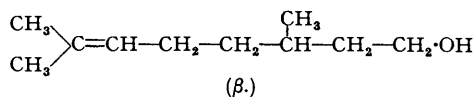
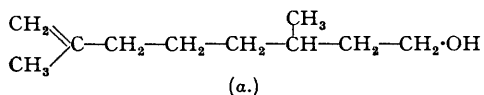


287. The Infra-red Examination of Some Terpenoid Substances.

By H. W. THOMPSON and D. H. WHIFFEN.

The infra-red absorption spectra of some terpenoid substances have been measured, with the object of determining the nature of terminal groupings in such compounds as citronellol, where *isopropenyl* and *isopropylidene* structures may arise. Characteristic absorption bands occur for these two groupings, and it has been found that in many of these compounds both the structures are present, which seems adequate proof that the substances are mixtures of the two forms. The proportions of the two isomeric forms are different in different compounds, although the *isopropylidene* type seems as a rule to be in excess. Different samples of the same substance may also contain different proportions of the two forms.

THERE has been some discussion about the structure of citronellol and other related terpenoid substances, with particular reference to the nature of the terminal groupings which may be *isopropenyl* (α) or *isopropylidene* (β).



The chemical evidence has been discussed fully by Simonsen and Owen ("The Terpenes", 2nd Edn., Vol. I, p. 2; Simonsen, *J.*, 1935, 784). Ozonolysis leads to both acetone and formaldehyde (Kuhn and Roth, *Ber.*, 1932, 65, 1258), which suggests that both forms exist simultaneously, but others have argued that migration of the double bond may occur during oxidation, and that the substances concerned have sharp melting points and behave like single compounds.

Dr. Simonsen recently inquired whether this dilemma might be resolved by measuring the infra-red absorption spectra, which has the advantage that the substances are examined without the possibility of intramolecular rearrangement. Fortunately, too, characteristic infra-red absorption bands appear to exist for the two types of olefinic group involved. It has been found from measurements on the spectra of unsaturated hydrocarbons that four classes may be distinguished, having fairly strong absorption bands at the approximate positions given in the table (Thompson and Torkington, *Proc. Roy. Soc.*, 1945, 184, A, 3; *Trans. Faraday Soc.*, 1945, 51, 247; Rasmussen and Brattain, *J. Chem. Physics*, 1947, 15, 120, 131, 135).

Type of group.	Positions (cm. ⁻¹) of characteristic bands.
(a) R-CH=CH ₂	910 and 990
(b) R ₁ -CH=CHR ₂	965
(c) R ₁ R ₂ C=CH ₂	890
(d) R ₁ R ₂ C=CHR ₃	810—840

In the hydrocarbons themselves, those bands which are associated with deformational motions of the C-H bonds contiguous to the double bond, usually stand out strongly against the remainder of the spectrum, and they are useful in studying the structure of complex molecules such as polybutadiene, polyisoprene or rubber (Thompson and Torkington, *loc. cit.*). In oxygenated compounds, other intense bands may occur, so that thinner layers of the absorbing substances have to be used if all the features of the spectrum are to be seen, but experience has shown that the characteristic olefinic bands just listed are as a rule clearly discernible.

