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SHORT COMMUNICATION

4,4-DIMETHYL-2-CYCLOHEPTEN-1-ONE IN THE CORTICAL OLEORESIN OF *ABIES BALSAMEA*

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In the course of our investigations of the volatile components from the oleoresins of Pinaceae, we encountered among the oxygenated monoterpenoids from *Abies balsamea* (L.) Mill. cortex a component which could not be related to any known compound by the GLC data. Isolation of this material by preparative GLC gave a colorless liquid with a strong odor. The compound exhibited a strong absorption at 1685 cm^{-1} in the IR suggestive of an unsaturated aldehyde or ketone. In the UV it absorbed at 228 nm (EtOH), indicating a monosubstituted double bond (calculated value: 227 nm). The IR peaks at 3075–3095 cm^{-1} and at 885–895 cm^{-1} characteristic of $R_2C{=}CH_2$ group were absent, suggesting the β substitution of the double bond. The presence of a geminal dimethyl group was indicated by the IR doublet at 1370 and 1385 cm^{-1}.

The NMR spectra were obtained at 60, 100 and 220 MHz. A barely resolved doublet corresponding in terms of its position and relative area to two methyl groups was present at δ 0·97–1·00 ppm from TMS, in good agreement with IR information. As the J for an isopropyl group is usually around 5 cps, and as the distance between the two methyl peaks was dependent upon the field strength used (14·09, 23·50, or 51·7 kG) the separation of the two methyl groups is associated with slight magnetic nonequivalence rather than with spin–spin coupling and is suggestive of their attachment to a quarternary carbon atom. At the low magnetic field area, two doublets were encountered, at δ H_a 6·05 and δ H_b 6·95 ppm, arising from protons of a *cis*-disubstituted double bond (J_{ab} 10·5 cps). Since neither doublet showed any additional splitting, a quarternary carbon atom, presumably the one carrying two methyl groups, was indicated in a position α to the double bond. The remaining NMR absorption peaks were in positions expected for methylene groups (δ 1·6–3·0 ppm), but otherwise contributed no further information.

Low and high resolution mass spectra of the compound showed a fragmentation pattern characteristic of cyclic α,β-unsaturated ketones. The molecular ion was identified as m/e 138 ($C_9H_{14}O$), and prominent peaks were observed at m/e 123 (M-15) and m/e 96 (base peak, M-42) positions. The M-15 fragment is due to a methyl group loss and occurs in most monoterpenes. The intense M-42 peaks are prevalent in the spectra of many alkyl or aryl substituted cyclohexenones,[1] and arise from the elimination of ketene from the molecule.

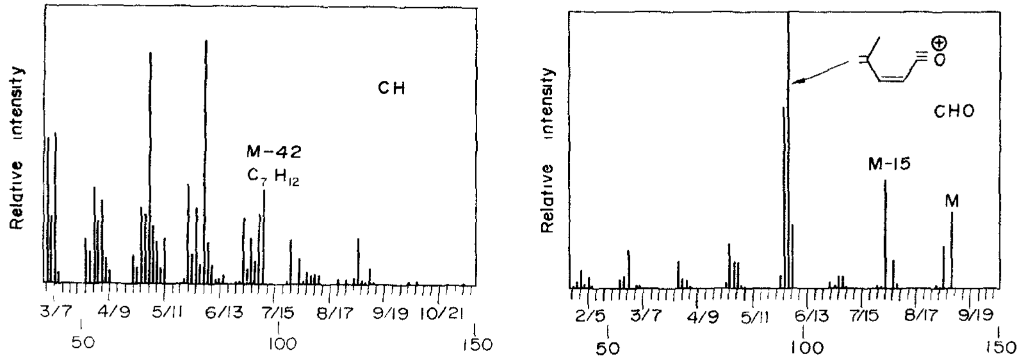

FIG. 1. C/H AND C/HO PLOTS OF HIGH RESOLUTION MASS SPECTRAL DATA.

The examination of the base peak at high resolution (Fig. 1) revealed that it consists of approximately 10% C_7H_{12} and 90% C_6H_8O fragment ions. Thus ketene elimination took place affording the C_7H_{12} fragment while the formation of the strong C_6H_8O ion (accidentally also a M-42 fragment) should be attributed to a retro-Diels-Alder type of reaction which is characteristic in a large number of cyclic ketones.[2] Combining the foregoing proton NMR and MS data, the evidence points to the presence of a seven-numbered ring system in the molecule.

The steric conformation of the isolated unknown follows unequivocally from the ^{13}C NMR data (Table 1). Figure 2 shows the noise decoupled ^{13}C spectrum consisting of 9

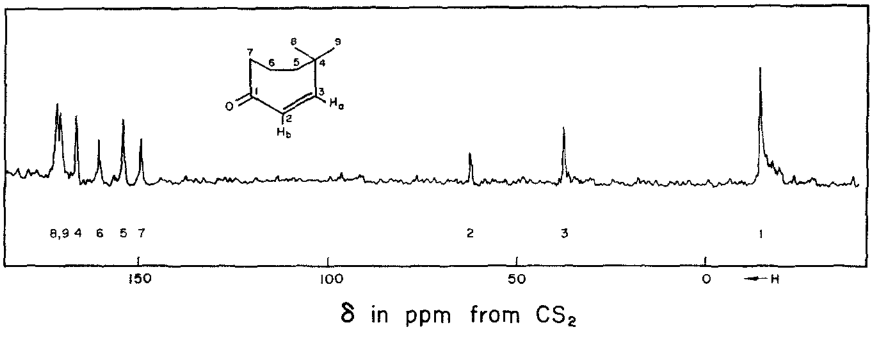

FIG. 2. NOISE DECOUPLED ^{13}C NMR SPECTRUM.

