678. *Infra-red Examination of Terpenoid Substances.*

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In a previous paper infra-red measurements were applied to determine the nature of the end groups in certain terpenoid compounds. The characteristic vibration bands for the *iso*propenyl and *iso*propylidene groups were explained. This work has now been extended by a more systematic study with compounds of known origin and method of purification. It has been found that citronellal, citronellol, and geraniol obtained from the natural oils occur exclusively with the *iso*propylidene structure. A sample of citronellal prepared by dehydration of the hydroxy-derivative was largely in the *iso*propenyl form. The contaminant in natural oils giving rise to the *iso*propenyl groups has been separated, and is not an alcohol, although its exact nature has not been determined.

It has already been shown (Thompson and Whiffen, *J.*, 1948, 1412) that the infra-red absorption spectra of alicyclic terpenoid substances may be used to determine the presence of the *iso*propenyl ($CH_2{:}CMe{\cdot}$) or *iso*propylidene ($CMe_2{:}$) end groups in such compounds. Measurements with several substances such as citronellal, citronellol, and geraniol suggested that the specimens contained both types of group, but, whilst different samples varied in the relative proportions of the two types, the *iso*propylidene group seemed predominant. It was stated clearly that the matter required further examination on compounds of known origin and method of purification before it could be finally clarified.

We have therefore re-examined this problem, using samples of citronellal, citronellol, and geraniol prepared by different methods, and have used the infra-red absorption spectra to follow the changes during the purification processes. Our results now show that when these substances are prepared in a pure state from the natural oils the *iso*propenyl group is hardly detectable. When citronellal is prepared by the dehydration of hydroxycitronellal, however, the *iso*propenyl end group is formed predominantly. The component in Java citronella oil which appears to be mainly responsible for the *iso*propenyl group found in the crude sample of geraniol has been extracted, and although it is impossible to decide whether it is a single compound or a mixture by this method the spectrum indicates the presence of ketonic material and the absence of hydroxyl groups.

Recently, and after the present measurements were completed, Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland (*J.*, 1950, 915) described similar measurements on this problem, and used the correlation rules and methods which were given by Thompson and Whiffen. They reached the same conclusions as ourselves, namely that the *iso*propylidene structure is in general the important one. Our approach has been somewhat different, however, and more systematic, and we have traced the details of separation of the pure substances from several sources and are now able to explain the whole matter more exactly. The main contribution of the above authors is perhaps to draw attention to the comparatively high value of the extinction coefficient of the C–H bending vibration of the *iso*propenyl group at 890 cm.$^{-1}$, strengthening the argument that few such groups can be present, although it will be shown later that this consideration is scarcely relevant now. It may also be noted that we seem to have obtained rather better spectral resolution in some cases.

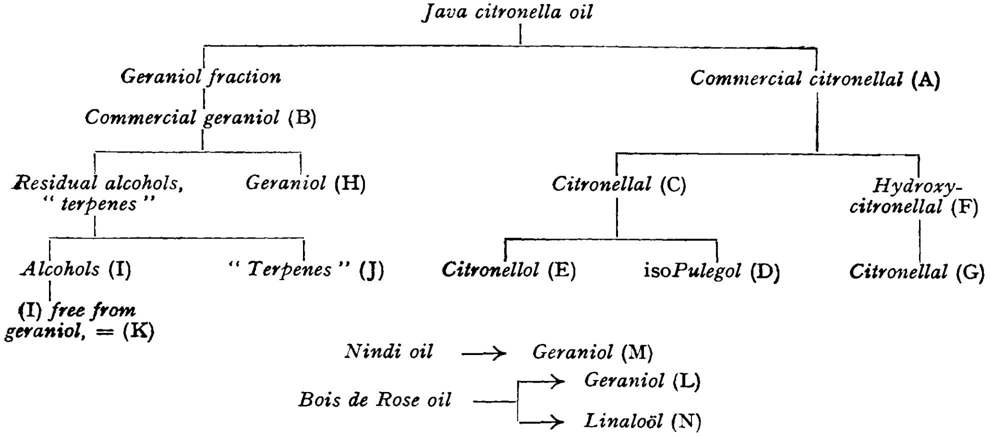
The spectra were measured with a Perkin Elmer spectrometer, model 12C, which was dried out sufficiently to make the water band at 6 μ. extremely weak. The substances were measured as liquids in rock-salt absorption cells of varying thickness (0·03—0·1 mm.). A rock-salt prism was used. Measurements in the region of 3 μ. with a lithium fluoride prism were not made since, although some of the substances have a band due to hydroxyl groups in addition to those due to the stretching modes of C–H bonds, little further information pertinent to the problem is likely to be obtained here. Details of the methods of extraction and purification of the compounds are given below.

