Phytochemistry, Vol. 28, No. 11, pp. 3073–3080, 1989.
Printed in Great Britain.

0031-9422/89 \$3.00+0.00

CHARACTERIZATION OF LASIOCARPENONOL AND CONFORMATION OF FOUR SESQUITERPENOIDS FROM ALPINE FIR

JOHN F. MANVILLE, TAMARA FRASER and ALAN S. TRACEY*

Forestry Canada, Pacific Forestry Centre, 506 West Burnside Road, Victoria, British Columbia, Canada V8Z 1M5; *Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

(*Received* 16 *January* 1989)

Key Word Index—*Abies lasiocarpa*; Pinaceae; lasiocarpenone; lasiocarpenonol; *E* and *Z*-α-atlantones; ^{1}H and ^{13}C NMR; conformation.

Abstract—A new sesquiterpenoid alcohol, lasiocarpenonol, from the whole wood of *Abies lasiocarpa* has been isolated and characterized. Lasiocarpenone, lasiocarpenonol, *E*- and *Z*-α-atlantone were analysed by ^{1}H and ^{13}C NMR experiments, assignments made, and the results interpreted in terms of the conformational preferences exhibited by the molecules. Revision of the conformation of *Z*-α-atlantone which exhibits an unexpected conformation in which the C_8 side chain was found to be perpendicular to the plane of the cyclohexene ring. This conformation invokes a strong but localized effect between H-4 and the carbonyl oxygen resulting in a 1.62 ppm deshielding of H-4 and an 8.3 ppm shielding of C-4 in *Z*-α-atlantone. Similar conformations are not favoured by the other compounds.

INTRODUCTION

Z- and *E*-α-Atlantones (**1, 2**) [1–5], lasiocarpenone (**3**) [6], together with juvabione (**5**) and epijuvabione (**6**) type compounds [7–12] are significant lipophilic extractives of the whole wood of balsam fir [*Abies balsamea* (L.) Mill.] [7, 8], interior or Rocky Mountain type alpine fir (*A. bifolia* A. Murr.) [2, 6] and coastal type alpine fir [*A. lasiocarpa* (Hook.) Nutt.] [13]. Lasiocarpenone (**3**) is an Ehrlich-positive component of alpine fir wood extractives used to differentiate alpine fir solid-wood products from that of other west coast species [6]. A second Ehrlich-positive component, lasiocarpenonol (**4**), has now been isolated and characterized for the first time.

While extensive NMR spectroscopic investigations of the juvabione type sesqiterpenoids have been carried out [6–13], neither lasiocarpenone (**3**) [6] nor **1** and **2** [1–5] had been fully characterized by NMR spectroscopy. In order to characterize the newly isolated lasiocarpenonol (**4**) and to determine the conformational preferences of these molecules, ^{1}H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively.

RESULTS AND DISCUSSION

Details of similar isolations of hexane-soluble whole wood components have been described elsewhere [7–11]. The compounds of interest were given numerical assignments in accordance with their GC elution order on a non-polar bonded-phase capillary column, DB-1. Compound **4** was isolated in admixture with several juvabione-type sesquiterpenoid compounds by silica gel column chromatography and purified by alumina column chromatography. The assigned structure of **4** is based on similarities of its chromatographic behaviour with that of lasiocarpenone (**3**) and on its MS, IR, ^{1}H, and ^{13}C NMR spectra.

Compound **4** was observed to elute after **3** on silica gel and alumina TLC plates as well as by capillary GC on DB-1 and a polar Supelcowax-10 column; in accordance with the fact that **4** is more polar and of higher M_r than **3**. Compounds **4** and **3** are both Ehrlich positive, confirming a similar structural feature (furan ring) in both. In contrast with the published report of Fraser and Swan [6], these compounds were stable when kept away from acids or acid-washed glassware, but unstable when in prolonged contact with chloroform-d_1.

