4. Agrawal, P. K., Agarwal, S. K. and Rastogi, R. P. (1980) *Phytochemistry* **19**, 893.
5. Audier, H. (1966) *Bull. Soc. Chim. Fr.* **9**, 2892.
6. Erdtman, H. (1963) in *Chemical Plant Taxonomy* (Swain, T., ed.) Chap. 4. Academic Press, London.
7. Pearl, I. A. and Darling, S. F. (1971) *Can. J. Chem.* **49**, 49.
8. Raghunathan, K., Rangaswani, S. and Seshadri, T. (1974) *Indian J. Chem.* **12**, 1126.
9. Rabesa, Z., Voirin, B., Favre-Bonvin, J. and Lebreton, Ph. (1978) *Phytochemistry* **17**, 1810.
10. Rabesa, Z. and Voirin, B. (1979) *C. R. Acad. Sci. Ser. C* **289**, 167.
11. Rasamoelisendra, R., Voirin, B., Favre-Bonvin, J., Andriantsiferana, M. and Rabesa, Z. (1985) *Pharmazie* **40**, H1, 59.
12. Rabesa, Z. and Voirin, B. (1983) *Phytochemistry* **22**, 2092.
13. Jay, M., Gonnet, J. F., Wollenweber, E. and Voirin, B. (1975) *Phytochemistry* **14**, 1605.

Phytochemistry, Vol. 25, No. 2, pp. 561–562, 1986.
Printed in Great Britain.

0031–9422/86 $3.00 + 0.00

A CHEMOTAXONOMIC STUDY OF FLAVONOIDS IN *THYMBRA CAPITATA*

F. A. T. BARBERÁN, L. HERNÁNDEZ and F. TOMÁS

(*Received* 7 *June* 1985)

Laboratorio de Flavonoides, Centro de Edafología y Biología Aplicada del Segura, C.S.I.C., Apdo. 195, Murcia 30003, Spain

Key Word Index—*Thymbra capitata*; Labiatae; 6-hydroxyflavones; chemotaxonomy.

Abstract—5,6,4′-Trihydroxy-7,3′-dimethoxyflavone, 5,6-dihydroxy-7,3′,4′-trimethoxyflavone, luteolin, diosmetin, vicenin-2 and luteolin 7-rutinoside have been isolated and identified from *Thymbra capitata*. The occurrence of these compounds supports the inclusion of this plant in the genus *Thymbra*, rather than *Thymus* or *Corydothymus*.

Thymbra capitata (L.) Cav. Lag. Griseb. [= *Thymus capitatus* (L.) Hoffmann and Link = *Corydothymus capitatus* (L.) Reichemb. fil.] is a Mediterranean plant that grows mainly in southern Spain and occasionally in eastern Spain (Alicante) and the Balearic islands. This plant constitutes a taxonomic problem that has been extensively discussed [1–3]. Several authors [4–6] have considered that there are two systematic groups sufficiently differentiated to sustain the existence of two separate genera, *Corydothymus* Reichemb. fil. and *Thymus* L. Other workers [2, 3, 7, 8] have considered that there is geobotanical, morphological, cytological and chemotaxonomic evidence to include *Thymus capitatus* in *Thymus*, but separating it as a distinct subgenus *Corydothymus*. Recently it has been suggested in agreement with Cavanilles, Lagasca and Grisebach, that it should be included in the genus Thymbra, on the basis of morphological and genetic similarities with *Thymbra spicata* [1] and has been renamed *Thymbra capitata*.

In this work we have studied the flavonoid compounds of *T. capitata* in order to establish a chemotaxonomic approach to this problem. The flavonoid aglycones 5,6,4′-trihydroxy-7,3′-dimethoxyflavone, 5,6-dihydroxy-7,3′,4′-trimethoxyflavone, luteolin and diosmetin and the glycosides vicenin-2 and luteolin 7-rutinoside, have been identified by UV and MS standard procedures [9–11].

5,6,4′-Trihydroxy-7,3′-dimethoxyflavone and 5,6-dihydroxy-7,3′,4′-trimethoxyflavone have been recently isolated as new naturally occurring compounds from *Thymbra spicata* [12], this being the second report in which the former flavonoid has been found in nature. The present chemical evidence thus supports the inclusion of the problematic plant in the genus *Thymbra* as *Thymbra capitata*. Also, these unusual methylated flavones have not been found in *Thymus* species *sensu lato* [13] (35 species studied). However, 5,6-dihydroxy-7,3′,4′-trimethoxyflavone has been identified in *Thymus piperella* (section *Piperella*) [14], a peculiar thyme which contains unusual flavones compared with other *Thymus* species, and which lacks the typical *Thymus* flavones, thymonin and thymusin [13].

