

Studies Related to Pristane

IV. Infra-Red Spectra

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In the course of their work on the constitution of the saturated aliphatic hydrocarbon pristane from the liver oil of the basking shark, J. S. Sørensen and N. A. Sørensen^{1,2} determined the physical constants of a series of aliphatic hydrocarbons C₁₉—C₂₀. On the basis of their careful measurements these authors concluded that pristane is probably identical with *norphytane*, i. e. 2,6,10,14-tetramethylpentadecane.

In order to obtain conclusive confirmation of this identity, the infra-red spectra of pristane, *norphytane*, phytane and crocetane were measured. The results of these measurements are discussed in the present communication.

EXPERIMENTAL

The isolation of *pristane* from the unsaponifiable matter of the liver oil of the basking shark and its purification has been described in the first communication of this series³.

Norphytane and *phytane* were obtained from phytol as described in the third communication of this series².

Crocetane "A" was prepared according to Fischer and Löwenberg⁴ as described in Part I³.

Crocetane "B" was obtained from carefully purified 2,6,11,15-tetramethylhexadecatetraene-2,6,10,14 (digeranyl)⁵.

The physical constants of the samples used for measurement are given in Table 1 (cf. also ref. 1—3).

Table 1. Physical constants of the samples investigated.

	d_4^{20}	n_D^{20}
Pristane	0.7827	1.4385
<i>Norphytane</i>	0.7833	1.4386
Phytane	0.7907	1.44225
<i>Crocetane</i> "A"	0.7858	1.44055
<i>Crocetane</i> "B"	0.7888	1.4410

The infra-red spectra were measured on a Perkin-Elmer infra-red spectrometer, model 12B, with a 60° rock-salt prism. The substances were examined in the liquid state at room temperature.

RESULTS AND DISCUSSION

As may be seen from Fig. 1, the infra-red spectra of pristane (curve I) and *norphytane* (curve II) are practically identical. Although this close coincidence of the spectra might have been considered proof of the identity of these hydrocarbons, it was thought worth while to examine the spectra of phytane (2,6,10,14-tetramethylhexadecane) and crocetane (2,6,11,15-tetramethylhexadecane) as well, to make sure that the differences between the infra-red spectra of such closely related hydrocarbons are sufficient to permit their safe identification.

As would be expected, the differences found were most marked in the case of hydrocarbons which differ in their terminal groups, *e. g.* *norphytane* and phytane, or crocetane and phytane, since the terminal groups give rise to characteristic absorption bands; the strong band at 1170 cm^{-1} with a shoulder at about 1150 cm^{-1} is due to skeletal vibrations of the *isopropyl* groups, $(\text{CH}_3)_2\text{CH}-$ ⁶. In the spectrum of phytane a moderately strong band is found at 770 cm^{-1} which is characteristic of the terminal ethyl group⁷.

On the other hand, the hydrocarbons *norphytane* and crocetane differ only in the number of the CH_2 -groups in the middle of the chain. Their spectra therefore show many common features. Nevertheless, even in this case the homologues may safely be distinguished from one another by means of their infra-red spectra. In the spectra of the crocetanes (curves IV and V), the strong bands at 735 cm^{-1} , which may probably be assigned to the CH_2 -rocking vibrations in the chain $\text{R}_1-\text{CH}_2\text{CH}_2\text{CH}_2-\text{R}_2$ ^{8,9}, show distinct and readily reproducible shoulders at about 727 cm^{-1} , whereas these shoulders are definitely absent in the spectra of pristane and *norphytane* (as well as of phytane). Because of the natural width of these hydrocarbon bands it has not been possible to resolve the 735 cm^{-1} and the overlapped 727 cm^{-1} bands although our instrument is capable of resolving bands separated by about 2 cm^{-1} in this region. Resolution of these bands might be achieved at very low temperatures. The overlapped band at 727 cm^{-1} may be assigned to the CH_2 -rocking vibrations in the group $\text{R}_1-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{R}_2$ ^{7,9}. Some further dissimilarities in the spectra may also serve to distinguish between *norphytane* and crocetane, *e. g.* the distinct broad band at 970—80 cm^{-1} in the spectra of the crocetanes (*cf.* curves IV and V).

