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A NEW CHROMONE FROM SEEDS OF *Cydonia oblonga*[a]

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*The new chromone 5,7-dihydroxy-2-*n*-pentacosanylchromen-4-one (**1**) in addition to the three known compounds ursolic acid (**2**), tormentic acid (**3**), and* β*-daucosterol (**4**) were isolated from seeds of* Cydonia oblonga*. Their structures were determined based on their 1D and 2D NMR and HR-ESI-MS spectral data.*

Keywords: *Cydonia oblonga*, 5,7-dihydroxy-2-*n*-pentacosanylchromen-4-one, ursolic acid, tormentic acid, *β*-daucosterol.

Until now the plant *Cydonia oblonga* (Rosaceae) was the only representative of the genus *Cydonia* that included about 50 widely distributed varieties [1]. Six types of this genus are found in Xinjiang Autonomous Region of China [2]. The plant *C. oblonga* Mill. var. *maliformis* is one of them. Its seeds are used in folk medicine to treat various skin diseases, dysphoria, lung tuberculosis, cough, and sore throat [3]. For many years mainly fruit of *C. oblonga* was studied. According to the literature, it contains essential oils, organic acids, amino acids, phenolic acids, flavonoids, terpenoids, and steroids [4–7].

Herein we report the isolation from seeds of this plant and the structure determination of the new chromone **1** and the identification of the three known compounds ursolic acid (**2**) [8], tormentic acid (**3**) [9], and *β*-daucosterol (**4**) [10]. Compounds **2**, **3**, and **4** were isolated for the first time from *C. oblonga*.

The structure of **1** was established based on spectral data (1D and 2D NMR, HR-ESI-MS) and confirmed by comparison with related compounds [11].

Compound **1** ($C_{34}H_{56}O_4$) was obtained as a white powder, mp 101–103°C. The mass spectrum of **1** had strong peaks for ions with *m*/*z* 527.8 (18) $[M - H]^-$, 190.1 (100) $[M - H - C_{24}H_{49}]^-$, and 203.1 (53) in addition to peaks with *m*/*z* 217.3 (6), 231.0 (8), 246.4 (5), 259.1 (16), 273.0 (10), 287.2 (9), 303.4 (5), 315.2 (9), 329.1 (5), 343.0 (6), 357.1 (8), 371.2 (8), 399.4 (3), 413.0 (3), 441.1 (3), 427.3 (6), 455.2 (3), 469.2 (7), 497.4 (5).

The ^{13}C NMR spectrum showed resonances for 34 C atoms that appeared in the DEPT spectrum as 1 methyl, 24 methylenes, 3 methines, and 6 quaternary C atoms.

The PMR spectrum of **1** contained two 1H broad singlets at δ 13.3 and 13.6 ppm that were due to two hydroxyls. The PMR, ^{13}C NMR, HMBC, and HSQC spectra of **1** (Table 1, Fig. 1) were consistent with the presence of an alkyl side chain CH_2–$(CH_2)_{23}$–CH_3 and three aromatic protons (δ_H 6.24, s, H-3; δ_C 108.5, d, C-3); (δ_H 6.72, d, J = 1.6 Hz, H-8; δ_C 95.2, d, C-8; and δ_H 6.75, d, J = 1.6 Hz, H-6; δ_C 100.4, d, C-6). The last two doublets were typical of two *meta*-related protons (H-6 and H-8) of a chromone ring. These data and the presence of singlets at 171.1 and 183.3 ppm in the ^{13}C NMR spectrum indicated that **1** was an alkyl-substituted 5,7-dihydroxychromon-4-one.

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TABLE 1. NMR Spectra of **1** (^{1}H, 600 MHz; ^{13}C, 150 MHz; C_5D_5N, δ, ppm, J/Hz)

C atom	δ_H	δ_C	DEPT	HMBC
2		171.1	C	
3	6.24 (1H, s)	108.5	CH	C-1′, C-2, C-4, C-10
4		183.3	C	
5		163.7	C	
6	6.75 (1H, d, J = 1.6)	100.4	CH	C-5, C-8, C-10
7		159.4	C	
8	6.72 (1H, d, J = 1.6)	95.2	CH	C-4, C-6, C-7, C-10
9		166.3	C	
10		105.3	C	
1′	2.48 (2H, t, J = 7.2)	34.5	CH_2	C-2, C-3, C-2′, C-3′
2′	1.60 (2H, m)	27.4	CH_2	C-1′, C-3′
3′–24′	1.27–1.33 (44H, m)	29.6–32.6	$(CH_2)_{22}$	C-2′, C-25′
25′	0.89 (3H, t, J = 7.2)	14.7	CH_3	C-(23′, 24′)

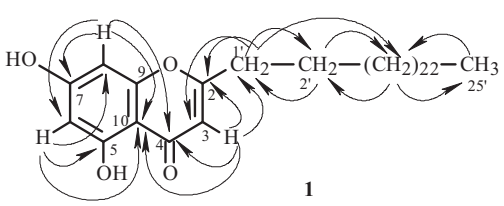

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Fig. 1. Structure and main HMBC correlations of **1**.

