32. A New Xanthone Diglucoside from *Swertia perennis* L.

by **Kurt Hostettmann**[1]) and **Iwao Miura**

Department of Chemistry, Columbia University, New York, N.Y. 10027

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Summary

A new xanthone diglucoside (1) has been isolated from the aerial parts of *Swertia perennis* L. (*Gentianaceae*) by means of column chromatography on polyamide, followed by preparative TLC. on silica gel. From UV. and NMR. data, its structure has been established as 1,3-di-β-D-glucopyranosyl-7,8-dihydroxyxanthone or norswertianine-1,3-diglucoside.

1. Introduction. – In connection with our work on polyphenolic constituents of *Gentianaceae*, we undertook investigation of *Swertia perennis* L., the only *Swertia* species distributed in Europe. Recently, we reported the identification of ten xanthones and four glycoflavones [1]. In addition a trace compound (**1**) has now been isolated. The present paper deals with the structure determination of this minor constituent.

2. Results. – Extraction of the dried plant material (150 g) has been reported previously [1]. Polyamide column chromatography of the methanol extract starting with MeOH/H_2O 1:1 and increasing the percentage of MeOH afforded glycoflavones and xanthone glycosides. Compound **1** was eluted from the column with MeOH/H_2O 7:3 and subsequently purified by preparative TLC. on silica gel using AcOEt/MeOH/H_2O 21:4:3 as solvent. Filtration on Sephadex LH20, followed by recrystallization in MeOH afforded finally 4.0 mg of yellow needles, m.p. 210–212°. The UV. spectrum was characteristic of 1,3,7,8-tetraoxygenated xanthones [2]. The bathochromic shift observed by adding $AlCl_3$ indicated the presence of a free hydroxyl group *peri* to the carbonyl function (position 1 or 8). As no change in the curve is observed by adding NaOAc, position 3 must be substituted by a group other than OH. Compound **1**, when subjected to acid hydrolysis or treatment with β-D-glucosidase, furnished glucose and 1,3,7,8-tetrahydroxy-xanthone or norswertianine (**2**) (identified by comparison with an authentic sample [3]). The high Rf value on polyamide TLC. suggested that **1** must be a diglucoside. This is evidenced from its ^{1}H-NMR. spectrum[2]) which showed the presence of two glucose units, four aromatic protons (two *meta* coupled and two *ortho* coupled protons) and two aromatic hydroxyl protons at δ 9.30 and

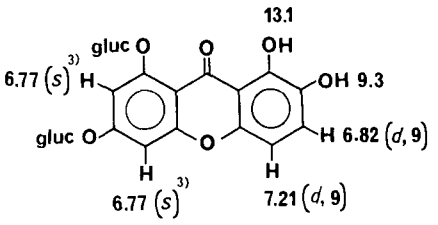
[1]) On leave from *Institut de Chimie, Université de Neuchâtel*, CH–2000 Neuchâtel.

[2]) Measured at 100 MHz in DMSO-d_6.

13,10. The latter value is typical of a chelated hydroxyl group. Thus, one glucose unit must be attached to the xanthone ring either at position 1 or 8 and the other at position 3 (evident from UV. data by comparison of the spectra of **1** before and after cleavage of the sugars). Thus, only two structures remain: 1,3-di-β-D-glucopyranosyl-7,8-dihydroxyxanthone and 3,8-di-β-D-glucopyranosyl-1,7-dihydroxyxanthone. Comparison of the UV. spectra of **1** with those of known xanthone glycosides having a methoxyl group at position 3 and a sugar residue either at position 1 (1-primeverosyl-3-methoxy-7,8-dihydroxyxanthone (**3**)) [3] or position 8 (8-glucosyl-3-methoxy-1,7-dihydroxyxanthone (**4**)) [4] showed that the curve of **1** is similar to that

UV. spectra of compounds **1–4** (max. in nm, solvent = MeOH)

