Pergamon 0031-9422(95)00572-2 *Phytochemistry*, Vol. 41, No. 1, pp. 337–338, 1996

0031-9422/96 $15.00 + 0.00

LUTEOLIN 7-*O*-SOPHOROSIDE FROM *PTERIS CRETICA*

FILIPPO IMPERATO*† and ROBERTO NAZZARO‡

*Dipartimento di Chimica dell'Università della Basilicata, 85100 Potenza, Italy; ‡Dipartimento di Biologia Vegetale dell'Università Federico II, 80139 Napoli, Italy

(*Received* 15 *March* 1995)

Key Word Index—*Pteris cretica*; Pteridaceae; flavone *O*-diglycosides; luteolin 7-*O*-sophoroside; luteolin 7-*O*-gentiobioside.

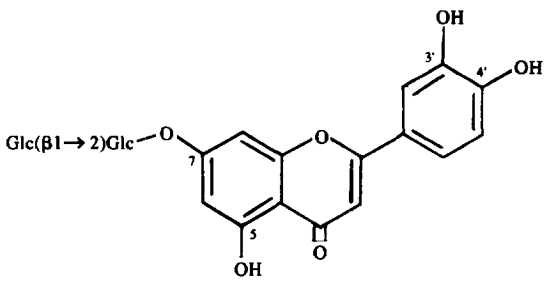
Abstract—A new flavone *O*-glycoside from aerial parts of *Pteris cretica* was characterized as luteolin 7-*O*-β-sophoroside by chemical and spectral methods. In addition, luteolin 7-*O*-β-gentiobioside was identified in this plant material.

INTRODUCTION

Flavonoid data of ferns are of taxonomic and phylogenetic interest but the distribution of these compounds in most fern families, including the Pteridaceae, is not well known [1]. Previous work on the flavonoids of *Pteris cretica* L. reported the presence of flavone *O*-glycosides (not identified) based on apigenin and luteolin [2]. Recently, luteolin 8-*C*-rhamnoside-7-*O*-rhamnoside [3] and three flavone *O*-glycosides (7-*O*-glucoside, 7-*O*-rutinoside and 7-*O*-robinobioside of luteolin) [4] have been found in this fern. The present paper describes the characterization of a new flavone *O*-glycoside (**1**) from *P. cretica*. In addition, the presence of luteolin 7-*O*-β-gentiobioside (**2**) is reported in the same plant.

RESULTS AND DISCUSSION

Compounds **1** and **2** were isolated from an ethanolic extract of aerial parts of *Pteris cretica*. Colour reactions (brown to yellow in UV + NH_3), chromatographic behaviour (see Experimental) and UV spectral analysis in the presence of the customary shift reagents [5]: λ_{max}^{MeOH} nm: 256, 266 (*sh*), 350; + $AlCl_3$ 278, 298 (*sh*), 432; + $AlCl_3$/HCl 278, 294, 370, 388; + NaOAc 258, 268 (*sh*), 367, 410; + NaOAc/H_3BO_3 259, 365; + NaOMe 263, 271 (*sh*), 403 suggested that **1** was a flavone glycoside with free hydroxyl groups at positions 5, 3′ and 4′. Total acid hydrolysis gave luteolin and D-glucose and controlled acid hydrolysis gave sophorose in addition to the products of total acid hydrolysis. Enzyme hydrolysis with β-glucosidase gave small amounts of luteolin and D-glucose. These results suggest that **1** is luteolin 7-*O*-β-sophoroside, a new natural product. The structure of **1** was confirmed as follows. The FAB mass spectrum



1

showed a quasimolecular ion $[M + H]^+$ at *m/z* 611 ($C_{27}H_{30}O_{16}$ required 610). The ^{1}H NMR spectrum (DMSO-d_6) showed a multiplet at δ3.10–3.85 (sophorosyl 12 protons), a doublet at δ4.52 (J = 8 Hz, glucosyl anomer), a doublet at δ5.26 (J = 8 Hz, glucosyl anomer), a doublet at δ6.43 (J = 2.1 Hz, H-6), a singlet at δ6.73 (H-3), a doublet at δ6.78 (J = 2.1 Hz, H-8), a doublet at δ6.92 (J = 8 Hz, H-5′) and a doublet at δ7.45 (J = 8 Hz, H-2′ and H-6′). The presence of an 1 → 2 interglucosidic linkage in **1** was confirmed by the ^{13}C NMR (Table 1) in which C-2″ showed a 7.9 ppm downfield shift and C-1″ showed a 2.8 ppm upfield shift [6] in comparison with the corresponding carbons of glucose in the spectrum of luteolin 7-*O*-glucoside [7].

