($C_{15}H_{22}O_4$), 230 $[M-H_2O]^+$ (14), 215 $[230-Me]^+$ (11), 204 $[248-CO_2]^+$ (9), 175 $[204-CHO]^+$ (53), 55 $[C_4H_7]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-25 \quad -25 \quad -28 \quad -45} \; (\text{CHCl}_3;\ c = 0.26).$$

4 mg **1** was heated with 0.1 ml Ac_2O for 1 hr at 70°. TLC (Et_2O–petrol, 3:1) afforded 3 mg **2**, colourless gum, IR $\nu^{\text{CCl}_4}_{\text{max}}$ cm^{-1}: 1785 (γ-lactone), 1745, 1240 (OAc), 1645 ($C=CH_2$); MS *m/z* (rel. int.): 350 $[M]^+$ (0.2), 290 $[350-HOAc]^+$ (6), 230 $[290-HOAc]^+$ (100), 215 $[230-Me]^+$ (9), 202 $[230-CO]^+$ (12).

3-*Desacetyl*-10,14-*desoxoarctolide* (**3**). Colourless gum, IR $\nu^{\text{CHCl}_3}_{\text{max}}$ cm^{-1}: 3620 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 262.121 $[M]^+$ (3) ($C_{15}H_{18}O_4$), 244 $[M-H_2O]^+$ (23), 226 $[244-H_2O]^+$ (11), 216 $[244-CO]^+$ (22), 201 $[216-Me]^+$ (14), 192 (31), 138 (48), 91 (72), 55 (78), 53 (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365}{+40 \quad +43 \quad +49 \quad +85 \quad +141} \; (\text{CHCl}_3;\ c\ 0.44).$$

REFERENCES

1. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes* p. 439. Academic Press, London.
2. Samek, Z., Holub, M., Drozdz, B. and Grabarczyk, H. (1977) *Collect. Czech. Chem. Commun.* **42**, 2217.
3. Halim, A. F. and Zaghloul, A. M. (1980) *Planta Med.* **38**, 183.
4. Bohlmann, F. and Le Van, N. (1977) *Phytochemistry* **16**, 487.
5. Halim, A. F., Zaghloul, A. M. and Bohlmann, F. (1980) *Phytochemistry* **19**, 2767.
6. Grabyrczyk, H. and Makowska, B. (1973) *Pol. J. Pharmacol. Pharm.* **25**, 477.

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A DITERPENIC ACID FROM *STEVIA LUCIDA*[*]

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Key Word Index—*Stevia lucida*; Compositae; Eupatorieae; labdane-type diterpene.

Abstract—A new furan diterpenic acid was isolated from *Stevia lucida*. On the basis of IR, ^1H NMR and mass spectra, as well as chemical evidence, the acid was assigned the structure 5β,9β*H*,10α,-labda-7,13(16),14-trien-15,16-epoxy-19-oic-acid.

INTRODUCTION

In the course of a phytochemical survey of Mexican Eupatorieae [1–4], we have isolated and elucidated the structure of a new labdane diterpenic acid from the leaves of *Stevia lucida* Lag var Bipontini, a wild herb which is plentiful in the semi-arid area of Oaxaca, Mexico.

RESULTS AND DISCUSSION

The new diterpenic acid (**1**) decomposed rapidly and its purification by CC over Si gel was only accomplished with a loss of large amounts of material. The molecular formula of **1**, was determined to be $C_{20}H_{28}O_3$. The IR spectrum revealed the presence of a hydroxyl group (3300–2700 cm^{-1}), a carbonyl function (1690 cm^{-1}) and a furan ring [5] (1440, 1020 and 870 cm^{-1}). The ^1H NMR spectrum showed three multiplet signals at δ 7.30, 7.17 and 6.22 which were assigned to two α-furan protons and a β-furan proton. A vinyl proton at δ 5.35 interacting with a vinylic methyl at 1.70 was also observed establishing the presence of a trisubstituted double bond.

