

ON THE CO-OCCURRENCE OF LEVOJUNENOL AND ZIZANENE[(+)- α -AMORPHENE]*

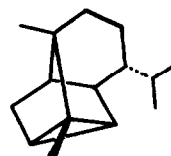
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Evidence for the existence of two chemically distinct races of *Vetiveria zizanioides* (Gramineae) has been presented.¹ The North Indian "Khus" variety elaborates antipodal cadinenes (III, and oxygenated derivatives) and levojunenol (IV), whereas the typical varieties produce largely nootkatanes, vetispiranes,² and substances of the tricyclic zizane skelton.³ This communication presents the first evidence of similarity for these varieties.

Typical vetiver oils have been shown to contain cyclocopacamphene (I) and related oxygenated sesquiterpenes.³ They are the first sesquiterpene constituents of typical vetiver oils to bear a 7α -isopropyl group. In our recent work on the hydrocarbon fraction from Reunion Vetiver we encountered a fraction whose properties corresponded to "zizanene" isolated by Romanuk and Herout.⁴ On further purification by preparative glc on three different phases (FFAP, Carbowax 20-M, and Apiezon-L), a pure substance was obtained— $[\alpha]_D = +120^\circ$; $\delta_{CDCl_3} 0.92$, 0.95 (2CH₃,d), 1.63(vinyl-CH₃), 5.09(vinyl-H), and 5.34 ppm (vinyl-H); $\nu_{max}(-CH=C<)$ 3045, 1670 cm⁻¹—which was identical to α -amorphene ($[\alpha]_D = -126^\circ$) in all respects except rotation.⁵ Thus zizanene should be given structure II [(+)- α -amorphene].⁶ The other material of interest, is the component of typical vetiver oils which corresponds by glc to levojunenol from the Khus varieties (see ref. 1 for sample glc traces of different Vetiver oils). Isolation by repeated preparative glc afforded a still impure alcohol which is largely levojunenol by IR, NMR, glc, and ORD comparison.⁷ These findings are unexpected in light of the common occurrence of 7β -isopropyl-sesquiterpenes such as valencene, elemol, and β -eudesmol in typical vetiver oils.



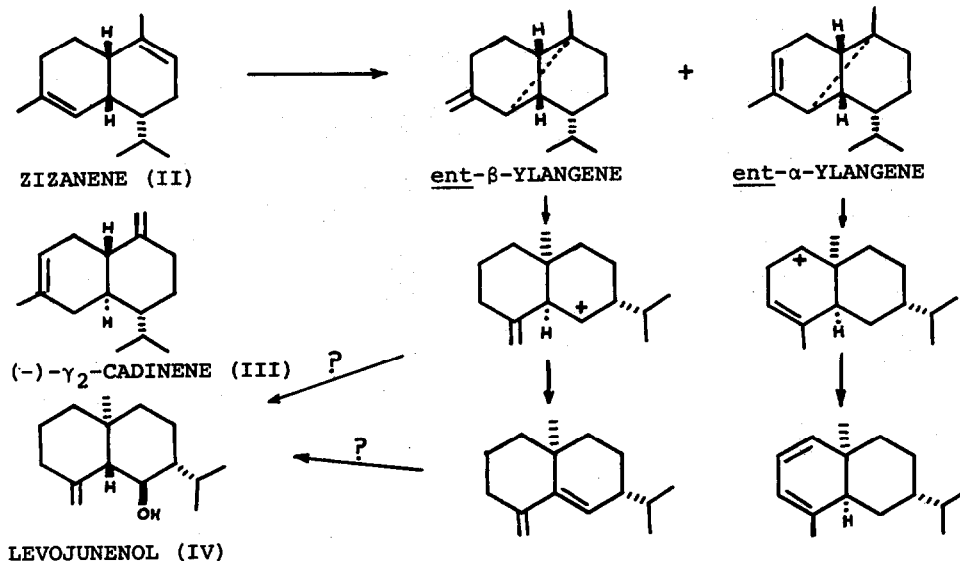
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In the case of the "Khus" varieties we have recently found elemol as significant alcoholic component. Thus these oils can no longer be viewed as strictly antipodal. Zizanene appears, not unexpectedly (in light of the prominence of antipodal cadinenes such as III), as a significant component in the hydrocarbon portion of the Bharatpur variety.^{7,8}

A working hypothesis for the genesis of levojunenol from zizanene via ent- β -ylangene is shown below.[#] By this proposal, the junenols would not be considered as relatives of the eudesmols and selinenes. This position is supported by the fact that junenols generally occur in oils containing cadalene-type sesquiterpenes rather than eudesmanes. Evidence for the existence of ent- β -ylangene (and of the two novel dienes shown) among the numerous minor components of vetiver oil is being sought.

* Paper V in the series "Vetiver Oil Constituents".

Data from our laboratory and that of Dr. E. Klein (Dragoco) indicates that zizanene is a relatively common sesquiterpene. Furthermore it occurs with ent- β -ylangene in oils producing 7β -isopropyl sesquiterpenes.



As to the prior steps leading to zizanene in plants producing normal (7 β -iPr) eudesmanes and the like, perhaps the double 1,2-hydride shift hypothesis of Hirose⁹ (later withdrawn when natural α -ylangene was shown to have a 7 β -isopropyl group)¹⁰ should be resurrected as a minor pathway in sesquiterpene biogenesis.¹⁰

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REFERENCES

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2. N. H. Andersen, M. S. Falcone, and D. D. Syrdal, Tetrahedron Letters, 1759 (1970).
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4. M. Romanuk and V. Herout, Coll. Czechoslov. Chem. Commun., **25**, 2540 (1960).
5. Authentic α -amorphene was the gift of Dr. Y. Hirose.
6. Dr. E. Klein of Dragoco has also arrived at this conclusion (Dragoco Reports, in press). The author wishes to thank Dr. Klein for information on the course of these studies prior to publication.
7. Authentic levojunenol was the gift of Professor Chakravarti (Poona). It was also isolated from a sample of the Bharatpur variety of vetiver oil (the gift of Professor P. S. Kalsi).
8. These discoveries appear to be exceptions to the "absolute configurational homogeneity rule,"¹¹ however they do not vitiate the biogenetic scheme that stands as a chemical rationale for the rule. See for example: N. H. Andersen and D. D. Syrdal, Tetrahedron Letters, 2277 (1970).
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