

INFRA-RED INVESTIGATIONS ON THE HYDROCARBON CYPERENE—II

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Received February 10, 1956

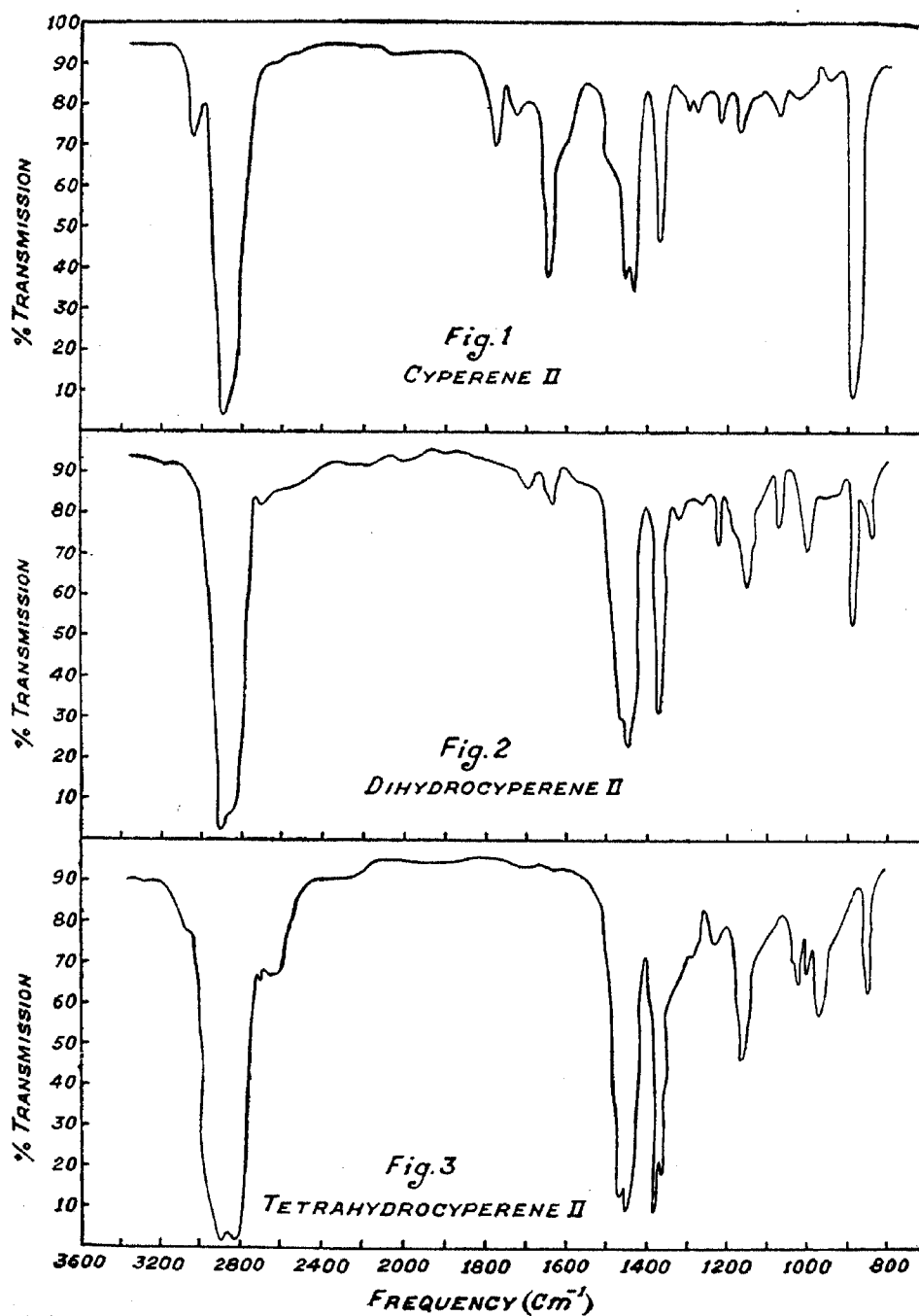
(Communicated by Prof. R. S. Krishnan, F.A.Sc.)

1. INTRODUCTION

KIMURA AND OHTANI (1928) gave the name cyperene to the hydrocarbon fraction of the oil extracted from the tubers of the weed plant *Cyperus rotendus* L. Subsequently Hegde and Rao (1935) followed up these investigations on the Indian variety but failed to confirm the presence of a hydrocarbon with properties ascribed by Kimura and Ohtani. Hegde and Rao, therefore, suggested that there were at least two different hydrocarbons present in the oil extracted from *Cyperus rotendus* L. Recently one of us (Senich) has carried out a systematic examination of the hydrocarbon fraction of the oil from Indian tubers (Madras variety) and it has been found that by fractional distillation four different hydrocarbon fractions could be obtained. Two of these fractions could be obtained in yields of 14% and 6% while the other two fractions are obtainable in much lower yields. The product which is available in maximum yield (14%) has been named cyperene II (M. Wt. 204). In this paper we shall describe the results of our investigations on the infra-red spectra of cyperene II and its hydrogenated products. However, before doing so it will be desirable to note the following facts regarding the chemical properties of these compounds which will enable us to discuss the structure of these molecules from the infra-red data.

