

from the other proteins of the anti *Naja nigricollis* horse immune-serum. They belong to the IgT immunoglobulins. By the same technique, when erabutoxin 'a' from *Laticauda semifasciata* is covalently linked to the Sepharose, antibodies reacting with both this toxin

and the  $\alpha$  toxin were separated from the same immune-serum. This confirms that an immunological relationship exists between the  $\alpha$  toxin of an Elapidae: *Naja nigricollis*, and the erabutoxin 'a' of an Hydrophiidae *Laticauda semifasciata*.

## SPECIALIA

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### Constituents of Labiatae XIX<sup>1</sup>. Structure of Galdosol, a New Diterpene from *Salvia canariensis* L.

In previous papers we reported the isolation of the 3 new triterpenes, anagadiol, nivadiol and  $\alpha$ -amyradienyl acetate, from *Salvia broussonetii* Benth.<sup>2-4</sup>. Continuing our investigations on the Labiatae endemic to the Canary Isles, we have studied *Salvia canariensis* L., collected near Arucas (Gran Canaria) in spring. From the aerial part we have isolated the new diterpene galdosol (I) as a powder which would not crystallise. It has IR absorptions indicative of hydroxyl,  $\gamma$ -lactone and keto functions (3350, 1780 and 1700  $\text{cm}^{-1}$  in  $\text{CHCl}_3$ ). Its NMR spectrum ( $\text{CDCl}_3$ , 60 MHz) displays singlets at  $\tau$  2.35 (1H, aromatic) 5.35 (1H, geminal to the lactone oxygen) and 7.60 (H-5), in addition to signals between 8.80 and 9.10 corresponding to 4 methyl groups.

Mild acetylation of I gave the diacetate II, white needles from MeOH, m.p. 223–224°,  $[\alpha]_D^{25} + 62^\circ$  (2.1%,  $\text{CHCl}_3$ );  $M^+$  428; analysis, found: C 67.21; H 6.50.  $\text{C}_{24}\text{H}_{36}\text{O}_7$  requires: C 67.28; H 6.59%. Structure II was established on the basis of the following considerations: a broad IR-absorption at 1780  $\text{cm}^{-1}$  (in KBr) is attributed to the carbonyl groups of the acetate and  $\gamma$ -lactone functions, while the bands at 1700 and 1605  $\text{cm}^{-1}$  are due to the system  $\text{Ph}-\text{C}=\text{O}$ . The NMR-spectrum ( $\text{CDCl}_3$ ) presents a one-proton singlet at  $\tau$  2.02 assigned to the aromatic H-14 conjugated with the keto group at C-7. The signals of the H-6 ( $\tau$  5.26) and H-5 (7.52) appear as singlets which indicates the existence of an angle of about 90° between these protons. Further signals correspond to the H-15 ( $\tau$  7.04 m), 2 acetate (7.68, 7.76, s) and 4 methyl groups (8.73, 8.85, 8.96 and 9.02).

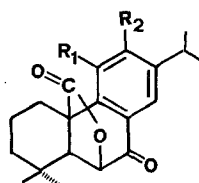
Structure I was confirmed as follows: reduction of II with Zn in HOAc to the ketoacid III and subsequent methylation with  $\text{CH}_3\text{N}_2$  gave IV, m.p. 146–150° (fine

white druses from light petroleum/*n*-hexane) which in the IR ( $\text{CHCl}_3$ ) presents absorptions at 2870, 1605 (aromatic), 1775, 1240 (OAc), 1720 (ester) and 1685 ( $\text{Ph}-\text{C}=\text{O}$ ). The NMR-spectrum ( $\text{CDCl}_3$ ) displays singlets at  $\tau$  1.96 (1H, aromatic), 6.46 (3H, OMe), 7.72 (6H, OAc) and a 1-proton multiplet at 7.02 (H-15). This compound proved to be identical (mixed m.p., TLC, IR- and NMR-spectra) with the oxidation product obtained by LINDE from carnosic acid<sup>5</sup>.

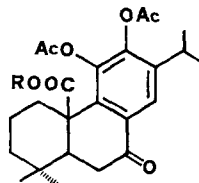
*Résumé.* Le nouveau diterpène galdosol (I) a été isolé de la *Salvia canariensis* L. et sa structure déterminée comme 7-oxo-11,12-dihydroxy-8,11,13-abiétatrién-20,6-olide.

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I  $R_1 = R_2 = \text{OH}$   
II  $R_1 = R_2 = \text{OAc}$



III  $R = \text{H}$   
IV  $R = \text{CH}_3$

<sup>1</sup> For Part XVIII see A. G. GONZÁLEZ, J. L. BRETÓN and C. R. FAGUNDO, *An. Quím.*, in press (1973).

<sup>2</sup> A. G. GONZÁLEZ, J. L. BRETÓN and B. M. FRAGA, *Chem. Commun.* 1971, 567.

<sup>3</sup> A. G. GONZÁLEZ, J. L. BRETÓN and B. M. FRAGA, *An. Quím.* 68, 709 (1972).

<sup>4</sup> A. G. GONZÁLEZ, B. M. FRAGA and A. G. RAVELO, *An. Quím.* 68, 1433 (1972).

<sup>5</sup> H. LINDE, *Helv. chim. Acta* 47, 1234 (1964).

<sup>6</sup> Acknowledgments. The authors thank Dr. H. LINDE (Universität Basel) for the sample of compound IV and Dr. W. WILDPRET (Departamento de Botánica, Universidad de La Laguna) for classifying the plant. This work was realized within the Programme of Chemistry 1971 conceded by the Foundation Juan March.