to a syrupy residue under red pres at 30° The syrup was partitioned between petrol (50–70°, 1 l), $CHCl_3$ (1 l), EtOAc (1 l) and H_2O (1 l) EtOAc and H_2O fractions containing flavonoids were further subjected to a Craig distribution with 70 steps in a two phase system as follows (1) EtOAc fraction, $CHCl_3$–MeOH–PrOH–H_2O (4 6 1 4, upper phase as mobile phase), and (2) H_2O fraction, EtOAc–PrOH–H_2O (4 3 5, upper phase as mobile phase) Individual fractions were monitored using Si gel rapid plates, Woelm F 254, using mobile phase (upper layer) as solvent system from the Craig two phase system Flavonoid containing fractions were pooled and further chromatographed

Chromatography CC cellulose microcrystalline, ashless quality, acid washed (solvents 0 05–0 1% HOAc, 10% MeOH), Sephadex LH 20 (solvent MeOH) TLC cellulose plastic sheets without fluorescent indicator (solvents 15% HOAc, 25% HOAc, BAW, upper phase), spray reagent NA

Hydrolysis and acid isomerization 5 ml 0 1 N TFA [10] and 10 mg flavonoid heated in a stream bath for 1 hr PC of sugars, Whatman 3 MM (solvent pyridine–EtOAc–HOAc–H_2O, 36 36 7 1) Spray reagent Aniline hydrogen phthalate

UV spectroscopy As described in ref [11]

^1H- and ^{13}C NMR spectroscopy The spectra were recorded in DMSO-d_6 at 30°

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A FLAVANONE GLYCOSIDE FROM THE FRONDS OF *CETERACH OFFICINARUM*

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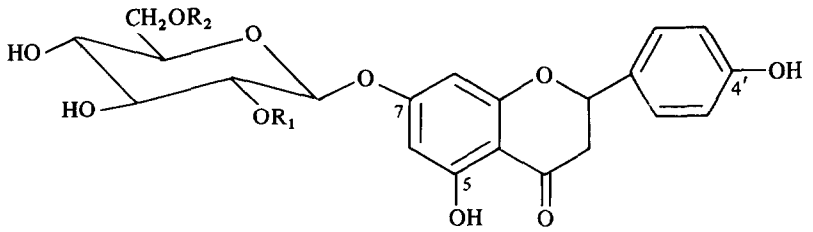
Key Word Index—*Ceterach officinarum*, Polypodiaceae, naringenin 7-[*O*-L-arabinopyranosyl-(1 → 6) glucoside]

Abstract—From the fronds of the fern *Ceterach officinarum* naringin and a new flavanone, naringenin 7-[*O*-L-arabinopyranosyl-(1 → 6) glucoside], have been characterized

Early investigations of the chemical constituents of *Ceterach officinarum* Lam et DC have led to the identification of lignin [1], higher alkanes (the entire series from C_{19} to C_{31}) [2], triterpenoids [22 (29)-hopene and cyclolaudenol] [3] and by using neutron activation analysis, the sodium, potassium, chlorine and manganese levels have been determined in a pharmacological study [4] on diuretic drugs Recently an examination of its polyphenolic constituents in this laboratory has led to the identification of three hydroxycinnamic acid–sugar derivatives (1-caffeyl glucose 6-sulphate, 1-caffeylglucose 3-sulphate and 1-caffeylglucose 2-sulphate) [5], and four flavonol glycosides quercetin 3-glucoside, quercetin 3-gentiobioside, kaempferol 3-(6″-malonyl) glucoside and kaempferol 3-(6″-malonyl) galactoside) [6]

In the present study another flavonoid band was isolated from an ethanolic extract of fresh fronds of *C officinatum* The UV spectral data λ_{max}^{MeOH} nm 267 (sh), 282,



