowering heads of *Xyris indica*. Their structures were established as 3-*n*-propyl-6,7-(methylenedioxy)-1H-2-benzopyran-1-one and 3-(1′-oxopropyl)-6,7-(methylenedioxy)-1H-2-benzopyran-1-one by means of spectroscopic analyses.

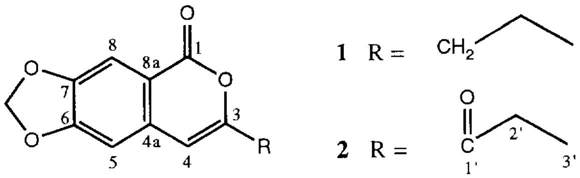
INTRODUCTION

The genus *Xyris* Gronov. ex L. in the Xyridaceae family is composed of *ca* 250 species distributed primarily in tropical and subtropical regions [1]. *Xyris indica* L. (tall yellow-eyed grass) is one of the five species found throughout Thailand and is known locally as ‘Kra thin thung’ [2]. It is a weed which is widespread in paddy fields of Prachin buri. In Bengal, the plant has been used in folklore medicine as a cure for ringworm, itch and leprosy [3,4]. Phytochemical study of the genus *Xyris* has previously led to the isolation of two anthraquinones; chrysazin and 3-methoxy chrysazin from *X. semifuscata* [5]. Herein, we report the structure determination of two new isocoumarins isolated from a non-polar chromatographic fraction obtained from the flowering heads of *X. indica*.

RESULTS AND DISCUSSION

Purification of a chloroform soluble extract of the flowering heads of *X. indica* with silica gel column chromatography resulted in the isolation of two new isocoumarins (**1** and **2**).

Compound **1**, mp 67–68°, was obtained as pale yellow plates. The molecular formula of **1** was deduced to be $C_{13}H_{12}O_4$ (calcd 232.0732 amu) from its molecular ion at *m/z* 232.0731 in the high resolution mass spectrum. The benzopyrone structure was evident from its UV absorptions at 334 and 282 nm (log ε 3.65 and 3.77) [6], and the pyrone-carbonyl stretching frequency was found in the region 1725 cm^{-1} of the IR spectrum [7, 8]. The presence of a methylenedioxy group at C-6 and C-7 was indicated from the isolated methylene proton signal at δ6.03 (*s*) and the aromatic proton resonances of H-5 at δ6.66 (*s*), H-8 at δ7.51 (*s*) and H-4 at δ6.09 (*s*) in the ^{1}H NMR spectrum. Analysis of the ^{13}C NMR and DEPT spectra of **1** revealed the presence of three methylene carbons at (δ20.2, 35.2 and 102.0), three aromatic methine carbons (δ103.0, 103.5 and 107.2), one methyl carbon (δ13.4), and six quaternary carbons (δ114.5, 135.2, 147.7, 153.5, 157.0 and 162.6) including one carbonyl carbon. The *n*-propyl side chain could be assigned from ^{1}H NMR signals at δ0.93, 1.66 and 2.42 (*t*, J = 7.3 Hz; *tq*, J = 7.3, 7.3 Hz; *t*, J = 7.3 Hz). It could be inferred from the above data that there are alternative structures of **1**: (i) a 3-*n*-propyl or 4-*n*-propyl-6,7-(methylenedioxy)-1H-2-benzopyran-1-one and (ii) a 3-*n*-propyl or 4-*n*-propyl-6,7-(methylenedioxy)-2H-1-benzopyran-2-one. In order to evaluate the structure more explicitly, a detailed examination of the HMBC of **1** was undertaken. The significant long range ^{1}H–^{13}C correlations contour are indicated by arrows in Fig. 1. The quaternary carbon at δ157.0 (C-3) is correlated with the methylene protons at δ2.42 (H-1′) and δ1.66 (H-2′), and with the olefinic proton at δ6.09 (H-4). The carbonyl carbon at δ162.6 (C-1) is correlated with the olefinic proton at δ7.51 (H-8). The quaternary carbon at δ114.5 (C-4a) is correlated with the olefinic protons at δ6.09 (H-4) and δ6.66 (H-5). The quaternary carbon at δ135.2 (C-8a) is correlated with the olefinic proton at δ7.51 (H-8).