RESULTS AND DISCUSSION.

The plan of this work is explained schematically in Fig. 1, and the spectra are shown in Figs. 2 and 3. Commercial citronellal (*A*) obtained by the fractionation of Java oil shows the bands near 830/1675 and 890/1645 cm.$^{-1}$ associated with *iso*propylidene and *iso*propenyl groups respectively. The band near 1725 cm.$^{-1}$ is due to the carbonyl group. Pure citronellal (*C*) made by extraction with sodium hydrogen sulphite shows no bands at 890/1645 cm.$^{-1}$ and we therefore conclude that the substance is free from *iso*propenyl groups. The bands at 830/1675 cm.$^{-1}$ due to the *iso*propylidene group remain. This spectrum of pure citronellal shows rather greater detail than others so far reported.

Similarly, the citronellol (*E*) obtained by the reduction of pure citronellal (*C*) shows only bands due to the *iso*propylidene group, and again the spectrum now given seems rather better resolved than those previously measured.

FIG. 1.



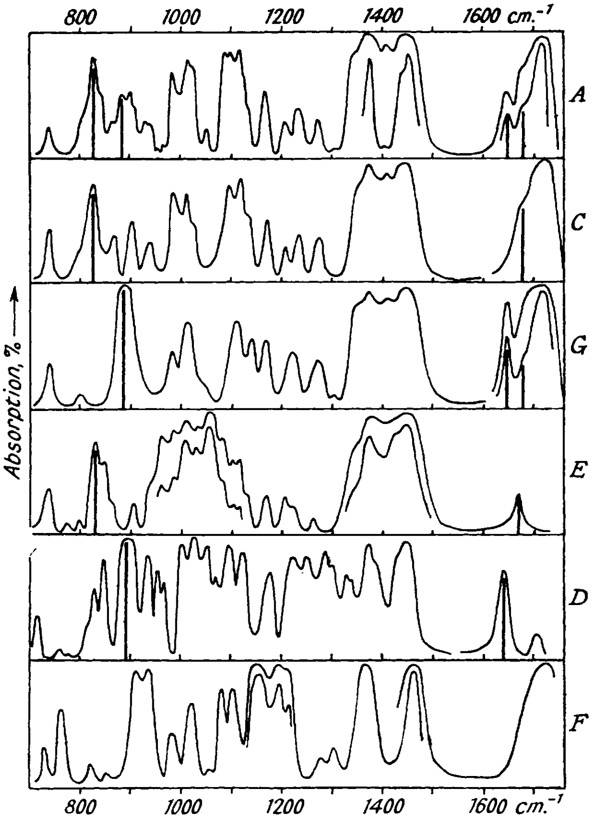
Citronellal (*G*) has also been prepared from the commercial product (*A*) by a different route, hydroxycitronellal (*F*) being first obtained by hydration and sodium hydrogen sulphite extraction, followed by dehydration. The hydroxycitronellal (*F*) shows, as expected, no bands near 1645, 1675 cm.$^{-1}$ due to C=C bonds in the *iso*propenyl or *iso*propylidene groups, and none at 890 cm.$^{-1}$. It may be noted, however, that it has a weak band at 824 cm.$^{-1}$ which must be due to some vibration other than the characteristic olefinic C–H deformation. The contrast between the spectra of (*F*) and (*C*) as regards position of many other bands is noteworthy in view of the comparatively small structural change between these molecules. The citronellal (*G*) formed by dehydration of (*F*) is strikingly different from (*C*) in that it seems to be almost exclusively in the *iso*propenyl form, the bands at 890 and 1645 cm.$^{-1}$ being very intense and those due to the *iso*propylidene group hardly detectable. The possibility that the double bond might have migrated during the dehydration so as form a compound including the linkage CH:CH seems to be excluded since there is no strong band near 965 cm.$^{-1}$. It seems therefore that, whereas the naturally occurring citronellal is in the *iso*propylidene form, the compound obtained by dehydration has very largely at least the alternative structure. It would be expected that dehydration of such a tertiary hydroxy-compound should give roughly equal amounts of the two isomers, and the fact that the *iso*propylidene form is absent is probably due to the relative ease with which it is formed *iso*pulegol (see below) which was present in quantity in the crude pyrolysed product.

