

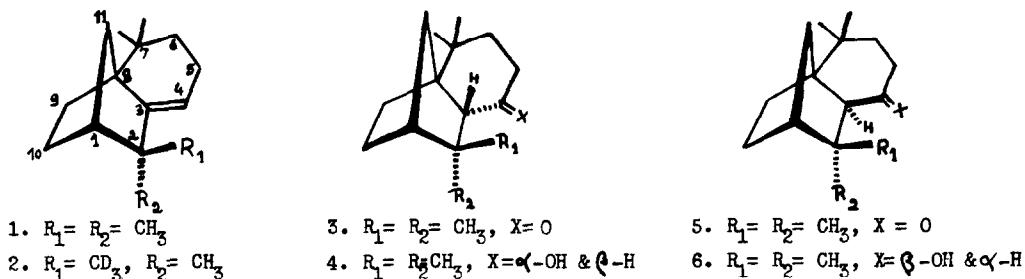
STEREOCHEMISTRY OF ISOLONGIFOLENE KETONES

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A recent communication<sup>1</sup> by Banthorpe, Curtis and Fordham prompts us to place on record our results concerning the dispute<sup>2-4</sup> over the stereochemistry of isolongifolene ketones. The main controversy centres around the stereochemistry at C<sub>3</sub> of the ketone epimer obtained from the rearrangement of isolongifolene epoxide. Dev's<sup>2</sup> original assignment 5 to this ketone has been supported by Lala<sup>3</sup> but contradicted by Eschinasi and coworkers,<sup>4</sup> who assign it the opposite stereochemistry depicted in 3. We present evidence that is compatible with unexpected<sup>5</sup> and exclusive endo-attack on the isolongifolene 1 double bond and also delineates the stereochemistry of the derived ketones.

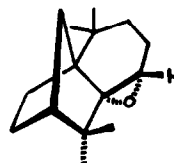


The LiAlH<sub>4</sub> reduction of the ketone obtained from the isolongifolene epoxide rearrangement gave a single alcohol,<sup>6</sup> which on further treatment with Pb(OAc)<sub>4</sub> in refluxing benzene gave a tetracyclic ether<sup>7,8</sup> in 50% yield. This tetracyclic ether and its precursor alcohol<sup>9</sup> can be assigned structures 7 or 8 and 4 or 6 depending upon the stereochemistry 3 or 5 of the starting ketone. A distinction between ether structures 7 or 8 has been achieved as follows. Preparation of the methyl labelled ketone from deuterated isolongifolene 2<sup>10</sup> and repetition of the sequence (vide supra) gave the deuterated tetracyclic ether 9, which exhibited low field signals at δ 3.7-4.15 (3H, m, H<sub>2</sub>-C-O-C-H) along with two methyl singlets at δ 0.95 and 0.99 in the PMR spectrum. These spectral features are consistent with structure 9 and 8 for the tagged and

parent ether and rule out the alternate formulation 7.



7

8.  $R_1 = \text{CH}_3$ 9.  $R_1 = \text{CD}_3$ 

10

The above results lead to structure 3 for the ketone epimer from 1. The thermodynamically more stable ketone epimer<sup>4,12</sup> obtained from 3 and isolongifolene epoxide should therefore be represented by 5 and 10 respectively.

#### REFERENCES

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2. T.S. Santhanakrishnan, R.R. Sobti, U.R. Nayak and S. Dev, *Tetrahedron*, **26**, 657 (1970).
3. L.K. Lala, *J. Org. Chem.*, **36**, 2560 (1971).
4. E.H. Eschinasi, G.W. Shaffer and A.P. Bartels, *Tetrahedron Letters*, 3523 (1970).
5. The camphene like olefinic linkage in 1 is expected to undergo preferential *exo*-addition, see, H.C. Brown and K.T. Liu, *J. Amer. Chem. Soc.*, **89**, 466 (1967).
6.  $\text{C}_{15}\text{H}_{26}\text{O}$ , IR:  $\nu^{\text{O-H}}$  3410  $\text{cm}^{-1}$ , PMR:  $\delta$  0.93, 1.06, 1.15 (12H, s,  $\text{CH}_3\text{-C-}$ ); 4.21 (1H, m,  $\text{H-C-OH}$ ).
7. This ether has been prepared by Lala<sup>3</sup> along similar lines but his structural assignment and conclusions are at variance from those reported here. We wish to thank Dr. Lala for sending us the PMR spectrum of his ether for comparison.
8.  $\text{C}_{15}\text{H}_{24}\text{O}$ , IR:  $\nu^{\text{C-O}}$  905, 1060  $\text{cm}^{-1}$ , PMR:  $\delta$  0.93, 1.01 (9H, s,  $\text{CH}_3\text{-C-}$ );  $\delta$  3.7-4.10 (3H, m,  $\text{-CH}_2\text{-O-CH}$ ).
9. The stereochemistry of hydroxyl group in 4 and 6 follows from the hydride attack from the less hindered side of the molecule as revealed by the examination of Drieding models. Furthermore, the alcohols from 3 and 5 with opposite hydroxyl configuration do not fulfill the steric requirement for the formation of a cyclic ether.
10. Deuterated 2 was obtained by the rearrangement of longifolene with  $\text{D}_2\text{SO}_4\text{-D}_2\text{O-AcOD}$  reagent. The deuterium exchange of the methyl group at  $\text{C}_2$  was apparent from the PMR and mass spectra of various compounds of the series. The location of the tagged methyl in *exo*-position at  $\text{C}_2$  in 2 is unambiguous and follows from the mechanism<sup>11</sup> of longifolene  $\rightarrow$  isolongifolene rearrangement.
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12. R. Ranganathan, U.R. Nayak, T.S. Santhanakrishnan and S. Dev., *Tetrahedron*, **26**, 621 (1970).

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