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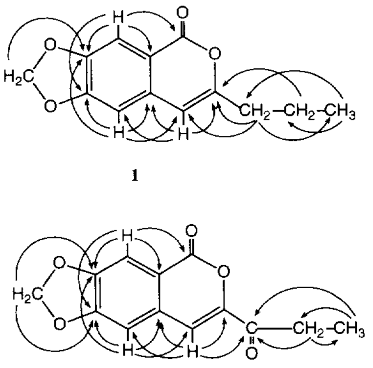

1

2

Fig. 1. ^{13}C–^{1}H correlation observed in the HMBC spectra of **1** and **2**.

These results strongly support the proposed structure of **1** as 3-*n*-propyl-6,7-(methylenedioxy)-1H-2-benzopyran-1-one, a new isocoumarin named xyridin A.

Compound **2**, mp 198–199°, was obtained as plates, possessing the molecular formula $C_{13}H_{10}O_5$ as determined by the high resolution mass spectrum. A variety of spectroscopic techniques were employed to determine the structure of **2** and indicated a close structural relationship with **1** as both exhibited the same carbon framework. The UV spectrum of **2** showing absorption maxima (log ε) at 333 (4.16) and 262 (4.57) nm, suggested a benzopyrone [6]. The two carbonyl stretching frequencies were found in the regions 1695 and 1733 cm^{-1} in the IR spectrum [7]. The ^{1}H NMR spectrum of **2** indicated the presence of three aromatic protons at δ7.24 (*s*), 6.92 (*s*) and 7.62 (*s*), and two methylene protons at δ6.11 (*s*) and 2.92 (*q*), suggested a close resemblance to **1** based on the 6,7-methylenedioxy-1H-2-benzopyran-1-one skeleton. Further, the triplet at δ1.14 and quartet at δ2.92 ($J = 7.3$ Hz) indicated the Me-CH_2 side chain. In the ^{13}C NMR and DEPT spectra, it was shown that **2** consisted of two methylene carbons (δ31.6 and 102.7), three methine carbons (δ106.3, 108.1 and 108.5), one methyl carbon (δ7.3) and seven quaternary carbons (δ118.4, 132.6, 148.7, 150.3, 153.9, 160.4 and 194.9 (including two carbonyl carbons). It is clearly shown that **2** has an additional carbonyl on the propyl side chain of **1** as an oxopropyl group from the NMR and mass spectral data. Confirmation by ^{13}C–^{1}H long range connectivity of **2** in the HMBC spectrum indicated that the carbonyl carbon (C-1′) at δ194.9 of the oxopropyl side chain is correlated with the olefinic proton at δ7.24 (H-4), methylene proton at δ2.92 (H-2′) and methyl proton at δ1.14 (H-3′). The quaternary carbon at δ148.7 (C-3) is correlated with the olefinic proton at δ7.24 (H-4). The carbonyl carbon at δ160.4 (C-1) is correlated with the olefinic proton at δ7.62 (H-8). The quaternary carbon at δ118.4 (C-4a) is correlated with the olefinic protons at δ7.24 (H-4) and 6.92 (H-5). The quaternary carbon at δ132.6 (C-8a) is correlated with the olefinic proton at δ7.6 (H-8). The structure of **2** was thus determined to be 3-(1′-oxopropyl)-6,7-(methylenedioxy)-1H-2-benzopyran-1-one unambiguously and named xyridin B.

Table 1. ^{1}H NMR spectral data for **1** and **2** ($CDCl_3$; 500 MHz; TMS)

H	**1**	**2**
4	6.09 *s*	7.24 *s*
5	6.66 *s*	6.92 *s*
8	7.51 *s*	7.62 *s*
-O-CH_2-O-	6.03 *s*	6.11 *s*
1′	2.42 *t* (7.3)	—
2′	1.66 *tq* (7.3, 7.3)	2.92 *q* (7.3)
3′	0.93 *t* (7.3)	1.14 *t* (7.3)

δ (ppm). Coupling constants (*J* in Hz) in parentheses.

