Phytochemistry, Vol. 22, No. 4, pp. 1044–1045, 1983.
Printed in Great Britain.

0031–9422/83/041044–02$03.00/0

TRITERPENE ACIDS FROM *SALVIA* AND *TEUCRIUM* SPECIES

Salvatore Passannanti, Mariapia Paternostro and Franco Piozzi*

Istituto di Chimica Organica, Università di Palermo, Via Archirafi 20, 90123 Palermo, Italy

(*Revised received* 30 *July* 1982)

Key Word Index—*Salvia grandiflora*; *S. menthaefolia*; *S. splendens*; *S. lavandulifolia*; *Teucrium marum*; *T. fruticans*; Labiatae; pentacyclic triterpenes; ursolic acid; oleanolic acid; micromeric acid; maslinic acid; 3-epi-maslinic acid.

Abstract—The pentacyclic triterpene acids ursolic acid, oleanolic acid, micromeric acid, maslinic acid and 3-epi-maslinic acid have been isolated from several *Salvia* and *Teucrium* species.

For several years our group has been interested in the terpenoids of many genera of the Labiatae. The present communication deals with some triterpene acids isolated from species of the genera *Salvia* and *Teucrium*.

Salvia grandiflora which has not been studied previously†, is a shrub 1 m high, with long ovate leaves. It is a native of south-west Asia and the Balkan peninsula and it is now acclimatized in Sicily. The acetone extract of the air-dried aerial part gave a residue that was subjected to chromatographic separation. No diterpenoid was isolated, whereas the extract was rich in triterpene acids. Repeated chromatography of the free acids and then their methyl esters yielded three fractions. The first fraction contained methyl oleanolate and methyl ursolate, identified by GC and by conventional methods. The third fraction, not volatile on GC under the conditions used for methyl ursolate, yielded a more polar methyl ester. Mass spectrometry and NMR investigations allowed this compound to be identified as methyl maslinate [1] (methyl-2α, 3β-dihydroxyolean-12-en-28-oate). The second minor fraction yielded another polar methyl ester which was not volatile on GC. It was identified as methyl 3-epi-maslinate [2] (methyl-2α,3α-dihydroxyolean-12-en-28-oate).

The occurrence of these two rare acids is worthy of remark. Maslinic acid occurs only in *Crataegus oxyacantha* (Rosaceae) [3], *Olea europaea* (Oleaceae) [1], *Dryobalanops aromatica* (Dipterocarpaceae) [4] and *Chamaenerion angustifolium* (Onagraceae) [5]. 3-Epi-maslinic has been isolated only from *Shorea acuminata* (Dipterocarpaceae) [2] and *Holoptelea integrifolia* (Ulmaceae) [6].

Salvia menthaefolia previously unstudied, is an exotic herb with small red flowers, whose original habitat is unknown. It has been cultivated in Sicily for many years as an ornamental plant for hedges. It does not contain diterpenes, but a triterpene fraction was isolated. Usual work-up showed the occurrence of methyl oleanolate, methyl ursolate and a third product, methyl micromerate. Micromeric acid is a rare triterpene, with the structure 3β-hydroxy-ursa-12,20(30)-dien-28-oic acid. It has been isolated only from *Micromeria benthami* [7], *Salvia horminum* [8] and *Rosmarinus officinalis* [9], all belonging to the Labiatae family.

Salvia splendens, previously investigated for its content of diterpenes [10, 11], is a shrub with beautiful clusters of bright red flowers. It is originally from Brazil and was acclimatized in Europe as a decorative plant. The triterpene fraction is composed of ursolic acid and small quantities of oleanolic acid.

Salvia lavandulifolia, which is widespread in Spain, is sometimes incorrectly called *S. hispanica*‡. It also contains no diterpenoids and the triterpene fraction is composed of almost equal amounts of oleanolic acid and ursolic acid.

The genus *Teucrium* seems to contain only minor amounts or even traces of triterpenes. *Teucrium marum* was shown previously [12] to contain a monoterpene lactone. We have now shown that a sample collected in Spain contained no diterpenes, whereas the triterpene fraction consisted of ursolic acid, oleanolic acid and small amounts of micromeric acid. This is the first time that micromeric acid has been detected in this genus.

Teucrium fruticans is widespread in Sicily and it contains some diterpenes [13, 14]. The only triterpenes isolated were ursolic acid and oleanolic acid in the ratio 3 : 1.

Only traces of unidentified triterpene acids were observed in *T. flavum* L., *T. gnaphalodes* L'Her., *T. Spinosum* L., *T. eriocephalum* Willk., *T. polium* L. subsp. *aureum* (Schreber) Arcangeli.

EXPERIMENTAL

S. grandiflora Etling., *S. menthaefolia* Tenore, *S. splendens* L. and *T. fruticans* L. were cultivated and identified in the Botanic Garden of the University of Palermo; voucher specimens are deposited in the herbarium. *S. lavandulifolia* Vahl and *T. marum* L. were collected in central and south-east Spain, respectively; voucher specimens are deposited in the Herbarium of the Faculty of Pharmacy, Madrid 'Complutense' University. The other *Teucrium* species were collected in Sicily or in Spain some years ago and their botanical identification reported in previous papers dealing with their diterpene content.

---

*To whom correspondence should be addressed.

†A recent paper [15] deals with the isolation of several flavonoids from the leaves of *Salvia tomentosa* Mill., claimed to be synonymous with *S. grandiflora* Etling. Indeed, only *S. grandiflora* Etling. is listed in *Flora Europaea*, whereas *S. tomentosa* Mill. is mentioned as a synonymous with *S. officinalis* L. in the index of *Flora Europea*, p. 362.

‡This incorrect name should not be used in order to prevent confusion with *S. hispanica* L. which grows in tropical America.

