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DEODARONE, A NOVEL SESQUITERPENE TETRAHYDRO-γ-PYRONE FROM *CEDRUS DEODARA* ESSENTIAL OIL

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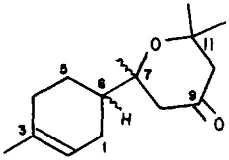
IN continuation of our earlier investigations[1] on the essential oil from the wood of *Cedrus deodara* Loud., we wish to report on the structure of *deodarone*, a sesquiterpene constituent of the essential oil. Deodarone is present to the extent of ~ 2% in the essential oil and, has an intense odour characteristic of the wood.

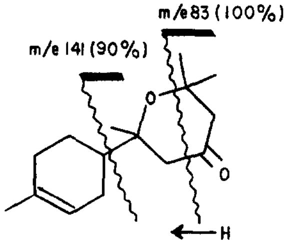
Deodarone (n_D^{30} 1.4951; $[\alpha]_D$ +6.3 in $CHCl_3$) analyses for $C_{15}H_{24}O_2$ (M^+, m/e 236) and shows in its IR spectrum (smear) absorptions for C=O (1725 cm^{-1}) and C=C (1625 cm^{-1}), but no OH band. Since, the compound remains unaffected by 10% alc. KOH (3 hr, N_2) an ester or a δ-lactone grouping is ruled out and hence, the second oxygen function must occur as an ether. Its PMR spectrum displays signals at 1.16 ppm (3H, s) and 1.28 ppm (6H, s) assignable to three tertiary methyls attached to carbons linked to oxygen, besides revealing the structural features: $CH_3-\underset{|}{C}=C$ (3H, broad s, 1.62 ppm), $-\overset{|}{C}-C\underline{H}_2-\overset{\overset{O}{\|}}{C}-$ (~ 2H, s, 2.28 ppm), $CH_3-\underset{|}{C}=C\underline{H}-CH_2-$ (1H, ill-resolved m, 5.26 ppm, W 1/2 = 8 Hz) Since, its PMR spectrum does not show any signal for $\underline{H}C=O$, deodarone must be a ketone.

From its UV absorption (no strong absorption above 220 nm) it is clear that deodarone is not an $\alpha\beta$-unsaturated ketone. That, in all likelihood, the olefinic linkage is also not located at $\beta\gamma$ to the carbonyl, became evident from the fact that, deodarone remained unchanged (UV) on exposure to t-BuOK in t-BuOH (attempted equilibration to $\alpha\beta$-isomer). Deodarone undergoes no change on treatment with Zn and AcOH, and hence, the ether linkage cannot be located α to the carbonyl. That the ketone function in deodarone is flanked by two methylene groups was evident from deuterium exchange studies, which revealed the incorporation of 4D (M^+, m/e 240. PMR: loss of ~ 4H signals in the 2.10 - 2.40 ppm region).

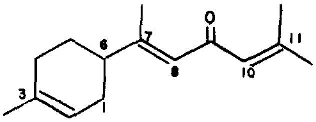
All the known sesquiterpene constituents of the *Cedrus deodar* essential oil appear to have been derived from *cis*-farnesyl pyrophosphate, either by a 1,6-cyclization (bisabolane type) or a 1,11-cyclization (himachalane, longibornane types)[2]. Arguing, that deodarone also may belong to either one of these groups, it was found that, only on the basis of a bisabolane skeleton (1,6-cyclization), can one draw up a working structure (I) meeting all the structural requirements disclosed above. This structure (I) is clearly supported by electron-impact-induced fragmentation of deodarone, the main features of which are summarised in II. This fragmentation is supported by the mass spectrum of the deuterated derivative, described earlier.



I



II



III

Chemical support in favour of I was obtained by a direct correlation with trans-atlantone (III)[1]. Atlantone on treatment with H_2O_2-NaOH aq. gave 7-8, 10-11 diepoxide. The latter product, in hexane, on long (40 hr) exposure to 10% H_3PO_4 aq. at ~ 60° yielded a complex mixture of keto alcohols. This was acetylated and the product on treatment with Ca-liq.NH_3 gave as one of the compounds, deodarone, which was identified in the usual manner (PMR, Mass).

Further work is in progress to define the stereochemistry of I.

REFERENCES

1 B.S. Pande, S. Krishnappa, S.C. Bisarya and Sukh Dev, Tetrahedron **27**, 841 (1971), and the references cited therein.

2 S.C. Bisarya, Ph.D Thesis, Agra University (1965).