Even after hydrogenation with $\text{Pd}(\text{OH})_2$ as catalyst, cyperene II reacts to tests for unsaturation (tetranitromethane), that is, the compound shows the presence of more than one unsaturated bond in the molecule. However, after hydrogenation with PtO_2 as catalyst and acetic acid as solvent, the compound becomes completely saturated and thus the presence of two unsaturated bonds in the molecule was inferred. The product obtained after hydrogenation by $\text{Pd}(\text{OH})_2$ as catalyst is termed as dihydrocyperene II (M. Wt. 206), while the completely hydrogenated product is termed as tetrahydrocyperene II

(M. Wt. 208). The chemical investigations on these compounds which will be published elsewhere, have shown that the skeletal structure of these compounds is the same as that of eudalene. Since the infra-red spectra of these hydrocarbons can give us valuable evidence regarding molecular structure we have undertaken the study of the same and in what follows it will be seen that certain important conclusions can be arrived at from these studies. It



FIGS. 1-3.

may be noted here that the Raman spectra of these compounds have already been studied by Hariharan and Senich (1955).

2. EXPERIMENTAL

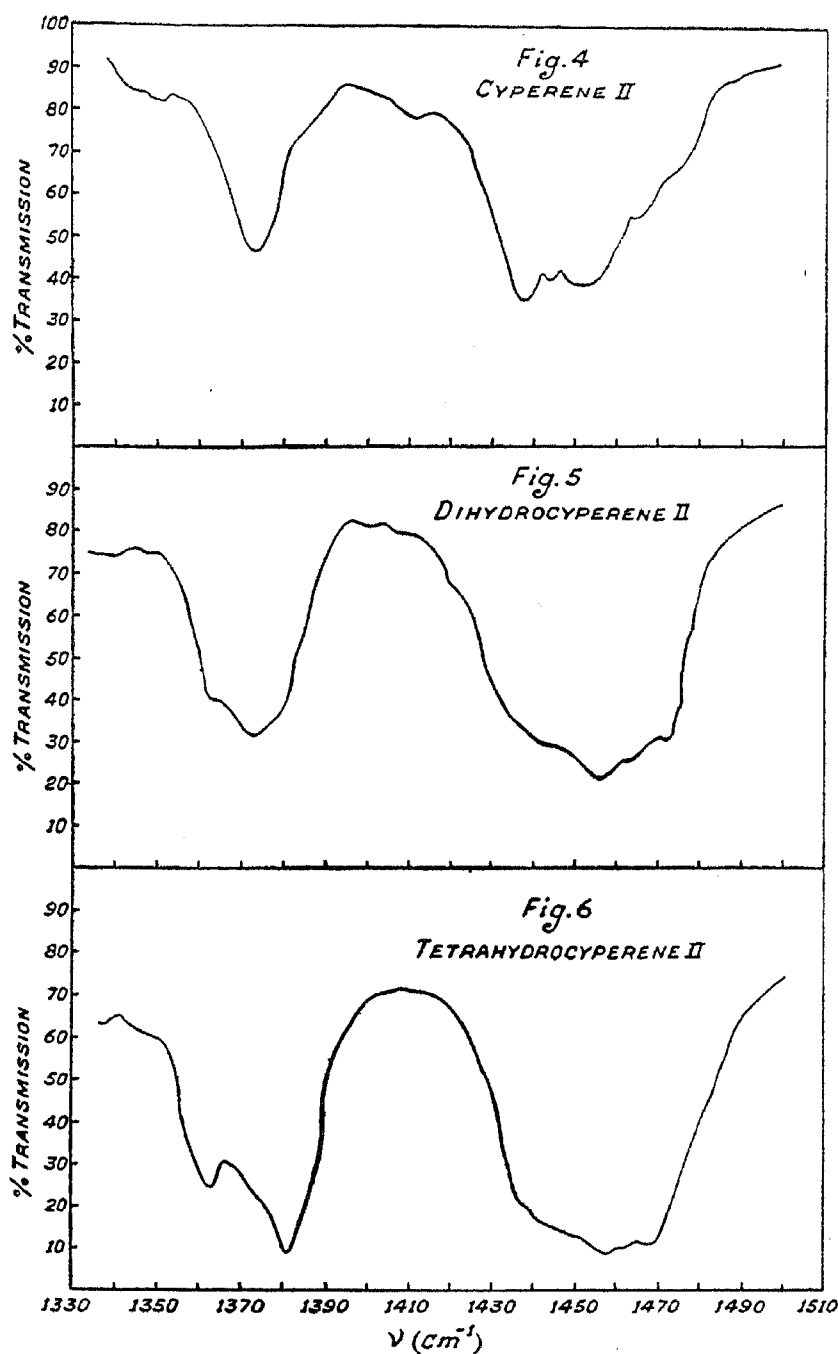
The compounds were examined in the form of thin liquid films between NaCl windows separated by a spacer 0.012 mm. thick. A Perkin-Elmer model 112 single beam double pass infra-red spectrometer with NaCl optics was used for recording the spectra. The region examined was between 800 and 3,500 cm^{-1} and the resolution with the slit width employed was approximately as follows: 800–1,500 cm^{-1} — 4 cm^{-1} ; 1,500–2,000 cm^{-1} — 8 cm^{-1} ; 2,000–3,500 — 20 cm^{-1} . The liquids were freshly distilled over sodium before examination. Owing to their high boiling points (cyperene II — 129° C. at 10 mm.) trouble on account of evaporation in the cell was absent. Some of the physical properties of these compounds are listed here. Cyperene II — n_D^{20} 1.5072; α_D^{30} + 13° 48'. Dihydrocyperene II n_D^{25} 1.4920; α_D^{25} + 12° 0'. Tetrahydrocyperene II n_D^{25} 1.4838; α_D^{25} + 1° 24'.

