Phytochemistry, Vol. 25, No. 3, pp. 772–774, 1986.
Printed in Great Britain.

0031–9422/86 $3.00 + 0.00

FLAVONOIDS OF *PHLOMIS AUREA* AND *P. FLOCCOSA*

SABRY I. EL-NEGOUMY, MOHAMED F. ABDALLA and NABIEL A. M. SALEH*

National Research Centre, El-Dokki, Cairo, Egypt

(*Revised received* 17 *August* 1985)

Key Word Index—*Phlomis aurea*; *P. floccosa*; Labiatae; flavonoid *O*-glycosides; *C*-glycosides; *p*-coumaroyl derivatives.

Abstract—The leaves of *Phlomis aurea* proved to contain the 7-glucosides, 7-rutinosides and 7-*p*-coumaroylglucosides of naringenin, apigenin, luteolin and chrysoeriol, hispidulin 7-glucoside, luteolin 7-diglucoside, vicenin-2 and lucenin-2. The microscopic hairs on the leaves only contained the 7-monoglucosides and their acylated derivatives. *Phlomis floccosa* showed a similar flavonoid pattern, but with no flavanones.

Phlomis aurea Decne and *P. floccosa* D. Don belong to the Labiatae. *P. aurea* is restricted to the rocky places in Sinai, while *p. floccosa* is found in the north coastal region of Egypt, west of Alexandria. The Labiatae is rich in flavonoids and has been reported to contain flavanones [1, 2], flavone *C*-glycosides [3, 4], flavonols and flavones [4–8] and 6- and 8-methoxyflavones [4, 9–11].

We present here the first flavonoid investigation of *P. aurea*. Sixteen flavonoid compounds were isolated and identified in *P. aurea* as apigenin 7-glucoside, apigenin 7-rutinoside, apigenin 7-*p*-coumaroylglucoside, 6-methoxyapigenin 7-glucoside (hispidulin 7-glucoside), luteolin 7-glucoside, luteolin 7-rutinoside, luteolin 7-diglucoside, luteolin 7-*p*-coumaroylglucoside, chrysoeriol 7-glucoside, chrysoeriol 7-rutinoside, chrysoeriol 7-*p*-coumaroylglucoside, 6,8-di-*C*-glucosylapigenin (vicenin-2), 6,8-di-*C*-glucosylluteolin (lucenin-2), naringenin 7-glucoside, naringenin 7-*p*-coumaroylglucoside and free naringenin.

Phlomis is reported to have star-shaped hairs [12]. The fresh leaf surface of *P. aurea* was found to have a powdery like material, which separated on touch. This proved to be microscopic star-shaped hairs (0.2–0.5 mm) (see Fig. 1). The fresh leaves were quickly dipped in ethanol, and the ethanol filtered separating the microscopic hairs. These were blended with 70% ethanol, warmed and filtered. The extract proved to contain only the 7-*O*-glucosides of naringenin, apigenin, luteolin and chrysoeriol as well as their *p*-coumaroyl derivatives (Table 1). *Phlomis floccosa* showed a very similar flavonoid pattern as *P. aurea* but with the absence of naringenin, its 7-glucoside and *p*-coumaroyl derivative (Table 1).

The flavonoid monoglycosides, diglycosides and *C*-diglucosides were identified by standard chemical methods, UV and co-chromatography with authentic samples.

The four acylated flavonoids gave rise to *p*-coumaric acid and their corresponding 7-monoglucosides on alkaline hydrolysis. The UV data (see Experimental) indicates the presence of a free 5-hydroxyl group ($AlCl_3$–HCl) and a free 4′-hydroxyl group (shoulder at ~ 390 with NaOAc and increased intensity of band I with NaOMe). Although they are very likely the 7-*p*-coumaroylglucosides, the small amounts prevented any further investigations. The 7-diglucoside of luteolin did not co-chromatograph with luteloin 7-gentiobioside or 7-sophoroside.

EXPERIMENTAL

Plant material. A fresh leaf sample of *Phlomis aurea* Decne was collected from Mount Moses, Sinai. The plant was identified by Professor Dr. M. N. El-Hadidi of the herbarium, NRC, where a voucher specimen has been deposited. *Phlomis floccosa* D. Don. was a herbarium sample from NRC collected from the region between Mersa Matruh and Agiba, Täckholm, Gassar and Abdel-Aziz, 5/3/1976.

Isolation and identification of flavonoids. The plant material was extracted with 70% EtOH. The dry extract was fractionated on a polyamide column using H_2O followed by increasing concns of EtOH. The fractions were further purified using elution techniques. Flavonoids were identified according to standard methods [13–15]. Acid hydrolysis was carried out with 2 N HCl, mild acid hydrolysis with 0.1 N HCl, alkaline hydrolysis with 2 N KOH and enzymic hydrolysis with β-glucosidase (Fluka).

UV data of acylated flavonoids. Naringenin 7-*p*-coumaroyl glucoside: λ_{max}^{MeOH} nm: 284, 305 (sh); + NaOH: 284, 360. Apigenin 7-*p*-coumaroylglucoside (MeOH): 268, 294 (sh), 316, 355 (sh); + NaOMe: 270, 300 (sh), 366 (with increased intensity); + NaOAc: 268, 294 (sh), 316, 390; + NaOAc–H_3BO_3: 268, 294 (sh), 316, 355 (sh); + $AlCl_3$ + $AlCl_3$–HCl: 276, 297, 326, 380. Chrysoeriol 7-*p*-coumaroylglucoside (MeOH): 269, 295 (sh), 317, 355 (sh); + NaOMe: 260, 300 (sh), 366 (with increased intensity); + NaOAc: 262, 295 (sh), 308, 394; + NaOAc–H_3BO_3: 269, 295 (sh), 317, 355 (sh); + $AlCl_3$: 278, 296, 314 (sh), 388; + $AlCl_3$–HCl: 278, 286, 314 (sh), 386.