The IR spectrum of the methyl ester (**2**) exhibited the expected shift from 1690 to 1730 cm^{-1} in the parent carbonyl absorption band. The characteristic absorption pattern [6] for an equatorial carboxylic methyl ester with a strong band at 1245 cm^{-1} was clearly observed between 1030 and 1000 cm^{-1}. Analysis of the ^1H NMR spectrum showed a singlet δ 1.20 for an axial Me-4 on a carbon atom bearing an equatorial carboxyl group [7, 8]. The alcohol (**3**) prepared from the ester, **2**, exhibited hydroxyl group absorption in the IR at 3360, 1240 and 1050 cm^{-1} and the ^1H NMR spectrum exhibited an AB system (δ 3.2, $J = 11$ Hz) assigned to the new methylene formed in the reduction reaction.

The spectroscopic and chemical behaviour of the above substances including the acetate derivative (**4**), are very similar to those of bicyclic diterpenes possessing the labdane nucleus [9, 10] and related to polyalthic acid

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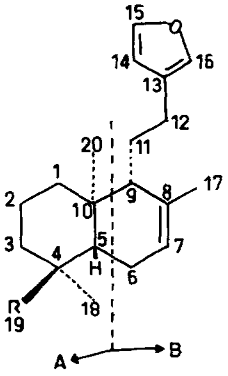

	R
1	COOH
2	COOMe
3	CH_2OH
4	CH_2OAc

[10–12]. Electron impact breakdown into ions A and B of **1**–**4** by a facile retro-Diels–Alder type reaction [13] located the trisubstituted double bond between C-7 and C-8 confirming the labdane skeleton of the acid, **1**.

Hydride reduction of the equatorial COOMe to CH_2–OH at C-4 was indicated by an upfield shift of $\Delta\delta$ *0.37 in the C-4-methyl resonance position. The chemical* shift values of the AB system of the methylene group formed in **3**, as well as the corresponding acetate derivative **4**, are very similar to those methylenes with equatorial stereochemistry [11, 14]. Finally, the negative rotations of these compounds suggest that the acid, **1**, and its derivatives have the same configuration about C-9 and C-10 as is found in polyalthic acid [9, 12].

EXPERIMENTAL

IR: film; ^{1}H NMR: 80 MHz, $CDCl_3$ with TMSi as int. reference; MS: 70 eV (probe); UV: EtOH; $[\alpha]_D$: $CHCl_3$ (conc. g/100 ml). TLC and CC separations were performed in Si gel 60-F 254 Merck.

Plant material. S. lucida Lag var Bipontini was collected 3 km S. of Sinaxtla (Oaxaca, Mexico) in July 1980 (MEXU-305281 on deposit in the Herbarium of the Instituto de Biología, U.N.A.M.).

Extraction and isolation of 5*β*,9*β*H,10*α*,-*labda*-7,13(16),14-*trien*-15,16-*epoxy*-19-*oic acid* (**1**). Dried leaves (300 g) were extracted with cold MeOH and the MeOH soln was concd to dryness. A suspension of the residue (70 g) in H_2O–MeOH (4:1) was extracted with $CHCl_3$. The $CHCl_3$ layer was evaporated to dryness and the residue (20 g) was chromatographed on Si gel. Elution with (C_6H_6-EtOAc, 17:3) gave **1** as an oil (150 mg 0.0075 % of dry plant wt). (Found: C, 76.40; H, 8.77; O, 14.96. $C_{20}H_{28}O_3$ requires: C, 75.95: H, 8.86; O, 15.18 %.) UV $\lambda^{CHCl_3}_{\max}$ 220 nm (ε 8300); $[\alpha]_D - 7.03°$ ($CHCl_3$; *c* 0.2132) IR $\nu^{\text{film}}_{\max}\,\text{cm}^{-1}$: 3300–2700, 1690, 1440, 1020, 870; ^{1}H NMR: δ 0.79 (3H, *s*), 1.20 (3H, *s*), 1.70 (3H, *br s*), 5.35 (1H *br s*), 6.22 (1H, *br s*), 7.17 (1H, *br s*) 7.30 (1H, *dd J* = 1.8 Hz); MS *m/z* (rel. int.): 316 $[M]^+$ (25), 234 (70), 133 (100).

