Dihydropanaxacol (2). $[\alpha]_D^{22}$ +13.5° (MeOH, *c* 1.0), IR ν_{max} cm^{-1}: 3500 ~ 3300, 2910 (*s*), 2850 (m), 2220 (w), 1485 (w), 1450 (m), 1370 (m); UV λ_{max} nm (log ε): 230 (2.73), 242 (2.69) 255 (2.52); EIMS 70 eV, *m/z* (rel. int): 280 $[M]^+$ (2.5), 262 $[M-H_2O]^+$ (11.3), 233 $[M-C_2H_7O]^+$ (21.3), 159 $[M-C_8H_9O]^+$ (25.0), 104 $[M-C_9H_{20}O_3]^+$ (100).

Reduction of 1 *with* $NaBH_4$. An excess amount of $NaBH_4$ (4.0 equivalents) was added to a soln of 1 (74 mg) in MeOH (1.0 ml) with stirring at room temp. After 1 hr, a satd NaCl soln (10 ml) was added and the mixture extracted with EtOAc (20 ml × 3). The combined organic layer was washed with satd NaCl soln (10 ml), dried over Na_2SO_4 and concd under red. pressure to leave an oil which was purified by HPLC [Nucleosil 50-5 (Senshu), 8 × 300 mm, flow rate: 3.0 ml/min, hexane–EtOAc, 1:1] to give 2 (50 mg, R_t, 9 min). The ^{1}H NMR and GC/MS spectra of 2 were identical with those of the natural product.

Preparation of dihydropanaxacol acetonide (3). A mixture of 2 (3 mg) and a catalytic amount of camphor sulphonic acid in 2,2-dimethoxypropane (500 μl) was stirred for 30 min at room temp. After completion of the reaction, a satd $NaHCO_3$ soln (2 ml) was added and the mixture extracted with EtOAc (5 ml × 3). The combined organic layer was washed with satd NaCl soln (5 ml × 2), dried over Na_2SO_4 and concentrated *in vacuo* to give 3 mg of 3. ^{1}H NMR (400 MHz, $CDCl_3$ + D_2O): δ0.89 (3H, *t*, *J* = 7.1 Hz, H-17), 1.01 (3H, *t*, *J* = 7.3 Hz, H-1), 1.20–1.40 (10 H, *br*, *m*, $W_{1/2}$ = 25 Hz, H-12–H-16), 1.41 (6H, *s*, *gem*-dimethyl), 1.56 (2H, *m*, H-11), 2.58 and 2.62 (2H, *ABq*, *J* = 5.4, 16.9 Hz, H-8), 1.74 (2H, *m*, H-2), 3.73 (1H, *ddd*, *J* = 5.4, 5.4, 7.8 Hz, H-9), 3.81 (1H, *ddd*, *J* = 4.2, 7.8, 7.8 Hz, H-10), 4.37 (1H, *t*, *J* = 6.1 Hz, H-3); EIMS 70 eV, *m/z* (rel. int): 305 $[M-Me]^+$ (15.3), 245 $[M-C_3H_7O_2]^+$ (16.3), 199 $[M-C_8H_9O]^+$ (100).

Detection of n-*octyl alcohol from* 2. To a stirred mixture of 2 (10 mg), THF (300 μl), H_2O (300 μl) and $NaIO_4$ (74 mg) were added at room temp. After 20 min, a satd NaCl soln (10 ml) was added and the mixture extracted with EtOAc (20 ml × 3). The combined organic layer was dried over Na_2SO_4 and concd under red. pressure to give an oil. This oil was dissolved in MeOH (500 μl) and an excess $NaBH_4$ (5 mg) was added with stirring. After 20 min, a satd NaCl soln (10 ml) was added and the mixture extracted with EtOAc (20 ml × 3). The combined organic layer was dried over Na_2SO_4, and then concentrated under reduced pressure to leave an oil. *N*-Octyl alcohol was detected in the oil by GC/MS [column OV-1, 1.0 m × 3 mm, temp. programmed: 50–250° at 10°/min, injection temp. 200°: *m/z* (rel. int): 130 $[M]^+$ (3.0), 112 $[M-H_2O]^+$ (10.0), 84 $[M-C_2H_4O]^+$ (100).

