Pyrolysis of *cis*-Pinocarveol

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Summary Pyrolysis of *cis*-pinocarveol gives an extensively rearranged acyclic aldehyde, the mode of formation of which was determined by deuterium labelling.

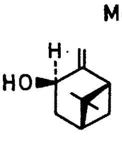
PYROLYSIS of *cis*-pinocarveol (**1**; $[\alpha]_D - 40°$) on passage through a stainless steel tube at 510° (contact time 0·1 sec.) gave a crude product (*ca.* 92%) shown by g.l.c. to consist of 12 components. Five of these were identified as diene (**2**; 9%), hydroxy-triene (**3**; 42%), *cis*-pinocarveol (**1**; 3%), *cis*-carveol (**4**; 16%), and the aldehyde (**5**; 14%) by i.r., u.v., n.m.r., and mass spectra.

N.m.r. data for aldehyde* (**5**)

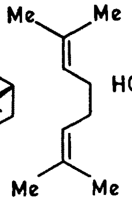
Functional group	Position of signal(s) (p.p.m.)	Nature of signal	Apparent coupling constants (c./sec.)
C-3–CH_3	1·06	doublet	$J(CH_3,H^3)$ 6·8
trans-C-6–CH_3	1·59	singlet	
cis-C-6–CH_3	1·67	doublet	$J(CH_3,H^5)$ 1
C-4–H_2	*ca.* 2·05	multiplet	
C-3–H	2·70	quintuplet	$J(H^3,CH_3) = J(H^3,H^{4a}) = 7$ $J(H^3,H^{4b}) = 0$
C-5–H	5·05	doublet of triplets	$J(H^5,H^4) = 7·3$; $J(H^5,CH_3) = 1$
C=C–H^c	5·98	doublet	$J(H^c,H^d)$ 0·6
C=C–H^d	6·22	triplet	$J(H^d,H^c) = J(H^d,H^3) = 0·6$
-CHO	9·55	singlet	

* Determined at 60 MHz for a 10% solution (w/v) in $CDCl_3$ with $CHCl_3$ and Me_4Si as internal standards.

The detailed structure of the extensively rearranged aldehyde (**5**; *M* 152) was deduced as follows. The Δ^5-position of the isolated double bond was defined from the n.m.r. spectrum (Table). The multiplicity of the 5-H signal requires the presence at C-4 of two protons, and signal(s) for which was located at *ca.* δ 2·05 p.p.m. by double irradiation experiments. The nature of the conjugated aldehyde structure [ν_{max} 2720, 1696 cm^{-1}; λ_{max} (cyclohexane) 218·5 nm, ε 5700] followed from the n.m.r. analogy[1] with the simple aldehyde (**6**). The observed multiplicity of the C-3 methine proton arises from coupling with the C-3 –CH_3 and *one* 4-H proton; the second 4-H–3-H dihedral angle is *ca.* 80° in the preferred conformation (**7**) of the aldehyde (**5**).



(1)



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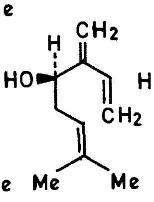

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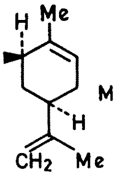

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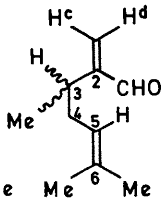

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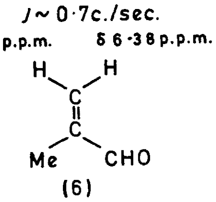
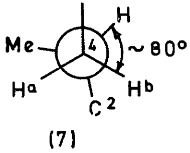


(6)



(7)

Results from deuterium labelling experiments demonstrated the origin of some of the hydrogen atoms in the aldehyde (Figure 1) and afforded evidence for its mechanism of formation (Figure 2). This reaction scheme is in accord with the formation of the diene (**2**) and the isolation of *racemic* (o.r.d.) aldehyde (**5**).

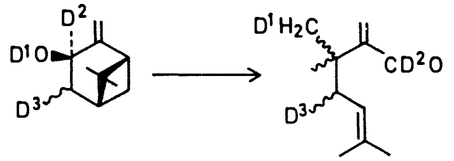


FIGURE 1

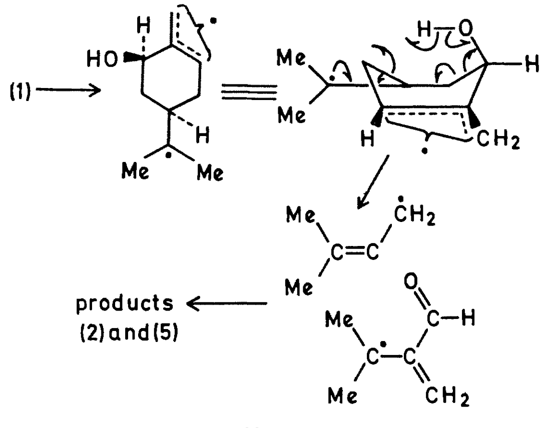


FIGURE 2

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[1] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 1960, 2881.