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MINOR XANTHONES OF *HYPERICUM MYSORENSE**

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Key Word Index—*Hypericum mysorense*; Hypericaceae; Guttiferae; xanthones; 6, 7-dimethoxy-1-hydroxyxanthone; 2-hydroxy-3-methoxyxanthone; 2-hydroxyxanthone; 1-hydroxy-7-methoxyxanthone; 1, 7-dihydroxyxanthone; 1, 2-dimethoxyxanthone; 2-methoxyxanthone; 2, 3-dimethoxyxanthone; chemotaxonomy.

Abstract—2-Hydroxyxanthone, 1,7-dihydroxyxanthone, 1-hydroxy-7-methoxyxanthone, 6,7-dimethoxy-1-hydroxyxanthone and a new natural product, 2-hydroxy-3-methoxyxanthone, have been isolated and characterized from the phenolic fraction of the chloroform extract of the timber of *Hypericum mysorense*. The presence of simple xanthones in this genus supports the classification of *Hypericum* in the subfamily Hypericoideae in Guttiferae.

INTRODUCTION

As a part of our continuing chemical and biological studies on medicinal and related plants of Sri Lanka, we have investigated the phenolic fraction derived from the timber of *Hypericum mysorense* Wight and Arn, and in this paper we report the isolation and characterization of several simple xanthones including a new natural product, 2-hydroxy-3-methoxyxanthone (**4**). Our previous studies resulted in the isolation of 2, 3-dimethoxyxanthone (**1**) from the neutral fraction [1].

RESULTS AND DISCUSSION

The hot $CHCl_3$ extract of the timber of *H. mysorense* was separated into neutral and phenolic fractions. The former fraction contained mainly 2, 3-dimethoxyxanthone [1]. The phenolic fraction on TLC indicated the presence of at least seven pigments and these were separated by CC followed by repeated prep. TLC. All these compounds had UV (Table 1) and IR spectra characteristic of xanthones.

The least polar pigment eluted from the column with 1% EtOAc–petrol was further purified by TLC ($CHCl_3$–MeOH, 99.5 : 0.5) to give a pale yellow crystalline solid, $C_{13}H_{12}O_5$, mp 189–190°, which was identified as 6, 7-dimethoxy-1-hydroxyxanthone (**2**) from its physical data. The next polar compound eluted from the column with the same solvent mixture, after further purification by prep. TLC, afforded 1-hydroxy-7-methoxyxanthone (**3**) whose identity was confirmed by comparison with an authentic sample prepared by methylation of euxanthone (1, 7-dihydroxyxanthone).

Further elution of the column with 5% EtOAc–petrol gave a new pigment which was purified by prep. TLC to afford a pale yellow crystalline solid, mp 174–175°, $C_{14}H_{10}O_4$, which gave a green colour with $FeCl_3$ indicative of a phenol. The IR spectrum was characteristic of a phenolic xanthone and the ^1H NMR spectrum indicated the presence of one OMe group. Methylation gave a methyl ether which was identified as 2, 3-dimethoxyxanthone (**1**) (mp, mmp and co-TLC). The pigment was shown to be different from authentic 3-hydroxy-2-methoxyxanthone [2] thus confirming it to be 2-hydroxy-3-methoxyxanthone (**4**). The following xanthones have also been isolated and identified: 2-hydroxyxanthone (**5**) and 1, 7-dihydroxyxanthone (**7**). From the methylated mixture (see Experimental) were isolated the following xanthones: 1, 2-dimethoxyxanthone (**1**), 2-methoxyxanthone (**6**) and 1-hydroxy-7-methoxyxanthone (**3**).

