

## NEW CYCLOHEXANE DERIVATIVE FROM *ISOPLEXIS CANARIENSIS* VAR. *TOMENTOSA*

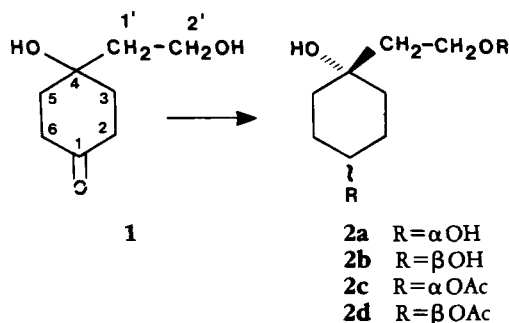
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Of the four species comprising the genus *Isoplexis* (1), *Isoplexis canariensis* var. *glaberrima* Kuntze (Scrophulariaceae) (2) has been investigated most thoroughly (3); however, no phytochemical study of the variety *tomentosa* Kuntze has been carried out until now because of its small habitat. In order to complete the knowledge of this genus, it seemed worthwhile to undertake such a study.

Two recent papers reported the isolation from *Isoplexis chalcantha* of a salidroside (4) and two cyclohexanetriols, **2a** and **2b** (5). Continuing our study of

tions and a peak at  $1700\text{ cm}^{-1}$  characteristic of a cyclohexanone. In the hrms the ion at the highest mass appeared at  $m/z = 158.0961$ , corresponding to the formula  $\text{C}_8\text{H}_{14}\text{O}_3$ . The  $^1\text{H-nmr}$  spectrum displayed two triplets coupled together (2H each,  $J = 5.7\text{ Hz}$ ) centered at  $\delta 4.01$  ( $\text{CH}_2\text{OH}$ ) and  $\delta 1.83$  ( $\text{CH}_2$ ). The remaining eight protons produced a series of multiplets centered at 2.75 (2H, 2a,6a), 2.15 (4H, 2e,6e, 3e,5e), and 1.81 (2H, 3a,5a), partially overlapped with the signal at 1.83, identical with reported values (7). The  $^{13}\text{C-nmr}$  spectrum showed five signals which, on the



this type of product from the genus *Isoplexis*, we have isolated and identified two compounds that are chemically related to the above triols. The less polar compound, obtained as an oil, was identified by spectroscopic methods as halteridone, a cyclohexanone previously found in *Hallerida lucida* L. (Scrophulariaceae) (6).

The second, slightly more polar, was also obtained as an oil that could not be crystallized. Its ir spectrum displayed a broad absorption band ( $3500\text{-}3200\text{ cm}^{-1}$ ) corresponding to alcoholic func-

basis of the molecular formula and the above-mentioned spectral data, indicated the presence of some element of symmetry in the molecule. The said signals confirmed the existence of a carbonyl carbon, 213.72 ppm (singlet), two carbon atoms carrying hydroxyl groups, one, totally substituted, 70.12 ppm, singlet, and the other terminal, 58.65 (triplet) and a methylene group, 42.22 (triplet). The remaining four carbon atoms produced a single very intense signal at 36.74 ppm, triplet, and must, therefore, be methylene groups. All these data suggested that the new compound was 4-(2-hydroxyethyl)-4-hydroxycyclohexanone [1].

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Reduction of **1** with  $\text{NaBH}_4$  in MeOH afforded a mixture of alcohols **2a** and **2b** in a 4:1 ratio, as determined by gc of the mixture of their acetates.

The most polar substances, which could not be isolated because of their low yields, were identified as **2a** and **2b** on the basis of their chromatographic behavior (tlc, several eluents, and comparison with authentic samples).

## EXPERIMENTAL

**GENERAL EXPERIMENTAL PROCEDURES.**—Mps were determined on a Kofler block and were uncorrected. Ir spectra were run in  $\text{CHCl}_3$ .  $^1\text{H}$ -nmr and  $^{13}\text{C}$ -nmr spectra were recorded in  $\text{CDCl}_3$  with TMS as internal standard. Ms analyses were obtained at 70 eV with an ion source temperature of 200°. Gc was performed on a capillary column. Cc was carried out on Si gel 60 (Merck) (0.063 mm) under pressure.

**ISOLATION OF THE COMPOUNDS.**—Leaves of *I. canariensis* var. *tomentosa*, collected in Güimar, Tenerife, in June 1983, were dried at room temp. A voucher specimen was deposited in the Herbarium of the Department of Botany, Faculty of Biology, University of La Laguna (TFC 21.937). The dry, powdered leaves (1000 g) were extracted first with  $\text{C}_6\text{H}_6$  and then with EtOH in a Soxhlet extractor. The  $\text{C}_6\text{H}_6$  extract, after concentration under vacuum, afforded a syrupy residue (25 g) that was separated by chromatography using mixtures of hexane/EtOH of increasing polarity as eluents. The least polar fractions afforded halleridone and the new compound, 4-(2-hydroxyethyl)-4-hydroxycyclohexanone [**1**], which showed the following characteristics: colorless oil; ir  $\text{cm}^{-1}$  3520, 3000, 2592, 1710, 1440, 1330, 1230, 1120, 1080, 900; ms  $m/z$  (rel. int. %) 158.0961 ( $\text{M}^+$ , 7), (calcd for  $\text{C}_8\text{H}_{14}\text{O}_3$ ) 158.0943, 140 ( $\text{M}^+$  - 18, 24), 113 (47), 112 (39), 101 (83);  $^1\text{H}$  nmr  $\delta$  4.01 (2H, t,  $J=5.7$  Hz), 1.83 (2H, t,  $J=5.7$  Hz), 1.70-2.80 (8H,

m);  $^{13}\text{C}$  nmr 36.74 (t, C-2, C-3, C-5, C-6), 42.22 (t, C-1'), 58.65 (t, C-2'), 70.12 (s, C-4), 213.72 (s, C-1).

Two other minor compounds were detected in the most polar fractions and were identified by chromatographic analysis to be **2a** and **2b**.

**REDUCTION OF 1.**—To **1** (107 mg) dissolved in MeOH was added  $\text{NaBH}_4$  (36.5 mg), and the reaction proceeded with stirring for 1 h. The reaction mixture was poured into  $\text{H}_2\text{O}$  (100 ml) and submitted to continuous extraction for 30 h in a liquid-liquid extractor with EtOAc. Chromatography of the residue afforded two products identical with **2a** and **2b** (mp mixed, ir, and nmr superimposable).

Part of the reaction product was acetylated in the usual way with  $\text{Ac}_2\text{O}$  and  $\text{C}_3\text{H}_5\text{N}$  for 24 h. After extraction the mixture was submitted to gc in order to determine the proportions of the two isomers. The first eluted isomer was compound **2d** (retention time 8.60, 20%), and the second eluted was **2c** (retention time 8.95, 80%).

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