REFERENCES

1. Wagner, H., Hörhammer, L., Aurnhammer, G. and Farkas, L. (1967) *Tetrahedron Letters* 1837.
2. Brieskorn, C. H. and Riedel, W. (1977) *Planta Med.* **31**, 308.

*Author to whom correspondence should be addressed.

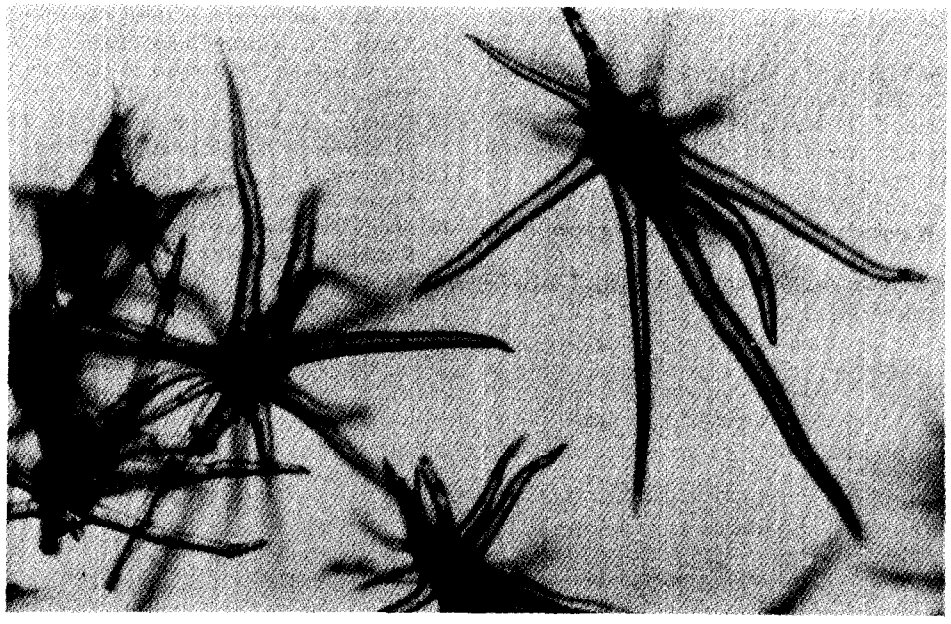

Fig. 1. Star-shaped hairs on leaves of *Phlomis aurea* (× 90).

Table 1. Chromatographic and relative amounts of flavonoids in *Phlomis aurea* and *P. floccosa*

Compound	Relative amounts*			R_f values (× 100)†		
	Phlomis aurea		*P. floccosa*			
	leaves	hairs	leaves	BAW	15%	PhOH
Naringenin	+	+	—			
7-glucoside	t	+	—			
7-*p*-coumaroylglucoside	+ + +	+ + +	—	88	37	—
Apigenin						
7-glucoside	+ +	+ +	t	47	17	81
7-rutinoside	+	—	+	36	28	73
7-*p*-coumaroylglucoside	+ + +	+ + +	+ + +	83	7	92
Luteolin						
7-glucoside	+ +	+	+ +	36	11	58
7-rutinoside	+	—	+ +	30	22	66
7-diglucoside	+	—	+	30	37	42
7-*p*-coumaroylglucoside	+	+	+	72	3	80
Chrysoeriol						
7-glucoside	+	+	+	34	13	86
7-rutinoside	+	—	+	28	21	78
7-*p*-coumaroylglucoside	+ + +	+ + +	+ + +	78	3	89
Hispidulin						
7-glucoside	t	—	?	48	22	93
Vicenin-2	+	—	+ +	11	63	51
Lucenin-2	t	—	t	6	52	30

*+ + + = major; + + = strong; + = present; t = traces; — = absent.

†BAW = *n*-butanol–acetic acid–water (4:1:5 top layer); 15% = acetic acid–water (3:17); PhOH = phenol–water (1:4).

3. Raynaud, J. and Chouikha, M. (1976) *Plant. Med. Phytother.* **10**, 199.
4. Abdalla, M. F., Saleh, N. A. M., Gabr, S., Abu-Eyta, A. M. and El-Said, H. (1983) *Phytochemistry* **22**, 2057.
5. Wollenweber, E. (1974) *Phytochemistry* **13**, 753.
6. Hörhammer, L., Aurnhammer, G. and Wagner, H. (1970) *Phytochemistry* **9**, 899.
7. Harborne, J. B. (1969) *Phytochemistry* **8**, 419.
8. Glennie, W. and Harborne, J. B. (1971) *Phytochemistry* **10**, 1325.
9. Ulubelen, A., Miski, M., Neuman, P. and Mabry, T. J. (1979) *J. Nat. Prod.* **42**, 261.
10. Tomas, F. and Ferreres, F. (1980) *Phytochemistry* **19**, 2039.
11. Xaasan, C. C., Xaasan-Cilmi, C. Faarax, M. X., Passannanti, S., Piozzi, F. and Paternostro, M. (1980) *Phytochemistry* **19**, 2229.
12. Polunin, O. and Huxley, A. (1966) *Flowers of the Mediterranean.* Houghton Mifflin, Boston.
13. Harborne, J. B. (1967) *Comparative Biochemistry of the Flavonoids.* Academic Press, London.
14. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids.* Springer, New York.
15. Markham, K. R. (1982) *Techniques of Flavonoid Identification.* Academic Press, London.