Another region of the infra-red which can be used for diagnosis is that around

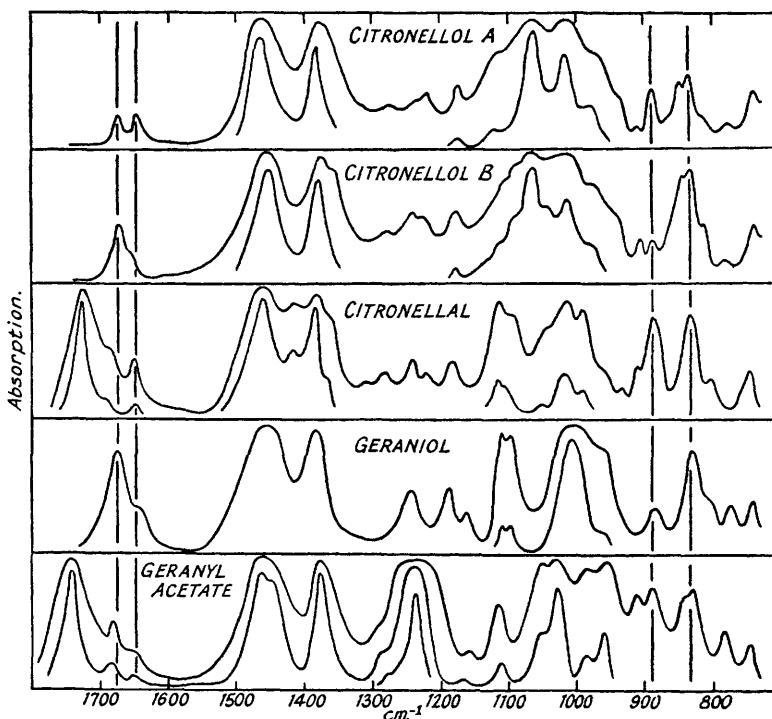
1600—1700 cm^{-1} , where the band due to the stretching of the carbon-carbon double bond occurs. Measurements with simple olefins have shown that with compounds containing the group $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ there is a band near 1640 cm^{-1} , whereas with those of the type $\text{R}_1\text{R}_2\text{C}=\text{CHR}_3$ the corresponding band lies near 1670 cm^{-1} . This result corresponds to that found with the Raman spectra of similar compounds (Hibben, "The Raman Effect", p. 166; Dupont, Desreux, and Dulon, *Bull. Soc. chim.*, 1937, 4, 2016; Dupont and Desreux, *ibid.*, p. 422; Gredy, *Compt. rend.*, 1932, 195, 313; Naves, Brus, and Allard, *ibid.*, 1935, 200, 1112).

In applying correlations of this kind to the determination of the structure of molecules, it is of course important to realise that other vibrations of the structure may give rise to bands which fall accidentally in the same positions as those of the key bands. On the other hand, the persistence of these key bands through a series of molecules is good evidence for their reliability. The present results appear to confirm the hypothesis that many of these substances are in fact mixtures of the two forms with *isopropenyl* and *isopropylidene* groupings, which occur in varying proportions in different compounds and which may vary in different samples of any given compound.

EXPERIMENTAL.

The substances were obtained from several sources, more than one sample of each compound being studied whenever possible. Many were provided by Dr. J. L. Simonsen and Dr. E. R. H. Jones;

FIG. 1.



others were laboratory specimens of purified commercial samples. They will be more conveniently listed below. All except geranamide were examined as liquids in thin layers between rock-salt plates. Geranamide was studied as a thin solid film on rock-salt.

The spectrometers have been described elsewhere. One was a single beam recorder with prism of rock-salt (Whiffen and Thompson, *J.*, 1945, 268), the other a double-beam recorder with prism of calcium fluoride (Sutherland and Thompson, *Trans. Faraday Soc.*, 1945, 51, 178; Thompson, Whiffen, Richards, and Temple, in the press). The region 5—15 μ was studied in each case.

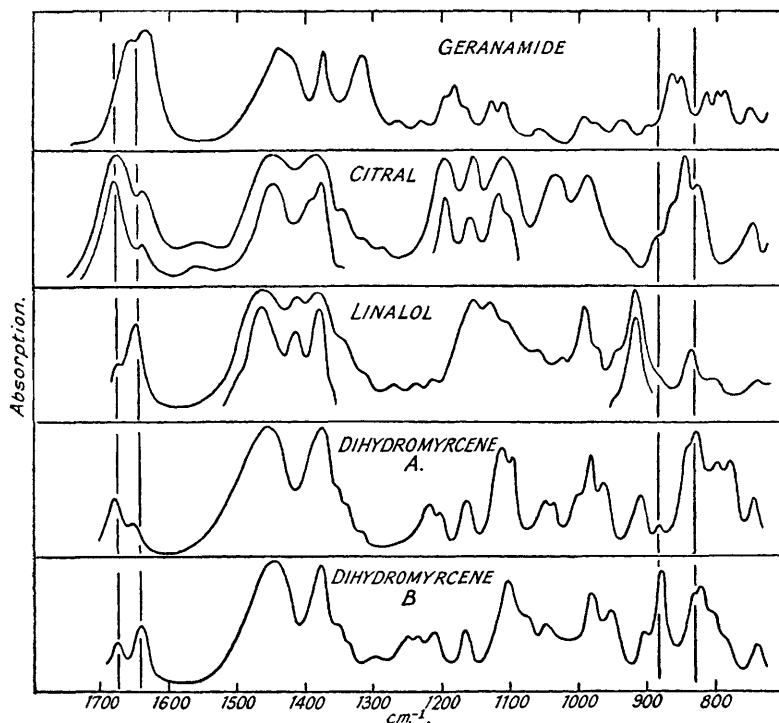
Results.—The spectra are shown in Figs. 1 and 2. Most of the substances examined have a fairly strong band near 830 cm^{-1} , and many have a band near 890 cm^{-1} , which can be correlated with the olefinic groupings concerned, but the relative intensities of these bands vary in different cases. There are also bands connected with the carbon-carbon double-bond vibrations in the region of 1650 cm^{-1} . The compounds are best considered individually.

