Phytochemistry **20**, 1567.
3. Ito, T., Takahashi, T., Oshima, Y., Takusari, H. and Odagiri, S. (1979) *Agric. Biol. Chem.* **43**, 413.
4. Guedes, M. E. M., Kuč, J., Hammerschmidt, R. and Bostock, R. (1982) *Phytochemistry* **21**, 2987.
5. Fuchs, A., Slobbe, W., Mol, P. C. and Posthumus, M. A. (1983) *Phytochemistry* **22**, 1197.
6. Uegaki, R., Fujimori, T., Kaneko, H., Kubo, S. and Kato, K. (1980) *Phytochemistry* **19**, 1543.
7. Hammerschmidt, R. and Kuč, J. (1979) *Phytochemistry* **18**, 874.
8. Fujimori, T., Tanaka, H. and Kato, K. (1983) *Phytochemistry* **22**, 1038.
9. Uegaki, R., Fujimori, T., Kaneko, H., Kubo, S. and Kato, K. (1980) *Phytochemistry* **19**, 1229.
10. Burden, R. S., Bailey, J. A. and Vincent, G. G. (1975) *Phytochemistry* **14**, 221.
11. Bailey, J. A., Burden, R. S. and Vincent, G. G. (1975) *Phytochemistry* **14**, 597.
12. Cruikshank, I. A. M., Perrin, D. R. and Madryk, M. (1976) *Annu. Rep. Plant Ind. CSIRO Aust.* **1975**, 65.
13. Budde, A. D. and Helgeson, J. P. (1980) *Phytopathology* **71**, 206.
14. Uegaki, R., Fujimori, T., Kubo, S. and Kato, K. (1983) *Phytochemistry* **22**, 1193.
15. Tomita, B. and Hirose, Y. (1970) *Tetrahedron Letters* 235.
16. Gerber, N. N. and Denney, D. Z. (1977) *Phytochemistry* **16**, 2025.
17. Nakatsuka, T. and Hirose, Y. (1956) *Bull. Agric. Chem. Soc. Jpn.* **20**, 215.
18. Hortmann, A. G. and De Roos, J. B. (1969) *J. Org. Chem.* **34**, 736.
19. Hortmann, A. G., Daniel, D. S. and Martinelli, J. E. (1973) *J. Org. Chem.* **38**, 728.

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MARIOLIN, A GERMACRANOLIDE FROM *ANACYCLUS RADIATUS**

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Key Word Index—*Anacyclus radiatus*; Compositae; sesquiterpene lactone; germacranolide; mariolin.

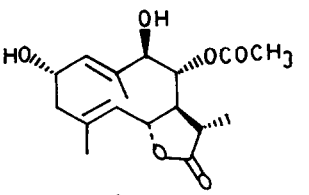
Abstract—A new sesquiterpene lactone, the germacranolide mariolin, was isolated from the aerial part of *Anacyclus radiatus* along with several known compounds. The structure of mariolin was determined by spectroscopic methods.

INTRODUCTION

The genus *Anacyclus* (tribe Anthemideae) with about eight species is mainly distributed in the southern part of the Iberian Peninsula and in North Africa. This genus has not been investigated chemically; therefore we have studied the constituents of *Anacyclus radiatus* Loisel. The aerial parts afforded two flavonoids: isorhamnetin [1] and quercetin [2], a coumarin: isoscopoletin [3], a triterpene: taraxasterol, three sterols: sitosterol, campesterol and stigmasterol, and the new germacranolide mariolin **1**, whose structure was determined from its spectroscopic data.

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of mariolin **1** showed a two-proton multiplet at δ4.36 assigned to geminal hydrogens of allylic hydroxy groups. The presence of an acetate group was confirmed by a three-proton singlet at δ2.05. A broad singlet (3H) at δ1.89 and a doublet (3H, J = 2 Hz) at δ1.82 are attributable to the characteristic vinylic methyls of a germacranolide skeleton. A doublet at δ1.31



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*Part 6 in the series "Structure and Chemistry of Secondary Metabolites from Compositae". For part 5 see González Collado, I., Macias, F. A., Massanet, G. M. and Rodriguez Luis, F., *J. Nat. Prod.* (in press).

(2H, $J = 7$ Hz) and the absence of two typical lowfield doublets of the α-methylene-γ-lactone grouping allowed a clear assignment of the C-11 methyl group.

