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Xanthones from *Triperospermum chinense* (Migo)

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Five xanthones including 1,3-dihydroxy-5,8-dimethoxyxanthone (**1**), 1,3,7-trihydroxy-8-methoxy xanthone (**2**), 8-hydroxy-1,2,6-trimethoxy xanthone (**3**), 1,7-dihydroxy-3,8-dimethoxyxanthone (**4**), 1,2,8-trihydroxy-5,6-dimethoxyxanthone (**5**) were isolated from 95% ethanolic extract of *Triperospermum chinense* (Migo) by chromatographic techniques. The structure of these compounds were determined by spectral techniques (UV, IR, MS and NMR). All the compounds were isolated from this genus for the first time.

Key Words: *Tripterospermum chinense*, Xanthone.

INTRODUCTION

The genus *Tripterospermum(Gentianacea)* comprises more than 10 species in China[1]. Previous study showed that the main constituents of this genus were xanthones, flavonoids, iridoids and triterpenes[2]. *Tripterospermum chinense* (Migo) H. Smith, widely distributed in the southeast of China, is traditionally used for the treatment of coughs, haemoptysis and pulsonary disease by local inhabitants[3]. In this study, five xanthones including 1,3-dihydroxy-5,8-dimethoxyxanthone (**1**), 1,3,7-trihydroxy-8-methoxyxanthone (**2**), 8-hydroxy-1,2,6-trimethoxyxanthone (**3**), 1,7-dihydroxy-3,8-dimethoxyxanthone (**4**), 1,2,8-trihydroxy-5,6-dimethoxyxanthone (**5**) were isolated from the 95% EtOH extracts of this plant.

EXPERIMENTAL

UV spectra were obtained on a Shimadzu UV-2401PC spectrophotometer, IR spectra were recorded on a Nicolet Manga-750 spectrophotometer. Melting points were determined using a SGW-X4 melting point apparatus and uncorrected. The NMR spectra were taken on Buker AM-400 instrument with TMS as an internal standard. The EI-MS experiment was conducted at MAT-95 mass spectrometer. Column chromatography (CC) and preparative TLC were carried out on silica gel (200-300 mesh) and GF_{254} plates at 254 nm, respectively. The visualization of TLC was processed by spraying 5% H_2SO_4 regeant. All the solvents were distilled prior to use. Petroleum ether: 60-90ºC.

Plant material: *Tripterospermum chinense* was collected from Yongshun county, Hunan Povince of China in May, 2004 and identified by Prof. Jingui Shen of Shanghai Institute of Materia Medica. A voucher specimen (No. 2004053205) is deposited at the herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Science.

Extraction and Purification: The air-dried powdered aerial part of *T. chinense* (10 kg) was extracted with 95 % EtOH (80 L × 3, 2 d each) at room temperature. After removal of solvent in *vacuo*, an extract of 550 g was afforded. The extract was suspended in H_2O (2 L) and partitioned with petroleum ether (2 L × 5), EtOAc (2 L × 5) and *n*-BuOH (2 L × 5) to give corresponding fractions A (3 g), B (120 g) and C (220 g).

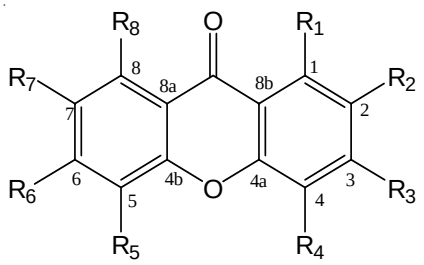
Fraction A was subjected to silica gel column (150 g, 100 - 200 mesh, ϕ50 mm × L 250 mm). Gradient elution using petroleum ether-acetone (20:1, 12:1, 8:1 each 2000 mL) to yield three subfraction A1 - A3. A1 (0.8 g) was separated over silica gel column (40 g, 200 - 300 mesh, ϕ30 mm × L 250 mm) with petroleum ether-EtOAc (12:1) to give **3** (260 mg); A2 (1.8 g) was chromatographied by silica gel column (80 g, 200-300 mesh, ϕ40 mm × L 250 mm) with petroleum ether-EtOAc (10:1) afforded **4** (830 mg).

Fraction B was divided into five subfraction B1-B5 by silica gel column (2500 g, 100 - 200 mesh, ϕ80 mm × L 850 mm), using $CHCl_3$-CH_3OH (50:1, 25:1, 10:1, 5:1, each 8000 mL) and methanol (8000 mL) as solvents. B1 (5.8 g) was separated over silica gel column column (280 g, 200-300 mesh, ϕ60 mm × L 550 mm) with petroleum ether-acetone (10:1) to give **1** (180 mg); Separation of B2 (6.8 g) by silica gel column (320 g, 200-300 mesh, ϕ60 mm × L 550 mm) with petroleum ether-actone (6:1) afforded **2** (530 mg); B3 (7.3 g) was chromatographied by silica gel column (350g, 200-300 mesh, ϕ60 mm × L 450 mm) eluted with petroleum ether-EtOAc (2:1) to yield **5** (430 mg).

RESULTS AND DISCUSSION

1,3-Dihydroxy-5,8-dimethoxyxanthone (**1**) yellow crystal ($CHCl_3$), m.p. 192.5-193.5°C; EIMS m/z 288 $[M]^+$; UV(MeOH) λ_{max} (nm): 220, 224, 305, 376; IR (KBr) ν_{max} (cm^{-1}): 3360, 2950, 2860, 1650, 1610, 1470, 1435, 1320, 1300, 1210, 1160, 1100, 1060, 825. ^1H NMR and ^{13}C NMR data (Tables 1 and 2) was in accordance with those reported[4].