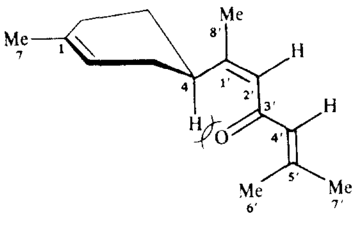
Ion-Trap® MS spectra of **3** and **4** exhibit a strong $[M+1]^+$ peak at m/z 233 and 249, respectively, consistent with a general formula, $[C_{15}H_{20}O_n+H]^+$, where $n=2$ or 3, respectively. Compound **4** had its base peak at m/z 123 which is indicative of a $[C_7H_7O_2]^+$ moiety formed by loss of the di-substituted furan, the C_8 side chain $[M-123]^+$ and two hydrogen atoms to form a stable dihydroxy tropyllium ion. Lasiocarpenone (**3**) gave a base peak of m/z 109 $[C_7H_9O]^+$ which is consistent with the loss of an identical, di-substituted furan, C_8 side chain (loss of m/z 123). The aromatization process observed in **4** was not apparent in **3**. Other major fragments from **4** were observed at m/z 107, 95, 79, 53, and 39.

The gas phase IR spectrum of **4** showed a hydroxyl band at 3510 cm^{-1} (3476 cm^{-1}, solid phase, KBr) and a strong carbonyl band at 1693 (1674 cm^{-1}, solid phase, KBr), cf. 1697 cm^{-1} for **3**.

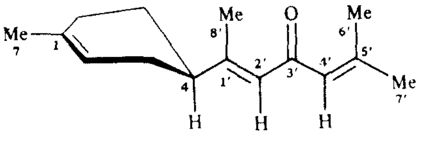
All these features support structural similarities between **4** and **3**; differences can be accounted for by the simple addition of a single oxygen atom to form a hydroxyl group. Many features of the ^{1}H NMR spectrum of **4** in $CDCl_3$ (Table 1) also support this deduction. Extensive homonuclear decoupling experiments were conducted to completely assign all ^{1}H resonances.* Protons attached to C-2 of both **3** and **4** were found at $\delta 6.74$, those attached to C-6′ at $\delta 7.03$, and those attached to C-4′ at $\delta 5.86 \pm 0.1$. The methyl groups bonded to C-1 were

---

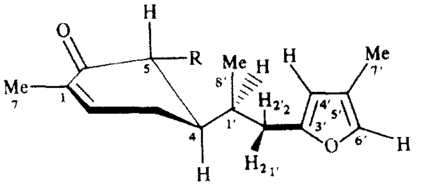
*Numbering of positions was made to conform with that used for the juvabiones [6–12].



1 (*Z*)



2 (*E*)



3 R = H
4 R = OH

found at $\delta 1.81$ and 1.72, bonded to C-1' at $\delta 0.98$ and 0.89, and to C-5' at $\delta 1.98 \pm 0.2$ for **3** (Table 2) and **4**, respectively. The two C-2' methylenic protons in **4** were observed to have coincidental chemical shifts in chloroform-d_1 and in benzene-d_6. This was unexpected as C-1' is a chiral centre and methylenic protons adjacent to chiral carbons are normally non-equivalent. These methylenic protons were observed to be non-degenerate in acetone-d_6 which allowed for the accurate measurement of geminal and vicinal coupling constants. The most notable difference between **4** and **3** was the observation in **4** of a doubleted doublet ($J = 13$ and 1.7 Hz) at $\delta 4.01$ and a doublet ($J = 1.7$ Hz) at $\delta 3.76$. These chemical shifts and coupling constants are consistent with a cyclohexenonol ring. A single proton resonance was observed at $\delta 4.01$ as a quartet prior to, and as a doublet after, the addition of D_2O. This data places the hydroxyl at C-5 and the observed H-5 to H-4 coupling constant of 13.0 Hz requires that H-5 be axial.

The occurrence of the hydroxyl group was further demonstrated by a ^{13}C NMR resonance at $\delta 74.3$ while the resonance at $\delta 201.4$ confirmed the presence of the carbonyl group (Table 2). All carbon assignments were made on the basis of a ^{13}C–^1H 2D carbon correlation experiment [14] and comparisons to related compounds [7–13].