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Phytochemistry, Vol. 26, No. 10, pp. 2852–2854, 1987.
Printed in Great Britain.
0031–9422/87 $3.00 + 0.00

FOUR TERPENOIDS FROM *CEDRUS LIBANOTICA*

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(*Revised received* 3 *February* 1986)

Key Word Index—*Cedrus libanotica*; Pinaceae; sesquiterpenes.

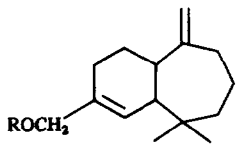
nAbstract—Structures are proposed for four new terpenoids, α-torosol, β-torosol, andirolactone and *trans*-atlanton-6-ol, isolated from the neutral fraction of the petroleum ether extract of *Cedrus libanotica* wood.

INTRODUCTION

Cedar (*Cedrus libanotica*), which is a needle-leaf tree, grows in southern Turkey and Lebanon. The tar, which is obtained from its wood, is used to cure various diseases [1]. Though several studies have been made on the other two cedars (*C. deodora* and *C. atlantica*) [2–7], a detailed chemical study has not yet been performed on *C. libanotica*. We now wish to report the isolation and structures of four new terpenoids, named α-torosol, β-torosol, andirolactone and *trans*-atlanton-6-ol, from the neutral fraction of the petroleum ether extract of *C. libanotica.*

RESULTS AND DISCUSSION

Two sesquiterpene alcohols, α-torosol (1) and β-torosol (2), were isolated as a mixture from a silica gel column and were separated using preparative thin layer chromato-



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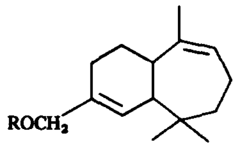
1a R = Ac
1b R = Ts



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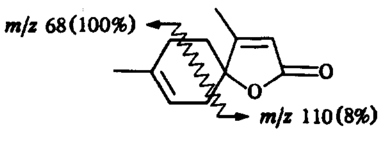

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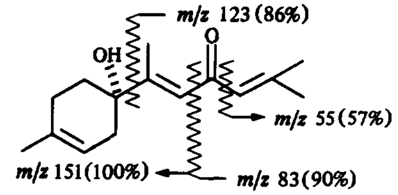

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graphy. Their structures were determined from IR, ^{1}H NMR and mass spectrometric analyses.

The wide peak at 3600–3250 cm^{-1} in the IR spectrum of α-torosol (**1**) suggested the existence of an hydroxy group. It formed a monoacetate (**1a**) with pyridine–acetic anhydride. The ^{1}H NMR spectrum of **1** showed the presence of two quarternary methyl groups (δ0.97, *s*, 3H and 1.02, *s*, 3H), two protons attached to a carbon linked to oxygen (δ3.92, *s*, 2H) and three olefinic protons (δ4.72, *br s*, 2H and 5.72, *s*, 1H). Since the double bond equivalent of the molecule was four, the molecula had two fused rings. The structure of α-torosol (**1**) was also proved by means of reduction with lithium aluminium hydride of its tosylate (**1b**) to α-himachalene [5].

The wide peak in the range of 3600–3250 cm^{-1} in the IR spectrum of β-torosol (**2**) indicated the existence of hydroxy group. It reacted with pyridine–acetic anhydride to form a monoacetate (**2a**). The ^{1}H NMR spectrum showed the presence of two quarternary methyl groups (δ1.00, *s*, 3H and 1.05, *s*, 3H), one methyl group linked to olefinic carbon (δ1.73, *s*, 3H), two protons attahced to a carbon linked to oxygen (δ4.03, *s*, 2H) and two olefinic protons (δ5.52, *m*, 1H and 5.88, *d*, 1H). The structure of β-torosol (**2**) was also proved by means of reduction with lithium aluminium hydride of its tosylate (**2b**) to γ-himachalene [8].

