XANTHONES FROM *Comastoma pedunlulatum*

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Comastoma pedunlulatum (Rogle ex D. Dou) Holub (Gentianaceae), widely distributed in the northwest of China, is traditionally used for the treatment of hepatitis and gallstone by local inhabitants. The bioactive substance is unknown since phytochemical studies on the species has not been carried out until recent years [1]. In continuation of our research on bioactive compounds of the title plant, eight xanthones were isolated from the aerial parts of *C. pedunlulatum*. Herein we describe the isolation and structure determination of the isolated compounds.

C. pedunlulatum was collected in Xining city, Qinghai province, People′s Republic of China, in June 2007. The identity of the plant material was verified by Prof. Jian Cui, and a voucher specimen (HMH200708) was deposited in the Key Laboratory of China Minority Traditional Medicine Center, Central University for Nationalities. Dried and chipped aerial parts (1 kg) of *C. pedunlulatum* were extracted with boiling aqueous ethanol (95%). The solvent was evaporated in vacuum and then the concentrated extract was successively partitioned with ethyl acetate and *n*-butanol. The ethyl acetate fraction was successively purified on silica gel with $CHCl_3$–MeOH gradient as eluent to yield compounds **1–5**. The *n*-butanol extract was purified on ODS with MeOH–H_2O gradient as eluent to give compounds **6–8**.

1,8-Dihydroxy-3,5-dimethoxyxanthone (1), yellow crystal, mp 184–186°C. EI-MS *m/z*: 288 (M^+). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.32 (1H, d, J = 2.4, H-2), 6.47 (1H, d, J = 2.4, H-4), 7.33 (1H, d, J = 8.1, H-6), 6.76 (1H, d, J = 8.1, H-7), 3.91 (3H, s, 3-OCH_3), 3.82 (3H, s, 5-OCH_3). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 161.9 (C-1), 97.8 (C-2), 166.9 (C-3), 92.8 (C-4), 157.5 (C-4a), 144.0 (C-4b), 137.5 (C-5), 123.5 (C-6), 109.4 (C-7), 151.7 (C-8), 107.5 (C-8a), 102.1 (C-8b), 184.1 (C-9), 56.3 (3-OCH_3), 56.5 (5-OCH_3) [2].

1,8-Dihydroxy-3,7-dimethoxyxanthone (2), yellow crystal, mp 190–192°C. EI-MS *m/z*: 288 (M^+). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.37 (1H, d, J = 2.4, H-2), 6.57 (1H, d, J = 2.4, H-4), 6.93 (1H, d, J = 8.1, H-5), 7.54 (1H, d, J = 8.1, H-6), 3.88 (3H, s, 3-OCH_3), 3.82 (3H, s, 7-OCH_3). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 162.1 (C-1), 97.8 (C-2), 167.1 (C-3), 92.8 (C-4), 157.8 (C-4a), 149.7 (C-4b), 105.5 (C-5), 121.5 (C-6), 142.4 (C-7), 148.7 (C-8), 107.1 (C-8a), 101.7 (C-8b), 184.1 (C-9), 56.3 (3-OCH_3), 56.5 (7-OCH_3) [3].

1-Hydroxy-3,7,8-trimethoxyxanthone (3), yellow crystal, mp 157–159°C. EI-MS *m/z*: 302 (M^+). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.25 (1H, d, J = 2.1, H-2), 6.30 (1H, d, J = 2.1, H-4), 7.13 (1H, d, J = 8.4, H-5), 7.34 (1H, d, J = 8.4, H-6), 3.98 (3H, s, 3-OCH_3), 3.92 (3H, s, 7-OCH_3), 3.86 (3H, s, 8-OCH_3). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 163.1 (C-1), 97.1 (C-2), 166.1 (C-3), 92.3 (C-4), 157.1 (C-4a), 149.7 (C-4b), 113.0 (C-5), 121.5 (C-6), 148.4 (C-7), 150.3 (C-8), 115.1 (C-8a), 103.7 (C-8b), 181.1 (C-9), 56.3 (3-OCH_3), 57.5 (7-OCH_3), 60.8 (8-OCH_3) [4].

1,3,8-Trihydroxy-7-methoxyxanthone (4), yellow crystal, mp 298–299°C. EI-MS *m/z*: 274 (M^+). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.23 (1H, d, J = 2.4, H-2), 6.37 (1H, d, J = 2.4, H-4), 6.97 (1H, d, J = 8.8, H-5), 7.44 (1H, d, J = 8.8, H-6), 3.81 (3H, s, 7-OCH_3); ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 162.1 (C-1), 98.3 (C-2), 166.6 (C-3), 93.8 (C-4), 157.8 (C-4a), 149.2 (C-4b), 105.5 (C-5), 121.5 (C-6), 142.4 (C-7), 148.7 (C-8), 107.0 (C-8a), 100.7 (C-8b), 184.0 (C-9), 56.4 (7-OCH_3) [2].

1-*O*-*β*-D-Glucopyranosyl-3,8-dihydroxy-7-methoxyxanthone (5), yellow crystal, mp 284–286°C. ESI-MS (negative) *m/z*: 435 $[M–H]^-$. PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.42 (1H, d, J = 2.7, H-2), 6.57 (1H, d, J = 2.7, H-4), 6.93 (1H, d, J = 8.8, H-5), 7.41 (1H, d, J = 8.8, H-6), 5.06 (1H, d, J = 7.5, H-1′), 3.83 (3H, s, 7-OCH_3). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 160.1 (C-1), 99.8 (C-2), 166.1 (C-3), 96.8 (C-4), 158.8 (C-4a), 150.7 (C-4b), 105.5 (C-5), 120.5 (C-6), 142.4 (C-7), 148.7 (C-8), 108.1 (C-8a), 104.2 (C-8b), 181.5 (C-9), 56.5 (7-OCH_3), 102.1 (C-1′), 73.5 (C-2′), 77.8 (C-3′), 70.0 (C-4′), 76.2 (C-5′), 61.1 (C-6′) [2].

