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STRUCTURE AND SYNTHESES OF A NEW KETONE FROM THE ESSENTIAL OIL OF *CEDRUS* SPECIES

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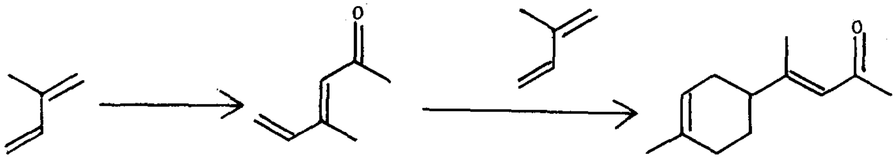
We wish to report the isolation of a new ketone from the oxygenated components of the essential oils of *Cedrus atlantica* Manet and *C. deodara* Loud. It is present to the extent of *ca.* 0.1% and 0.15% respectively and has a pleasant odour characteristic of the oil.

The ketone ($[\alpha]_D^{20}$ + 25° in $CHCl_3$) has M^+ 178 a.m.u. ($C_{12}H_{18}O$). Its n.m.r. spectrum (100 MHz in CCl_4, internal TMS) shows τ:4.04 brs (1H); 4.67 brm (1H); 7.7-8.7 brm, on which is superimposed 7.95s and 8.36 brs (16H). Its i.r. spectrum (in CCl_4) shows absorptions for an α,β-unsaturated ketone (1690 cm^{-1}) and C = C (1613 cm^{-1}). Its u.v. spectrum confirms the presence of an α,β-unsaturated ketone (λ_{max} 237 nm).

The mass spectrum supports the assignment of structure (1), with major fragments at: 178(M^+, 39%); 43(100%); 95(95%); 67(53%); 68(52%); 41(52%); 109(45%); 135(42%); 93(40%) and 79, 120(39%).

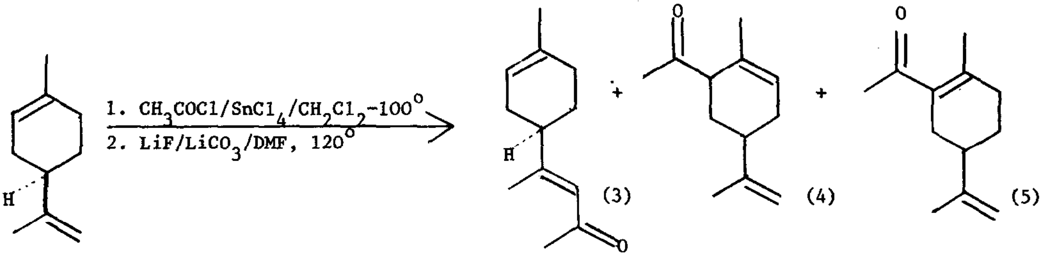
The structure (1) has been confirmed by two syntheses.

Isoprene (0.062 mol) in dichloromethane was added during 1h to acetyl chloride (0.05 mol) in dichloromethane containing stannic chloride (0.045 mol) at -78°. After a further ½h at -78°, excess of pyridine in ether was added, the mixture was filtered and the filtrate worked up. The crude product was treated with lithium carbonate and lithium fluoride in dimethylformamide at 120° for 1h to afford the dienone (2).



(2) (1)

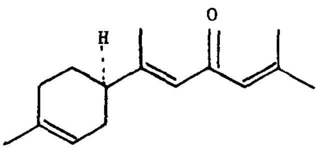
To this crude dienone (2) in dichloromethane containing aluminium chloride (0.036 mol) at 20° was added isoprene (0.15 mol) in dichloromethane over a period of 5h. After a further 8h, isolation and chromatography over silica gel gave the (±)-ketone (1) in an overall yield (based on acetyl chloride) of 40%. An alternative synthesis involving acylation of (+)-limonene ($[\alpha]_D^{20}$ + 110° in $CHCl_3$) with acetyl chloride at -100° and subsequent dehydrochlorination gave the (+)-ketone ($[\alpha]_D^{20}$ + 30° in $CHCl_3$) in an estimated yield of *ca.* 30% (glc).



(3) (4) (5)

The other major monoacylation products in this reaction were the non-conjugated ketone (3) (22%) and the conjugated ketone (4) (28%). This synthesis establishes the absolute configuration as (3),† corresponding to that of (+)-limonene.

† The possibility that the C_{12}-ketone (3) might have been formed from (+)-atlantone (6) during isolation of the oil by steam distillation seemed to be supported by the claim (A.S. Pfau and P. Plattner, <u>Helv. Chim. Acta</u>, 1934, <u>17</u>, 129) that acetyldipentene (1) is produced by treatment of atlantone with alcoholic alkali (although the reported b.p. is too low). However, in our hands, treatment of atlantone with 3% alcoholic KOH for 10 min gave only 4-acetyl-1-methylcyclohex-1-ene, with no trace of (1). That the atlantone from the oil is largely racemised also tells against its being the precursor of (1) during isolation. Presumably atlantone or a related sesquiterpene is the biogenetic precursor of the C_{12}-ketone (3).



(6)

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