(1) *Citronellol*. This substance may have either of the formulæ (α) and (β) given above. Sample A was provided by Simonsen and Jones, and showed bands at 885 and 830 cm^{-1} , of about equal intensity.

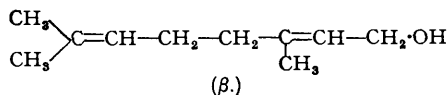
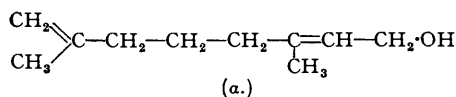
It also had bands at 1640 and 1670 cm^{-1} , also of about equal intensity. Both results imply the simultaneous occurrence of α - and β -forms. Sample B, from British Drug Houses Ltd., showed an almost identical spectrum to sample A, but the relative intensities of the bands at 885–830 and 1640–1670 were changed, the bands at 885 and 1640 cm^{-1} being weakened relatively to the other two. This is in agreement with what would be expected if the sample contained less of the α -form and relatively more of the β -variety.

(2) *Citronellal*. The spectrum shown relates to a sample from British Drug Houses Ltd., and has the bands at 885 and 830 cm^{-1} almost equally intense, and similarly the bands at 1640 and 1670 cm^{-1} about equally strong. Another specimen (Light and Co.) appeared to have become much oxidised, but again gave the characteristic pairs of bands of about equal intensity. In these cases, therefore, there seem again to be mixtures of the α - and β -forms. An exact determination of the proportions is not at present possible without pure samples of the isomers, since measurements on simpler olefins have suggested that the "group" extinction coefficients of the characteristic absorption bands do not remain strictly constant in different molecules. It seems certain, however, that the proportions of the α - and β -forms vary in the different samples.

FIG. 2.



(3) *Geraniol*. The formula of geraniol and nerol can be either of the following :



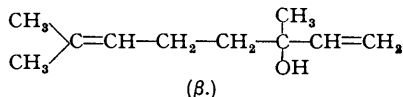
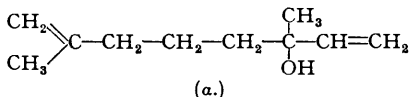
The spectrum is shown of a sample from Simonsen and Jones. The bands near 830 and 1670 cm^{-1} are strong compared with those at 885 and 1640 cm^{-1} , indicating a greater proportion of the *isopropylidene* (β) form. Two other samples, a purified laboratory product and a sample from the British Drug Houses Ltd., were measured and gave similar results, although other small differences in the spectra suggested that slight oxidation had occurred.

(4) *Geranyl acetate*. The sample was a purified commercial product. It showed the characteristic ester group absorption bands near 1230 and 1740 cm^{-1} . Bands at 830 and 885 cm^{-1} appeared about equally intense, and there are bands at 1640 and 1675 cm^{-1} . Again, therefore, both isomeric forms α and β appear to be present. In this case the relative intensities of the bands in each pair are more difficult to assess owing to the occurrence of neighbouring absorption bands which overlap.

(5) *Citral*. Two samples were examined with similar results, the spectrum shown being that of a sample from Simonsen and Jones. In this case the characteristic olefinic bands appear as before and seem roughly parallel in intensity to those found with geraniol, but there are some complications which may arise from conjugation of the carbon-carbon double bond with that of the carbonyl link in the aldehyde group. This conjugation appears to lower the characteristic frequency of the carbonyl link so

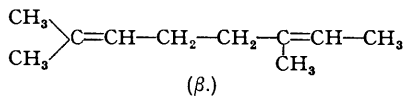
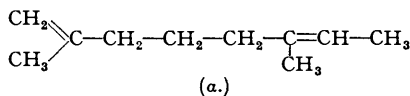
that its band overlaps the region of the band of the carbon-carbon double bonds, and the electronic effects may also give rise to the complex systems of bands near 850 cm^{-1} where another band appears.