Compound	Pure solvent	Solvent with added	
		$AlCl_3$	NaOAc
1	242,268 312,380	245,278 343	242,270 312,380
2	238,265 329,385	244,278 360	270,360
3	240,270 312,380	248,280 341	240,274 312,380
4	236,264 315,382	238,276 328	240,266 313,400



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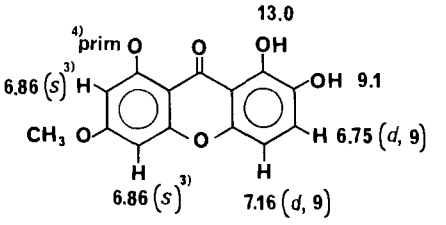

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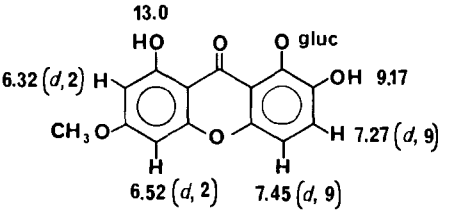

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3) These singlets constituted an *AB*-type quartet ($J = 2$) upon addition of 20% C_6D_6 to the DMSO-d_6 solution.

4) prim = primeverose or 6-*O*-(β-D-xylopyranosyl)-β-D-glucopyranose.

of **3** (see Table). In addition, a comparison of the ^{1}H-NMR. spectra of **1** and **3** showed that the *ortho* coupled protons in ring B have similar chemical shifts, whereas they are substantially low-field shifted in compound **4**. It is to be noted that ring A protons of **1** and **3** are at δ 6.77 and 6.86 whereas those of **4** are at the higher field of δ 6.52 and 6.32 in contrast, the ring B protons of **1** and **3** are at δ 7.21/6.82 and 7.16/6.75 whereas those of **4** are now at the lower field of δ 7.45/7.27. Namely, protons on the aromatic ring containing the chelated hydroxyl group absorb at higher fields. This can be ascribed to the increased electron density of the chelated hydroxyl group and may be of diagnostic value in structural studies.

Therefore, the structure of compound **1** is represented by 1,3-di-β-D-glucopyranosyl-7,8-dihydroxyxanthone or norswertianine-1,3-diglucoside. Compound **1** is the first xanthone diglucoside encountered in nature. The glycosides reported so far are monoglucosides or xanthones containing the disaccharides rutinose or primeverose.

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Experimental Part

NMR. spectra were recorded at 100 MHz on a *Varian* HA-100 using DMSO-d_6 as solvent. Chemical shifts are expressed in ppm with tetramethylsilane as internal standard. UV. spectra were taken on a *Perkin-Elmer* Model 202 spectrophotometer in MeOH. Shift reagents were prepared according to [5]. Micro m.p. were obtained on an *American Optical Corporation* Model 60.

The plant material was collected in the Gantrisch region (Switzerland). 150 g of dried leaves and stems were extracted by refluxing with solvents of increasing polarity [1]. The methanol extract was chromatographed over a polyamide (*Macherey-Nagel* SC_6) column (6.5 cm × 100 cm) starting with MeOH/H_2O 1:1 and increasing the percentage of MeOH. Compound **1** was eluted from the column with MeOH/H_2O 7:3 and purified by preparative TLC. on *Merck* silica gel 60 developed with AcOEt/MeOH/H_2O 21:4:3 and eluted from the plate with MeOH. Filtration on Sephadex LH20 afforded 4 mg of compound **1**: m.p. 210–212°, recrystallized from MeOH; Rf = 0.84 on polyamide *Macherey-Nagel* DC_{11}, MeOH/H_2O 9:1; Rf = 0.20 on silica gel 60 F_{254} *Merck*, AcOEt/MeOH/H_2O 21:4:3.

Acid or enzymatic hydrolysis was carried out as described previously [1]. Compound **2** (1,3,7,8-tetrahydroxyxanthone) was identified by comparison with an authentic sample (TLC., UV., m.p.) [3].

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