3. RESULTS

In Figs. 1, 2 and 3 are reproduced the infra-red spectra of cyperene II, dihydrocyperene II and tetrahydrocyperene II respectively. Figs. 4, 5 and 6 show the enlarged spectra in the region 1,330 — 1,500 cm^{-1} so as to bring out the details which are discussed later. Table I summarises the infra-red data on these compounds.

TABLE I
Infra-red absorption frequencies

Cyperene II	Dihydrocyperene II	Tetrahydrocyperene II
858 (W)	847 (W)	855 (W)
886 (S)	885 (M)	978 (M)
1070 (W)	1001 (W)	1100
1171 (W)	1072 (W)	1030
1220 (W)	1151 (W)	1164 (S)
1372 (S)	1222 (W)	1224
	1373 (S)	1367/1381 (S)
1436/1452 (S)	1456/1472 (S)	1458 (S)
1644 (S)	1644 (W)	
1728 (W)		2640 (W)
1775 (W)	2700 (W)	2700 (W)
2890 (S)	2890 (S)	2820/2900 (S)
3050 (W)		



FIGS. 4-6.

4. DISCUSSION

The appearance of a strong absorption band at 886 cm.⁻¹ in cyperene II clearly indicates the presence of the grouping >C=CH_2 since this frequency is easily ascribed to the C—H out of plane deformation in this group especially on account of its intensity (Bellamy, 1954). In dihydrocyperene II this

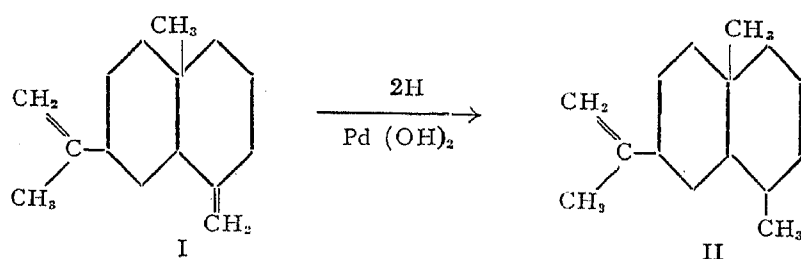
band is no doubt present but is very much less intense while in the completely hydrogenated compound this band is absent. (Compare Figs. 1, 2 and 3). A corroboration of this fact can also be obtained from the C=C stretching frequency of $1,644\text{ cm.}^{-1}$ in the abovementioned grouping (Sheppard and Simpson, 1952). The absence of this band in tetrahydrocyperene is noteworthy. It will be seen that remarks made earlier regarding the intensity of the 886 cm.^{-1} band apply equally to the $1,644\text{ cm.}^{-1}$ band also. These facts are in good agreement with the chemical point of view, *viz.*, that hydrogenation of cyperene II removes in the first instance one of the two double bonds while in the last case the compound (tetrahydro-) is completely saturated and hence shows no absorption in these regions. It will be shown subsequently that this proof of the presence of the grouping >C=CH_2 in cyperene II and in dihydrocyperene II goes a long way in elucidating the structure of these molecules.