An analysis of the HMBC and HSQC spectral data showed that the alkyl side chain was bonded to C-2 of the chromone core (Table 1). This was consistent with the presence in the HMBC spectrum of **1** of cross peaks between H-1′ and the resonances of C-2 and C-3. Correlation peaks between resonances of H-3 and C-1′, C-2, C-4, and C-10; between H-8 and C-4, C-6, C-7, and C-10; between H-6 and C-5, C-8, and C-10 were observed in the HMBC spectrum. Furthermore, the chemical shifts of resonances for C-7 (δ 159.4) and C-5 (δ 163.7) in the ^{13}C NMR spectrum showed that the two hydroxyls were bonded to C-5 and C-7.

Thus, **1** was determined as 5,7-dihydroxy-2-*n*-pentacosanylchromen-4-one based on the spectral data.

EXPERIMENTAL

General Comments. Melting points were determined on a Buchi B-540 Melting Point instrument. PMR, ^{13}C NMR, and 2D NMR spectra were recorded in C_5D_5N with TMS internal standard on a Varian VNMRS-600 spectrometer (600 MHz for ^{1}H; 150 MHz for ^{13}C). Mass spectra and high-resolution mass spectra (HR-ESI-MS) were measured on a Bio-TOF Q spectrometer (QStar Elite Hybrid LC/MS/MS). Column chromatography was performed over silica gel (G and H grades, Qingdao Ocean Chemical Factory, China), silica gel (RP-18 grade, Merck), and LH-20 Sephadex (Merck).

Plant Material. Seeds of *C. oblonga* Mill. var. *maliformis* were collected in October 2009 in Atush, Xinjiang Autonomous Region, PRC. The specimen was identified by Sulayman Khalik, Chief Pharmacist of Xinjiang-Uighur Autonomous Regional Institute for Control of Products and Medicines.

Extraction and Isolation. Dried and ground seeds of *C. oblonga* (2 kg) were extracted (3×) with refluxing MeOH for 2 h each time. The solvent was vacuum distilled. The combined extracts (470 g) were suspended in H_2O and extracted successively with petroleum ether (15 g), EtOAc (95 g), and *n*-BuOH (200 g). The EtOAc fraction (80.0 g) was chromatographed over a column of silica gel. Compounds were eluted by petroleum ether, petroleum ether:CH_2Cl_2 (9:1, 8:2, 7:3, 6:4, 1:1, 1:2, 1:3, etc.), CH_2Cl_2, and CH_2Cl_2:MeOH (9:1, 8:2, 7:3, 6:4, etc.). Fractions of 200 mL were collected to afford 15 fractions (1–15).

Fraction 4 was chromatographed over silica gel with elution by a hexane:EtOAc gradient (10:1, 7:1) to afford **1** (11 mg) and **2** (8 mg) [8]. Fraction 5 was separated by chromatography over silica gel with elution by $CHCl_3$:MeOH (20:1) and then over a column of Sephadex LH-20 with elution by $CHCl_3$:MeOH (1:1) to afford **3** (100.9 mg). Fraction 6 was separated by chromatography over silica gel with elution by CH_2Cl_2:MeOH (9:1) to isolate new compound **1** (80 mg), mp 101–103°C.

Compounds **2**, **3**, and **4** were identified as ursolic acid (**2**) [8], tormentic acid (**3**) [9], and *β*-daucosterol (**4**) [10] based on PMR, ^{13}C NMR, HSQC, and HMBC spectral data, which agreed well with those reported.

5,7-Dihydroxy-2-*n*-pentacosanylchromen-4-one (1), white powder, mp 101–103°C. HR-ESI-MS: calcd for $C_{34}H_{55}O_4$, 527.8083; found, 527.8081 $[M - H]^-$. Table 1 presents the PMR, ^{13}C NMR, HSQC, and HMBC spectra.

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REFERENCES

1. B. Zeng, Y. Hebibulla, and E. Kerim, *Strain Economy Animals and Plants*, **8**, 29 (2005).
2. Y. Dejun, *Chinese Carpology*, Agriculture Press, 1979, p. 169.
3. *Editorial Committee of Chinese Medical Encyclopedia, Encyclopedia of Chinese Medicine-Uighur Medicine*, Shanghai Science and Technology Press, Shanghai, China, 2005, p. 177.
4. T. Tomoyuki, I. Masakazu, S. Haruyasu, and S. Minoru, *Agric. Biol. Chem.*, **47**, 1525 (1983).
5. B. M. Silva, P. B. Andrade, R. M. Seabra, P. Oliveira, M. A. Ferreira, and F. Ferreres, *Nat. Prod. Res.*, **19**, 275 (2005).
6. N. De Tommasi, S. Piacente, F. De Simone, and C. Pizza, *J. Agric. Food Chem.*, **44**, 1676 (1996).
7. A. Fiorentino, B. D'Abrosca, S. Pacifico, C. Mastellone, S. Piccolella, and P. Monaco, *Chem. Biodiversity*, **4**, 973 (2007).
8. J.-Y. Wu, G.-C. Li, and D.-Y. Wang, *J. South. Med. Univ.* [*Nanfang Yike Daxue Xuebao*], **27**(2), 226 (2007).
9. M. H. Yang, G. Blunden, M. J. O'Neill, and J. A. Lewis, *Planta Med.*, **58**, 227 (1992).
10. Z. F. Zhang, B. L. Ben, J. Yang, and X. F. Tian, *China J. Chin. Mater. Med.*, **29**, 237 (2004).
11. M. J. Gonzalez, M. M. Pinto, A. Kijjoa, S. Kengthong, I.-O. Mondanondra, A. M. S. Silva, G. Eaton, and W. Herz, *Phytochemistry*, **61**, 995 (2002).