1 R_1 = α-L-Rhamnopyranosyl, R_2 = H
2 R_1 = H, R_2 = α-L-Arabinopyranosyl

326 (sh), +NaOAc 266 (sh), 283, 330 (sh), +NaOAc–H_3BO_3 266 (sh), 281, 328 (sh), +$AlCl_3$ 261 (sh), 313, 377, +$AlCl_3$–HCl 257 (sh), 310, 377, +NaOMe 285, 415 and colour reactions (brown to yellow in UV +NH_3) are consistent with those of a flavanone skeleton with a free hydroxyl group at position 5 [7] Total acid hydrolysis gave naringenin, glucose, rhamnose and arabinose On controlled acid hydrolysis the band gave, in addition to the products of total acid hydrolysis, two disaccharides which were identified as neoesperidose (2-*O*-α-L-rhamnopyranosyl-D-glucose) and vicianose (6-*O*-α-L-arabinopyranosyl-D-glucose) Enzymic hydrolysis with α-rhamnosidase gave naringenin 7-glucoside Kuhn methylation followed by acid hydrolysis gave 2,3,4-tri-*O*-methyl-L-rhamnose, 2,3,4-tri-*O*-methyl-L-arabinose, 3,4,6-tri-*O*-methyl-D-glucose, 2,3,4-tri-*O*-methyl-D-glucose and naringenin 5,4′-dimethyl ether The above results show that the band must be a mixture of naringin (**1**) and naringenin 7-[*O*-L-arabinopyranosyl-(1 → 6) glucoside] (**2**) which is a new natural product The identification of naringin was confirmed by direct comparison with authentic material Attempts to further separate **1** and **2** from the isolated band met with no success

Naringin is well-known for its bitterness, it is a common flavanone glycoside and has already been reported in ferns (e g in *Evodiopanax innovans*) [8] Vicianose (6-*O*-α-L-arabinopyranopyranosyl-D-glucose), the disaccharide component of the flavonoid (**2**), does not appear to have been reported before in the flavanone series though it has been found in the 3-position of quercetin in *Nymphoides peltata* [9] From the biosynthetic point of view it appears that **1** and **2** may arise from the same intermediate, naringenin 7-glucoside

EXPERIMENTAL

Plant material Fronds of *Ceterach officinarum* Lam et DC were collected in Catania, Sicily

Isolation Fresh fronds (800 g) of *C officinarum* were homogenized and extracted × 3 with 95% EtOH The combined extracts were filtered, concd to a small vol *in vacuo* and re-filtered The mixture (10 mg) of **1** and **2** was isolated by prep PC in BAW, the band was cut out eluted with 70% EtOH, concd and re-chromatographed in 10% HOAc and BEW R_f values (on Whatman No 1 paper) are BAW, 0 60, 30% HOAc, 0 88, H_2O, 0 65

Hydrolysis procedures Total acid hydrolysis was carried out with 2 M HCl (2 hr at 100°) Controlled acid hydrolysis was carried out with 10% HOAc (2 hr reflux) Naringenin was identified by co-PC with an authentic sample (four solvents) and UV spectral analysis with the usual shift reagents [7], D-glucose, L-rhamnose, L-arabinose, neoesperidose and vicianose were identified by co-PC (four solvents) and TLC on Si gel (*n*-BuOH–HOAc–Et_2O–H_2O, 9 6 3 1) Enzymic hydrolysis with α-rhamnosidase was carried out in H_2O by using Koch-Light pectinase ex *A niger* which has some α-rhamnosidase activity [10], naringenin 7-glucoside was identified by UV spectral analysis with shift reagents [7], total acid hydrolysis (which gave naringenin and glucose identified as above) and co-PC with authentic material (three solvents)

Methylation The isolated band was methylated with MeI in $HCONMe_2$ in the presence of Ag_2O and subsequently hydrolysed with 0 3 M HCl (4 hr reflux) 2,3,4-Tri-*O*-methyl-L-rhamnose, 2,3,4-tri-*O*-methyl-L-arabinose, 3,4,6-tri-*O*-methyl-D-glucose and 2,3,4-tri-*O*-methyl-D-glucose were identified by PC [11] and TLC on Si gel Naringenin 5,4′-dimethyl ether was identified by UV spectral analysis with shift reagents [7] and co-PC with authentic material (three solvents)

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