The $1,370\text{ cm.}^{-1}$ band in cyperene II and in dihydrocyperene II can be ascribed to the symmetrical deformation mode of the C—CH₃ group. In the dihydrogenated compound this band appears with greater intensity while in the tetrahydrogenated compound some additional features are to be noticed (compare Figs. 4, 5 and 6). The $1,370\text{ cm.}^{-1}$ absorption band of tetrahydrocyperene II has two sharp peaks, the positions of which are $1,363$ and $1,381\text{ cm.}^{-1}$ respectively. These arise from the resonance splitting of the C—H deformation frequencies of the two C—CH₃ groups in $\text{—HC}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ (McMurray and Thornton, 1952; Sheppard and Simpson, 1953). The presence of a strong band at 1164 cm.^{-1} (skeletal vibration of $\text{—HC}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$) in the completely saturated compound is again in agreement with this assignment. We may, therefore, conclude that the molecule of tetrahydrocyperene II contains the grouping $\text{—HC}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$.

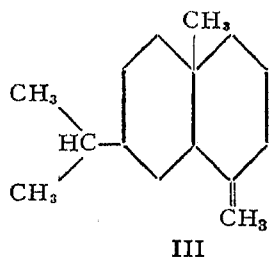
The symmetrical mode of the C—H vibration in C—CH₃ group generally gives rise to a broad band near $1,450\text{ cm.}^{-1}$. The appearance of this band in the three compounds studied and the increase in intensity of this band with hydrogenation point out to the increase in the number of methyl groups. The intense absorption band near $2,890\text{ cm.}^{-1}$ has a very broad coverage and on account of the lower resolution (20 cm.^{-1}) of the spectrometer in this region and owing to the overlapping of the C—H stretching frequencies of CH₃, CH₂ and CH (tertiary) groupings it is very difficult to differentiate these frequencies. Generally speaking this band is to be ascribed

to the C—H stretching frequencies and here again the qualitative correlation in intensity with progressive hydrogenation is clearly seen.

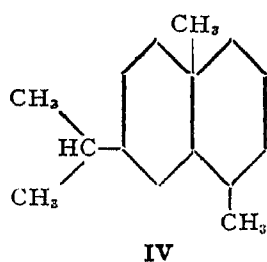
Having discussed the main features of the infra-red spectra of these three compounds it now remains for us to see how best the observed spectra could be correlated to the molecular structures. It was stated earlier that the chemical evidence points out to the skeletal structure of eudalene for these molecules. Based on this we can now postulate for cyperene II structure I which on hydrogenation first gives dihydrocyperene II (struc-



ture II). The appearance of two kinks in the $1,370\text{ cm.}^{-1}$ band of dihydrocyperene II may be due to the formation of (III) but this is certainly extre-



mely small and the evidence is mainly spectroscopic. The structure of



tetrahydrocyperene II can be, therefore, given by IV. Other structures with double bond inside the ring can be postulated for cyperene II but the infra-red spectral data do not then lend themselves to satisfactory interpretation.

Particular mention should be made of the $\text{>C}=\text{CH}_2$ group and its strong intensity and the resonance splitting of the $1,370\text{ cm.}^{-1}$ band due to the $\text{—HC} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ grouping with its appearance in the tetrahydrogenated compound.

Structure I accounts satisfactorily for the following bands. 886 cm^{-1} ; 1,372 cm^{-1} ; 1,430–1,450 cm^{-1} ; 1,644 cm^{-1} and 2,890 cm^{-1} —in fact for all the observed strong infra-red bands. Structure II accounts for the following bands: 885 cm^{-1} , 1,373 cm^{-1} ; 1,430–1,450 cm^{-1} and 2,890 cm^{-1} . It also accounts for the decrease in the intensity of the 885 cm^{-1} , the persistence of the weak 1,644 cm^{-1} band and the increase in intensity of the 1,373 cm^{-1} band. Even the presence of the two kinks (see Fig. 5) in the 1,373 cm^{-1} band of this compound (dihydro-) may be accounted for on the basis of the presence of traces of III formed from I during hydrogenation. Structure IV accounts completely for the observed infra-red spectrum of tetra-hydro-cyperene II and in particular for the appearance of the two maxima in the 1,370 cm^{-1} band and its increase in intensity.

5. SUMMARY

The infra-red spectra of cyperene II [hydrocarbon isolated from oil extracted from *Cyperus rotendus* (Indian variety)], dihydrocyperene II and tetrahydrocyperene II have been studied in the form of thin liquid films in the region 800–3,500 cm^{-1} . The skeletal structure of the molecules is of the eudalene type. The probable structures of these molecules are discussed in the light of the infra-red data and tentative assignments have been made.

The authors' grateful thanks are due to Prof. R. S. Krishnan, Head of the Department of Physics, for his valuable help and guidance in the progress of this work. Their thanks are also due to Prof. D. K. Banerjee, Head of the Department of Organic Chemistry, and to Dr. Suk Dev, for valuable help. They also wish to thank Dr. P. S. Narayanan, for helpful discussions.

6. REFERENCES

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