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δ - ELEMENOL AND EPI- δ -ELEMENOL

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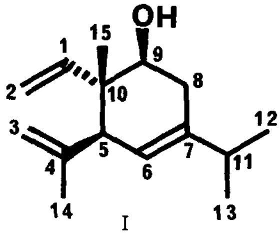
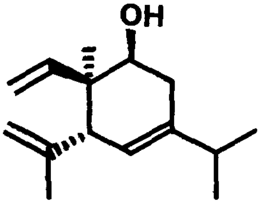
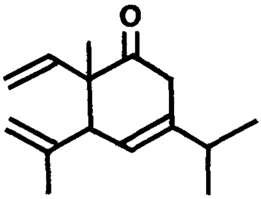
The volatile oil of the dried fruits of Kadsura japonica Dunal (Magnoliaceae) contains more than thirty sesquiterpene hydrocarbons and several oxygenated sesquiterpenoids, among which δ-elemene being the main component. Two sesquiterpene alcohols, named δ-elemenol and epi-δ-elemenol, both $C_{15}H_{24}O$, were isolated in nearly the same amount from the high boiling fraction of the oil, and the authors are going to present chemical and spectroscopic evidences in favor of the structures I and II for δ-elemenol and epi-δ-elemenol, respectively.



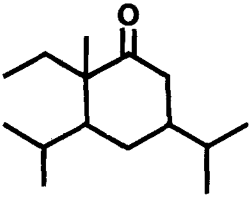
I



II



III



IV

δ-Elemenol (I), $[\alpha]^{24}_{D}$ -13.1° (c, 0.26 in MeOH), and epi-δ-elemenol (II), $[\alpha]^{24}_{D}$ +184.1° (c, 1.23 in MeOH), show the following spectral properties.

IR : cm^{-1}

(I) : 3450, 3075, 1638, 918, 895 and 840

(II): 3390, 3075, 1635, 910, 895 and 839

MS : m/e (%)

(I) : 220 (4.9): M^{+}, 137 (95), 136 (63), 121 (100) and 84 (91)

(II): 220 (3.0): M^{+}, 137 (88), 136 (67), 121 (100) and 84 (72)

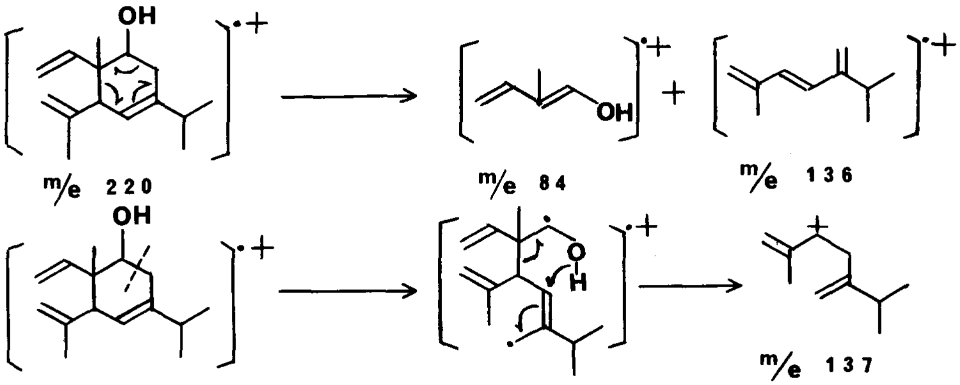
NMR : ppm in CCl_4

proton at	C-8	C-5	C-9	C-6
(I) :	2.08 (2H, broad d.),	2.74 (1H),	3.52 (1H, q., J_1 =10 cps, J_2 = 6 cps),	5.13 (1H)
(II) :	2.15 (2H, broad d.),	2.80 (1H),	3.53 (1H, t., J = 5 cps),	5.10 (1H)

Both alcohols gave the same ketone (III)[*1], $\nu_{max}^{liq.}$ = 1710 cm^{-1}, on oxidation with chromic anhydride in pyridine at room temperature. Therefore, I and II are isomeric with regard to the orientation of hydroxyl group. In NMR spectra, double doublet signals of one proton of δ-elemenol at 3.52 ppm (J_1= 10 cps and J_2= 6 cps) and triplet signals of one proton of epi-δ-elemenol at 3.53 ppm (J = 5 cps) suggest that the hydroxyl group is oriented equatorial in the former and axial in the latter.

Each alcohol gave a corresponding hexahydro derivative on catalytic hydrogenation, which, on oxidation with chromic anhydride in pyridine, gave a corresponding hexahydro ketone (IV). The ketone (IV) was subjected to Wolff-Kishner reduction to yield elemane. The product showed the same IR and MS spectra with those of authentic sample obtained from β-elemene.

The MS cracking patterns of both alcohols resemble with each other and their degradation modes are essentially the same with that of δ-elemene, except for m/e 137 ion species. This, together with the information from their NMR spectra, furnish a strong evidence for the relative location of both the hydroxyl group and the double bond on ring.



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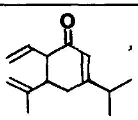
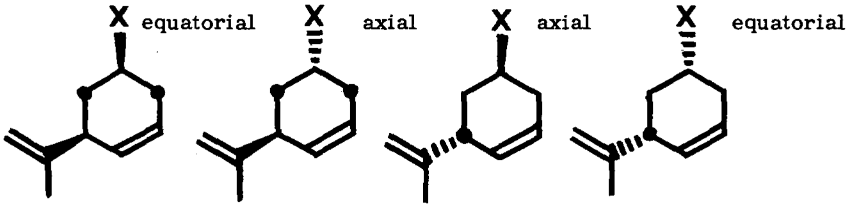
*1) A minor amount of the conjugated isomer, , ν = 1670 cm^{-1}, was obtained.

Intensity of the ion, m/e 137, is negligible in δ-elemene, acetates of both δ-elemenol and epi-δ-elemenol and δ-elemenone (III), supporting such hydrogen transfer as depicted above.

According to Brewster[1)], the gross values of optical rotation in the model compounds, A, B, C and D, are expected as follows:

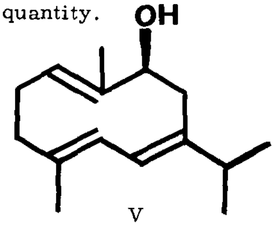


	A	B	C	D
X term	+ 160°	+ 80°	- 80°	- 160°
isopropenyl term	- 303°	- 303°	+ 303°	+ 303°
$[M]_D$ calc.	- 143°	- 223°	+ 223°	+ 143°

The X term includes the contribution of ring asymmetry and, therefore, the asymmetry at C-10 would claim a correction term, calculation of which is not easy though.

The difference of the observed $[M]_D$ values of II and I, $\Delta[M]_D = 434°$, is far greater than that could be expected on the basis of different orientation of hydroxyl group in the same enatiomorphic skeleton. Now, we can chose a set of antipodal epimers, I and II, for (-)-δ-elemenol and (+)-epi-δ-elemenol, respectively, as the main contribution to the optical rotation of these compounds is effected by the asymmetry of the cyclohexene ring conformation and of C-5.

Further elaborate studies are now under progress and will be reported elsewhere, though the tentative conclusion seems quite natural, because a single precursor (V) could afford two optically active products, while a set of epimeric precursors would result in nearly inactive products so far as in about the same quantity.



V

Acknowledgements - We wish to thank Sionogi Research Laboratory, Shionogi & Co., Ltd., for the measurements of optical rotation.

REFERENCE

1) J.H. Brewster, J. Amer. Chem. Soc., 81, 5475 (1959).