The proposed conformation of **4** resulted from analysis of the appropriate ^1H coupling constants in a variety of solvents. The vicinal coupling of 3.0 ± 0.2 Hz between H-4 and H-1' indicates that they are *gauche* to each other with the angle between H-4 and H-1' greater than 90° but less than 120°. Couplings between H-1' and H-$2'_1$ or H-$2'_2$ totalled 15.5 Hz in all three solvents but due to obvious second order distortions they could not be determined individually in chloroform-d_1 or benzene-d_6. Furthermore, no significant changes in other couplings were found for any solvent which indicates no change in conformational preference with solvent. In acetone, first order vicinal H-1' to H-2' couplings of 8.0 and 7.5 Hz indicate that the projected angles between these adjacent protons are close to 120° (Fig. 1). This suggests a C-1'–C-2' rotamer with nearly eclipsed substituents. These observations indicate that the stereoconfiguration at C-1' is most likely *S*, since the *R* configuration would require C-3' and C-4 to be nearly eclipsed, clearly a less favourable structure.

This proposed structure for **4** is supported by a series of NOE experiments. Irradiating the methyl group attached to C-1', at $\delta 0.98$ ($CDCl_3$) or at $\delta 0.94$ [$(CD_3)_2CO$], showed: (i) no NOE on H-4, (ii) a strong NOE on H-5a, and (iii) a slightly smaller enhancement on H-3a. This places the 8'-methyl between H-5a and H-3a but slightly closer to H-5a. This is in agreement with a conformation in which H-4 and the 8'-methyl group are *trans* to each other. Manipulation of a CPK Precision Molecular Model of **4** also suggests that this is the favoured conformation. Moderately strong effects were noted ($CDCl_3$) for protons attached to C-1' and C-2'. As expected from the proposed structure, only one of the C-2' protons, as observed in acetone-d_6, showed a NOE enhancement when the 8'-methyl group was irradiated. The lower-field H-$2'_1$ proton at $\delta 2.52$ failed to show a NOE; it is therefore remote from the irradiated 8'-methyl. A moderate enhancement of intensity in H-4' on the furan ring and a very small intensity enhancement in H-6' indicates approach of the furan ring to the irradiated 8'-methyl group. Irradiation of H-4' at $\delta 5.83$ (C_6D_6) caused enhancements of 7'-methyl, H-1' and H-2'. A very small NOE was noted for the C-8' methyl group*. These data agree with the proposed rotamer conformation (Fig. 1) which allows for H-4' to approach the 8'-methyl group as a result of

---

*Irradiation of H-5a at $\delta 3.69$ (in C_6D_6) caused strong NOEs on the hydroxyl proton at $\delta 3.98$, the 8'-methyl group at $\delta 0.88$, and H-3a. In addition a notable but atypical effect on the signal from H-4 was observed. In this instance the low-field portion of the multiplet was positively enhanced, the central portion was not enhanced, and the high-field portion was negatively enhanced. The net effect, on H-4, was zero.

Table 1. Proton chemical shifts and interproton coupling constants measured for compound **4**

	Chemical shift (δ)			Coupling constant (Hz)												
H*	$CDCl_3$	C_6D_6	$(CD_3)_2CO$	3e	3a	4	5a	7	1′	$2'_1$	$2'_2$	4′	6′	7′	8′	OH
2	6.74	5.97	6.82	5.7	2.5	*s*	—	1.38	—	—	—	—	—	—	—	—
3_e	2.31	1.72	2.37		18.5	5.5	—	1.4	—	—	—	—	—	—	—	—
3_a	2.23	1.61	2.27			10.5	—	2.5	—	—	—	—	—	—	—	—
4	2.03	1.99	1.95				13.0	—	3.0	—	—	—	—	—	—	—
5_a	4.01	3.69	4.01					—	—	—	—	—	—	—	—	1.7
7	1.81	1.70	1.73						—	—	—	—	—	—	—	—
1′	2.47	2.67	2.45							8.0†	7.5†	—	—	—	6.7	—
$2'_1$	2.54	2.42	2.58								14.3†	0.6†	—	—	—	—
$2'_2$			2.52									0.75†	—	—	—	—
4′	5.87	5.82	5.93										1.2	*s*	—	—
6′	7.03	6.98	7.10											1.2	—	—
7′	1.96	1.83	1.92												—	—
8′	0.98	0.88	0.94													—
OH	3.76	3.98	4.01													

* For numbering see **4**.

† Coupling constants are from $(CD_3)_2CO$, the only solvent in which the signals from H-$2'_1$ and H-$2'_2$ were not degenerate.

s = small coupling.

