Phytochemistry, 1980, Vol. 19, pp. 2029–2030. © Pergamon Press Ltd. Printed in England. 0031–9422/80/0901–2029 $02.00/0

A 5-METHYLCOUMARIN GLUCOSIDE FROM *ETHULIA CONYZOIDES**

ZEINAB F. MAHMOUD,† TAHA M. SARG,† MASOUDA E. AMER,† SAAD M. KHAFAGY† and FERDINAND BOHLMANN‡

† Department of Pharmacognosy, Alexandria University, Egypt; ‡ Institute for Organic Chemistry, Technical University Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, W. Germany

(*Received* 21 *December* 1979)

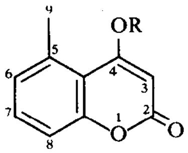
Key Word Index—*Ethulia conyzoides*; Compositae; 5-methylcoumarin glycoside.

Ethulia conyzoides L. var. *gracilis* has been investigated before [1]. It is apparent that unusual 5-methylcoumarins are characteristic for this species. We have now examined the water-soluble fraction of an ethanolic extract of the aerial parts. Among other compounds, a crystalline glucoside, mp 150° (water), was isolated. The ^{1}H NMR data (see Table 1) of the tetraacetate clearly show that it is the coumarin **3**. Therefore the natural compound is **2**, the β-D-glucoside of the precursor **1** of all 5-methylcoumarins so far isolated from *Ethulia conyzoides* [1] and other composites [2–6]. The presence of a β-glucoside clearly follows from the observed coupling constants in the ^{1}H NMR spectrum of the tetraacetate, while in the spectrum of **2** the corresponding signals overlap. The signals of the aromatic protons are very similar to those of the known coumarins [1, 2]. Also the chemical shift of the 5-methyl group is in agreement with the proposed structure.

Table 1. ^{1}H NMR data of **1** and **2** (270 MHz, TMS as internal standard)

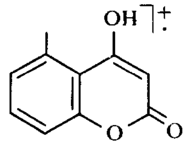
	1 ($CDCl_3$–DMSO)	**2** ($CDCl_3$)
3-H	5.83 *s*	5.83
6-H	7.00 *d*(*br*)	7.05 *d*(*br*)
7-H	7.36 *dd*	7.41 *dd*
8-H	7.08 *d*(*br*)	7.20 *d*(*br*)
9-H	2.62 *s*	2.57 *s*
1′-H	5.37 *d*	5.34 *d*
2′-H	5.06 *m*	5.43 *dd*
3′-H		5.33 *dd*
4′-H		5.19 *dd*
5′-H	3.18 *m*	3.95 *ddd*
6_1′-H	3.67 *m*	4.33 *dd*
6_2′-H		4.12 *dd*
OAc	—	2.13 *s*
		2.08 *s*
		2.07 *s*
		2.05 *s*

J (Hz): 6,7 = 7,8 = 8; 1′,2′ = 7; 2′,3′ = 9; 3′,4′ = 10; 4′,5′ = 9; 5′,6_1′ = 6.5; 5′,6_2′ = 2.5.

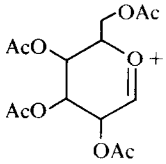


1 R = H
2 R = Glc
3 R = Glc $(OAc)_4$

A =



B =



EXPERIMENTAL

^{1}H NMR: 270 MHz; MS: 70 eV. Aerial parts (4.75 kg; collected near Alexandria on the banks of the Nile) were chopped and extracted with EtOH (room temp.). After evapn the residue was extracted with H_2O and the H_2O-soluble fraction was extracted several times with EtOAc yielding 11.3 g extract, which was separated by column chromatography (SiO_2) with EtOAc–2% MeOH. **1** (60 mg) was obtained as colourless crystals, mp 150° (from H_2O). IR ν_{max}^{nujol} cm^{-1}: 3500–3200 (OH), 1680, 1615 and 1605 (coumarin); MS: M$^+$ *m/e*—; **A** 176.047 (61%) ($C_{10}H_8O_3$); 134 (100) (176 − ketene).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-117.5 \quad -119.6 \quad -137.5 \quad -254.6}$$

(c = 0.76, MeOH).

1 (20 mg) was acetylated with 1 ml Py and 0.2 ml Ac_2O (24 hr, room temp.) yielding 20 mg **2**, colourless crystals, mp 115–117° ($CHCl_3$–Et_2O). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760 and 1255 (OAc); 1717, 1620 and 1605 (coumarin); MS: M$^+$ *m/e*—; **B** 331 (1%); **A** 176 (12); 134 (19) (176 − ketene); 43 (100) ($MeCO^+$); CI (isobutane): M$^+$ + 1501 (4%) ($C_{24}H_{26}O_{12}$); **B** 331 (100); 271 (22) (331

---

* Part 20 in the series "Naturally Occurring Coumarin Derivatives". For Part 19 see Rustaiyan, A., Nazarians, L. and Bohlmann, F. (1980) *Phytochemistry* **19**, 2007.

