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# A XANTHONE GLYCOSIDE FROM *SWERTIA SPECIOSA*

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**Key Word Index**—*Swertia speciosa*; Gentianaceae; high altitude plants; 1-hydroxy-8-glucosyloxy-3,5-dimethoxyxanthone; 1,8-dihydroxy-3,7-dimethoxyxanthone; 3-methoxy- 1,5,8-trihydroxyxanthone; ursolic acid.

**Abstract**—A new xanthone glycoside, 1-hydroxy-8-glucosyloxy-3,5-dimethoxyxanthone, alongwith 1,8-dihydroxy-3,7-dimethoxyxanthone, 3-methoxy-1,5,8-trihydroxyxanthone and ursolic acid have been isolated and identified from the aerial parts of *Swertia speciosa*.

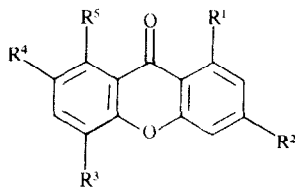
## INTRODUCTION

The crude extracts of most *Swertia* plants show mutagenetic activity [1, 2] and the xanthone glycosides, their aglycones and steryl derivatives have produced varying responses to central nervous and cardiovascular systems [3–5]. Fifteen species of this genus are found to occur in Kumaon Himalayan region and a few, e.g. *S. chirata*, *S. paniculata* and *S. alata*, are used medicinally [6, 7]. *Swertia speciosa*, an alpine herb, has only been studied with a chemotaxonomic point of view and only one report exists in the literature [8]; it contains 1,7-dihydroxy-3-methoxyxanthone, 1,3-dihydroxy-7-methoxyxanthone, 1-hydroxy-3,7-dimethoxyxanthone, 1,7,8-trihydroxy-3-methoxyxanthone, 1,7-dihydroxy-3,8-dimethoxyxanthone, 1,8-dihydroxy-3,5-dimethoxyxanthone and 2-*C*-glucosyl-1,3,6,7-tetrahydroxyxanthone in its roots. In a research programme [9, 10] on high altitude flora, aerial parts of *S. speciosa* have been found to contain a new xanthone glucoside, two known xanthones and ursolic acid.

## RESULTS AND DISCUSSION

Compound (**1**) $C_{21}H_{22}O_{12}$ which appeared as a brown purple spot on TLC did not move either in HOAc–$H_2O$ (3:17, 3:7, 3:2), HOAc–$H_2O$–HCl (30:10:3), isopropanol–$H_2O$ (3:2) or in phenol–$H_2O$ (4:1). It gave positive Molisch, Feigl [11] and $FeCl_3$ tests and MS did not show any prominent molecular ion peak but peaks at 288 and 270 were intense. The immobile behaviour, [12] colour reactions and mass spectral results indicated the glycosidic nature of the compound [1]. It was further supported by a broad IR band in the region 1150 to 950 $cm^{-1}$ due to *O*-glycosylation.

On emulsin hydrolysis, **1** gave an aglycone **1a** mp 191° and glucose (PPC). The aglycone **1a** was similar to xanthones in its colour reactions. The UV spectrum of **1a** was of the pattern of 1,3,5,8-tetraoxygenated xanthone [13]. Its UV maxima in methanol underwent a bathochromic shift with aluminium trichloride (not destroyed by the addition of HCl) and showed two low field $^1H$ NMR signals at $\delta$ 12.15 and 11.98 due to two chelated OH groups placed at $C_1$ and $C_8$. The compound **1a** was insoluble in sodium carbonate and the UV maxima in MeOH remained unchanged by the addition of sodium acetate [14] or sodium acetate–boric acid showing the absence of free OH groups at $C_3$ and $C_5$. The two signals at $\delta$ 4.09 and 3.98 were indicative of two methoxyl groups. The $^1H$ NMR spectra revealed four aromatic protons, exhibiting two pairs of *ortho* ($C_6$ and $C_7$) and *meta* ($C_2$ and $C_4$) coupled protons attached to two different rings at 6.64, 7.15 (2H, *dd*, $J = 9$ Hz) and 6.34, 6.52 (2H, *dd*, $J = 2$ Hz) respectively. On complete methylation with dimethyl sulphate and potassium carbonate followed by hydrolysis **1** afforded 8-hydroxy-1,3,5-trimethoxyxanthone (**1b**) indicating the linkage of sugar at $C_8$ of the aglycone. Thus **1** was identified as 1-hydroxy-8-glucosyl-