1,3,7-Trihydroxy-8-methoxyxanthone (**2**) yellow crystal (ethonol), m.p. 250-252°C; UV(EtOH) λ_{max} (nm): 242, 264, 322, 383; IR (KBr) ν_{max} (cm^{-1}): 3425-3325, 1640, 1595, 1500, 1300, 1170, 1150, 1060, 945, 835. ^1H NMR and ^{13}C NMR data (Tables 1 and 2); EIMS m/z: 274$[M]^+$, 245 $[M\text{-}CHO]^+$, 244$[M\text{-}CH_2O]^+$, 231$[M\text{-}C_2H_3O]^+$ and 123$[M\text{-}CO]^{2+}$. The mass information and NMR data resembled closely to those reported[5].



	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
1	OH	H	OH	H	OMe	H	H	OMe
2	OH	H	OH	H	H	H	OH	OMe
3	OMe	OMe	H	H	H	OMe	H	OH
4	OH	H	OMe	H	H	H	OH	OMe
5	OH	OH	H	H	OMe	OMe	H	OH

Fig. 1. Chemical structure of **1-5**

TABLE-1
^{1}H-NMR SPECTRAL DATA OF 1-5 (DMSO-d_6, 400 MHz)

Position	1 δ *J* (Hz)	2 δ *J* (Hz)	3 δ *J* (Hz)	4 δ *J* (Hz)	5 δ *J* (Hz)
1	-	-	-	-	-
2	6.35(d, 1.8)	6.21(d, 2.0)	-	6.31(d, 2.2)	-
3	-	-	7.36(d, 9.1)	-	7.34(d, 9.0)
4	6.39(d, 1.8)	6.30(d, 2.0)	7.17(d, 9.1)	6.38(d, 2.2)	6.91(d, 9.0)
5	-	7.14(d, 8.9)	6.35(d, 2.1)	7.14(d, 9.1)	-
6	7.40(d, 9.0)	7.35(d, 8.9)	-	7.40(d, 9.1)	-
7	7.18(d, 9.0)	-	6.28(d, 2.1)	-	6.61(s)
8	-	-	-	-	-
OMe	4.06(s)	3.81(s)	3.88(s)	3.95(s)	3.83(s)
	3.93(s)		3.94(s)	4.03(s)	3.91(s)
			4.00(s)		
OH-1	13.21(s)	13.30(s)	-	13.10(s)	11.70(s)
OH-3	6.03(br)	-	-	-	-
OH-7	-	-	-	-	-
OH-8	-	-	13.24(s)	-	11.80(s)

8-Hydroxy-1,2,6-trimethoxyxanthone (**3**) yellow crystal ($CHCl_3$), m.p. 159-161°C; UV(EtOH) λ_{max} (nm): 240, 261, 318, 378; IR (KBr) ν_{max}(cm^{-1}): 3390, 1650, 1610, 1300, 1170, 1150,1070; EIMS m/z: 302 $[M]^+$, 287$[M-CH_3]^+$, 273$[M-CHO]^+$, 259$[M-C_2H_3O]^+$, ^{1}H NMR and ^{13}C NMR data (Tables 1 and 2) was in well agreement with reported results[6-8].

1,7-Dihydroxy-3,8-dimethoxyxanthone (**4**), yellow crystal, $C_{15}H_{12}O_6$, m.p. 192-193°C; UV(EtOH) λ_{max} (nm): 239, 262, 311, 372; IR (KBr) ν_{max}

(cm^{-1}): 3440, 1640, 1615, 1590, 1300, 1170, 1140; EIMS m/z: 288$[M]^+$, 270$[M-H_2O]^+$, 259$[M-CHO]^+$, 245$[M-C_2H_3O]^+$. ^1H NMR and ^{13}C NMR data (Tables 1 and 2) was in accordance with those reported[9,10].

1,2,8-Trihydroxy-5,6-dimethoxyxanthone (**5**), yellow needles (MeOH), m.p. 233-235°C; UV(MeOH) λ_{max} (nm): 238, 312, 344, 404; IR (KBr) ν_{max} (cm^{-1}): 3420, 1640, 1595, 1290, 1160, 1120, EIMS m/z: 304$[M]^+$, 289$[M-CH_3]^+$, 275$[M-CHO]^+$, 261$[M-C_2H_3O]^+$; ^1H NMR and ^{13}C NMR data (Tables 1 and 2) corresponded well to those reported[11].

TABLE-2
^{13}C NMR SPECTRAL DATA OF 1-5 (DMSO-d_6, 100 MHz)

Position	1	2	3	4	5
	δ_C	δ_C	δ_C	δ_C	δ_C
1	157.4	156.8	140.9	157.3	147.1
2	104.3	97.7	149.2	97.0	140.5
3	150.8	149.3	120.5	150.8	124.3
4	94.6	93.7	112.6	92.1	106.3
5	163.4	113.0	91.9	113.9	128.3
6	97.1	124.1	166.3	122.5	160.3
7	92.4	163.0	96.8	163.0	95.1
8	166.6	165.1	163.7	166.6	157.6
C=O	180.6	180.1	181.0	180.6	184.6
4a	144.5	146.8	148.8	145.6	148.0
4b	145.7	145.2	157.0	144.4	149.0
8a	122.7	114.8	103.8	114.8	101.2
8b	113.9	102.4	115.7	104.1	107.2
OMe	55.9	61.0	55.6	55.8	56.6
	62.9	57.1	60.8	60.9	61.6

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