Xanthones of various structural types have been previously encountered in several *Hypericum* species. Investigation of *H. maculatum* resulted in the isolation of a new pyranoxanthone, maculatoxanthone [3], whereas *H. androsaemum* yielded several simple xanthones along with 1, 3, 6, 7-tetrahydroxy-8-prenylxanthone, toxyloxanthone B and another

Table 1. UV absorption maxima of xanthones **1–8**

Xanthone	λ_{max}^{EtOH} nm (log ϵ)
1	242.5(4.52), 272(3.84), 307(4.02), 349(4.98)
2	253(4.57), 275(4.10), 291(3.80), 370(3.90)
3	235(4.35), 264(4.29), 227(4.30), 307(3.58), 375(3.58)
4	238(3.45), 255(3.95), 272(4.80), 277(2.80)
5	238(4.83), 252(4.58), 300(3.33), 358(3.98)
6	237(4.21), 250(4.51), 360(3.33)
7	240(4.48), 360(3.30)
8	240(4.48), 260(4.10), 360(3.30)

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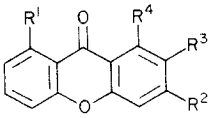

1	$R^1=R^4=H$,	$R^2=R^3=OMe$	
2	$R^1=OH$,	$R^2=R^3=OMe$,	$R^4=H$
3	$R^1=OH$,	$R^2=R^4=H$,	$R^3=OMe$
4	$R^1=R^4=H$,	$R^2=OMe$,	$R^3=OH$
5	$R^1=R^2=R^4=H$,	$R^3=OH$	
6	$R^1=R^2=R^4=H$,	$R^3=OMe$	
7	$R^1=R^3=OH$,	$R^2=R^4=H$	
8	$R^1=R^2=H$,	$R^3=R^4=OMe$	

pyranoxanthone, kielcorin, which has previously been reported from *Kielmeyera coriacea*, a plant belonging to the Guttiferae [4]. The presence of xanthones in *H. mysorense* further supports the inclusion of Hypericoideae within the Guttiferae.

EXPERIMENTAL

General procedures. Mps: uncorr; IR: KBr disc; TLC: 0.25 mm Si gel (Merck), prep. TLC 1 mm Si gel. Petrol refers to the fraction of bp 60–80°.

Extraction and separation of the phenolic fraction. The timber of *H. mysorense* collected at Horton Plains, Sri Lanka, after defatting with hot petrol, was extracted with hot $CHCl_3$. The hot $CHCl_3$ extract (21 g) after evaporation *in vacuo* was separated into neutral (11 g) and phenolic (9 g) (NaOH-soluble) fractions by the usual procedure.

2, 3-*Dimethoxyxanthone* (**1**). TLC analysis of the neutral fraction indicated it to consist of a single compound. Recrystallization from $CHCl_3$–petrol afforded **1** as colourless crystals, mp and mmp 165–167°, lit. 165–167° [1], identical (IR, co-TLC) with an authentic sample.

6, 7-*Dimethoxy*-1-*hydroxyxanthone* (**2**). The phenolic fraction (3 g) was chromatographed over Si gel (60 g). Fractions eluted with petrol–EtOAc (99 : 1) were further purified by prep. TLC to yield xanthone **2** (26 mg, 9.3×10^{-3}%), mp 189–190°, lit. 187–189° [5]; UV data see Table 1; IR ν_{max}^{KBr} cm^{-1}: 2970–3000 (OH), 1640 (γ-pyrone C=O); ^1H NMR ($CDCl_3$): δ 12.73 (1H, *s*), 7.60 (1H, *d*, *J* = 8 Hz), 6.72 (1H, *d*, *J* = 1.5 Hz), 6.75 (1H, *d*, *J* = 1.5 Hz), 6.85 (1H, *d*, *J* = 8 Hz), 4.02 (3H, *s*), 3.97 (3H, *s*). (Found: C, 66.01; H, 4.41%. $C_{13}H_{12}O_5$ requires: C, 66.01; H, 4.40%.)

1-*Hydroxy*-7-*methoxyxanthone* (**3**). Elution of the column with the same solvent mixture afforded crude **3** which was purified by prep. TLC to obtain dark yellow needles (42 mg, 1.5×10^{-2}%), mp 124–126° (from $CHCl_3$), lit. 128–129° [6]; UV data see Table 1; IR ν_{max}^{KBr} cm^{-1}: 2995–3000 (OH), 1640 (γ-pyrone C=O); MS *m/z* (rel. int.): 242 $[M]^+$ (100), 227(35), 212(17), 171(15); ^1H NMR (Me_2CO-d_6): δ 12.66 (1H, *s*), 7.72–7.46 (4H, *m*), 7.10–6.69 (2H, *m*), 3.95 (3H, *s*). Sample identical (co-TLC, mmp and ^1H NMR) with a sample of **3** prepared by methylation (CH_2N_2) of euxanthone [7].