The above spectral data are in close correspondence with an 11,13-dihydrolactone of the germacrane type with an acetate and two free hydroxyl groups. The C-6 lactonic proton, coupled with H-5 and H-7 ($J_{5,6} = J_{6,7} = 10$ Hz) appeared as a typical triplet at δ4.61. The large coupling constants exhibited by signals corresponding to the C-5, C-6 and C-7 protons, indicate that the H-6 bears a transdiaxial relationship with both H-5 and H-7. The stereochemistry at C-11 was also inferred from the large coupling ($J_{7,11} = 9.5$ Hz) between H-7 and H-11. The observation of the value of the coupling constants $J_{7,8}$ and $J_{8,9}$ (Table 1) led us to the conclusion that the transdiaxial relationship is also extended to H-7, H-8 and H-9 [4, 5]. Finally, the β-orientation of the remaining oxygen function followed from the shape of H-1 (doublet at δ5.24) and the couplings observed.

From the chemical shift of H-1 and the value of the coupling constant $J_{6,7}$ the skeletons of heliangolide, melampolide and *cis,cis*-germacranolide can be ruled out [6, 7]. Furthermore, the close relationship between the coupling constants (H-5, H-6, H-7, H-8 and H-9) is in good agreement with a crown conformation in a germacrolide skeleton [8].

Table 1. ^{1}H NMR spectral data for mariolin 1 (360 MHz, $CDCl_3$, TMS as internal standard)

H-1	5.24 *d*	H-8	5.42 *dd*
H-2	4.36 *m*	H-9	4.36 *m*
H-3	2.36 *dd*	H-11	1.74 *dq*
H-3′	2.30 *dd*	H-13	1.31 *d*
H-5	4.86 *d*	H-14	1.82 *d*
H-6	4.61 *dd*	H-15	1.89 *s* (*br*)
H-7	2.15 *ddd*	AcO	2.04 *s*

J (Hz): 1, 2 = 10.1; 2, 3 = 3, 3′ = 7.5; 2, 3′ = 10.1; 5, 6 = 6, 7 = 8, 9 = 10; 7, 8 = 7, 11 = 9.5; 11, 13 = 7.

EXPERIMENTAL

Anacyclus radiatus was collected near Puerto Real, Cádiz on March 1981. A voucher is on deposit at the Herbarium of the Department of Botany (SEVF), Faculty of Pharmacy, Sevilla (Spain).

The air-dried plant material (6 kg) was extracted with hot EtOH and the resulting extract was separated by CC (silica gel) and eluted with petrol and petrol–EtOAc mixtures. From the less polar fractions eluted with petrol–EtOAc (9:1) isoscopoletin (35 mg), taraxasterol, a mixture of sitosterol, stigmasterol and campesterol and 4 mg mariolin (1) were isolated. From the medium polar fractions eluted with petrol–EtOAc (1:4) isorhamnetin (50 mg) and quercetin (45 mg) were isolated.

Mariolin (1). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 3300, 1775, 1735, 1675, 1645, 1200. MS *m/z* (rel. int.) 324.1566 $[M]^+$ (2%), ($C_{17}H_{24}O_6$ requires 324.3706), 306 $[M-18]^+$ (3%), 264 $[M-60]^+$ (5%), 246 $[M-60-18]^+$ (5.4%), 228 $[M-60-2\times18]^+$ (10%).

Isoscopoletin, isorhamnetin and quercetin were identified according to their spectroscopic data as well as by the study of their acetates.

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REFERENCES

1. González, A. G., Barroso, J. T., Díaz Chico, E., Rodríguez Luis, J. and Rodríguez Luis, F. (1977) *An. Quim.* **73**, 858.
2. Bleier, W. and Chirikdjian, J. J. (1972) *Planta Med.* **22**, 145.
3. Nakano, T., Terao, S. and Jin, K. D. (1966) *J. Chem. Soc.* (*C*) 1805.
4. Quijano, L., Calderón, J. S., Gómez G., F. and Rios C., T. (1979) *Phytochemistry* **18**, 843.
5. Gershenzon, J. and Mabry, T. J. (1984) *Phytochemistry* **23**, 1959.
6. Bohlmann, F., Singh, P. and Jakupovic, J. (1982) *Phytochemistry* **21**, 2122.
7. Herz, W. and Wahlberg, J. (1973) *Phytochemistry* **12**, 1421.
8. Fischer, N. H., Olivier, E. J. and Fischer, H. D. (1979) *The Biogenesis and Chemistry of Sesquiterpene Lactones. Progress in the Chemistry of Organic Natural Products*, pp. 88–92. Springer, Austria.