Table 2. Proton shifts and interproton coupling constants measured for compound **3**

		Coupling constant (Hz)												
H*	δ	3_e	3_a	4	5_e	5_a	7	1′	$2'_1$	$2'_2$	4′	6′	7′	8′
2	6.74	6.2	2.4	—	—	—	1.2	—	—	—	—	—	—	—
3_e	2.29		18.0	4.4	1.6	*s*	1.2	—	—	—	—	—	—	—
3_a	2.07			10.8	—	—	2.5	—	—	—	—	—	—	—
4	1.98				3.5	13.6	—	5.2	*s*	—	—	—	—	—
5_e	2.46					15.8	*s*	—	—	—	—	—	—	—
5_a	2.17						—	—	*s*	—	—	—	—	—
7	1.72							—	—	—	—	—	—	—
1′	1.75								5.7	8.3	—	—	—	6.9
$2'_1$	2.63									15.0	0.8	—	—	—
$2'_2$	2.38										0.8	—	—	—
4′	5.85											1.0	0.4	—
6′	7.03												1.2	—
7′	2.00													—
8′	0.89													

*For numbering see **3**.
s = small coupling.

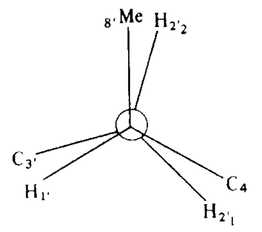


Fig. 1.

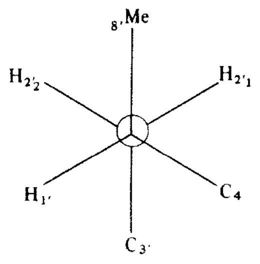


Fig. 2.

essentially free rotation about the C-2′–C-3′ bond as implied from this NOE experiment. Close approach of H-4′ is not possible in the other rotamer (staggered) (Fig. 2) obtained by a *ca* 60° rotation about the C-1′–C-2′ bond. The staggered arrangement would result in a less favoured conformation with the furan ring at approximately right angles to the plane of the six-membered ring.

Assuming that the configuration of the cyclohexene ring of **4** is as indicated and the same as previously noted for the juvabione (**5**) and epijuvabione (**6**) series of compounds [6–12]; the stereo configuration at C-4 would be *R*. With the configuration at C-4 fixed, the confirmation of the assignment of the *S* configuration to C-1′ was made following a series of NOEs on **4** in benzene-d_6. First, the C-2′ methylenic protons at δ2.42 were irradiated and NOE effects noted, in order of magnitude, on H-4, H-3e, H-4′ and the C-1′ methyl (8′). Second, the C-1′ methine proton was irradiated, resulting in NOE enhancements on H-4, H-4′ and a small effect on H-5. These results place the C-2′ methylenic protons in close proximity to H-3e and the C-1′ methine proton (H-1′) remote from H-3e. The configuration about C-1′ is therefore *S*, the configuration previously reported for the epijuvabione series of compounds (**6**) [7–11]. The configuration at C-5 is *R*.

The isolations of lasiocarpenone (**3**), *E*-(**2**) and *Z*-α-atlantones (**1**) afforded us the opportunity to confirm previous structural assignments and to determine respective conformational preferences. A preliminary assignment of proton signal positions and of interproton coupling constants of **3** was obtained by extensive use of homonuclear decoupling experiments, at 400 MHz, while selective off-resonance heteronuclear decoupling experiments provided the carbon chemical shift assignments of **3**. The results of these experiments were confirmed by a carbon correlation study. Tables 2 and 3 list the proton and carbon chemical shifts and the interproton coupling constants obtained for **3** in $CDCl_3$. The couplings from H-4 to H-3a and H-5a are of particular interest. Their respective magnitudes of 10.8 and 13.6 Hz requires that H-4 occupies an axial position in the predominant conformation. Therefore C-4 is out of the plane of the molecule since C-1, C-2, C-3, C-5 and C-6 are essentially co-planar because of the α,β-unsaturated cyclohexenone structure. The H-4 to H-3e and H-5e coupling constants of 4.4 and 3.5 Hz are fully consistent with this half-chair conformation. Further support for this assignment was gleaned from the observed long-range coupling of 1.6 Hz between H-3e and H-5e which is of a magnitude typical for 1,3-diequatorial protons [15].

