

## LONGIPINENE DERIVATIVES FROM *LAVANDULA STOECHAS* SUBSP. *STOECHAS*

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**Key Word Index** — *Lavandula stoechas* L. subsp. *stoechas*; Labiatae; longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one; longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one 9-monoacetate.

**Abstract** — The aerial parts of *Lavandula stoechas* subsp. *stoechas* afforded two longipinene derivatives one of which is a new compound. The structures were elucidated by spectral methods and the compounds identified as longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one and longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one 9-monoacetate.

### INTRODUCTION

Recent literature has described the isolation and structure determination of some longipinene derivatives and their stereochemistries were discussed [1-3]. These compounds were found mainly in *Stevia* [4-7], *Critonia* [5], *Polypterus* [8] and *Artemisia* [1] species of the Compositae family. We have isolated two longipinene derivatives longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one and longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one 9-monoacetate, the latter being new, from *Lavandula stoechas* L. subsp. *stoechas*. This is the first isolation of longipinenes from a plant in Labiatae family.

### RESULTS AND DISCUSSION

Chloroform extracts of the aerial parts of *L. stoechas* subsp. *stoechas* afforded two longipinene derivatives, one was a known compound longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one (**1**) [2], the other was a new substance: longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one 9-monoacetate (**2**). The structures of both compounds were established by spectral methods.

The mass spectrum of compound **2** gave a molecular ion peak at *m/z* 292 ( $C_{17}H_{24}O_4$ ). Its IR spectrum showed ester bands at 1735, 1240  $\text{cm}^{-1}$ , enone bands at 1675, 1620  $\text{cm}^{-1}$  and hydroxyl absorption at 3460  $\text{cm}^{-1}$ . The

$^1\text{H}$  NMR spectrum of **2** indicated its structure. A signal at  $\delta$  5.78 (1H, *q*,  $J$  = 1.5 Hz, H-2) together with the methyl group signal at  $\delta$  2.03 (3H, *d*,  $J$  = 1.5 Hz,  $C_{15}$  Me) indicated the enone part of ring A. The doublets at  $\delta$  2.50 (1H, *d*,  $J$  = 6 Hz, H-4) and 3.18 (1H, *d*,  $J$  = 6 Hz, H-11), the broad singlet at 2.16 (1H, *br s*, H-5) together with methyl signals at 0.95 (3H, *s*,  $C_{12}$  Me), 0.96 (3H, *s*,  $C_{13}$  Me) and 1.05 (3H, *s*,  $C_{14}$  Me) and an acetyl signal at 2.14 (3H, *s*,  $OCOMe$ ) were in agreement to those of literature values. The signals at  $\delta$  3.95 (1H, *dd*,  $J$  = 10 Hz and 2 Hz, H-7) and 5.14 (1H, *d*,  $J$  = 5 Hz, H-9) after studying a Dreiding model and measuring the *J* values indicated the H $\alpha$ -7 and H $\beta$ -9 configurations.

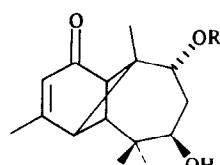
The spectroscopic data of the known compound **1** was similar to those of literature values [2].

### EXPERIMENTAL

*Lavandula stoechas* L. subsp. *stoechas* was collected from the Marmara region of Turkey in July 1986; it was identified by Dr K. Altipinar and a voucher specimen is deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul (ISTE 46352).

The  $\text{CHCl}_3$  extract of the dried and powdered aerial parts of plant material (200 g) yielded 20 g of a residue upon evapn *in vacuo*. The residue was separated by CC (silica gel) eluting with  $\text{CH}_2\text{Cl}_2$ , a gradient of EtOH was added up to 10%. The mixture of longipinenes were further separated by TLC plates (E. Merck) with  $\text{Et}_2\text{O}$ -petrol  $C_6\text{H}_6$  (1:1:1). Thus longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one (10 mg) and longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one 9-monoacetate (8 mg) were obtained.

*Longipin-2-ene-7 $\beta$ ,9 $\alpha$ -diol-1-one-9-monoacetate* (**2**). UV  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  nm: 215 (log  $\epsilon$  3.75). IR  $\nu_{\text{cm}^{-1}}$   $\text{cm}^{-1}$ : 3460, 2960, 2940, 2875, 1735, 1675, 1620, 1460, 1455, 1387, 1240, 1020, 840.  $^1\text{H}$  NMR given in the text. MS 70 eV (probe) *m/z* (rel. int.): 292 [ $M]^+$  ( $C_{17}H_{24}O_4$ ) (1.8), 264 [ $M - CO$ ]<sup>+</sup> (1), 232 [ $M - AcOH$ ]<sup>+</sup> (5), 189 [ $M - AcOH - Me - CO$ ]<sup>+</sup> (20), [ $C_4H_9CO$ ]<sup>+</sup> (40), 59 [ $AcO$ ]<sup>+</sup> (68), 57 [ $C_4H_9$ ]<sup>+</sup> (100), 55 [ $83 - CO$ ]<sup>+</sup> (96).