The isolated andirolactone was purified by prep. TLC. Spectroscopic investigations indicated that the structure of andirolactone should be **3**. The peaks which were observed at 1765, 1755 and 1650 cm^{-1} in the IR spectrum of **3** led to the conclusion that it was an α, β-unsaturated γ-lactone. Furthermore, the absorption observed in the UV spectrum (λ_{max} 225 nm) confirmed the presence of an α,β-unsaturated lactone structure. The ^{1}H NMR spectrum showed the existence of two methyl groups linked to olefinic carbons (δ1.73, *s*, 3H, $H_3C{-}\overset{|}{C}{=}\overset{|}{C}{-}$ and 2.02, *s*, 3H, $H_3C{-}\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}O$) and two olefinic protons (δ5.40, *m*, 1H and 5.74, *d*, 1H, *J* = 1.5 Hz, $H_3C{-}\overset{|}{C}{=}C\underline{H}{-}CO$). The mass spectrum also supports this structure.

trans-Atlanton-6-ol, after being isolated by means of silica gel column chromatography, was purified by prep. TLC. The spectroscopic studies indicated that, the structure of *trans*-atlanton-6-ol should be **4**. The absorptions in the UV spectrum (λ_{max} 246, 253, 297 and 308 nm) and in the IR spectrum (3600, 1670 and 1623 cm^{-1}) indicated the existence of the group, $-\overset{|}{C}=\overset{|}{C}-CO-\overset{|}{C}=\overset{|}{C}-$, and an hydroxy group. However, it did not react with pyridine–acetic anhydride. Moreover, the absence of any signal for a proton attached to a carbon linked to oxygen, in the ^{1}H NMR spectrum showed that the alcohol must be tertiary. The ^{1}H NMR spectrum of **4** showed the presence of four methyl groups linked to three olefinic carbons (δ1.72, *s*, 3H; 1.88, *s*, 3H and 2.13, *s*, 6H) and three olefinic protons (δ5.33, *m*, 1H; 6.13, *br s*, 1H and 6.48 *br s*, 1H). The mass spectrum of the compound also supported this structure.

EXPERIMENTAL

The ^{1}H NMR spectra were taken in CDCl$_3$ with TMS as int. reference. The cedar wood was supplied by K. Maras (Turkey).

The isolation and separation of **1**, **2**, **3** and **4**. Cedar wood (2 kg), 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 using 10% Na$_2$CO$_3$ soln. After this extraction, 93 g of the mixture of neutral terpenoid compounds remained. This mixture (28 g) was separated on a silica gel column, eluting with *n*-hexane–ether whose polarity was constantly increased from 99:1 to 50:50. The 34 fractions obtained were tested by TLC and GC. The fractions which were found to be impure were repurified by prep. TLC. α-Torosol (**1**) and β-torosol (**2**) were isolated together (483 mg) and the mixture was separated by prep. TLC with *n*-hexane-EtOAc (1:1) to yield 232 mg of **1** and 54 mg of **2**.

α-Torosol (**1**). $[\alpha]^{25}_{D}$ − 180.2° (CHCl$_3$; *c* 2.7). MS *m/z* (rel. int.): 220 [M]$^+$ (69), 205 (66), 202 (17), 189 (100), 187 (30), 159 (26), 135 (57), 91 (83) and 69 (91). (Observed *m/z* 220.1830, calculated for C$_{15}$H$_{24}$O, 220.1827). When 95 mg of **1** was tosylated with pyridine (2 ml) and TsCl (165 mg), 127 mg of **1b** was obtained.

Reduction of (**1b**) *to α-himachalene*. The mixture of 80 mg (**1b**) and 17 mg $LiAlH_4$ was stirred in dry Et_2O for 2 hr. Wet Et_2O was added to the mixture and it was acidified with 5% HCl. The Et_2O phase was washed with H_2O and after evaporation of Et_2O, 35 mg of α-himachalene [5] was obtained.