**1** $R^1$=OH, $R^2$=$R^3$=OMe, $R^4$=H, $R^5$=OGlu
**1a** $R^1$=$R^5$=OH, $R^2$=$R^3$=OMe, $R^4$=H
**1b** $R^1$=$R^2$=$R^3$=OMe, $R^4$=H, $R^5$=OH
**2** $R^1$=$R^3$=$R^5$=OH, $R^2$=OMe, $R^4$=H
**3** $R^1$=$R^5$=OH, $R^2$=$R^4$=OMe, $R^3$=H

Part 2 in the series 'Constituents of High Altitude Himalayan Herbs'. For Part 1 see: Khetwal, K. S. and Manral, K. (1987) *Planta Med.* (in press).

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oxy-3,5-dimethyoxyxanthone. Compound (**2**) $C_{14}H_{10}O_6$ mp 262° was identified as 3-methoxy-1,5,8-trihydroxyxanthone on the basis of UV, IR, $^1$H NMR and MS results [1] as well as by preparing 1,3,5,8-tetramethoxyxanthone mp 225° [17] by treating with dimethyl sulphate and potassium carbonate. Compound **3**, $C_{15}H_{12}O_6$ mp 190°, belonged to the 1,3,7,8-tetraoxygenated series of xanthones on the basis of UV spectra [15]. The presence of two methoxyl groups at $\delta$3.85 and 3.95 and two chelated hydroxyl groups at $\delta$11.82 and 11.93 as well as conversion of **3** to tetramethoxy derivative mp 214° confirmed its structure to be 1,8-dihydroxy-3,7-dimethoxyxanthone [17]. Compound **4**, colourless needles mp 288° responded to Liebermann–Burchard reagent (pink blue) and was identified as ursolic acid by comparing its UV, IR $^1$H NMR and MS spectral results.

## EXPERIMENTAL

Mps: uncorr. Silica gel G (Glaxo 60–120 mesh) was used for CC and TLC. Whatman No. 3 chromatographic paper was used for PPC. Water Associates HPLC along with variable wavelength (190–750 nm) UV detector, 6000 psi pump and steel and Z-module $\mu$ bonda Pak $C_{18}$ column/cartridge was used with $CHCl_3$–MeOH (49:1) solvent for checking the purity and for isolation. TLC spots were visualized either by their fluorescence in long range UV light (365 nm), $I_2$ vapour, $FeCl_3$, or with 15% $H_2SO_4$. Sugar was analysed by PC using *p*-anisidine and benzidine as visualizing reagents.

*Extraction and isolation. S. speciosa* was collected from Pindari glacier area at 4000 m. The material was authenticated at the Department of Botany, Kumaun University, Nainital where the voucher specimen is deposited. The shade dried aerial parts of the plant were pulverized, dried and Soxhlet extracted with 90% EtOH. The EtOH extract was partitioned with $CHCl_3$ and $H_2O$. The $CHCl_3$ fraction was further extracted with petrol (bp 60–80°) and $H_2O$ fraction with EtOAc and *n*-BuOH. The petrol fraction on silica gel chromatography (petrol–benzene) yielded, 1,8-dihydroxy-3,7-dimethoxyxanthone, 3-methoxy-1,5,8-trihydroxyxanthone besides ursolic acid whereas *n*-BuOH fraction ($CHCl_3$: MeOH), 1-hydroxy-8-glucosyloxy-3,5-dimethoxyxanthone.

*1-Hydroxy-8-glucosyloxy-3, 5-dimethoxyxanthone* (**1**). Yellow crystals mp 249–252°, UV $\lambda_{max}^{MeOH}$ nm: 260, 295, 300, 308, 330, 370, 375, IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3450, 1660, 1605, 1580, 1450, 1250, 1200, 1110, 1085, 1045, 955. Hydrolysis of **1** with emulsin gave an aglycone (**1a**) and glucose [16]. Glucose was identified by direct comparison with an authentic sample.