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#### REFERENCES

- Bohlmann, F., Ates, N., Jakupovic, J., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 2691.
- Roman, L. U., Del Rio, R. E., Hernandez, J. D., Cerdá, C. M., Cervantes, D., Castaneda, R. and Joseph-Nathan, P. (1985) *J. Org. Chem.* **50**, 3965.
- Joseph-Nathan, P., Cerdá, C. M., Del Rio, R. E., Roman, L. U. and Hernandez, J. D. (1986) *J. Nat. Prod.* **49**, 1053.
- Bohlmann, F., Zdero, C. and Schönweiss, S. (1976) *Chem. Ber.* **109**, 3366.
- Bohlmann, F., Suwita, A., Natu, A. A., Czerson, H. and Suwita, A. (1977) *Chem. Ber.* **110**, 3572.
- Bohlmann, F., Dutta, I. N., Dorner, W., King, R. M. and Robinson, H. (1979) *Phytochemistry* **18**, 673.
- Roman, L. U., Del Rio, R. E., Hernandez, J. D., Joseph-Nathan, P., Zabel, V. and Watson, W. H. (1981) *Tetrahedron* **37**, 2769.
- Bohlmann, F. and Zdero, C. (1975) *Chem. Ber.* **108**, 3543.

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## TERPENE ACIDS FROM *CEDRUS LIBANI*

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**Key Word Index**—*Cedrus libani*; Pinaceae; sesquiterpenes; terpenes.

**Abstract**—Structures are proposed for three new terpene acids, atlantonic acid, dihydroatlantonic acid and libanotic acid, isolated from the acidic fraction of the petrol extract of *Cedrus libani* wood. In addition, three resin acids, abietic acid, dehydroabietic acid and isodextropimaric acid were isolated from the same source.

#### INTRODUCTION

The terpenoids of two cedars (*Cedrus deodora* and *C. atlantica*) have been the subject of a number of investigations [1–6]. Recently, we reported [7] the isolation and structural elucidation of four terpenoids from the petrol extract of *C. libani* wood. In continuation of our work on this cedar species, we have isolated three new terpene acids, named atlantonic acid, dihydroatlantonic acid and libanotic acid and three resin acids, abietic acid, dehydroabietic acid and isodextropimaric acid. The structures of the terpene acids were established by UV, IR, <sup>1</sup>H NMR and mass spectroscopic studies.

#### RESULTS AND DISCUSSION

The petrol extract of *C. libani* wood was extracted with 10% NaHCO<sub>3</sub> soln. followed by 10% Na<sub>2</sub>CO<sub>3</sub> soln. to give two terpenic acid fractions. The acids were converted

to methyl esters with CH<sub>2</sub>N<sub>2</sub>. GC examinations showed that both acid fractions contained three components.

The methyl ester mixture of atlantonic acid (1), dihydroatlantonic acid (2) and libanotic acid (3) was separated by silica gel CC.

The UV spectrum ( $\lambda_{\text{max}}$  238 nm) and the IR spectrum (1690, 1685, 1650, 1610  $\text{cm}^{-1}$ ) of the methyl ester of atlantonic acid (1a) indicated the presence of the groups,  $-\text{C}=\text{C}-\text{CO}$  and  $-\text{C}=\text{C}-\text{COOR}$ . The <sup>1</sup>H NMR spectrum of 1a showed the presence of a isopropyl group ( $\delta$  0.91, *d*, 6H, *J* = 7 Hz), one methyl group linked to an olefinic carbon ( $\delta$  2.11, *s*, 3H), one methyl group linked to oxygen ( $\delta$  3.70, *s*, 3H, Me—OCO) and two olefinic protons ( $\delta$  6.02, *s*, 1H,  $\text{H}-\text{C}=\text{C}-\text{Me}$  and 6.96, *t*, 1H,  $-\text{CH}_2-\text{CH}=\text{C}-\text{COOR}$ ). The mass spectrum of the compound also supported this structure.

The characteristic peaks in the UV spectrum