

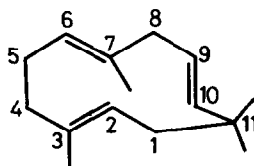
TERPENES AND RELATED SYSTEMS XII. A FASCINATING REARRANGEMENT
OF HUMULENE TO EUDESMANE-TYPE SKELETON (δ -SELINENE)

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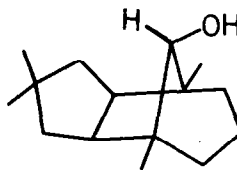
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In several recent communications, we have drawn attention to the ability of various polyisoprenoids to undergo novel molecular rearrangements in strong acid medium under the conditions that are propitious for the formation of stable carbocations.¹ The monocyclic triisoprenoid humulene (I), bearing a unique 11-membered carbon framework, is an intriguing substrate for the study of cationic rearrangements as it can generate a variety of carbocyclic skeletons. Furthermore, (I) has also been implicated² as the biogenetic precursor of several marine^{2a} and fungally derived^{2b} sesquiterpenoids. Recent reports from numerous groups³ on the rearrangement of (I) to apollanol (II)^{3a} and bicyclic diene (III),^{3b-d} employing systems of varying acidity, prompts us to place on record our preliminary results about the rearrangement of (I) to eudesma-4-6-diene (δ -selinene)⁴ (IV). This, to our knowledge, is the first direct acid catalysed cyclisation of humulene to a naturally occurring carbon skeleton. It is noteworthy that among the various alternatives, humulene chooses a cyclisation pathway to eudesmane-types, a ring system to which (I) cannot eventuate in vivo according to the Ruzicka-Hendrickson biogenetic theory.⁵

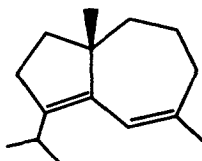


(I)

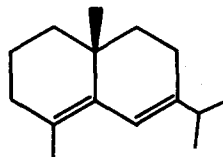


(II)

When a solution of (I) in CH_2Cl_2 was rapidly dispersed at $0-5^\circ$ in conc. H_2SO_4 (98%) a clear saffron colored solution was obtained. Quenching of this



(III)



(IV)

solution (30 min) in iced aq. Na_2CO_3 led to nearly 50% recovery of an olefinic mixture from which the major component (IV) was obtained pure ($\text{AgNO}_3\text{-SiO}_2$ column) in 60% yield. The structure of (IV) was evident from its spectral data: $\text{C}_{15}\text{H}_{24}$, $\lambda_{\text{max}}^{\text{MeOH}}$ 241, 249 and 256 nm, δ 0.92 (3H,s), 1.06 (6H,d, $J=7\text{Hz}$), 1.67 (3H, br,s) and 6.17 (1H, br,s). A direct comparison (UV, IR, NMR) of (IV) with authentic δ -selinene prepared⁴ from dehydration of eudesmols established their mutual identity.

Although a direct pathway from (I) to (IV) via the protonation of $\text{C}_6\text{-C}_7$ bond and participation by $\text{C}_2\text{-C}_3$ π bond is conceivable, the geometry of humulene (I) precludes this possibility. Several other mechanistic schemes including one involving the (I) \rightarrow (III) \rightarrow (IV) type pathway are possible and appropriate experiments are underway to elucidate the mechanism of this cyclisation.

- References** : 1. G. Mehta and D. G. Farnum, *Chem. Commun.* 1643 (1968); G. Mehta and S. K. Kapoor, *Tetrahedron Letts.*, 4947 (1972); G. Mehta and S. K. Kapoor, *Tetrahedron Letts.*, 2385 (1973); D. G. Farnum, R. A. Mader and G. Mehta, *J. Amer. Chem. Soc.*, 95, 8692 (1973); G. Mehta and B. P. Singh, *Tetrahedron Letts.*, 1585 (1975); G. Mehta, B. P. Singh and B.G.B. Gupta, Unpublished results.
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