The air-dried aerial parts of the plants were powdered and extracted with cold Me_2CO for 1 week. The solvent was removed from the extracts and the residues chromatographed on Si gel columns. The acids were methylated with CH_2N_2 in Et_2O soln. GC of the methyl esters was performed on a 1.5 m × 3 mm column packed with 3% OV-1 on Chromosorb at 260°, detector and injector temp. 300°, carrier gas N_2 at 20 ml/min.

Methyl oleanolate and methyl ursolate were identified by their GC, MS and ^1H NMR data. Methyl maslinate and methyl 3-epi-maslinate were isolated and identified by comparison with the physical, MS and ^1H NMR data in the lit. [2, 4, 5].

The separation of micromeric acid from ursolic and oleanolic acids was as described previously [7], by chromatography of the mixture of the acetylated methyl esters on a Si gel–$AgNO_3$ column. Methyl acetylmicromerate was identified by mmp, MS, and GC, in comparison with an authentic specimen.

Acknowledgements—This work was supported by the 'C.N.R. Institute for the Chemistry of Natural Products of Nutritive and Pharmaceutical Interest', Catania. We thank Professor A. G. Gonzalez (I.P.N.O., Tenerife) and Professor C. H. Brieskorn (Würzburg University) for samples of methyl acetylmicromerate.

REFERENCES

1. Caglioti, L., Cainelli, G. and Minutilli, F. (1961) *Gazz. Chim. Ital.* **91**, 1387.
2. Cheung, H. T. and Yan, T. C. (1972) *Aust. J. Chem.* **25**, 2003.
3. Tschesche, R. and Pugmann, R. (1951) *Chem. Ber.* **84**, 810.
4. Cheung, H. T. and Feng, M. C. (1968) *J. Chem. Soc. C* 1047.
5. Glen, A. T., Lawrie, W., McLean, J. and Younes, M. E. (1967) *J. Chem. Soc. C* 510.
6. Misra, G., Bhatnagar, S. C. and Nigam, S. K. (1975) *Planta Med.* **27**, 290.
7. Bermejo, J., Breton, J. L., De La Fuente, G. and Gonzalez, A. G. (1967) *Tetrahedron Letters* 4649.
8. Ulubelen, A. and Brieskorn, C. H. (1975) *Phytochemistry* **14**, 820.
9. Brieskorn, C. H. and Zweyrohn, G. (1977) *Pharmazie* **25**, 488.
10. Savona, G., Paternostro, M., Piozzi, F., Hanson, J. R., Hitchcock, P. B. and Thomas, S. A. (1978) *J. Chem. Soc. Perkin Trans.* 1, 643.
11. Savona, G., Paternostro, M., Piozzi, F. and Hanson, J. R. (1979) *J. Chem. Soc. Perkin Trans.* 1, 533.
12. Pagnoni, U. M., Pinetti, A., Trave, R. and Garanti, L. (1976) *Aust. J. Chem.* **29**, 1375.
13. Savona, G., Passannanti, S., Paternostro, M., Piozzi, F., Hanson, J. R., Hitchcock, P. B. and Siverns, M. (1978) *J. Chem. Soc. Perkin Trans.* 1, 356.
14. Savona, G., Passannanti, S., Paternostro, M., Piozzi, F., Hanson, J. R. and Siverns, M. (1978) *Phytochemistry* **17**, 320.
15. Ulubelen, A., Miski, M., Neuman, P. and Mabry, T. J. (1979) *J. Nat. Prod.* **42**, 261.

Phytochemistry, Vol. 22, No. 4, pp. 1045–1047, 1983.
Printed in Great Britain.

0031-9422/83/041045-03$03.00/0

STEROL AND TRITERPENOID GLYCOSIDES FROM THE ROOTS OF *PATRINIA SCABIOSAEFOLIA*

WON SICK WOO, JAE SUE CHOI, OTTO SELIGMANN* and HILDEBERT WAGNER*

Natural Products Research Institute, Seoul National University, Korea; *Institut für Pharmazeutische Biologie der Universität München, West Germany

(*Received* 24 *September* 1982)

Key Word Index—*Patrinia scabiosaefolia*; Valerianaceae; triterpenoid glycosides; sterol glucosides; 2′-*O*-acetyl-3-*O*-α-L-arabinopyranosyl-hederagenin.

Abstract—From the roots of *Patrinia scabiosaefolia*, oleanolic acid, hederagenin, 3-*O*-α-L-arabinopyranosyl-oleanolic acid, 3-*O*-α-L-arabinopyranosyl-hederagenin, 2′-*O*-acetyl-3-*O*-α-L-arabinopyranosyl-hederagenin and a mixture of sitosterol and campesterol-D-glucosides were isolated.

Patrinia scabiosaefolia is a perennial weed, roots of which have been used as an indigenous medicine for edema, appendicitis, endometritis and inflammation and several pertaining pharmacological activities were reported [1]. On the other hand, a methanol extract caused a significant prolongation of hexobarbital-induced sleeping time, elevation of serum transaminase activities and severe histopathological changes in the liver in mice [2].

In the course of a search for the hepatotoxic substances, six compounds numbered **1**–**6** in order of increasing polarity were isolated from the chloroform-soluble fraction of a methanol extract of the roots.

Compound **1**, mp 310°, $[\alpha]_D^{23} + 58.6°$ and **2**, mp 330–334°, $[\alpha]_D^{20} + 90°$ were identified as oleanolic acid and hederagenin, respectively, by direct comparison with authentic samples. Compound **3**, mp 226–229°, $[\alpha]_D^{20} + 68°$ gave a positive reaction in the Libermann–Burchard and Molish tests and showed ester (1725 and