$-$HOAc); 1 A + 1 177 (23); 169 (41) (271 $-$ ketene and HOAc); 109 (35) (169 $-$ HOAc).

REFERENCES

1. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 1092.
2. Balbea, S. I., Halim, A. F., Halaweish, F. T. and Bohlmann, F. (1979) *Phytochemistry* **18**, 912.
3. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 1261.
4. Bohlmann, F. and Zdero, C. (1977) *Chem. Ber.* **110**, 1755.
5. Bohlmann, F., Zdero, C. and Franke, H. (1973) *Chem. Ber.* **106**, 382.
6. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 239.

Phytochemistry, 1980, Vol. 19, pp. 2030–2031. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0901-2030 $02.00/0

A XANTHONE-*O*-GLYCOSIDE FROM *ASPLENIUM ADIANTUM-NIGRUM*

FILIPPO IMPERATO

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Universita' di Catania, Catania, Italy

(*Revised received* 1 *February* 1980)

Key Word Index—*Asplenium adiantum-nigrum*; Aspleniaceae; 3,7,8-trihydroxyxanthone-1-*O*-β-laminaribioside.

Abstract—A new xanthone-*O*-glycoside isolated from the fern *Asplenium adiantum-nigrum* has been identified as 3,7,8-trihydroxyxanthone-1-*O*-β-laminaribioside by chemical and spectroscopic methods.

Recently a new hydroxycinnamic acid–sugar derivative, 1-caffeyllaminaribiose has been characterized from *Asplenium adiantum-nigrum* L. [1]. The present paper describes the identification of a new xanthone-*O*-glycoside, which has the same dissaccharide present, from the same fern.

The xanthone (colour reactions: orange–brown to yellow in UV + NH_3) was isolated by prep. PC of an ethanolic extract of the fronds of *Asplenium adiantum-nigrum*. The UV spectral data: λ_{max}^{MeOH} 240, 260, 315 and 364 nm; +NaOAc 260, 360 nm (increase in intensity); +$AlCl_3$ 245, 264, 349 (sh), 405 nm; +$AlCl_3$/HCl, 243, 262, 340 (sh), 405 nm; +NaOAc/H_3BO_3 242, 258, 355 (sh), 418 nm, are consistent with a xanthone skeleton. The presence of a 3-hydroxyl group and an *ortho*-dihydroxyl group in the 7,8-position is indicated by the shifts with NaOAc, $AlCl_3$, $AlCl_3$/HCl and H_3BO_3/NaOAc [2]. Both total acid hydrolysis and treatment with β-glucosidase gave D-glucose and an aglycone identified as 1,3,7,8-tetrahydroxyxanthone (norswertianin). This xanthone was first isolated in the free state from *Swertia japonica* [3] but has since been reported from *Gentiana bavarica* L. [4]. Norswertianin has been found as the 1-*O*-glucoside and 1-*O*-primeveroside in some *Swertia* and *Gentiana* species [5]. Controlled acid hydrolysis gave D-glucose and a disaccharide which was identical with an authentic sample of laminaribiose (3-*O*-β-glucosyl-D-glucose) synthesized according to Bächli and Percival [6]. Thus the isolated compound must be 3,7,8-trihydroxyxanthone-1-*O*-β-laminaribioside, a new natural product. The structure of this substance was confirmed by methylation followed by acid hydrolysis to give 2,4,6-tri-*O*-methyl-D-glucose, 2,3,4,6-tetra-*O*-methyl-D-glucose and a partially methylated aglycone identified as 1-hydroxy-3,7,8-trimethoxyxanthone (decussatin) [7–9]. Xanthones have only been reported twice in ferns, in *Asplenium montanum* [10] and *Athyrium mesosorum* [11, 12]. However, the presence of a xanthone-*O*-glycoside in ferns is here reported for the first time. The absence of xanthones in *Asplenium adiantum-nigrum* L. collected in Astorias, Spain [10] was not confirmed in the present study. The chemical differences in plants from this locality may be due to phytogeographical factors. Since xanthones have been found previously only in *Asplenium montanum* among the several species of *Asplenium* surveyed [10], the isolation of a xanthone from *A. adiantum-nigrum* L. may suggest a relationship to *A. montanum*. Laminaribiose is here reported for the first time in association with xanthones. The other disaccharides found to date in xanthone-*O*-glycosides [5] are rutinose and primeverose.