*1,8-Dihydroxy-3,5-dimethoxyxanthone* (**1a**). $C_{15}H_{12}O_6$ mp. 188°, MS *m/z* 288 ($M^+$) UV $\lambda_{max}^{MeOH}$ nm: 203, 250, 276 and 336, $\lambda_{max}^{MeOH+AlCl_3}$ nm: 243, 290, 316, 373, $\lambda_{max}^{MeOH+NaOAc/+H_3BO_3}$ nm: 203, 250, 276 and 335, IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3450, 1665, 1640, 1605, 1580, $^1$H NMR ($CDCl_3$: TMS int. standard, 400 MHz), 4.09, 3.98 (2 × OMe), 12.15, 11.98 (2 × OH, chelated), 6.64, 7.15 (2H, *dd*, *J* = 9 Hz, *ortho* H), 6.34, 6.52 (2H, *dd*, J = 2 Hz *meta* H).

*8-Hydroxy-1,3,5-trimethoxyxanthone* (**1b**). On complete methylation with $Me_2SO_4$ and $K_2CO_3$ followed by hydrolysis with 15% $H_2SO_4$, **1** gave (**1b**) $C_{16}H_{14}O_6$ mp 204°, UV $\lambda_{max}^{MeOH}$ nm: 202, 246, 276 and 315, IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3500, 1660, 1590, MS *m/z* (rel. int.) 302 ($M^+$), $^1$H NMR ($CDCl_3$), 6.34, 6.60 (*dd*, *J* = 2.4 Hz $C_2$, $C_4$, *meta* H), 7.16, 6.67 (*dd*, *J* = 8.9 Hz; $H_6$, $H_7$, *ortho* H) 3.98, 3.97, 3.92 (3 × OMe: 9H) which was identified as 8-hydroxy-1,3,5-trimethoxyxanthone.

*3-Methoxy-1,5,8-trihydroxyxanthone* (**2**). Crystallized in EtOAc, $C_{14}H_{10}O_6$ mp. 262°, MS *m/z* 274 ($M^+$), UV $\lambda_{max}^{MeOH}$ nm: 202, 253, 277, 332, IR $\nu_{max}^{KBr}$ cm$^{-1}$, 3450, 1660, 1635, 1610, 1590, $^1$H NMR ($CDCl_3$) 6.40, 6.62 (2H, *dd*, *J* = 2 Hz, *meta* H), 7.26, 6.64 (2H, *dd*, *J* = 8.8 Hz, *ortho* H), 11.9, 11.10 (2 × OH, chelated), 9.7 (OH), 3.88 (OMe). Treatment of **2** with $Me_2SO_4$–$K_2CO_3$ in $Me_2CO$ and after usual work-up afforded a tetramethyl ether. $C_{17}H_{16}O_6$ mp. 225°, MS *m/z* 316 $[M]^+$ $FeCl_3$(−) which was similar to 1,3,5,8-tetramethoxyxanthone in its UV, IR and $^1$H NMR values [17].

*1,8-Dihydroxy-3,7-dimethoxyxanthone* (**3**). The $CHCl_3$ soluble fraction afforded yellow crystals mp 198°, $FeCl_3$(+), MS *m/z* 288 ($M^+$), UV $\lambda_{max}^{MeOH}$ nm: 202, 236, 268, 327, IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3450, 1660, 1605, 1590, $^1$H NMR ($CDCl_3$), 3.85, 3.95 (2 × OMe), 11.82, 11.93 (2 × OH chelated), 6.38, 6.58 (2H, *dd*, *J* = 2.2 Hz, *meta* H), 7.49, 6.97 (2H, *dd*, *J* = 8.8 Hz, *ortho* H). The tetramethoxy ether. $C_{17}H_{16}O_6$ colourless crystals mp 214° prepared [17] after usual work-up was identical with of 1,3,7,8-tetramethoxyxanthone in its UV, IR and NMR results. Ursolic acid (**4**): mp 288–291°, MS *m/z* 456 ($M^+$) Acetate ether mp 246–247° identified by direct comparison of UV, IR, $^1$H NMR results with authentic sample.

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