Pure citronellal (*C*) was converted into *iso*pulegol (*D*) which is known to have the *iso*propenyl side chain, this being borne out by its spectrum. The bands at 890 and 1645 cm.$^{-1}$ are very intense and there is no band at 1675 cm.$^{-1}$. Here again, there is a band near 830 cm.$^{-1}$ which might be attributed to the *iso*propylidene radical, but the absence of a band at 1675 cm.$^{-1}$ suggests that it is in reality due to some other skeletal vibration.

Commercial geraniol (*B*) obtained from Java oil contains both types of olefinic end group. The pure geraniol (*H*) obtained from (*B*) by extraction with calcium chloride had only extremely feeble bands at 890/1645 cm.$^{-1}$ indicating again an exclusively *iso*propylidene structure. In the spectrum of (*H*) the fairly strong bands at 1057 and 1155 cm.$^{-1}$ shown by (*B*) are absent, and there are other minor changes of band intensity and position. The residue from (*B*) was separated further. Fraction (*I*) (other alcohols) appeared to contain almost exclusively the *iso*propylidene end groups; it also had a band near 1057 cm.$^{-1}$ to which reference has just been made. The product (*K*) [(I) free from geraniol] has a spectrum almost identical with that of (*I*), but there appears to be a further strengthening of the band at 1057 cm.$^{-1}$. This might well be assigned to a vibration of an alcoholic hydroxyl group, and could well be due to citronellol.

The fraction (J) ("terpenes") may either be a single compound or a mixture, but it is rich in the *iso*propenyl group (890/1645 cm.$^{-1}$) and it also has the strong band near 1155 cm.$^{-1}$ present in crude geraniol (*B*). (*J*) also contains ketonic or ester material (1730 cm.$^{-1}$) and there is a band near 795 cm.$^{-1}$ which cannot immediately be explained. The ketonic or ester material was not detected in sample (*B*) and may have been produced during the later chemical operations, but, whatever the precise nature of (*J*), it seems to contain the compound or compounds responsible for the *iso*propenyl groups present in the crude geraniol. A further important point is that (*J*) shows no appreciable absorption between 3200 and 3300 cm.$^{-1}$ attributable to a hydroxyl group and found in the alcohols. Thus (*J*) cannot be an alcohol, and we therefore have additional evidence that the compound with *iso*propenyl end groups is not geraniol itself. This fraction should contain the acyclic sesquiterpenes, sesquicitronellin isolated by Semmler and Spornitz (*Ber.*, 1913, **46**, 4025), stated to be $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH_2$. The presence of the *iso*propylidene group is not borne out by the spectrum of (*J*), but in any case this fraction is not even physically homogeneous.

FIG. 2.

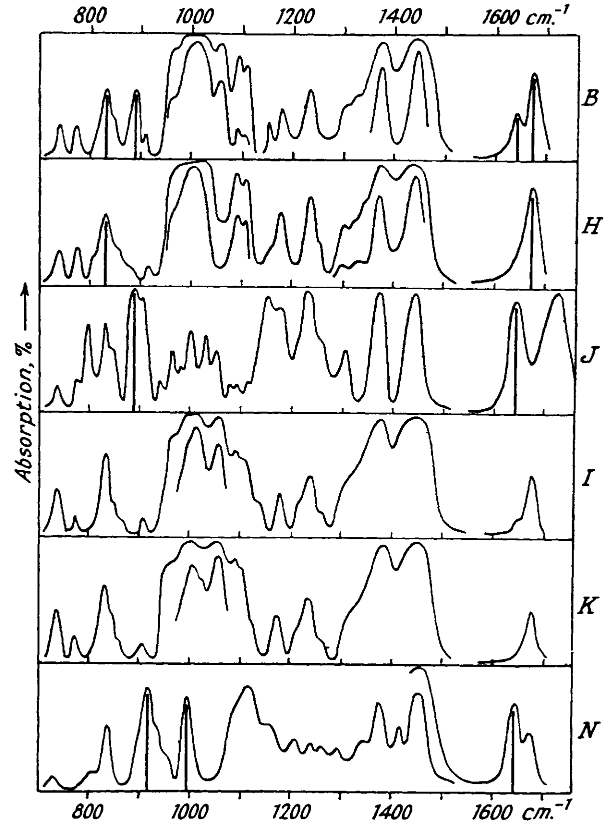


Two other samples of geraniol (*L* and *M*) have been prepared from natural oils. Each of these gave a spectrum identical with that of (*H*).