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[1] H. BUDZIKIEWICZ, C. DJERASSI and D. H. WILLIAMS, *Mass Spectrometry of Organic Compounds*, pp. 151–55, Holden-Day, San Francisco (1967); A. L. BURLINGAME, C. FENSELAU, W. J. RICHTER, W. G. DAUBEN, G. W. SHAFFER and N. D. VIETMEYER, *J. Am. Chem. Soc.* **89**, 3346 (1967).

[2] J. H. BOWIE, *Austral. J. Chem.* **19**, 1619 (1966).

resonance peaks over a span of 200 ppm. All carbon resonances were resolved from one another showing the presence of 9 carbon atoms in the molecule. Carbon-1, C-2 and C-3 were identified by their chemical shifts, which are characteristic of α,β-unsaturated ketones.[3] The identity of C-4, being a quarternary carbon, was deduced from a separate off-resonance spectrum (not shown). Carbon-5 and C-6 were assigned using structural analogies from the literature.[4]

TABLE 1. ^{13}C NMR SHIFTS* OF 4,4-DIMETHYL-2-CYCLOHEPTEN-1-ONE

Carbons	$\delta^{13}C$	Carbons	$\delta^{13}C$
C–1 (CO)	−15·0	C–6	161·2
C–2 ($—CH_b=$)	63·1	C–7 (α)	150·2
C–3 ($—CH_a=$)	38·1	C–8 (CH_3)	171·8
C–4	167·5	C–9 (CH_3)	173·2
C–5	155·4		

* From CS_2 in ppm.

The carbonyl group usually induces a strong downfield shift on adjacent carbon resonances which is often diagnostic for that carbon.[5] Steric interactions, on the other hand, are known to produce upfield shifts. It is highly probable therefore, that the chemical shift of C-7 found 6–8 ppm higher than the values most often reported for α carbon resonances is due to C-7-CH_3 steric interaction. The apparent planarity of the $O{=}C{-}CH{=}CH{-}$ structural unit shapes the seven membered ring to a more or less symmetrical conformation (a plane of symmetry passing through C-2 and between C-5 and C-6 atoms), and this twists one of the geminal methyls into close spatial proximity.

The assignment of C-8 and C-9 has to remain tentative because of the small difference in shifts. The compound is thus identified as 4,4-dimethyl-2-cyclohepten-1-one.

EXPERIMENTAL

Commercial 'natural' Canada balsam (1·8 kg), obtained from the British Drug Houses Ltd was distilled at the pressure of 5 mm to yield 360 g of materials boiling between 28 and 72°. The distillate was fractionated at 24 mm and stopped after the highest boiling monoterpenes (limonene and β-phellandrene) were collected. The distillation residue amounted to 1·5 g and was composed of a liquid containing only one major low boiling compound, identified here as 4,4-dimethyl-2-cyclohepten-1-one.

4-4-Dimethyl-2-cyclohepten-1-one was isolated by preparative GLC, using Varian Aerography Model A-90-C instrument in conjunction with a 30 ft × 0·25 in. column, filled with Chromosorb G 100/120, impregnated with 1% Carbowax 20 M. The compound isolated exhibited the following relative retention volumes: RRV = 1·39 relative to longifolene (= 29 min), Carbowax 20 M, 1% on Chromosorb G, 100/120, 21 ft × 0·125 in. o.d., $T = 125°$, flow 15 ml/min; RRV = 1·54, relative to menthol (= 24 min), OV-17, 20 ft × 0·125 in. o.d. column, $T = 150°$, otherwise as before.

For the NMR spectra, the small quantity of material available (2–4 mg) was dissolved in $CDCl_3$ in a 30 μl microbulb and immersed in D_2O with a special Teflon insert. The proton NMR spectrum was determined on a Varian HR-220 spectrometer with superconducting map net. The ^{13}C NMR spectra were obtained on a modified Varian HR-60 NMR spectrometer. For the spectrum free-induction decays following 400 W RF pulses were accumulated on a Fabri-Tek Model 1074 Signal Averager. The accumulated signal was then Fourier transformed into a magnitude spectrum electronically using a Spectrum Analyser. Details

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[3] D. H. MARR and J. B. STOTHERS, *Can. J. Chem.* **43**, 596 (1965).

[4] M. JAUTELAT, J. B. BRUTZNER and J. D. ROBERTS, *Proc. Natl. Acad. Sci.* **65**, 288 (1970).

[5] J. B. STOTHERS, *Quart. Rev. London* **19**, 144 (1965).

on equipment and operation have been reported elsewhere.[6–8] ^{13}C NMR conditions: pulse frequency 15·089500 MHz, pulse width 8·0 μsec; 100 μsec dwell time per data point; 5·0 sec pulse repetition rate, 37 927 scans.

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[6] D. M. WILSON, Ph.D. Dissertation, Univ. of California, Berkeley, Calif. (1971).

[7] D. E. JONES, Ph.D. Dissertation, Univ. of California, Berkeley, Calif. (1971).

[8] A. L. BURLINGAME, D. H. SMITH, T. O. MERREN and R. W. OLSEN, Real-time high resolution mass spectrometry, in *Computers in Analytical Chemistry* (edited by C. H. ORR and J. A. NORRIS), Plenum Press, New York (1970).

Key Word Index—*Abies balsamea*; Pinaceae; 4,4-dimethyl-2-cyclohepten-1-one.