

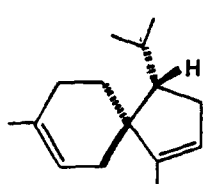
BIOGENETICALLY SIGNIFICANT COMPONENTS OF VETIVER OIL:  
OCCURRENCE OF (-)  $\alpha$ -FUNEBRENE AND RELATED COMPOUNDS

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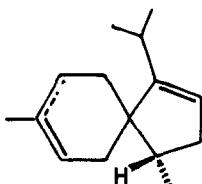
and

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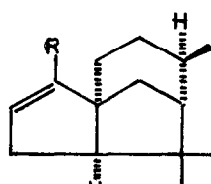
The isolation and structure determination of several minor but biogenetically interesting sesquiterpenes of vetiver oil (*Vetiveria zizanioides* Stapf.) has been recently reported by Kaiser and Naegli<sup>1,2</sup>. The compounds of special interest are acoradienes (1), (2) and seven new cedrene derivatives (3, a-d) and (4, a-c).



1

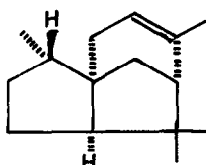


2



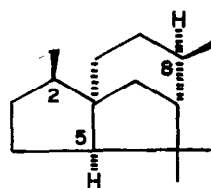
3, a-d

a, R=CH<sub>3</sub>  
b, R=CH<sub>2</sub>OH  
c, R=CHO  
d R=COOH



4, a-c

a, R=CH<sub>3</sub>  
b, R=CH<sub>2</sub>OH  
c, R=CHO



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In view of a recent report<sup>3</sup> concerning the revision of the absolute stereochemistry of acoradiene (1), we would like to place on record our conclusions regarding the structures, assigned to cedrene derivatives

<sup>†</sup>Communication No. 1943, National Chemical Laboratory, Poona, India.

(3, a-d)<sup>4</sup>. The data presented in sequel allows us to assign new structures (5, a-d) to these rare sesquiterpenes related to (+)  $\alpha$ -cedrene.

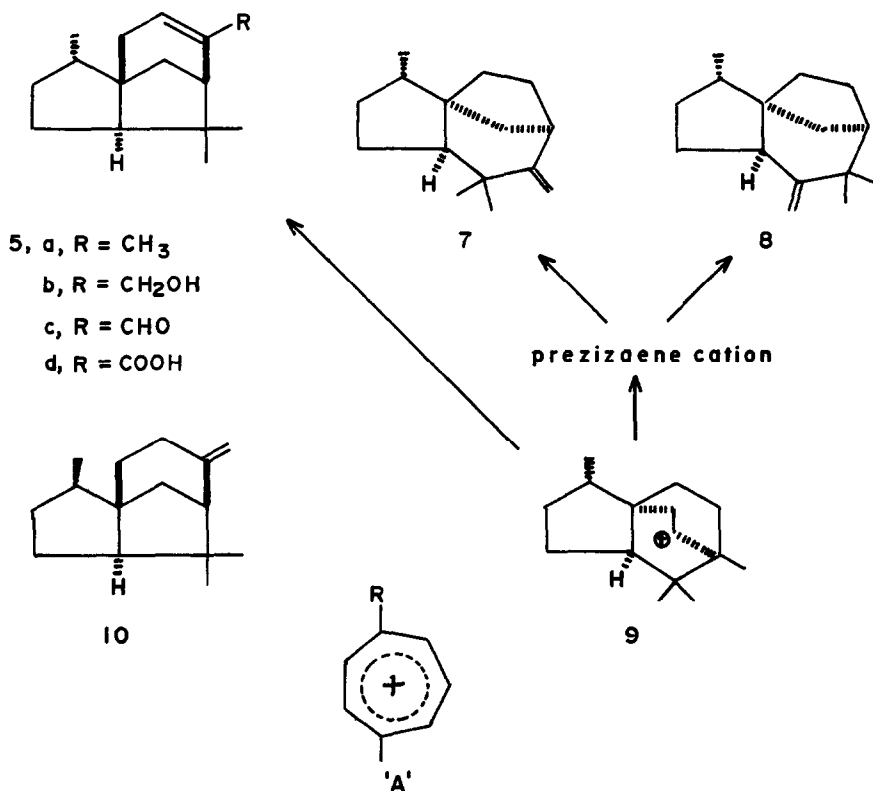
The assigned structures (3, a-d) to the so-called  $\Delta$ -2,8-epi-cedrene and its derivatives are far from convincing<sup>5</sup>, especially because of the biogenetically unsound structural features and the apparent discrepancy observed in the NMR spectral data on the parent saturated hydrocarbon and synthetic 8-epi-cedrane (6)<sup>2</sup>.

