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A CHALCONE GLYCOSIDE FROM *ACACIA DEALBATA*

FILIPPO IMPERATO

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Key Word Index—*Acacia dealbata*; Leguminosae; flowers; 4,2',4',6'-tetrahydroxychalcone 2'-[*O*-rhamnosyl-(1→4)-xyloside].

Abstract—A new yellow pigment isolated from the flowers of *Acacia dealbata* has been shown to be chalcononaringenin 2'-[*O*-rhamnosyl-(1→4)-xyloside] by chemical and spectroscopic methods.

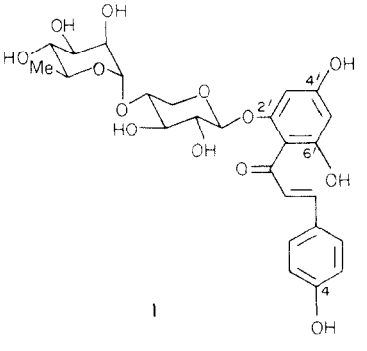
Recent work ([1]; Imperato, F., unpublished) has shown that anthochlor pigments contribute to the yellow colour of the flowers of *Acacia dealbata* and four such pigments have been found.

From an EtOH extract of the flowers of *A. dealbata*, another anthochlor has now been isolated by means of a combination of prep. PC and prep. TLC on Si gel. The UV spectrum of this pigment showed λ_{max}^{MeOH} 348 nm and bathochromic shifts with $AlCl_3$ (56 nm), $AlCl_3$/HCl (52 nm), NaOAc (39 nm) and NaOMe (62 nm; with increase in peak intensity). These spectral properties [2] and colour reactions (brown to orange in UV + NH_3) are consistent with those of a polyhydroxychalcone with free hydroxyl groups at positions 4 and 2'.

Total acid hydrolysis of the isolated pigment gave 1 mol each of naringenin, xylose and rhamnose. Methylation gave a methyl ether which on acid hydrolysis isomerized to flavanone since it gave naringenin trimethyl ether (identified after alkaline degradation to di-*O*-methylphloroglucinol and *p*-methoxycinnamic acid), 2,3-di-*O*-methyl-xylose and 2,3,4-tri-*O*-methyl-rhamnose.

Thus, the isolated pigment must be 4, 2', 4', 6'-tetrahydroxychalcone 2'-[*O*-rhamnosyl-(1→4)-side] (**1**) which is a new natural product. This structure was confirmed as follows. When heated in NaOAc solution [3], this chalcone isomerized to the corresponding flavanone (λ_{max}^{MeOH} 277 nm) which was identified as naringenin 5-*O*-rhamnoxyloside by UV spectral analysis with shift reagents [2], total acid hydrolysis (which gave naringenin, xylose and rhamnose) and controlled acid hydrolysis to give an intermediate which was further degraded into naringenin and xylose and identified as naringenin 5-*O*-xyloside by UV spectral analysis with shift reagents [2] and co-PC with an authentic sample.

4-*O*-Rhamnosyl-xylose is reported for the first time in association with chalcones. This disaccharide has been found only twice before in flavonoid glycosides; it has been found attached in the 3-position of kaempferol in *Euonymus alatus* [4] and in the 7-position of 6-hydroxyluteolin in *Pityrodia coerulea* [5]. Moreover,



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a partially characterized rhamnosyl-xylose has been found attached in the 3-position of quercetin in *Tilia argentea* [6].

From the biogenetic point of view, the co-occurrence in *A. dealbata* of chalcononaringenin 2'-xyloside [1] and of chalcononaringenin 2'-[*O*-rhamnosyl-(1→4)-xyloside] (**1**) suggests that in the biosynthesis of **1** the monosaccharides are attached to the appropriate chalcone one at a time rather than as a preformed disaccharide; this observation is in agreement with that on the biosynthesis of chalcone glycosides found in another species of the Leguminosae, *Ulex europaeus* [7].

The isolation of chalcone (**1**) confirms that *A. dealbata* has the capability of synthesizing anthochlor pigments with phloroglucinol-type A-ring structures since four anthochlors of the phloroglucinol type have already been found ([1]; Imperato, F., unpublished) in the flowers of this plant. From the taxonomic point of view, the occurrence of five such pigments in a single plant is quite exceptional since anthochlors of the family Leguminosae have generally resorcinol-based A-ring structures [8].

EXPERIMENTAL

Isolation. Fresh flowers (100 g) of *A. dealbata* (collected in Catania) were homogenized and extracted ×3 with hot 95% EtOH. The combined extracts were filtered, concd to a small vol. *in vacuo* and re-filtered. The pigment (30 mg) was isolated by prep. PC (*in* BAW, 5% HOAc and BEW) followed by prep. TLC on Si gel in EtOAc–MeCOEt–HCO_2H–H_2O (5:3:1:1). R_f values (on Whatman No. 1 paper) are: BAW 0.69, BEW 0.70, H_2O 0.20, PhOH satd with H_2O 0.59.

Hydrolysis. Total acid hydrolysis of the chalcone glycoside and of the corresponding flavanone was carried out with 2 M HCl (2 hr at 100°). Naringenin was identified by co-PC with an authentic sample (four solvents) and UV spectral analysis with usual shift reagents [2]. Xylose and rhamnose were identified by co-PC (four solvents) and TLC on Si gel (*n*-BuOH–HOAc–Et_2O–H_2O, 9:6:3:1). Quantitative examination [9] of hydrolysis products of the chalcone glycoside gave the following ratios: naringenin (1), xylose (1.15), rhamnose (1.12). Controlled acid hydrolysis of naringenin 5-*O*-rhamnoxyloside was carried out with 10% HOAc (30 min reflux). Naringenin 5-*O*-xyloside was identified by co-PC (four solvents), UV spectral analysis with shift reagents [2] and total acid hydrolysis with 2 M HCl (2 hr at 100°) to give naringenin and xylose which were identified as above.

Methylation. The chalcone glycoside was methylated with MeI in $HCONMe_2$ in the presence of Ag_2O and the permethylated product was hydrolysed with 0.3 M HCl (4 hr reflux). Alkaline degradation of naringenin trimethyl ether was achieved as in ref. [10]; *p*-methoxycinnamic acid was identified by PC [10] and TLC on Si gel; di-*O*-methylphloroglucinol was identified by comparison with an authentic sample (TLC; three solvents); 2,3,4-tri-*O*-methyl-rhamnose and 2,3-di-*O*-methylxylose were identified by PC [11] and TLC on Si gel.

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