Provided that one assumes that the stereo-configurations of **3** at C-4 and C-1′ are *R* and *S*, respectively, the same as those found in **4**, a preferred conformation for the C_8 side chain is also indicated by the observed interproton coupling constants. H-4 and H-1′ are *gauche* as indicated by their coupling of 5.2 Hz. Observed coupling constants between H-1′ and $H\text{-}2'_1$ or $H\text{-}2'_2$ are 5.7 and

Table 3. ^{13}C chemical shifts (δ in CDCl$_3$) measured for compounds **1–4** isolated from *A. lasiocarpa*

Compound	C*													
	1	2	3	4	5	6	7	1′	2′	3′	4′	5′	6′	7′	8′
Z-α-Atlantone (**1**)	133.6	120.4	29.3^{a}	36.0	27.4	30.2^{a}	23.3	161.4	126.2	191.0	126.6	153.8	20.4	27.5	20.5
E-α-Atlantone (**2**)	133.7	120.0	30.2	44.3	27.4	30.3	23.3	161.3	124.2	191.9	126.4	153.5	20.4	27.6	17.3
difference	−0.1	0.4	−0.9	−8.3	0.0	−0.1	0.0	0.1	2.0	−0.9	0.2	0.5	0.0	−0.1	3.2
Lasiocarpenone (**3**)	120.4	137.5	28.5	39.6	42.4	199.9	15.3	36.4	32.4	154.4	109.0	135.4	144.6	9.5	16.0
Lasiocarpenonol (**4**)	120.4	137.5	24.6	45.6	74.3	201.4	15.2	31.4	32.8	154.6	108.8	132.8	145.7	9.7	13.9
difference	0.0	0.0	3.9	−6.0	−31.9	−0.5	0.1	5.0	−0.4	−0.2	0.2	2.6	−1.1	−0.2	2.1

*For numbering see **1–4**.

^{a} Assignments may be interchanged.

8.3 Hz respectively. This indicates that the time averaged preferred orientation and overall conformation of **3** are similar to that determined for **4**, *vida supra.*

The NOE experiment in which the 8′-methyl group was irradiated caused effects on H-1′, H-2′$_2$, H-5a and H-3a. Small NOE enhancements were again observed for the H-4′ and H-6′ protons of the furan ring, indicating the close approach of the furan ring to this 8′-methyl group. In addition, effects of varying intensity were observed on H-3e and H-4. These observations indicate a conformationally more mobile structure for **3** than that observed for **4**.

Both *Z*-(**1**) and *E*-α-atlantone (**2**) in CDCl$_3$ gave NMR spectra which were not completely resolved at 400 MHz. Homonuclear proton decoupling enabled the assignment of most peak positions to be made (Table 4); some coupling constants, however, could not be obtained, in particular for **2**.

The proton coupling constants between analogous positions of the six-membered rings of the two atlantones are not significantly different (Table 4). In both cases, the proton at position 4 is in an axial environment as are H-3a, H-5a and H-6a. This assignment was derived from the large vicinal interproton couplings (from 10.2 to 12.1 Hz, dependent on position). Such values are those expected from a twist conformation for a mono-unsaturated six-membered ring.

The most notable feature of the proton spectrum of **1** was the observation of a complex multiplet at δ3.76. Pande *et al.* [3] had made no mention of this isolated resonance in their report on the structures and NMR spectra of the atlantones. In contrast, Plattier and Teisseire [4, 5] had noted and correctly assigned this resonance to H-4 but incorrectly placed this proton in an equatorial position. They invoked the conformational inversion in order to place H-4 equatorially in what they calculated as the deshielding region of the carbonyl group at C-3′. This invoked conformation would necessarily place C-4 in the same deshielding field, not observed (Table 2). However, since these researchers did not determine either the ^{13}C shift of C-4 nor the magnitude of the interproton couplings between H-4 and adjacent protons (Table 4) they postulated and reported an incorrect conformation for **1**.

