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ABSOLUTE STEREOCHEMISTRY OF THE INSECT ANTIFEEDANT CADINENE FROM EUPATORIUM ADENOPHORUM

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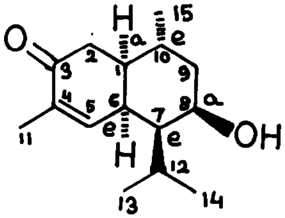
Summary: Chemical correlation studies and application of Horeau's method establish the absolute stereochemistry of the major cadinene from *E. adenophorum* as shown in 1.

Stereochemistry of cadinenes has always been a challenging problem, many structural and stereochemical assignments are dubious even till now[1]. Of the five cadinenes isolated from *E. adenophorum*[2], compound 1 was the major component. Since 1 exhibited appreciable antifeedant action against *Philasomia ricini* Hutt and also because of many other interesting biological properties associated with the cadinene group of compounds[3], it was of interest to us to establish its absolute stereochemistry.



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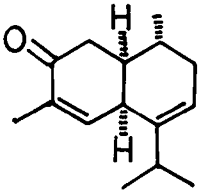

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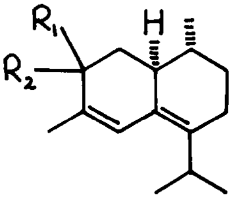

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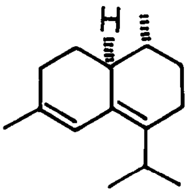
a $R_1, R_2 = O$

b $R_1 = H$
$R_2 = OH$

c $R_1 = H$
$R_2 = OTMS$



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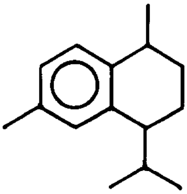

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Reaction of 1 with $POCl_3$ in pyridine furnished 2 in 70% yield which was isomerized to 3a in refluxing benzene containing a trace amount of toluene-p-sulphonic acid. Compound 3a was reduced with sodium borohydride in methanol to obtain 3b in 80% yield which on exposure to hexamethyldisilazane and chlorotrimethylsilane furnished 3c in quantitative yield. All attempts at reductive removal of the hydroxyl group in 3b with $LAH/AlCl_3$ or by LAH reduction of the tosylate of 3b led mainly to the formation of calamenene 5. However, when a solution of 3c in dry diglyme was stirred with nickel boride[4] for 8 hr at r.t., ent-10-epizonarene 4 was obtained in 80% yield[5]. This correlation established the absolute stereochemistry at C-1 and C-10 of 1. Since the relative stereochemistry at C-1, C_{10} and C_6 through C_8 is known[2a], 1 represents the absolute stereochemistry thus suggesting that it belongs to the amorphane group of compounds[6].

The same conclusion has been drawn by determining the absolute configuration at C-8 through Horeau's method[7]. Reaction of 1 with excess (±)-α-phenylbutyric anhydride gave (+)-α-phenylbutyric acid in 14% optical yield, implying that the configuration at C-8 is R.

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4. a) R B Boar, D W Hawkins, J F McGhie and D H R Barton, J. Chem. Soc., 654(1973) and references cited therein.
   b) Nickel boride reduction of several other allylic trimethylsilyl ethers has furnished the corresponding alkenes in excellent yield and these results are being published in a separate communication.
5. N H Anderson, D D Syrdal, B M Lawrence, S J Terhune and J W Hogg, Phytochemistry, 12(4), 827-33(1983).
6. Since cis-decalin can exist in two conformations, the small value of $J_{5,6}$ (≈2Hz) indicates that the dihedral angle between H_5 & H_6 in 1 is close to 90°, in which case H-6 must be equatorial.
7. A Horeau, Tetrahedron Lett., 506(1961); ibid., 965(1962).

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