Compound **2** was identified as luteolin 7-*O*-gentiobioside by colour reactions, UV spectral analysis in the presence of the customary shift reagents [5], total acid hydrolysis, controlled acid hydrolysis (which gave luteolin, D-glucose and gentiobiose), treatment with β-glucosidase, positive FAB mass spectrum and ^{1}H NMR spectrum (DMSO-d_6). The identification of **2** was confirmed by paper chromatography with anauthentic sample. Luteolin 7-*O*-gentiobioside is a new constituent of ferns. Gentiobiose has been reported previously in only one fern species, *Ceterach officinarum* [8], as sugar moiety of a flavonoid but a number of flavonoid

†Author to whom correspondence should be addressed.

Table 1. ^{13}C NMR spectral data (DMSO-d_6) of 1

Luteolin			
		Glucose at C-7	
2	164.6	1″	97.6
3	103.3[a]	2″	81.2
4	181.8	3″	76.6[b]
5	161.1	4″	70.0[c]
6	99.8	5″	76.6[b]
7	163.0	6″	61.0[d]
8	95.0		
9	156.9	*Glucose at C-2″*	
10	105.5		
1′	121.6	1‴	103.6[a]
2′	113.7	2‴	74.3
3′	145.7	3‴	76.7[b]
4′	149.8	4‴	70.4[c]
5′	116.1	5‴	76.8[b]
6′	119.1	6‴	61.3[d]

[a–d]Assignments with the same superscripts may be interchanged.

diglucosides (in which the interglucosidic linkage has not been determined) have been found in this group of plants [1].

EXPERIMENTAL

Plant material. Aerial parts (lamina with mature sporangia) of *P. cretica* L. were collected in the Botanic Garden of the University of Naples (Italy) in May 1991. The fern was identified by Dr R. Nazzaro (Dipartimento di Biologia Vegetale dell'Università Federico II, Naples, Italy). A voucher specimen has been deposited in the Herbarium Neapolitanum (NAP) of the University of Naples.

Isolation. Aerial parts of *P. cretica* L. were homogenized and extracted ×3 with hot EtOH. The combined extracts were filtered, concd and refiltered. Compounds **1** and **2** were separated by PPC on Whatman 3 MM paper in BAW, eluted with EtOH, concd and rechromatographed in 15% HOAc and BEW. Further purification was carried out on Sephadex LH-20 CC with MeOH as eluant. R_f values (on Whatman No 1 paper) for **1** were BAW 0.54; 15% HOAc 0.28 and H_2O 0.07.

Hydrolysis procedures. Total acid hydrolysis was carried out with 2M HCl (2 hr at 100°). Controlled acid hydrolysis was carried out with 10% HOAc (3.5 hr under reflux). Treatment with β-glucosidase was carried out in H_2O at 37° for 24 hr. Luteolin was identified by UV spectral analysis with the usual shift reagents [5], co-PC (4-solvent systems) and polyamide TLC. D-glucose, sophorose and gentiobiose were identified by silica gel TLC and PC (4-solvent systems) with authentic samples; sophorose could be separated by PC from all the other β-glucosylglucoses and gave the expected colours with appropriate sugar reagents [9].

Acknowledgements—The authors thank Servizio di Spettrometria di Massa del C.N.R.-Napoli for mass spectral measurements and Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Rome) for financial support.

REFERENCES

1. Markham, K. R. (1988) in *The Flavonoids: Advances in Research since* 1980 (Harborne, J. B., ed.), p. 427. Chapman and Hall, London.
2. Voirin, B. (1970) PhD thesis, University of Lyon, France.
3. Imperato, F. (1994) *Phytochemistry* **37**, 589.
4. Imperato, F. (1994) *Experientia* **50**, 115.
5. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) in *The Systematic Identification of Flavonoids*, p. 35. Springer, Berlin.
6. Markham, K. R., Ternai, B., Stanley, R., Geiger, H. and Mabry, T. J. (1978) *Tetrahedron* **34**, 1389.
7. Markham, K. R. (1982) in *The Flavonoids: Advances in Research* (Harborne, J. B. and Mabry, T. J., eds), p. 43. Chapman and Hall, London.
8. Imperato, F. (1981) *Chem. Ind. (London)* 695.
9. Bailey, R. W. (1962) *J. Chromatogr.* **8**, 57.