The most reasonable biosynthetic pathway which can account for the observed structural features and its co-occurrence with (+)  $\alpha$ -cedrene (4, a), (+) prezizaene (7) and (+) zizaene (9) would suggest structure (5, a) to Kaiser's vetiver oil hydrocarbon. In full support of this assignment, the reported spectral properties of the so-called  $\Delta$ -2,8-epi-cedrene are strikingly similar to those of  $\alpha$ -funebrene, a compound reported by one of us few years ago and which was assigned structure enantiomorphous with (5, a)<sup>6a,b</sup>. Direct spectral comparison (IR, NMR, Mass) of the two compounds under reference confirmed their identity as anticipated.

We have previously discussed<sup>6b</sup> the mass spectral fragmentation of  $\alpha$ -cedrene and  $\alpha$ -funebrene, a notable feature of which is the base peak due to tropilium ion 'A' (R=CH<sub>3</sub>, m/e 119). It may be pointed out that as expected, compounds (5, a-c) display in their mass spectra the ions m/e 119 (A, R=CH<sub>3</sub>), 135 (A, R=CH<sub>2</sub>OH), 133 (A, R=CHO) respectively as their base peaks. The mass spectrum of the methyl ester of (5, d) also shows base peak at m/e 163 (A, R=COOCH<sub>3</sub>).

On the basis of their co-occurrence with (+)  $\alpha$ -cedrene (4, a), (+) prezizaene (7), (+) zizaene (9) and the proposed biogenesis<sup>6b</sup> via allo-cedryl cation, (9), we assign absolute configurations as shown in (5, a-d) for these compounds. We propose that Kaiser's vetiver oil hydrocarbon should be called as (-)  $\alpha$ -funebrene<sup>7</sup>.

After our first report<sup>6a</sup> concerning the structure of  $\alpha$ -funebrene, the structure of 2,5-diepi- $\beta$ -cedrene (10) has been established by chemical and degradative results further supported by X-ray analysis<sup>8</sup>. It should be noted that  $\alpha$ - and  $\beta$ -funebrenes ( $\alpha$  and  $\beta$ -2,5-diepicedrenes) have been isolated from the same plant family Cupressaceae, and vetiver oil is yet another source for these compounds.



As the structure of 2,5-diepi- $\beta$ -cedrene has been established by X-ray analysis, a direct conversion of (5 a) to (10) is desirable. Efforts are being made in this direction.

We thank Dr. R. Kaiser, Givaudan-Esrolko Ltd., Zurich for the copies of IR, NMR and Mass spectra of vetiver  $\alpha$ -funebrene (5, a). One of us (S.K.P.) is indebted to UGC, India for financial assistance under National Associateship Scheme.

## REFERENCES

- 1 R. Kaiser and P. Naegeli, Tetrahedron Letters, 2009 (1972).
- 2 P. Naegeli and R. Kaiser, Tetrahedron Letters, 2013 (1972).
- 3 L.H. Zalkow and M.G. Clower, Jr., Tetrahedron Letters, 75 (1975).
- 4 S.V. Bhatwadekar, Ph.D Thesis, Poona University, Jan. (1975).
- 5 Structures assigned to compounds (3, b,c and d) are based on their conversion to (3, a).
- 6a J.K. Kirtany and S.K. Paknikar, 8th IUPAC Symposium on the Chemistry of Natural Products, New Delhi, Feb. 1972. Abstracts, C-44, 205.
- 6b J.K. Kirtany and S.K. Paknikar, Ind. J. Chem., 11, 508 (1973).
- 7 The specific rotation of  $\alpha$ -funebrene from Cupressus funebris Endl. was not measured. However, since it co-occurs with (-)  $\alpha$ -cedrene, we consider that the absolute configuration of  $\alpha$ -funebrene from C. funebris should be enantiomorphous to that shown in (5, a).
- 8 T. Norin, S. Sundin, P. Karlsson, A.P. Pillotti and A.G. Wiehager, Tetrahedron Letters, 17 (1973). These authors, however, did not refer to our work (cf. ref.6a).