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MOLECULAR STRUCTURE OF ISOLONGIFOLENE EPOXIDE

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ummary: An X-ray analysis on isolongifolene epoxide definitely settles the dispute over the tereochemistry in favor of the endo-formulation.

The stereochemistry of the sesquiterpene deriative, isolongifolene epoxide, has been a atter of considerable controversy in recent years. The epoxide was assigned[1] structure I, ssentially on the basis of the acid-catalyzed rearrangement[1b] to the olefinic alcohol II. his assignment was disputed[2] on the basis of chemical shift data from the two epimeric bi- yclic alcohols, derived from the epoxide, and the oxirane configuration III was proposed. oon after, results from a chemical study[3] were considered inconsistent with formulation III nd appeared to support structure I. Since then, two more chemical studies[4,5] have been car- ied out and it has been claimed that the results are consistent only with the stereochemistry II. None of the chemical studies cited above can be considered as conclusive* and the NMR tudy[2] depended largely on analogy to a much less substituted system. Clearly, a definite nswer is overdue and we here report the results of an X-ray study on isolongifolene epoxide hat settles the dispute in favor of the endo structure III.

Colorless crystals of (±) isolongifolene epoxide ($C_{15}H_{24}O$, m.p. 40.5 - 41.5°) sublimed

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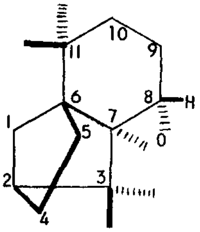
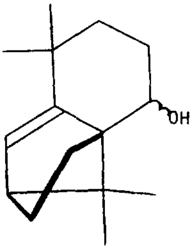
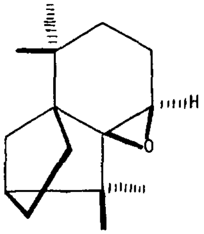
For example, Banthorpe et al.[4] extrapolate their stereochemical findings, from catalytic ydrogenation of 9-hydroxyisolongifolene, to epoxidation of isolongifolene. Mehta and Kapoor[5] se their results on the requirement that during D^+ -catalyzed isomerization of longifolene isolongifolene only the exo-methyl at C_3 gets selectively labelled; we find from our ex- nsive deuterium labelling studies that this is not the case and both methyls at C_3 incorpor- te D-label, though to different extents (note that considerable racemization occurs during omerization!)



I



II



III

upon exposure to air and had to be sealed in a thin-walled glass capillary. The crystals are triclinic with a = 8.405(1), b = 14.592(3), c = 6.163(1)Å, α = 113.66(1), β = 70.13(2), and γ = 103.02(1)°. There are two molecules in the unit cell and the space group is P$\bar{1}$, indicating that the epoxide exists as racemate in the crystal. A total of 1631 non-zero reflections ($2\theta \leq 125^\circ$) was collected on a Picker FACS-1 diffractometer (CuK$_\alpha$ radiation). The structure was solved by the symbolic addition method[6] and has been refined by full-matrix least squares to an R-factor of 0.060 on all non-zero reflections. Hydrogen atoms were easily located from a difference map and the final model contained anisotropic thermal parameters for the non-hydrogen atoms and individual isotropic parameters for the hydrogen atoms. The list of coordinates for the non-hydrogen atoms is given in Table 1. A stereoscopic drawing of a single molecule is shown in Figure 1. From the drawing, it can be seen that isolongifolene epoxide has the endo-structure (III).

The bond lengths and angles found in this analysis do not require extensive comment. However, it is worth pointing out that this is one of the most accurate determinations of the geometry of an epoxide ring fused to a six-membered ring, and it shows that the three bonds in the epoxide ring have nearly the same length, $C_7 - O_1$ 1.445(3), $C_8 - O_1$ 1.449(4), and $C_7 - C_8$ 1.454(4)Å and the internal angles are all within 0.3° of 60°. Additional structural data of comparable accuracy will be necessary to establish whether there are variations in these dimensions with molecular environment. The six-membered ring has a conformation with four coplanar atoms C_6, C_7, C_8, and C_9, and the other two, C_{10} and C_{11}, lying 0.684 and 0.388Å on opposite sides of this plane. As regards both the conformation of the six-membered ring and the C-C-C angles in the ring, the effect of the fused epoxide ring is rather similar to that of a carbon-carbon double bond.

Table 1: Final atomic coordinates for non-hydrogen atoms in Isolongifolene Epoxide. Standard deviations in parentheses.

Atom	x	y	z
O(1)	0.5209(2)	0.1527(1)	0.6862(3)
C(1)	0.4335(3)	0.2939(2)	0.3643(5)
C(2)	0.2581(3)	0.2552(2)	0.4944(5)
C(3)	0.2926(3)	0.1552(2)	0.4945(5)
C(4)	0.2283(4)	0.3360(2)	0.7489(6)
C(5)	0.4028(4)	0.3563(2)	0.7970(5)
C(6)	0.5216(3)	0.2954(2)	0.5498(4)
C(7)	0.4752(3)	0.1852(2)	0.5246(4)
C(8)	0.6050(3)	0.1164(2)	0.4237(5)
C(9)	0.7898(3)	0.1513(2)	0.3409(6)
C(10)	0.8151(4)	0.2490(2)	0.2948(5)
C(11)	0.7134(3)	0.3323(2)	0.5078(5)
C(12)	0.7546(4)	0.4264(2)	0.4390(8)
C(13)	0.7683(5)	0.3580(3)	0.7411(6)
C(14)	0.2877(5)	0.0709(3)	0.2498(7)
C(15)	0.1683(4)	0.1226(3)	0.7057(7)

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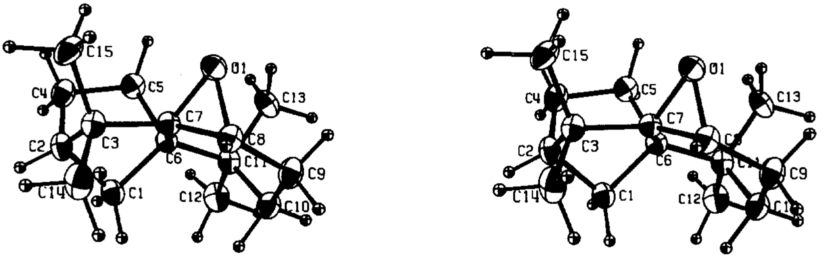

Figure 1: Stereoscopic drawing of the molecule of isolongifolene epoxide.

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