2-*Hydroxy*-3-*methoxyxanthone* (**4**). Fractions eluted with petrol–EtOAc (19 : 1) on further purification by prep. TLC afforded **4** as a pale yellow crystalline solid (160 mg, 4.7×10^{-2}%), mp 174–175°. UV data see Table 1; IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1640 (γ-pyrone C=O); MS *m/z* (rel. int.): 242 $[M]^+$ (100), 227 (78), 212(72), 199(30), 171(50), 121(37); ^1H NMR ($CDCl_3$): δ 8.30–8.35 (1H, *m*), 7.27–7.33(5H, *m*), 4.03(3H, *s*). Methylation (CH_2N_2) gave 2, 3-dimethoxyxanthone (**1**) (mp, mmp, IR and co-TLC).

2-*Hydroxyxanthone* (**5**). Column fractions eluted with petrol–EtOAc (9 : 1) consisted mainly of **5** which was subjected to further purification by prep. TLC to obtain a colourless solid (32 mg, 1.1×10^{-2}%). Recrystallization from petrol–$CHCl_3$ afforded white needles, mp 216–218°, lit. 240–242° [8]; UV data see Table 1; IR ν_{max}^{KBr} cm^{-1}: 3250(OH), 1650 (γ-pyrone C=O); MS *m/z* (rel. int.) 212 $[M]^+$ (100), 184(12), 128(7); ^1H NMR (Me_2CO-d_6): δ 8.28–8.16 (1H, *m*), 7.92–7.28 (6H, *m*).

2-*Methoxyxanthone* (**6**). Methylation (CH_2N_2) of **5** and usual work-up afforded 2-methoxyxanthone as colourless needles, mp 130–131°, lit. 130–131° [9]; UV data see Table 1; IR ν_{max}^{KBr} cm^{-1}: 1640 (γ-pyrone C=O) 1600, 1310, 1120, 825, 750; MS *m/z* (rel. int.): 226 $[M]^+$ (100), 196(31), 155(64); ^1H NMR($CDCl_3$): δ 8.46–8.28 (1H, *m*), 7.79–7.28 (6H, *m*), 3.97(3H, *s*). Identity confirmed by comparison (co-TLC, mmp) with an authentic sample [10].

1, 7-*Dihydroxyxanthone* (**7**). Fractions eluted with petrol–EtOAc (3 : 1) on evaporation and recrystallization from $CHCl_3$–Me_2CO gave **7** (68 mg, 2.4×10^{-2}%) as deep yellow needles, mp 238–240°; lit. 238–239° [11]; UV data see Table 1; IR ν_{max}^{KBr} cm^{-1}: 3250(OH), 1640 (γ-pyrone C=O); ^1H NMR ($CDCl_3$): δ 8.36–8.24 (2H, *m*), 7.29 (4H, *m*), 4.05 (3H, *s*), 3.67 (3H, *s*). Identity further confirmed by comparison (co-TLC, mmp) with an authentic sample.

1, 2-*Dimethoxyxanthone* (**8**). A portion of the above phenolic mixture was methylated with excess Me_2SO_4–K_2CO_3–Me_2CO and the resulting methylated xanthone mixture separated by CC on Si gel. Fractions eluted with petrol–CH_2Cl_2 (19 : 1) on further purification by prep. TLC afforded **8** as a colourless crystalline solid (44 mg, 1.5×10^{-2}%), mp 129–131°, lit. 130–131° [12]; UV data see Table 1. IR ν_{max}^{KBr} cm^{-1}: 1650 (γ-pyrone C=O); ^1H NMR ($CDCl_3$): δ 8.36–8.24 (2H, *m*), 7.29 (4H, *m*), 4.05 (3H, *s*), 3.67 (3H, *s*). The identity of **8** was further confirmed by comparison (co-TLC, co-IR and mmp) with an authentic sample [10].

The above methylated phenolic mixture on chromatography afforded in addition 2-methoxyxanthone (**6**, 22 mg, 7.9×10^{-3}%) and 1-hydroxy-7-methoxyxanthone (**3**, 68 mg, 2.4×10^{-2}%).

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