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STRUCTURE OF HUMULENE

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VARIOUS structures (I,[1] II,[2] III,[3] IV[4]) have been proposed for humulene. While the nature of the carbon-skeleton is well established,[5] the position of the ethylene linkages is not known with any certainty. Recently, we have demonstrated[6] that the closely related sesquiterpene ketone, zerumbone, has the structure (V). We have now examined the proton magnetic resonance (PMR) spectra of humulene, zerumbone and their hydroderivatives, and the data permit us to assign unequivocally the structure (IV) to humulene. The PMR spectrum* of zerumbone had peaks (all well-resolved) at 147.7

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[1] F. Sorm, M. Streibl, J. Pliva and V. Herout, Coll. Czech. Chem. Comm. **16**, 639 (1951).

[2] G. R. Clemo and J. O. Harris, Chem. & Ind. 799 (1951); R. W. Fawcett and J. O. Harris, Ibid. 18 (1953); J. Chem. Soc. 2673 (1954).

[3] Sukh Dev, Curr. Sci. **20**, 296 (1951).

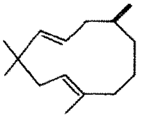
[4] P. Clarke and G. R. Ramage, J. Chem. Soc. 4354 (1954).

[5] F. Sorm et al., Coll. Czech. Chem. Comm. **19**, 570 (1954).

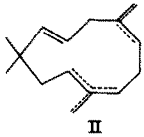
[6] Sukh Dev, Chem. & Ind. 1051 (1956).

* The spectra were determined at 40 mc on 25% solutions in carbon tetrachloride, with a Varian Model V-4300B high resolution spectrophotometer. The chemical shifts were measured relative to water. The assignments for zerumbone are confirmed by the PMR spectra of tetrahydrozerumbone, hexahydrozerumbone, and humulane.

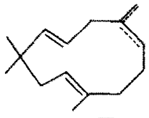
(two *gem*-dimethyl groups), 132.7 (one CH_3—C=C—group protons), 124.8 (second CH_3—C=C—), 104.3 (and minor peaks at 110.6 and 115.3 counts/sec; three —CH_2— groups protons*), -14.2 (a triplet; one olefinic proton), and -37.9 counts/sec (two olefinic hydrogens β to the carbonyl and one olefinic proton α to the carbonyl). It should be noted here that the 'saturated' methyl groups, 'olefinic' methyl groups and the methylene groups are well-separated in a characteristic manner. The PMR spectrum of humulene** is *almost identical* with that of zerumbone in the methyl and methylene proton region [peaks at 152, 137.8, 128.8, and 113.2 (with a small peak at 122.2) counts/sec with the areas approximately in the ratios 2:1:1:2] and this would indicate that *humulene also has four methyl groups*, which is in accord with structure (IV) only. Besides these bands, humulene showed the remaining 'extra' methylene group at position 9, as expected, at a still lower field strength (peaks at 90.8 and 98.6 counts/sec with



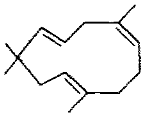
I



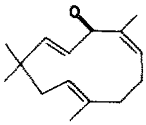
II



III



IV



V

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* These protons are well-separated from the =C-CH_3 peaks by virtue of all the methylene groups being allylic to the ethylenic linkages.

** Humulene was isolated from the essential oil of *Zingiber zerumbet* and after precise fractionation had: b.p. 114-115°/5 mm, n_D^{25} 1.5015, $[\alpha]_D^{25}$ -0.31, *nitrosochloride* m.p. 175-176°, *trioxide* m.p. 122°.

the areas approximately in the ratio 1:1 and roughly of one-third the intensity of a single methyl peak); the olefinic protons showed up as a complex group of bands, the major peaks being located at -1.0, -16.8, and -24.6 counts/sec.

According to previous workers, humulene contains one exo-cyclic $=CH_2$ group, and this contention is based on the infra-red data,[7] and $=CH_2$ group determinations involving ozonolysis.[7] Since, ozonolysis of certain systems is known to yield abnormal products, the results of $=CH_2$ group estimations do not constitute an argument against structure (IV). As for the infra-red data, we have re-examined the infra-red absorption of humulene quantitatively, and find the apparent ϵ of the relevant peaks as follows: 1665 (ϵ 20.8), 965 (ϵ 125), 885 (ϵ 32), and 820 cm^{-1} (ϵ 64). It would be clear from this data that the peak at 885 cm^{-1}, on which the presence of $=CH_2$ group had been based by these workers, is very weak,* and hence is not a forcing argument for the presence of $=CH_2$ group. Thus, the evidence presented in this paper allows the unequivocal formulation of humulene as (IV). This structure is directly related to that of zerumbone by an oxidation-reduction system, and we are currently trying to effect such transformations.

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[7] F. Sorm, J. Mleziva, Z. Arnold, and J. Pliva, *Coll. Czech. Chem. Comm.* **14**, 699 (1949).

* The usual value of the apparent ϵ for $\nu^{C=CH_2}$ is ~40 and for $\delta^{=CH_2}$ ~115. The intensities of the other bands at 965 (one *trans*- $-HC=CH-$) and 820 cm^{-1} (two $-HC{=}C-$) are as anticipated. (R. N. Jones and C. Sandorfy in A. Weissberger's *Technique of Organic Chemistry* Vol. IX, pp. 367-384. Interscience, New York (1956).

A fuller acount of this work will be reported shortly in Tetrahedron.

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