We also have assigned this low field, axial, ring proton at δ3.76 to H-4 following extensive homonuclear decoupling experiments. Corresponding resonances for H-4 in **2–4** occur at more normal values of about δ2.14, 1.98 and 2.03, respectively. By observing the differential chemical shifts of respective protons (Table 4) between the two α-atlantone isomers, it is apparent which proton(s) and carbon(s) are most affected and so determine the preferred orientation of the side chain. According to CPK molecular models, the carbonyl group of the side chain does not closely approach any of the ring protons in **2**, but in **1** it does to H-4, H-3, and H-5. Protons H-3 and H-5 do not exhibit abnormal differential chemical shifts, which indicate the lack of significant interaction between the carbonyl group of **1** and these protons. In contrast, the previously noted large downfield shift for H-4 of **1** must result from a strong intramolecular interaction of H-4 with the α,β; α′,β′ unsaturated carbonyl group. An alternate side chain conformation, the result of rotation by 180° about C-2′–C-3′, necessary to maintain conjugation, is not possible. This is because the 8′-methyl group is buttressed between H-3a and H-5a and the

Table 4. Proton chemical shifts and interproton coupling constants measured for compounds **1** and **2**

	E-α-Atlantone†	*Z*-α-Atlantone	Coupling constants (Hz) of *Z*-α-atlantone												
H*	δ	δ	3_e	3_a	4	5_e	5_a	6_e	6_a	7	2′	4′	6′	7′	8′
2	5.38	5.38	4.8	2.2	0.7	—	—	n	n	n	—	—	—	—	—
3e	1.92	1.96‡		n	6.0	n	—	—	—	n	—	—	—		—
3a	1.92	1.92‡			10.2	—	—	—	—	n	—	—	—	—	—
4	2.14	3.76				3.1	12.0	—	—	—	0.5	—	—	—	—
5e	1.76	1.64					12.0	n	n	—	—	—	—	—	—
5a	1.53	1.57						5.4	12.0	—	—	—	—	—	—
6e	2.18	2.10							n	1.2	—	—	—	—	—
6a	1.95	1.90‡								1.2	—	—	—	—	—
7	1.63	1.61									—	—	—	—	—
2′	6.03	5.97										—	—	—	1.3
4′	6.05	6.02											1.2	1.2	—
6′	2.14	2.13												*s*	—
7′	1.86	1.85													—
8′	2.13	1.78													

*For numbering see 1 and 2.

†Coupling constants (Hz) obtained for *E*-α-atlantone are: $J_{4,2'}=1.0$; $J_{4,5a}=12.1$; $J_{4,5e}=2.7$; $J_{5e,5a}=12.8$; $J_{5e,6e}=5.2$; $J_{5e,6a}=4.8$; $J_{5a,6a}=11.5$; $J_{5a,6e}=5.7$; $J_{2',8'}=1.2$; $J_{4',6'}=1.2$; $J_{4',7'}=1.2$; $J_{6',7'}=$small.

‡Assignments of resonance position is tentative.

s = small coupling.

n = coupling should be present but is not measurable because of signal overlap.

potential steric interactions between H-4 and H-4′ do not allow this alternative conformation to be attained. This molecule thus adopts a conformation in which C_8 side chain is oriented perpendicular to the plane of the cyclohexene ring, forcing the carbonyl oxygen into close proximity with H-4 as demonstrated by the 1.62 ppm deshielding of H-4.

Further support for this proposed conformation and resultant localized interaction in **1** between H-4 and the carbonyl oxygen, but not in **2**, was provided from their respective ^{13}C NMR spectra. Carbon assignments for **2** were made from a carbon correlation experiment and are listed in Table 3. The carbon shifts of compound **1** were assigned by analogy with those of **2**. The C-4 in **1** exhibited a chemical shift of $\delta 36.0$, a value $\delta 8.3$ to higher field than that observed for C-4 of **2**. The magnitude of this up-field shift is indicative of a rigid structure resulting in a strong intramolecular interaction between H-4 and the carbonyl oxygen of *Z*-α-atlantone (**1**) [16–18]. The cause of the noted deshielding of H-4, which is ascribed to a combination of the effect of the C=O anisotropy and, or, a sterically induced decrease in the electron cloud about H-4, would also result in the observed NMR shielding of C-4 caused by a concomitant increase in electron density about C-4. Increased electron density about C-4 could be stabilized by the α,β; α',β' unsaturated carbonyl group attached to C-4. In contrast, the corresponding shifts of C-3 and C-5 in **1** and **2** (Table 3) are within 1 ppm. These observations support a localized C=O anisotropy and, or, steric interaction in **1** centred on H-4.