EXPERIMENTAL

Plant material. Plants of *Thymbra capitata* were collected near Lanjarón (Granada) and Moraira (Alicante), and voucher specimens were deposited in the Herbarium of the Facultad de Ciencias de Murcia.

Extraction and isolation of flavonoids. The air-dried powdered aerial parts (*ca* 75 g) were extracted successively with $CHCl_3$ and EtOH. The extracts were concd under red. pres. The EtOH extract was redissolved in H_2O and extracted successively with Et_2O and *n*-BuOH. From the $CHCl_3$ extract two flavone aglycones were isolated by means of prep. PC on Whatman N°3 with 30% HOAc and prep. TLC on silica gel with toluene–HOAc (4:1).

5,6,4'-Trihydroxy-7,3'-dimethoxyflavone. UV λ_{max}^{MeOH} nm: 342 (1), 284 (0.9), 250 sh; + NaOMe, 392, 305 sh, 260 sh; + $AlCl_3$, 376, 295, 273; + $AlCl_3$ + HCl, 370, 294, 270 sh; + NaOAc, 397, 325, 277; + NaOAc + H_3BO_3, 340, 280, 271 sh. EIMS: 330 $[M]^+$ (100), 312 (33).

5,6-Dihydroxy-7,3',4'-trimethoxyflavone. UV λ_{max}^{MeOH} nm: 338 (1), 285 (0.9), 240 sh; + NaOMe, 400 sh, 328, 295 sh, 270 sh; + $AlCl_3$, 370, 298, 255 sh, 238 sh; + $AlCl_3$ + HCl, 364, 296, 255 sh, 238 sh; + NaOAc, 405 sh, 332, 289; + NaOAc + H_3BO_3, 334, 287. EIMS: 344 $[M]^+$ (100), 326 (31).

The Et_2O extract yielded luteolin and diosmetin that were identified by UV techniques and chromatographic comparison with authentic markers. From the *n*-BuOH extract, the flavones vicenin-2 and luteolin-7-*O*-β-D-rutinoside were isolated and identified by UV and EIMS standard procedures and by chromatographic comparison with authentic samples.

Acknowledgement—The authors are grateful to the Spanish CAICYT for financial support of this work (grant CSIC N° 608/126).

REFERENCES

1. Morales, R. (1985) *Taxonomia del Género Thymus L. Excluida la Sect. Serphyllum (Miller) Bentham en la Peninsula Ibérica.* Doctoral Thesis, Universidad Complutense, Facultad de Biología, Madrid.
2. Sibilio, E. (1961) *Delpinoa* **3**, 225.
3. Adzet, T. and Martínez, F. (1981) *Biochem. Syst. Ecol.* **9**, 293.
4. Pau, C. (1929) *Mem. R. Soc. Esp. Hist. Nat.* **15**, 65.
5. Del Villar, H. (1953) in *Diccionario de Botánica* (Font-Quer, P., ed.). Labor, Barcelona.
6. Font-Quer, P. (1961) *Plantas Medicinales.* Labor, Barcelona.
7. Jalas, J. and Kaleva, K. (1970) *Feddes Rep.* **81**, 53.
8. Jalas, J. (1972) in *Flora Europaea* (Tutin, T. G., Heywood, V. H., Burges, N. A., Moore, D. M., Valentine, D. H., Walters, S. M. and Webb, D. A., eds) Vol. 3. Cambridge University Press, Cambridge.
9. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids.* Springer, New York.
10. Mabry, T. J. and Markham, K. R. (1975) in *The Flavonoids* (Mabry, T. J., Harborne, J. B. and Mabry, H., eds.) p 79. Chapman & Hall, London.
11. Schmid, R. D. (1972) *Tetrahedron* **28**, 3259.
12. Miski, M., Ulubelen, A. and Mabry, T. J. (1983) *Phytochemistry* **22**, 2093.
13. Hernández, L. (1985) *Flavonoides en Especies Mediterráneas de Thymus L.* Doctoral Thesis, Universidad de Alicante, Facultad de Ciencias Químicas, Alicante.
14. Barberán, F. A. T., Hernández, L., Ferreres, F. and Tomás, F., *Planta Med.* (in press).