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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, ^{1}H NMR and mass spectroscopic studies.

RESULTS AND DISCUSSION

The petrol extract of *C. libani* wood was extracted with 10% $NaHCO_3$ soln. followed by 10% Na_2CO_3 soln, to give two terpenic acid fractions. The acids were converted to methyl esters with CH_2N_2. 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 λ_{max} 238 nm) and the IR spectrum (1690, 1685, 1650, 1610 cm^{-1}) of the methyl ester of altantonic acid (**1a**) indicated the presence of the groups, $-\underset{|}{C}=\underset{|}{C}-CO$ and $-\underset{|}{C}=\underset{|}{C}-COOR$. The ^{1}H NMR spectrum of **1a** showed the presence of a isopropyl group (δ 0.91, *d*, 6H, $J = 7$ Hz), one methyl group linked to an olefinic carbon (δ 2.11, *s*, 3H), one methyl group linked to oxygen (δ 3.70, *s*, 3H, Me–OCO) and two olefinic protons (δ 6.02, *s* 1H, $\underline{H}-\underset{|}{C}=\underset{|}{C}-Me$ and 6.96, *t*, 1H, $-CH_2-\underline{CH}=\underset{|}{C}-COOR$). The mass spectrum of the compound also supported this structure.

The characteristic peaks in the UV spectrum

(λ_{max} 222 nm) and in the IR spectrum (1695, 1685, 1645 cm^{-1}) of dihydroatlantonic acid methyl ester (**2a**) indicated the presence of a carbonyl group and the group, $-\underset{|}{C}=\underset{|}{C}-COOR$. The ^1H NMR spectrum showed the presence of an isopropyl group (δ 0.91, *d*, 6H, J = 7Hz), one methyl group (δ 0.97, *d*, 3H), one methyl group linked to oxygen (δ 3.72, 3H, Me–OCO) and one olefinic proton (δ 6.98, *t*, 1H). The mass spectrum also supports this structure.

The UV spectrum (λ_{max} 225 nm) and the IR spectrum (1705, 1650 cm^{-1}) of libanotic acid methyl ester (**3a**) showed the presence of the group, $-\underset{|}{C}=\underset{|}{C}-COOR$. The ^1H NMR spectrum indicated the existence of a methyl group (δ 0.87, *d*, 3H), one methyl group linked to a carbonyl group (δ 2.04, *s*, 3H), one methyl group linked to oxygen (δ 3.65, *s*, 3H, Me–OCO) and one olefinic proton (6.48, *t*, 1H, ROOC–C=CHCH$_2$–). The mass spectrum of the compound also supported this structure.

The resin acids in the Na_2CO_3 fraction were converted to methyl esters with diazomethane and separated by prep GC. They were identified as abietic acid methyl ester, dehydro abietic acid methyl ester and isodextropimaric acid methyl ester by their physical ($[\alpha]_D$) and spectroscopic (UV, IR, ^1H NMR, MS) data and by comparison (TLC, GLC) with authentic samples.

EXPERIMENTAL

The ^1H NMR spectra were taken in $CDCl_3$ with TMS as int. reference. The cedar wood was supplied by K. Maras (Turkey).

Isolation and separation of **1a, 2a** and **3a**. Cedar wood (2 kg) which had been dried in shade, was extracted with petrol in a Soxlet apparatus (15 hr). The 103 g of oil which remained after evapn of the petrol, was extracted with aq.10% $NaHCO_3$ and then with aq. 10% Na_2CO_3. Both extracts were neutralized with 10% HCl soln and the free acids extracted with Et_2O. After evapn of the solvent, 0.5 g of acids was obtained from the $NaHCO_3$ fraction and 9.8 g of acids from the Na_2CO_3 fraction.

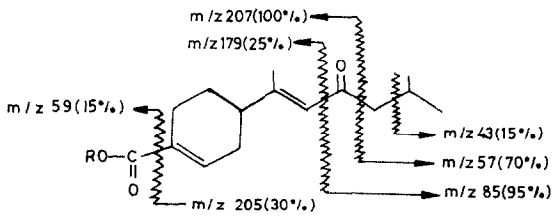
The 440 mg of terpene acids which remained in the $NaHCO_3$ fraction were converted to methyl esters using CH_2N_2 and separated on a silica gel column eluting with petrol–Me_2CO (5:1) to yield 102 mg **1a**, 88 mg **2a** and 52 mg **3a**. They were repurified by GC for spectroscopic investigations.

Atlantonic acid methyl ester (**1a**). Oily liquid, $[\alpha]_D^{25}$ 0.15 ($CHCl_3$, *c* 1.2), MS *m/z* (rel.int.): 264 $[M]^+$ (50), 207 (100), 180 (30), 164 (30), 147 (40), 95 (70), 85 (95), 57 (70) and 43 (15). (Observed *m/z* 264.1729, calcd for $C_{16}H_{24}O_3$, 264.1726).

Dihydroatlantonic acid methyl ester (**2a**). Oily liquid $[\alpha]_D^{25}$ 0.55 ($CHCl_3$, *c*. 1.2). MS *m/z* (rel.int): 266 $[M^+]^+$ (5), 234(25), 167 (20), 166 (20), 134 (100), 127 (15), 107 (15), 85 (15), 57 (25) and 43 (10). (Observed *m/z* 266.1884, calcd for $C_{16}H_{26}O_3$, 266.1882).

Libanotic acid methyl ester (**3a**). Oily liquid, $[\alpha]_D^{25}$ 0.6 ($CHCl_3$, *c*, 1.1). MS *m/z* (rel.int): 224 $[M]^+$(5), 192 (50), 166 (30), 165 (5), 139 (50), 134 (100), 107 (50), 85 (25), 79 (60), 59 (15) and 43 (95). (Observed *m/z* 224.1418, calcd for $C_{13}H_{20}O_3$ 224.1413).

Isolation and characterization of abietic acid methyl ester, dehydroabietic acid methyl ester and isodextropimaric acid methyl ester. The 1.2 g of resin acids present in the Na_2CO_3 fraction of the acidic part of *C. libani* wood were separated on a silica gel column (petrol–EtOAc, 5:1) to yield 398 mg of abietic acid fraction, 46 mg of dehydroabictic acid fraction and 320 mg of isodextropimaric acid fraction. They were converted to methyl esters using CH_2N_2 and purified by prep GC.



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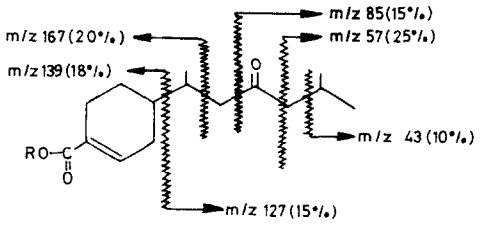
1a R = Me



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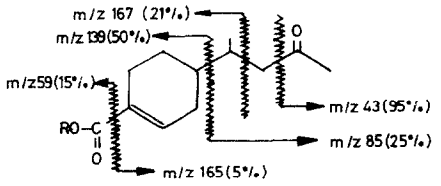

3 R = H

3a R = Me

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