Table 2. ^{13}C NMR spectral data for **1** and **2** ($CDCl_3$; 125.65 MHz; TMS)

C	**1**	**2**
1	162.6	160.4
3	157.0	148.7
4	103.0	108.5
4a	114.5	118.4
5	103.5	106.3
6	147.7	150.3
7	153.5	153.9
8	107.2	108.1
8a	135.2	132.6
-O-CH_2-O-	102.0	102.7
1′	35.2	194.9
2′	20.2	31.6
3′	13.4	7.3

δ (ppm). All carbons were assigned with the aid of ^{13}C–^{1}H and ^{13}C–^{1}H long range COSY.

From the biogenetic point of view, there seems to be no doubt that xyridin A (**1**) and xyridin B (**2**) arise from the acetate–malonate pathway through cyclization reactions of a C12-polyketide chain. The secondary metabolic route appears to be responsible for the other constituents which have so far been isolated from *Xyris* sp. [5].

EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were measured on a 500 MHz instrument and chemical shifts are given on a δ (ppm) scale with TMS as int.standard. MS were recorded at 70 eV using a direct inlet system. Mps are uncorr. Merck silica gel 60 F_{254} plates were used for analyt. TLC, kieselgel 60 CC was carried out at amounts equivalent to 50–100 the sample amount.

Plant material. Xyris indica L. was collected from Prachin Buri province Thailand in October 1991 and was identified by one of us (N.R.). A voucher specimen is deposited in the herbarium of the Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok, Thailand.

Extraction and isolation of **1** *and* **2**. The dried flowering heads (1 kg) were extracted with $CHCl_3$ (10 and 5 l) for 2 7-day periods and filtered. The combined filtrates were evapd *in vacuo* until dryness to yield a syrupy mass residue (45 g). The residue (10 g) was chromatographed on silica gel CC (8 x 12 cm) using petrol–EtOAc (8:1) as eluent and collecting 50 ml frs. Those frs containing homogeneous components, as judged by TLC, were combined and the solvent removed. Frs 20–41 and 59–176 afforded residues XV and XB, respectively. XV was rechromatographed on silica gel CC (2.5 x 26 cm) using $CHCl_3$ as eluent to furnish **1** (77 mg, 0.035%). XB was rechromatographed on silica gel CC (4.5 x 20 cm) using benzene–EtOAc (15:1) as eluent to yield 112 mg (0.05%) of **2**.

Compound **1**: mp 67–68°; UV λ_{max}^{MeOH} nm (log ε): 203 (4.26), 239 (4.60), 282 (3.77), 334 (3.65). IR ν_{max} cm^{-1}: 3090, 2960, 2925, 2865, 1725, 1662, 1595, 1503, 1484, 1412, 1358, 1261, 1110, 1031, 1015, 981, 920, 848: ^1H and ^{13}C NMR: Tables 1 and 2, respectively. EIMS 70 eV (probe) m/z (rel. int.): 232 $[M]^+$ (100), 204 (14), 203 (77), 175 (76), 162 (23), 161 (12), 133 (37), 75 (12). HREIMS found: $[M]^+$ 232.0731; $C_{13}H_{12}O_4$ requires 232.0732.

Compound **2**: mp 198–199°; UV λ_{max}^{MeOH} nm (log ε): 227 (4.09), 262 (4.57), 333 (4.16). IR ν_{max} cm^{-1}: 3080, 3055, 2980, 2925, 1733, 1695, 1632, 1613, 1505, 1490, 1412, 1346, 1275, 1243, 1192, 1048, 1015, 943, 908. ^1H and ^{13}C NMR: Tables 1 and 2, respectively. EIMS 70 eV (probe) m/z (rel. int.): 246 $[M]^+$ (80), 189 (16), 162 (2), 161 (16), 133 (100), 75 (3). HREIMS found: $[M]^+$ 246.0534; requires 246.0525.

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