4), 2.67 (2H, *t*, $J = 6$ Hz, H_2-7'), 3.80 (3H, *s*, OMe-3), 4.10 (2H, *t*, $J = 6$ Hz, $-CH_2OAc$-9'), 4.40 (2H, *m*, $-CH_2OAc$-9), 5.50 (1H, *d*, $J = 6.5$ Hz, H-7), 6.52–7.15 (6-ArH).

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6-*C*-GLUCOSYLNARINGENIN FROM FLOWERS OF *ACACIA RETINOIDE*

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Key Word Index—*Acacia retinoide*; Mimosaceae; 6-*C*-glucosylnaringenin; *C*-glycosylflavanone.

Abstract—From the flowers of *Acacia retinoide* 6-*C*-glucosylnaringenin has been identified.

C-Glycosylflavanones are rare plant constituents and only a few have been identified previously[1–5]. We now describe the characterization of 6-*C*-glucosylnaringenin (**1**) from the flowers of *Acacia retinoide*. This is the first report of a *C*-glycosylflavanone from the Mimosaceae.

1 showed colour reactions characteristic of a flavanone and its high R_f values in polar solvents and the results of the acid hydrolysis (extraction was possible with ethyl acetate or *n*-butanol but not with diethyl ether) suggested its *C*-glycosidic nature[6]. **1** had a UV spectrum and characteristic shifts of a flavanone with free hydroxyls in the C-5 and C-7 positions[7]. The mass spectrum of the PM derivative showed peaks at the following *m/z*: 546 $[M]^+$, 371 $[M - 175]^+$ (100%) and a series of characteristic peaks of *C*-hexosides[8] with losses from the $[M]^+$ at -161, -189, -191, -205 and -218. In a study of the retro-Diels–Alder fragmentation with respect to the ions derived from the A ring, a series of significant peaks were found at the following *m/z*: 237, 223, 207, 193 and 179 corresponding to the ions **n**, **i**, **j**, (**j** − 2), **k** and **l**[9] of permethylated *C*-glycosidic flavones with methoxy substituents in the C-5 and C-7 positions. The characteristic peaks of the exposed ions, together with fragmentation proposed by Itagaki *et al.*[10], can be derived from two ions with distinct types of fragmentation: ion A_2^+ and/or A_1^+. With respect to the ions derived from B ring, we found B_5^+ and $[B_5 - 28]^+$ at *m/z* 161 and 133; and B_1^+ at *m/z* 134.

In view of these results **1** is shown to be a *C*-hexoside of a flavanone with the *C*-sugar in the 6- or 8-position with free hydroxyl groups at C-5 and C-7 and an oxygenated substituent on the B ring. Alkaline degradation gave *p*-hydroxybenzoic acid, identified by co-TLC with an authentic sample, which showed the presence of a hydroxyl group at the 4'-position. The production of a chalcone on permethylation of **1** made the location of the *C*-sugar by mass spectrometry impossible, and the difficulty of hydrolysing *C*-glycosides made it necessary to refer to the chromatographic evidence. Thus co-chromatography with an authentic sample in six chromatographic systems led to the conclusion that **1** was 6-*C*-glucosylnaringenin.

EXPERIMENTAL

Flowers of *Acacia retinoide* Schlecht (Mimosaceae), cultivated in gardens at Cabo Roig, Alicante, Spain, were gathered during May 1980 (No. 3733, voucher on deposit in the Herbarium of the University of Murcia, Spain). Plant material was extracted with Et_2O and EtOAc. The EtOAc extract, dried under red. pres. and re-dissolved in H_2O, was chromatographed on a cellulose column using H_2O as eluant. The first eluate yielded needles of **1**, which were purified by TLC on cellulose with H_2O as solvent (a band at R_f 0.65).

Identification of 6-C-glucosylnaringenin (**1**). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 328sh, 291, 226; NaOMe: 327, 249; $AlCl_3$: 360, 310; $AlCl_3$–HCl: 364, 309; NaOAc: 328, 285sh, 254; NaOAc–H_3BO_3: 330, 293. MS (chalcone PM) 70 eV, direct inlet, *m/z* (rel. int. %): 546 $[M]^+$ (4.5), 385 (2.3), 371 $[M-175]^+$ (100), 370 (6), 257 $[M-189]^+$ (2.5), 355 $[M-191]^+$ (3.5), 341 $[M-205]^+$ (12), 328 $[M-218]^+$ (4.8), 251 (5), 237 (4.2), 236 (4), 235 (5.3), 223 (11), 209 (4.5), 207 (13), 205 (5.7), 193 (5.6), 179 (3.5), 161 (27), 151 (6.8), 147 (6.5), 134 (6.8), 133 (13), 121 (16). TLC: Polyamide (Macherey & Nagel, DC 6) H_2O–MeOH–MeCOEt–Ac_2CH_2 (10:6:2:1) (R_f: 0.67). Cellulose: H_2O (0.65), 15% HOAc (0.76), 30% HOAc (0.78), 60% HOAc (0.83). Si gel: EtOAc–MeOH–H_2O (21:4:3) (0.75).

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THE OCCURRENCE OF FLAVANONES IN THE FARINOSE EXUDATE OF THE FERN *ONYCHIUM SILICULOSUM*

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Key Word Index—*Onychium siliculosum*; Pteridophyta; frond exudate; chalcone isomerization; 5-hydroxy-7, 8-dimethoxyflavanone; 5-hydroxy-6, 7-dimethoxyflavanone.

Abstract—The yellow farina on fertile pinnules of *Onychium siliculosum* is composed of 2′,6′-dihydroxy-4′-methoxychalcone and 2′,6′-dihydroxy-4,5′-dimethoxychalcone. Heating of the crude extract brings about isomerization to pinostrobin and to 5-hydroxy-7,8-dimethoxyflavanone and 5-hydroxy-6,7-dimethoxyflavanone, respectively. The latter flavanone, recently reported as a constituent of this fern, is thus not a natural product.

Onychium siliculosum (Desv.) C.Chr. is a gymnogrammoid fern which according to Hooker [1] grows in the Himalayas and on the Malayan peninsula and islands. The fertile pinnules of its fronds bear a conspicuous yellow farina on the under surface. Two flavonoids, namely 2′,6′-dihydroxy-4′-methoxychalcone (**1**) and 2′,6′-dihydroxy-4′,5′-dimethoxychalcone (**2**) have been reported previously as 'constituents' of this fern (*Onychium auratum* Kaulf.) [2] without mention of the fact that they form the yellow farina (cf. ref. [3]). In the course of our chemotaxonomic studies on gymnogrammoid ferns we wanted to isolate chalcone **2** (pashanone) to have it available as an authentic marker. The orange-yellow farina was dissolved with acetone from one frond of *Onychium siliculosum* and the yellow solution was dried onto polyamide in an oven. The material became rather pale and after CC, it yielded a comparatively large amount of non-polar flavanone but only a small proportion of chalcone. One of the flavanones was readily identified as pinocembrin 7-methyl ether (pinostrobin, **3**). Two unknown flavanones, **4** and **5**,