

# TERPENOIDS OF CULTIVATED *SALVIA CANARIENSIS*

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*Salvia canariensis* L., endemic to the Canary Islands, was studied some years ago by Gonzalez (1). The aerial part of the plant, collected in Gran Canaria, yielded, among other things, the triterpenes oleanolic and ursolic acids (1) and the new diterpenes arucatriol (1), galdosol (1,2) and salviol (1).

Recently, we had the opportunity of examining a rich sample of *S. canariensis* growing in the Botanic Garden of the University of Palermo, which had sprung from seeds supplied by the Botanic Garden of the University of Coimbra (Portugal).

From this sample, we isolated a triterpene and a diterpene fraction, but, surprisingly, it was not possible to detect even one of the products described by Gonzalez.

The triterpene fraction contains neither oleanolic nor ursolic acid; on the contrary, maslinic acid (3) (2 $\alpha$ -hydroxy-oleanolic acid) and 2 $\alpha$ -hydroxy-ursolic acid (4) occur in the plant in small amounts. The diterpene fraction does not contain arucatriol, galdosol, and salviol; only one diterpenoid was isolated, the already known salvin (11, 12-dihydroxy-8, 11, 13-abietatrien-10-carboxylic acid), previously found in *S. officinalis* L. (5,6).

This finding is a remarkable example of how the change of region can affect the quantitative and qualitative content of the products in a species.

## EXPERIMENTAL<sup>1</sup>

Air-dried, powdered aerial parts of *S. canariensis* (1.3 kg) were extracted with cold acetone for one week. The residue from evaporation of the extract was chromatographed on a column of silica gel deactivated by 15% water. Elution with petroleum ether-EtOAc 85:15 and then 50:50 gave a diterpene fraction that was acetylated (Ac<sub>2</sub>O-pyridine at room temperature) and rechromatographed, yielding 2.5 g of diacetyl-salvin. Further elution with petroleum ether-EtOAc 50:50 yielded a triterpene fraction that was methylated with ether CH<sub>2</sub>N<sub>2</sub> and gave 250 mg of a mixture of methylesters.

Diacetyl-salvin has mp,  $\approx 210^\circ$  dec. [Lit. (5) 196°-215° dec.]; ms, M<sup>+</sup> 416; ir and uv spectra are identical with those reported (5); nmr (CDCl<sub>3</sub>, 60 MHz):  $\delta$  0.88 (s, tert. CH<sub>3</sub>), 0.98 (s, tert. CH<sub>3</sub>), 1.13 (d, J 6.5 Hz, sec. CH<sub>3</sub>), 1.25 (d, J 6.5 Hz, sec. CH<sub>3</sub>), 2.27 (s, 2  $\times$  OCOCH<sub>3</sub>), 6.45 (br, COOH), 7.03 (s, H-14). Treatment with ether CH<sub>2</sub>N<sub>2</sub> gave diacetyl-salvin methylester, mp, 157°-158° [Lit. (5) 158°-160°]; ms M<sup>+</sup> 430; its nmr spectrum (CDCl<sub>3</sub>, 60 MHz) is identical with the reported one (5).

The mixture of triterpene methylesters (ms, M<sup>+</sup> 486) was analyzed by hplc (Waters instrument, RI detector,  $\mu$ -Porasil column 30 cm  $\times$  3.9 mm id, eluent cyclohexane-EtOAc 50:50 2 ml/min): two peaks of similar intensity were observed, T<sub>r</sub> 11'30" resp. 11'40", which were identical (also co-injection) with authentic specimens of methyl 2 $\alpha$ -hydroxy-ursolate and methyl maslinate, respectively. However, micro-preparative separation was unsuccessful. The nmr spectrum (CDCl<sub>3</sub>, 60 MHz) of the mixture showed the overlapping of the spectra of methyl maslinate (7) and methyl 2 $\alpha$ -hydroxy-ursolate (7,8), especially for the signals of 18 $\beta$ -H, 2 $\beta$ -H, and 3 $\alpha$ -H. The spectra of the two pure products were run on authentic specimens, isolated from *Meriandra benghalensis* (Roxb.) Benth. (family Labiatae) (9).

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<sup>1</sup>Full details of the isolation and identification are available upon request to the authors.

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## STUDIES ON CHILEAN LICHENS, IV. ADDITIONS TO THE CHEMISTRY OF *LOBODIRINA CEREBRIFORMES*

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The study of *Lobodirina cerebriformes* (Mont.) Follm. (Roccellaceae) has been carried out by Huneck (1); roccellic acid and lobodirin were reported. We have since undertaken new research in order to obtain roccellic acid, which stimulates plant growth (2,3). Besides the aforementioned metabolite, portentol was obtained.

Portentol and acetylportentol are the only cycloaliphatic lactones found in lichens, and they have been described only in species of the family Roccellaceae (4).

The specimens analyzed by Huneck and those analyzed by us came from different geographical areas. It is possible that chemical differences among specimens are caused by the actual existence of chemical races (5,6). It may also be that these specimens exhibit a different chemistry due to hybridization (7).

### EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Kofler hot plate. Optical rotations were measured with a Schmidt-Haensch polarimeter. Spectra were recorded with the following instruments: ir, Perkin Elmer Model 683 and pmr, Varian XL-100; tlc were performed on silica gel from E. Merck.

PLANT MATERIAL.—*Lobodirina cerebriformes* (Mont.) Follm. (Roccellaceae) was collected on coastal rocks at the mouth of Limari River (Ovalle, Chile) in September 1980. Voucher specimens are deposited at University of Valparaíso.

EXTRACTION, ISOLATION, AND IDENTIFICATION OF ROCCELIC ACID AND PORTENTOL.<sup>1</sup>—The dried and ground thalli (500 g) were worked up by standard procedures (1). The compounds obtained were roccellic acid (102 g), identified by comparison with an authentic material (mmp, tlc, optical rotation, and ir spectrum) and portentol (0.85 g; 0.17%), which was identified by standard spectral and physical data (5) as well as by transformation in acetylportentol, which, in turn, was identified by comparison with an authentic sample (mmp, tlc, ir, and pmr spectra) (5).

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<sup>1</sup>Full details of the isolation and identification of the compounds are available on request to the senior author.