β-Torosol (**2**). $[\alpha]_D^{25}$ − 175° ($CHCl_3$; *c* 2.5). MS *m/z* (rel. int.): 220 $[M]^+$ (48), 205 (18), 189 (35), 161 (30), 133 (70), 91 (100) and 79 (70). (Observed *m/z* 220.1825, calc. for $C_{15}H_{24}O$, 220.1827). Compound **2** (87 mg) was tosylated as explained above and 114 mg **2b** was obtained.

Reduction of **2b** *to γ-himachalene.* As explained above, 81 mg of **2b** was reduced with $LiAlH_4$ and 21 mg of γ-himachalene [8] was obtained.

Andirolactone (**3**). After isolation from the silica gel column, **3** was purified by prep. TLC with $CHCl_3$–EtOAc (9:1) and 85 mg of pure **3** was obtained. $[\alpha]_D^{25}$ 3.2° ($CHCl_3$; *c* 2.1). MS *m/z* (rel. int.): 178 $[M]^+$ (48), 163 (10), 145 (8), 111 (46) and 68 (100). (Observed *m/z* 178.100, calc. for $C_{11}H_{14}O_2$, 178.099).

trans-*Atlanton-6-ol* (**4**). After isolation from the silica gel column, **4** was purified by prep. TLC with $CHCl_3$–Et_2O (8:2) and 79 mg of pure **4** was obtained. $[\alpha]_D^{25}$ 0.15° ($CHCl_3$; *c* 1.2). MS *m/z* (rel. int.): 234 $[M]^+$ (34), 216 (11), 151 (100), 123 (86), 83 (90), 55 (57) and 43 (70). (Observed *m/z* 234.1625, calculated for $C_{15}H_{22}O_2$, 234.1620).

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Phytochemistry, Vol. 26, No. 10, pp. 2854–2855, 1987.
Printed in Great Britain.

0031–9422/87 \$3.00 + 0.00
Pergamon Journals Ltd.

NEROLIDOL DERIVATIVES FROM *ASTERISCUS SERICEUS*

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(*Received* 20 *January* 1987)

Key Word Index—*Asteriscus sericeus*; Compositae; sesquiterpenes; nerolidol derivatives; asteriscunolide A–D.

Abstract—The aerial parts of *Asteriscus sericeus* afforded, as other species of this genus, the humulene derivatives asteriscunolide A–D and two new types of nerolidol derivative, their structures being elucidated by high field NMR techniques.

From the genus *Asteriscus* (Compositae, Inuleae, Inulinae) so far two of the three species have been studied chemically [1–3]. Typical constituents are humulene derivatives such as asteriscunolide A–D (**1**–**4**) [1–3]. The investigation of a further species, *A. sericeus* (L.f.) DC., afforded in addition to widespread compounds (see Experimental) also **1**–**4**. Furthermore two nerolidol derivatives (**5** and **6**) were present. Though in the mass spectra no molecular ions could be detected, the molecular formulae followed indirectly from the ^{13}C NMR spectra (Table 1) and the ^1H NMR spectral data (Table 2). The ^{13}C NMR signals of **5** indicated two olefinic double bonds, two oxygen bearing carbons and one carbonyl carbon which was replaced by a secondary hydroxyl in the case of **6** (71.4 *d*). Inspection of the ^1H NMR spectra clearly showed that a vinyl and a prenyl end group was present in both compounds. Furthermore, two singlets for tertiary methyls could be detected. The chemical shifts of the latter required methyl groups at oxygen bearing carbons. Thus the presence of nerolidol derivatives with a 3,7-ether linkage were likely. Spin decoupling in the case of **6** allowed the assignment of most signals and led to the sequences H-8 through H-12(13) and $-CH_2CH_2CH(OH)-$. The latter three carbons must be C-4 – C-6. The relative position of the oxygen function could be assigned by the observed NOE's between H-15, H-2 (2%), H-lt (2%) and H-4 (4%). The position of the keto group also followed from the observed McLafferty fragmentation in the mass spectrum of **5**. Similarly, the ketone **5** showed NOE's between H-15, H-2 (10%) and H-