Methylation of **1**. An excess of CH_2N_2 was added with stirring to a soln of **1** in Et_2O. After 1 hr the solvent was removed under red. pres. and by chromatographic separation **2** was isolated as a thick oil (70 mg, 67 %). UV $\lambda^{EtOH}_{\max}$ 215 nm (ε 4630); $[\alpha]_D - 36.97°$ (EtOH; *c* 0.119); IR $\nu^{\text{film}}_{\max}\,\text{cm}^{-1}$: 1725, 1245; ^{1}H NMR: δ 0.79 (3H, *s*), 1.2 (3H, *s*), 1.70 (3H, *br s*), 3.61 (3H, *s*), 5.35 (1H, *br s*), 6.25 (1H, *md*, *J* = 1.8 Hz), 7.2 (1H, *br* s), 7.33 (1H, *dd*, *J* = 1.8 Hz); MS *m/z* (rel. int.): 330 $[M]^+$ (10), 82 (100), 81.2 (73).

Methyl ester reduction. $LiAlH_4$ (100 mg) was added to a cold soln of **2** in dioxane. Work-up as usual yielded **3** as a thick oil (50 mg 91 %). $[\alpha]_D - 15.49°$ ($CHCl_3$; *c* 0.20); IR $\nu^{\text{film}}_{\max}\,\text{cm}^{-1}$: 3600–3200, 1240, 1460, 1380, 1050, 1025, 870, 750; ^{1}H NMR: δ 0.80 (3H, *s*), 0.83 (3H, *s*), 1.73 (3H, *s*), 3.05 and 3.36 (2H, AB, *J* = 11 Hz), 5.39 (1H, *br s*), 6.25 (1H, *br s*), 7.22 (1H, *br s*), 7.35 (1H, *br s*); MS *m/z* (rel. int.): 302 $[M]^+$ (6), 81.2 (100), 82.2 (61).

Acetate (**4**). A syrup was obtained when **3** was acetylated with isopropenylacetate *p*-toluene sulphonic acid (32 mg, 70 %); IR $\nu^{\text{film}}_{\max}\,\text{cm}^{-1}$: 1735, 1235; ^{1}H NMR: δ 0.79 (3H, *s*), 0.89 (3H, *s*), 1.71 (3H, *br s*), 2.03 (3H, *s*), 3.62 and 3.80 (2H, AB, *J* = 12 Hz), 5.39 (1H, *br s*), 6.25 (1H, *br s*), 7.2 (1H, *br s*), 7.30 (1H, *br s*); MS *m/z* (rel. int.): 344.4 $[M]^+$ (8), 82 (100), 81 (81).

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REFERENCES

1. Salmón, M., Díaz, E. and Ortega, A. (1973) *J. Org. Chem.* **38**, 1759.
2. Salmón, M., Ortega, A. and Díaz, E. (1975) *Rev. Latinoam. Quim.* **6**, 45.
3. Salmón, M., Díaz, E. and Ortega, A. (1977) *Rev. Latinoam. Quim.* **8**, 172.
4. Ortega, A., Martínez, R. and García, L. G. (1980) *Rev. Latinoam. Quim.* **11**, 45.
5. Kubota, T. (1958) *Tetrahedron* **4**, 68.
6. Bory, S. and Fétizon, M. (1964) *Bull. Soc. Chim. Fr.* 570.
7. Ayer, W. A., McDonald, C. E. and Stothers (1963) *Can. J. Chem.* **41**, 1113.
8. Ap Simon, J. W., Edwards, O. E. and Howe, R. (1962) *Can. J. Chem.* **40**, 630.
9. Dauben, W. G. and Herman, V. F. (1966) *Tetrahedron* **22**, 679.
10. Lombardi, R. and Haeuser, J. (1969) *C. R. Acad. Sci. Paris, Ser. C* **268**, 2234.
11. Henrick, C. A. and Jefferies, P. R. (1964) *Aust. J. Chem.* **17**, 915.
12. Gopinath, K. W., Govindachari, T. R., Parthansarathy, P. C. and Viswanathan, N. (1961) *Helv. Chim. Acta* **44**, 1040.
13. Enzell, C. R. and Ryhage, R. (1965) *Ark. Kemi* **23**, 367.
14. Gaudemer, A., Polonsky, J. and Wenkert (1964) *Bull. Soc. Chim. Fr.* 407.