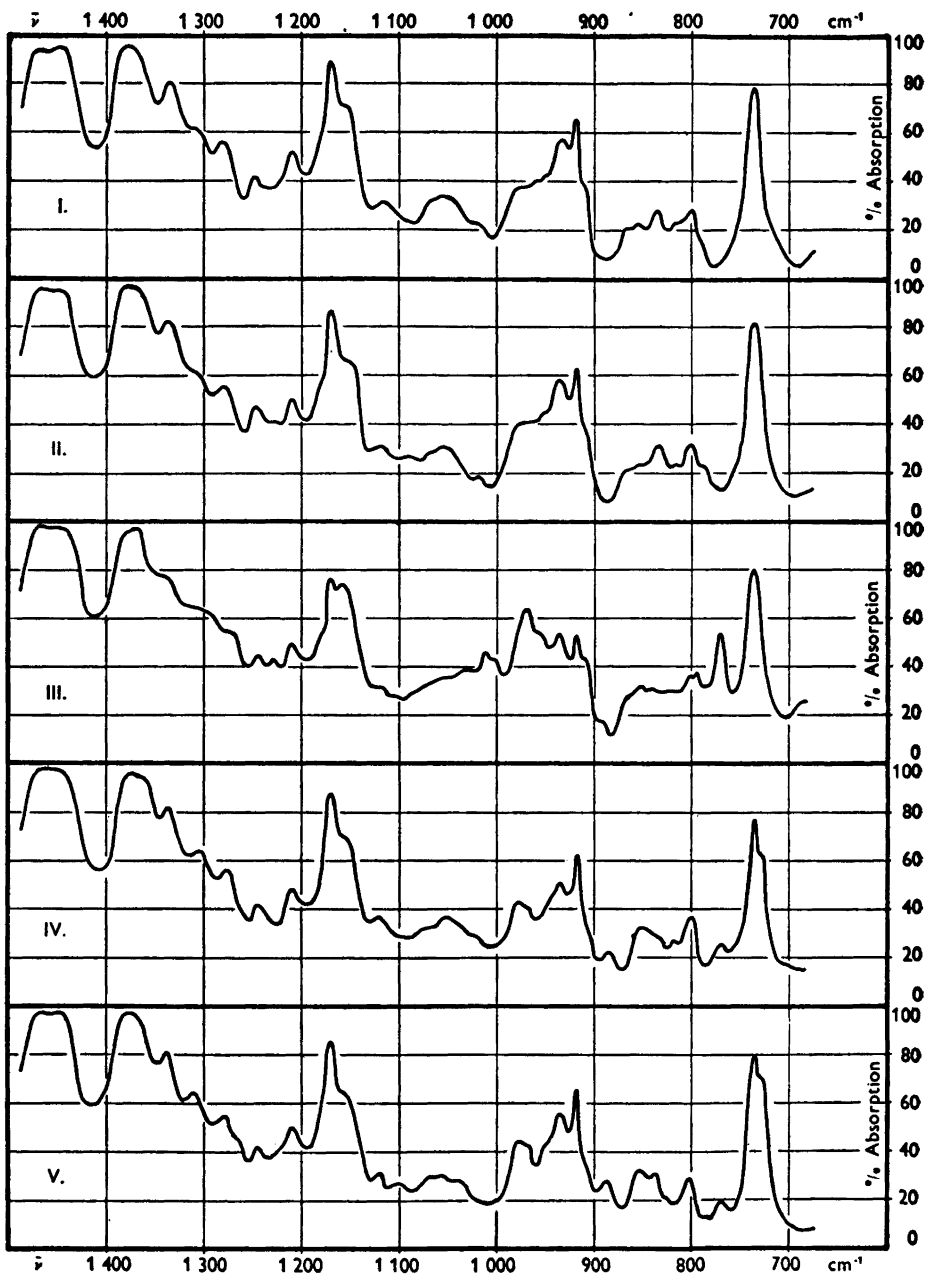


Fig. 1. I. Pristane. II. Norphytane. III. Phytane. IV. Crocetane "A". V. Crocetane "B". Cell thickness 0.15 mm.

It may be concluded that the infra-red spectrum is sufficiently sensitive to small changes in constitution, even in the case of aliphatic hydrocarbons of chain length as great as C_{19} or C_{20} , to serve for distinguishing between such very closely related hydrocarbons, if properly applied.

The coincidence of the infra-red spectra is therefore considered conclusive evidence for the identity of pristane and *norphytane*.

It may be added that the infra-red spectrum of phytane (2,6,10,14-tetramethylhexadecane) closely resembles the spectrum of farnesane (2,6,10-trimethyldodecane) and even that of hexahydromyrcene (2,6-dimethyloctane) which have been reported recently.⁸ All these hydrocarbons possess carbon skeletons consisting of regularly arranged isoprene residues and differ only in the number of these units.

SUMMARY

The infra-red spectra of the saturated hydrocarbons pristane, *norphytane*, phytane and of two samples of crocetane have been examined. These spectra furnish conclusive evidence for the identity of pristane and *norphytane* (2,6,10,14-tetramethylpentadecane) which had previously been suggested on the basis of measurements of physical constants.

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