EXPERIMENTAL

Isolations. The compounds used for this study were isolated from the whole woodof alpine fir [*Abies lasiocarpa* (Hook.)Nutt.] of Vancouver Island using methods described elsewhere [7–11].

General. ^1H and ^{13}C NMR spectra were determined, unless otherwise indicated, on samples dissolved in $CDCl_3$ ($\delta^1H = 7.26$ ppm and $\delta^{13}C = 76.88$ ppm) in 5 mm tubes at ambient temp. (21°). NOE difference and ^{13}C–^1H two dimensional correlation spectra were obtained using standard techniques [14]. Samples for proton spectra, *ca* 0.3 mg, were about a factor of 20 more dilute than those for the carbon spectra. Low resolution MS were determined on a Finnigan GC/MS at the Institute of Ocean Sciences, Sidney, B.C., and on a Finnigan mass spectrometric detector (Ion-trap®). Gas phase (200°) GC-FTIR analyses were conducted on a Nicolet 20 SXB spectrometer using a 30 m × 0.32 mm i.d. DB-5 fused silica capillary column. GC analyses were performed using a flame ionization detector (FID) and the Ion-trap. Columns used were 30 m × 0.25 mm (i.d.) DB-1 fused silica. The column oven was programmed as follows: 200° (1 min), 10° per min to 275° (15 min). The split/splitless injector was maintained at 250°; the injector used for the Ion-trap detector was a J&W cool on-column system. The FID was kept at 295°. The carrier gas was maintained at 150 psig at the split/splitless injector port and at 11 psig in the cool on-column injection port. Butane gas had a linear velocity of 22 cm/sec under these conditions. TLC was performed on silica gel using hexane–Et_2O (3:1) as developer or alumina plates using C_6H_6–EtOH (1%). Detection was facilitated with Ehrlich reagent or with H_2SO_4 and heat. Extractions and separations were similar to those reported earlier [7, 11], except for the purification of **4** which was accomplished by Al_2O_3 CC using 1% EtOH in C_6H_6.

Z-α-Atlantone (**1**), GC R_t 7.4 min. Identification made on the basis of its ^{13}C and ^1H NMR (Tables 3 and 4), MS and published information [2–5], noted ^1H NMR discrepancies are discussed above. IR ν cm^{-1}: 3014, 2973 (*m*), 2925 (*m*), 2871, 2850, 1677, 1627 (vs), 1451, 1381, 1220, 1209, 1145, 1111, 1045, 1010, 865, 761, 729, and 640.

E-α-Atlantone (**2**), GC R_t 7.9 min. Identification made on the basis of ^{13}C and ^1H NMR (Tables 3 and 4), mass spectra and published information [1–5]. IR ν cm^{-1}: 3014, 2974, 2924 (*m*), 2869, 1679 (*m*), 1628 (vs), 1450, 1386, 1354, 1212, 1151, 1104, 1053, 871, 799, and 641.

2-*Methyl*-5(R)-[1(S)-*methyl*-2-(4-*methyl*-2-*furanyl*)*ethyl*]-2-*cyclohexen*-1-*one* (*lasiocarpenone*) (**3**), GC R_t 8.3 min. Identification made on the basis of its ^1H and ^{13}C NMR (Tables 2 and 3), mass spectra and published information [6]. MS *m/z* (rel. int.): 232 (3), 149 (11), 136 (36), 123 (30), 109 (82), 95 (100), 81 (15), 79 (20), 77 (50), 65 (18), 55 (18), 53 (22) and 41 (62). Ion-trap: 245 (7) (?), 234 (13) (M + 2), 233 (100) (M + 1), 232 (18) (M), 215 (5), 137 (5), 136 (37), 135 (7), 124 (9), 123 (29), 122 (7), 121 (6), 110 (9), 109 (64), 97 (10), 96 (10), 95 (42), 67 (11), 65 (6), 53 (13), 43 (7), 41 (26), 39 (49). IR ν cm^{-1}: 3021, 2971 (*m*), 2939 (*m*), 2893 (*m*), 2843, 1697 (vs), 1549, 1478, 1459, 1447, 1367, 1247, 1230, 1123, 1105, 1084, 941, 795, 741, and 643.