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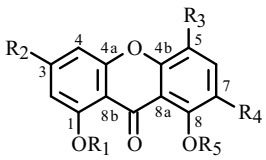

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1: $R_1 = R_4 = R_5 = H$, $R_2 = R_3 = OCH_3$; **2:** $R_1 = R_3 = R_5 = H$, $R_2 = R_4 = OCH_3$
3: $R_1 = R_3 = H$, $R_5 = CH_3$, $R_2 = R_4 = OCH_3$; **4:** $R_1 = R_3 = R_5 = H$, $R_2 = OH$, $R_4 = OCH_3$
5: R_1 = Glc, $R_3 = R_5 = H$, $R_2 = OH$, $R_4 = OCH_3$; **6:** R_1 = Glc-Xyl, $R_3 = R_5 = H$, $R_2 = R_4 = OCH_3$
7: R_1 = Glc-Xyl, $R_4 = R_5 = H$, $R_2 = R_3 = OCH_3$; **8:** R_1 = Glc-Xyl, $R_3 = H$, $R_5 = CH_3$, $R_2 = R_4 = OCH_3$

1-*O*-[*β*-D-Xylopyranosyl-(1-6)-*β*-D-glucopyranosyl]-8-hydroxy-3,7-dimethoxyxanthone (6), orange powder, ESI-MS (negative) *m/z*: 581 $[M–H]^-$. PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.73 (1H, d, J = 2.4, H-2), 6.75 (1H, d, J = 2.4, H-4), 6.93 (1H, d, J = 8.1, H-5), 7.44 (1H, d, J = 8.1, H-6), 5.06 (1H, d, J = 7.5, H-1′), 4.93 (1H, d, J = 7.5, H-1″), 3.91 (3H, s, 3-OCH_3), 3.87 (3H, s, 7-OCH_3); ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 159.1 (C-1), 98.8 (C-2), 165.7 (C-3), 94.8 (C-4), 158.8 (C-4a), 150.7 (C-4b), 108.5 (C-5), 120.5 (C-6), 142.4 (C-7), 148.1 (C-8), 104.1 (C-8a), 100.7 (C-8b), 181.1 (C-9), 56.2 (3-OCH_3), 56.5 (7-OCH_3), 104.1 (C-1′), 73.5 (C-2′), 75.7 (C-3′), 70.0 (C-4′), 76.2 (C-5′), 68.1 (C-6′), 104.5 (C-1″), 73.2 (C-2″), 76.3 (C-3″), 69.5 (C-4″), 65.2 (C-5″) [3].

1-*O*-[*β*-D-Xylopyranosyl-(1-6)-*β*-D-glucopyranosyl]-8-hydroxy-3,5-dimethoxyxanthone (7), orange powder, ESI-MS (negative) *m/z*: 581 $[M–H]^-$. PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.73 (1H, d, J = 2.4, H-2), 6.79 (1H, d, J = 2.4, H-4), 7.38 (1H, d, J = 8.1, H-6), 6.64 (1H, d, J = 8.1, H-7), 5.03 (1H, d, J = 7.5, H-1′), 4.93 (1H, d, J = 7.5, H-1″), 3.91 (3H, s, 3-OCH_3), 3.85 (3H, s, 5-OCH_3); ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 159.1 (C-1), 99.8 (C-2), 166.3 (C-3), 95.8 (C-4), 159.7 (C-4a), 144.7 (C-4b), 139.5 (C-5), 120.5 (C-6), 109.4 (C-7), 154.1 (C-8), 109.7 (C-8a), 105.7 (C-8b), 181.3 (C-9), 56.9 (3-OCH_3), 57.1 (5-OCH_3), 101.1 (C-1′), 73.5 (C-2′), 76.4 (C-3′), 70.0 (C-4′), 77.2 (C-5′), 66.1 (C-6′), 104.5 (C-1″), 73.8 (C-2″), 76.9 (C-3″), 69.9 (C-4″), 65.2 (C-5″) [5].

1-*O*-[*β*-D-Xylopyranosyl-(1-6)-*β*-D-glucopyranosyl]-3,7,8-trimethoxyxanthone (8), orange powder. ESI-MS (negative) *m/z*: 595 $[M–H]^-$. PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.71 (1H, d, J = 2.4, H-2), 6.75 (1H, d, J = 2.4, H-4), 7.23 (1H, d, J = 8.1, H-5), 7.54 (1H, d, J = 8.1, H-6), 4.98 (1H, d, J = 7.5, H-1′), 5.01 (1H, d, J = 7.5, H-1″), 3.91 (3H, s, 3-OCH_3), 3.87 (3H, s, 7-OCH_3), 3.84 (3H, s, 8-OCH_3); ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 158.5 (C-1), 99.8 (C-2), 164.3 (C-3), 94.8 (C-4), 157.7 (C-4a), 148.7 (C-4b), 112.5 (C-5), 119.5 (C-6), 147.4 (C-7), 149.1 (C-8), 117.0 (C-8a), 107.0 (C-8b), 174.6 (C-9), 55.5 (3-OCH_3), 56.1 (7-OCH_3), 60.5 (8-OCH_3), 104.1 (C-1′), 73.0 (C-2′), 75.8 (C-3′), 70.0 (C-4′), 76.2 (C-5′), 68.1 (C-6′), 102.5 (C-1″), 73.1 (C-2″), 75.5 (C-3″), 69.2 (C-4″), 65.1 (C-5″) [4].

All these xanthones were isolated from *C. pedunlulatum* for the first time.

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