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TRITERPENOIDS FROM *CARLINA CORYMBOSA* VAR. *GLOBOSA*

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Carlina corymbosa L. (Compositae) is a thistle largely widespread in Italy. We report here on the triterpenes and sterols isolated from *C. corymbosa* var. *globosa* Arc., growing in Southern Italy and specially in Sicily.

The unsaponifiable fraction of the light petrol extract gave a mixture that was submitted to repeated fractionation; the main constituents were lupeol, taraxasterol, and, in somewhat minor amounts, β-amyrin and α-amyrin. Further chromatography yielded a mixture of campesterol, stigmasterol and sitosterol (resolved by GLC); minor constituents isolated were 11-keto-β-amyrin, 30-nor-lupan-3β-ol-20-one, betulin and 11α-hydroxy-β-amyrin.

EXPERIMENTAL

The material was collected on the hills around Palermo and identified by Dr. A. Di Martino, Institute of Botany, University of Palermo. The aerial part and rhizome were dried, milled and extracted in a Soxhlet apparatus with light petrol for 72 hr. Solvent was removed under red pres and residue was extracted with EtOH: the filtrate was evaporated and new residue underwent saponification by refluxing with 10% ethanolic KOH for 6 hr. After the usual work-up, the unsaponifiable was purified over neutral alumina (grade III) giving 3 fractions.

The first fraction (85% of the total unsaponifiable) was acetylated and chromatographed on Si gel containing 20% $AgNO_3$. Elution gave, in the order: acetates of a mixture of β-amyrin and α-amyrin, taraxasterol and lupeol. The mixture was resolved by fractional crystallization giving pure β-amyrin acetate: the residue from the mother liquid was hydrolyzed, benzoylated and crystallized, yielding pure α-amyrin benzoate. The above triterpenols were identified as acetates, benzoates, free alcohols, related ketones; physical and spectroscopic data were in agreement with literature; direct comparison (mmp, IR, NMR, MS) was made with sure specimens. The products were homogeneous on GLC.

The second fraction (5% of the total wt) was not homogeneous on GLC: 3 peaks were observed and attributed to campesterol (approximately 8%), stigmasterol (27%) and sitosterol (65%), by co-injection with pure samples.

The third fraction (10% of the extract) contained more polar alcohols and was chromatographed many times on alumina; the first eluates were acetylated and chromatographed on Si gel, until 11-keto-β-amyrin acetate and 30-nor-lupan-3β-ol-20-one acetate were isolated; the last eluates were rechromatographed on alumina and resolved into betulin and 11α-hydroxy-β-amyrin. 11-Keto-β-amyrin [1] was identified as the free ketoalcohol and as acetate, by comparison (mmp, co-TLC, IR) with a synthetic specimen prepared as reported [2, 3]; NMR, UV and MS [4] confirmed the identity. 11α-Hydroxy-β-amyrin [5] was identified as diacetate, 3-monoacetate and free diol: physical data and NMR spectra agreed with previous reports [6, 7]. Betulin was identified as diacetate and free diol, by comparison (mmp, IR, NMR, MS) with sure samples. 30-Nor-lupan-3β-ol-20-one [8] and its acetate had physical data, MS and NMR spectra identical with those of sure specimens prepared [8] by oxidation of lupeol acetate. The products were homogeneous on GLC.

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REFERENCES

1. Wahlberg, I., Karlsson, K. and Enzell, C. R. (1972) *Acta Chem. Scand.* **26**, 1383.
2. Finucane, B. W. and Thompson, J. B. (1969) *Chem. Commun.* 1220.
3. Finucane, B. W. and Thompson, J. B. (1972) *J. Chem. Soc. Perkin I* 1856.
4. Wahlberg, I., Karlsson, K. and Enzell, C. R. (1971) *Acta Chem. Scand.* **25**, 3192.
5. Taylor, D. A. H. (1967) *J. Chem. Soc.* (C) 490.
6. Beynon, J. H., Sharples, K. S. and Spring, F. S. (1938) *J. Chem. Soc.* 1233.
7. Corsano, S. and Piancatelli, G. (1965) *Ann. Chim. (Rome)* **55**, 730.
8. Thompson, M. J. and Bowers, W. S. (1968) *Phytochemistry* **7**, 845.