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

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

FILIPPO IMPERATO

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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.

EXPERIMENTAL

Plant material. Fronds of *Asplenium adiantum-nigrum* L. were collected on Mount Etna, Sicily.

Isolation procedure. Fresh fronds of *Asplenium adiantum-nigrum* were homogenized and extrd 3 × with hot EtOH. The combined extracts were filtered, concd to small vol. *in vacuo* and re-filtered. The xanthone was isolated by successive prep. PC in BAW, 5% HOAc and BEW. R_f data are: BAW 0.45, 5% HOAc 0.25, BEW 0.17. Total acid hydrolysis was carried out with 2 N HCl (1 hr at 100° under N_2); controlled acid hydrolysis was carried out with 10% aq. HOAc (2.5 hr under reflux). Treatment with β-glucosidase was carried out in citrate–phosphate buffer, pH 4.5, at 37° for 20 hr. 1,3,7,8-Tetrahydroxyxanthone was identified by UV spectral analysis with shift reagents [2,4], MS and comparison with an authentic sample (TLC on Si gel: 3 solvents); D-glucose and laminaribiose were identified by Co-PC (4 solvents), TLC on Si gel (*n*-BuOH–HOAc–Et_2O–H_2O, 9:6:3:1) and GLC of their trimethylsilyl derivatives [13].

Methylation of xanthone. The xanthone was methylated (Me_2SO_4–K_2CO_3–Me_2CO) and hydrolysed with 0.3 N HCl (4 hr under reflux). The partially methylated aglycone was identified as 1-hydroxy-3,7,8-trimethoxyxanthone by UV spectral analysis with shift reagents [2,4], MS and comparison with an authentic sample (TLC on Si gel; 3 solvents); methylated sugars were identified by PC according to ref. [14] and TLC on Si gel (EtOAc–$CHCl_3$, 1:1).

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AN UNSYMMETRICAL DIARYLHEPTANOID FROM *CURCUMA LONGA*

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Key Word Index—*Curcuma longa*; Zingiberaceae; turmeric; diarylheptanoid; dihydrocurcumin; 1,7-bis-(4-hydroxy-3-methoxyphenyl)-hept-1-en-3,5-dione.

Earlier work on the pigments of turmeric (*Curcuma longa* L.) revealed the presence of three major phenolic diarylheptanoids, namely curcumin (**1**), feruloyl-(4-hydroxycinnamoyl)methane (**2**) and bis-(4-hydroxycinnamoyl)methane (**3**) [1,2]. Biosynthesis and metabolism of diarylheptanoids have recently attracted attention [2,3]. In the course of our work on the metabolism of curcumin [4], we have isolated a new diarylheptanoid from the benzene extract of *Curcuma longa* rhizomes.

This compound, $C_{21}H_{22}O_6$ (M^+ 370), had a UV maximum at 375 nm and its IR specrum showed bands at 3400 (OH), 1630 ($COCH_2CO$), 1600 and 1510 cm^{-1} (C=C and aromatic). It gave the rubrocurcumin reaction [5] with boric acid and oxalic acid (with visible max shifting to 420 nm), a characteristic reaction of β-diketones. The 270 MHz ^1H NMR spectrum in DMSO-d_6 showed signals for two phenolic hydroxyl protons at δ 9.65 and 8.76 (disappearing on exchange with D_2O), two singlets at 3.74 (3 H) and 3.83 (3 H) (OMe), two doublets at 7.48 and 6.64 (J = 14 Hz) for two *trans*-related olefinic protons, clusters of aromatic proton signals centred around 6.65,