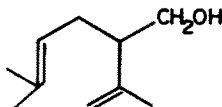
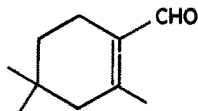


$\beta$ -CYCLOLAVANDULAL, A NEW NATURALLY OCCURRING  
MONOTERPENE TYPE

M.K. Logani and I.P. Varshney  
Department of Chemistry, Muslim University, Aligarh  
and  
R.C. Pandey and Sukh Dev  
National Chemical Laboratory, Poona (India)

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THE monoterpene fraction ( $\sim 80\%$ ) of the essential oil<sup>1</sup> from the seeds of Seseli indicum Wight and Arnold, has been found to contain upto 11% of a monoterpene aldehyde,  $C_{10}H_{16}O$ , now characterised as  $\beta$ -cyclolavandulal (I), a compound obtained synthetically earlier by Schinz and co-workers<sup>2-4</sup> from lavandulol (II). Since, a direct comparison could not be made, we briefly summarise the evidence, which provides, in itself, a complete and



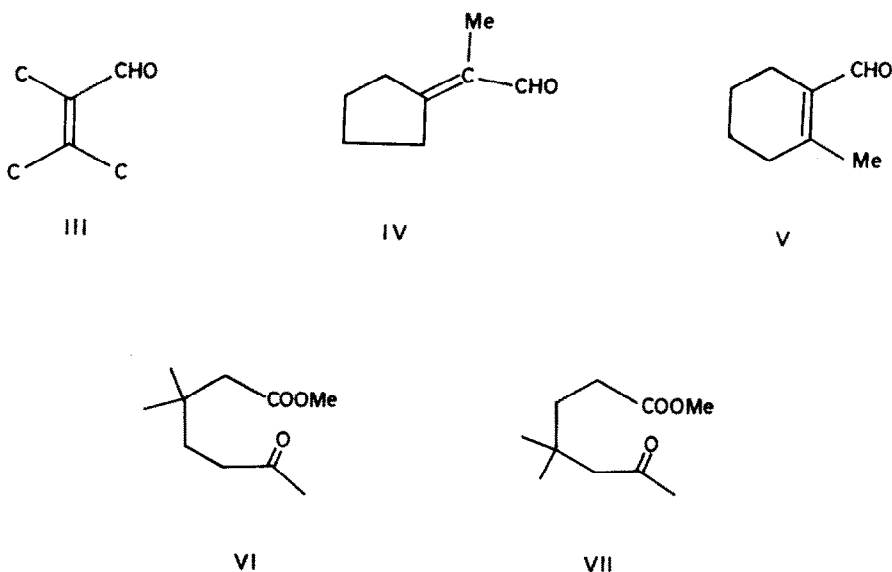
II

independent proof for structure I. Its occurrence in nature, reveals a new type of naturally occurring monoterpene framework, apparently, directly related, biogenetically, to the non-head-to-tail monoterpene, lavandulol (II).

The aldehyde [b.p. 100-105°(bath)/10 mm; semicarbazone, m.p. 219-221°;  $\nu^{CH=O}$  2750, 1680  $cm^{-1}$ ] is clearly  $\alpha\beta$ -unsaturated:  $\lambda_{max}^{EtOH}$  248  $m\mu$ ,  $\epsilon$ , 11,000. The compound is highly susceptible to air oxidation and soon deposits a crystalline solid,  $C_{10}H_{16}O_2$ , m.p. 106-107°,  $[\alpha]_D + 0$ , identified as the corresponding acid (methyl ester: b.p. 90-92°/3 mm,  $\lambda_{max}^{EtOH}$  229  $m\mu$ ,  $\nu^{C=O}$  1730  $cm^{-1}$ ,

$\nu^{C=C}$   $1650\text{ cm}^{-1}$ ). This conversion can be more efficiently carried out by catalytic air oxidation<sup>5</sup>. The methyl ester on reduction with  $\text{LiAlH}_4$  gave the corresponding alcohol (IR spectrum: OH  $3400, 1000\text{ cm}^{-1}$ ), which shows no UV maximum above  $215\text{ m}\mu$ .

The PMR spectrum<sup>6</sup> of the aldehyde shows signals for two quaternary methyls (6H singlet at  $56\text{ c/s}$ ), one vinylic methyl (3H, slightly split singlet at  $127\text{ c/s}$ ) and one aldehyde proton (1H singlet at  $610\text{ c/s}$ ); no olefinic proton is indicated. The PMR spectra of the corresponding acid, methyl ester and the alcohol ( $\text{CH}_2\text{OH}$  as a 2H singlet at  $241\text{ c/s}$ ) support these assignments. These data, coupled with the earlier results, require the presence of the grouping III in the molecule.



The mass spectrum of the methyl ester, shows  $M^+$  at  $m/e$  182, confirming the molecular formula  $\text{C}_{11}\text{H}_{18}\text{O}_2$  for the ester and hence,  $\text{C}_{10}\text{H}_{16}\text{O}$  for the aldehyde. This requires the aldehyde to be either monocarbocyclic or

diolefinic; the latter possibility is ruled out, as the remaining four carbon atoms, after the part structure III, must accommodate two quaternary methyls. It is also clear from this that these two quaternary methyls must be geminal, a conclusion which is supported by the presence of doublets, 1367, 1383  $\text{cm}^{-1}$  and 1369, 1392  $\text{cm}^{-1}$ , in the IR spectra of the aldehyde and the corresponding alcohol.

The above results require that the aldehyde must be represented by the part structure IV or V, the remaining two carbon atoms being located as a gem-dimethyl group on the alicyclic ring. Ozonolysis of the methyl ester, yielded an acid, isolated as the methyl ester ( $\text{C}_{10}\text{H}_{18}\text{O}_3$ ):  $\nu^{\text{C=O}}$  1715, 1745  $\text{cm}^{-1}$ . Its PMR spectrum shows signals for: two quaternary methyls (6H singlet at 218 c/s),  $\text{CH}_3\text{CO}$  (3H singlet at 125 c/s) and  $\text{COOCH}_3$  (3H singlet at 218 c/s). This rules out the possibility IV. The PMR spectrum of this keto ester also displays a sharp 2H singlet at 137 c/s, which is assigned to a methylene flanked by a fully substituted carbon on one side and a carbonyl function ( $\text{COCH}_3$  or  $\text{COOMe}$ ) on the other. Thus, this keto ester must be represented by either VI or VII. This was confirmed by the NaOBr oxidation of the keto acid to  $\beta\beta$ -dimethyladipic acid, m.p. 86-88 $^\circ$ , identified by comparison (mixed m.p., IR, GLC of the dimethyl ester) with an authentic sample. A distinction between VI and VII could be made on the basis of the PMR spectrum of its  $\text{KBH}_4$  product (hydroxy ester), which does not show the 2H singlet assignable to  $\text{C}-\underset{\text{C}}{\overset{\text{C}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{R}$  and hence VII must correctly represent the keto ester. The aldehyde, can now be represented by I.

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