2-*Methyl*-5(R)-[1(S)-*methyl*-2-(4-*methyl*-2-*furanyl*)-*ethyl*]-2-*cyclohexen*-6(R)-*ol*-1-*one* (*lasiocarpenonol*) (**4**), GC R_t 8.8 min. ^1H and ^{13}C NMR data are listed in Tables 1 and 3. MS *m/z* (rel. int.): no parent ion observed 135 (12), 124 (29), 123 (100), 122 (32), 109 (15), 107 (38), 96 (15), 95 (55), 79 (8), 77 (15), 67 (10), 65 (5), 55 (5), 41 (7). Ion-trap *m/z* (rel. int.): 249 (26) [M + 1], 248 (5) (M), 231 (5) [(M + 1) − H_2O], 135 (8), 126 (5), 125 (12), 124 (47), 123 (100), 122 (12), 109 (14), 108 (5), 107 (29), 96 (6), 95 (32), 79 (4), 67 (13), 65 (6), 55 (4), 54 (5), 53 (8), 43 (21), 41 (30), 39 (47). IR ν cm^{-1}: 3510 (w) −OH, 2970 (*m*), 2939 (*m*), 2903, 2845, 1693 (vs) C=O, 1548, 1464, 1439, 1384, 1468, 1351, 1329, 1244, 1211, 1181, 1169, 1142, 1125 (*m*), 1095, 1031, 988, 944, 929, 902, 876, 853, 800, 783, 769, 750, 737, 705, 680, 667, and 650.

Acknowledgements—Thanks are gratefully extended by AST to the Natural Sciences and Engineering Research Council of Canada for its financial support of this work. We also wish to thank Dr. W. Cretney for making available the Finnigan Mass Spectrometer at the Institute of Ocean Sciences, Sidney, B.C.

REFERENCES

1. Crawford, R. J., Erman, W. F. and Broaddus, C. D. (1972) *J. Am. Chem. Soc.* **94**, 4298.
2. Fraser, H. S. and Swan, E. P. (1973) *Can. For. Ser. Bi-Mon. Res. Notes* **29**, 13.
3. Pande, B. S., Krishnappa, S., Bisarya, S. C. and Dev, S. (1971) *Tetrahedron* **27**, 841.
4. Plattier, M. and Teisseire, P. (1972) *An. Acad. Bras. Cienc.* **44**, 392.
5. Plattier, M. and Teisseire, P. (1974) *Recherches* **19**, 153.
6. Fraser, H. S. and Swan, E. P. (1975) *Can. For. Ser. Bi-Mon. Res. Notes* **31**, 3.
7. Manville, J. F. (1975) *Can. J. Chem.* **53**, 1579.
8. Manville, J. F. (1976) *Can. J. Chem.* **54**, 2365.
9. Manville, J. F., Bock, K. and von Rudloff, E. (1977) *Phytochemistry* **16**, 1967.
10. Manville, J. F., Greguss, L., Slama, K. and von Rudloff, E. (1977) *Coll. Czech. Chem. Commun.* **42**, 3658.
11. Manville, J. F. and Kriz, C. D. (1977) *Can. J. Chem.* **55**, 2547.

12. Manville, J. F. and Bock, K. (1977) *Org. Magn. Reson.* **9**, 596.
13. Manville, J. F. and Tracey, A. S. (1989) *Phytochemistry* **28**, 2681.
14. Ernst, R. R., Bodenhausen, G. and Wokaun, A. (1987) *Principles of Nuclear Magnetic Resonance in One and Two Dimensions.* Oxford University Press, New York.
15. Sternhell, S. (1964) *Rev. Pure Appl. Chem.* **14**, 15.
16. Grant, D. M. and Cheney, V. B. (1967) *J. Am. Chem. Soc.* **89**, 5315.
17. Grant, D. M. and Cheney, V. B. (1967) *J. Am. Chem. Soc.* **89**, 6612.
18. Eggert, H. and Djerassi, C. (1973) *J. Org. Chem.* **38**, 3788.