(6) *Linalol*. This may have either of the structures (a) or (b). A sample (Bush and Co.) gave the



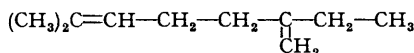
spectrum shown, but the presence of a fairly marked band near 1710 cm^{-1} suggested that it had become oxidised. However, the spectrum is interesting for the following reasons. It will be noticed that a band occurs at 835 cm^{-1} , and there may be a weaker shoulder at 890 cm^{-1} , but the latter is submerged in the onset of the strong band near 910 cm^{-1} . Another strong band occurs at 990 cm^{-1} . These bands at 910 and 990 cm^{-1} are obviously due to the vinyl groups at one end of the molecular chain. The *isopropylidene* groups are indicated by the band at 835 cm^{-1} , and the shoulder at 890 cm^{-1} may indicate some *isopropenyl* groups. There is again a strong band near 1640 cm^{-1} mainly due to the vinyl groups, and another near 1670 cm^{-1} connected with the *isopropylidene* structure. To summarise, therefore, while the situation here is somewhat masked by the presence of the vinyl groups at one end of the chain, both types appear to occur at the other end, with the *isopropylidene* groupings predominant.

(7) *Dihydromyrcene*. This substance may have either of the following formulæ :



Four samples were examined. Sample (i) was made for us by Dr. A. J. Birch by the reduction of geraniol, and sample (ii) by the same method after purification of the geraniol by means of its compound with calcium chloride. Both samples gave the same spectrum (curve A), except possibly for a small difference in the intensity of a band near 910 cm^{-1} . The band near 830 cm^{-1} is strong and that at 1680 cm^{-1} also well-marked, indicating the presence of *isopropylidene* groupings. There are also weak bands at 885 and 1645 cm^{-1} indicating a smaller amount of the *isopropenyl* type. A third sample was made for us by Dr. Birch by the reduction of linalol. This gave essentially the same result as regards the bands at 830 and 885 cm^{-1} , but showed small spectral differences from the two previous samples, particularly in the lower intensity of the band at about 910 cm^{-1} . The occurrence in all these cases of the two bands at 910 and 990 cm^{-1} raises the question as to whether the substance contains some vinyl groups, $-\text{CH}=\text{CH}_2$, present in a molecule of some impurity.

A fourth sample of dihydromyrcene (curve B) previously obtained from Dr. E. H. Farmer was examined. Its spectrum was given earlier in connexion with the spectra of some rubbers (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **51**, 247) but it is now clear from the bands near 1720 and 1000 cm^{-1} that this had become oxidised. The specimen was redistilled in a vacuum and this reduced the content of oxygenated groupings considerably, as shown by the spectrum. This sample, by contrast with those just discussed, had an intense band at 885 cm^{-1} and another at 1640 cm^{-1} , as well as those near 830 and 1675 cm^{-1} . It might therefore be concluded that this particular sample was relatively rich in the *isopropenyl* grouping. There is on the other hand another possible interpretation, namely that the compound has the formula



which could easily arise if the dihydromyrcene were made by reduction of myrcene, but not by its preparation from geraniol.

(8) *Geranamide*. The spectrum of a thin solid film from a sample provided by Dr. Jones is shown in Fig. 2, and appears anomalous in the series given, for there is no band at either 830 or 885 cm^{-1} , but a double band near 850 cm^{-1} . With a solution in ethylidene dichloride, a weak band was found at 885 cm^{-1} and another at 840 cm^{-1} . The region of the carbon-carbon double-bond stretching frequencies is obscured by the strong band due to the carbonyl link of the amide group near 1640 cm^{-1} . Although therefore the evidence is masked in this case, there is no reason to regard the case as abnormal, in the sense of all the results previously described.

Conclusions.—The conclusions which can be drawn from the above measurements are as follows.

(1) In general, the compounds examined appear to be mixtures of the two forms containing terminal *isopropenyl* and *isopropylidene* groups. This agrees with the measurements on Raman spectra in some cases.

(2) The proportions of the two forms vary in different cases, but it may be significant that in the majority the *isopropylidene* type is predominant.

(3) The exact amounts of the two isomeric forms cannot be determined until calibrations can be set up by using the pure isomers.

(4) None of the above results will be affected by any variation in the *cis-trans*-isomerism about the carbon-carbon double bonds, although this may account for some of the other spectral differences among the samples.

(5) No definite conclusions can be reached about the factors which control the proportions of the *isopropenyl* and *isopropylidene* types in a mixture, and in particular whether the mixture tends towards an equilibrium composition. If such an equilibrium exists, it must in some cases at least be attained very slowly.

It is evident that this problem might repay a more detailed study using a larger number of compounds, particular attention being paid to the origin or method of preparation, and to freedom from oxidation or impurities. The spectra already measured show that infra-red analysis of complex terpenoid derivatives could be developed successfully if required.

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