The spectrum of another sample of linaloöl (*N*) was also measured. It agrees with that given in Thompson and Whiffen's earlier paper; the bands near 915, 995 cm.$^{-1}$ due to the vinyl group are marked, and those due to the *iso*propylidene group are prominent, whilst there is a barely detectable amount of *iso*propenyl grouping.

The general conclusions of this work can be stated as follows: (1) The carefully purified samples of geraniol, citronellal, and citronellol obtained from natural oils of different kinds are homogeneous as regards the olefinic end group, which is the *iso*propylidene structure. (2) Preparation of compounds such as citronellal by dehydration of the corresponding hydroxy-compound may yield almost entirely the *iso*propenyl form. (3) The material in natural Java oil responsible for the *iso*propenyl end groups can be separated and is shown to be not only different from geraniol, but not an alcohol at all. (4) The present work shows that much of the evidence on the homogeneity of this class of compound must be regarded as misleading, presumably because of rearrangements or other chemical processes which take place during the determination.

FIG. 3.



EXPERIMENTAL.

Products isolated from Java Citronella Oil.—A standard grade of Java Citronella Oil, distilled *in vacuo*, gave two main fractions, the lower-boiling containing 90% of citronellal, and the higher alcohols, esters, sesquiterpenes, etc. The citronellal (*A*) was extracted by sodium hydrogen sulphite solution from which the aldehyde, obtained in 95% yield, had α_D^{20} +10·4°, n_D^{20} 1·4480, and d_4^{20} 0·856. Hydroxylamine titration showed citronellal 100%. The crude semicarbazone obtained in quantitative yield had f. p. 82—83° and m. p. 82—85°; after one crystallization this gave a good yield of pure product, m. p. 85° (cf. Carroll, *Perf. Ess. Oil Rec.*, 1947, 226).

The second fraction was hydrolysed with alcoholic potassium hydroxide and the recovered oil was distilled in a vacuum. The distillate (*B*) was treated with calcium chloride, the geraniol adduct treated with water, and the oil distilled. This oil was re-treated and then distilled without fractionation (Found: geraniol, by acetyl val., 100%; by Br val., 99·5%); α_D^{20} ±0·0°, n_D^{20} 1·4770. The purity of this material was checked by making the *p*-nitrophenylhydrazone of the acetoacetate (Carroll, unpublished work) in quantitative yield; it had f. p. 85°, and after one crystallization m. p. 91·5—92°.

The mother-liquors from the calcium chloride treatment were acetoacetylated (Carroll, XIth Internat. Congr. Pure Appl. Chem., Sect. 2, in the press) and the non-alcoholic portion was distilled off under a high vacuum. This material was re-treated with acetoacetate to remove traces of alcohols, and the recovered " terpenes " were boiled with alcoholic potassium hydroxide, and the extracted oil was distilled, to give sample (*J*), n_D^{20} 1·4921 (Br absorption, 1·47 g./g.).

The alcohols were recovered from the ester by alkaline hydrolysis. This fraction (1) was further treated with calcium chloride to remove as much geraniol as possible, giving the product (K), α_D^{20} +2·06°, n_D^{20} 1·4640, Br absorption 1·39 g./g., which corresponds to approx. 2 parts of citronellol to one of nerol (or geraniol).

Citronellol from Citronellal.—Citronellal (*C*) was reduced with aluminium *iso*propoxide, and the alcohol (*E*) obtained having α_D^{20} 3·6°, d_4^{20} 0·8570, n_D^{20} 1·45772 (Found : citronellol, by acetyl val., 100%).

Geraniol from Nindi Oil.—The oil was saponified with alcoholic potassium hydroxide, and the geraniol fraction separated by vacuum-distillation. The geraniol (*M*) obtained from this fraction by calcium chloride treatment had α_D^{20} ±0·0°, d_4^{20} 0·8848, n_D^{20} 1·4778 (Found : geraniol, by acetyl val., 99·7% ; by Br val., 99·5%). The *p*-nitrophenylhydrazone of the acetoacetate had f. p. 89·5—90° and after one crystallization m. p. 92·0°.

Geraniol from Bois de Rose Oil.—The alcoholic fraction obtained by removal of linaloöl (see below) was treated with calcium chloride as above. The recovered geraniol (*L*) had n_D^{20} 1·4784, d_4^{20} 0·8838 (Found : geraniol, by Br val., 98·7%). The acetoacetate *p*-nitrophenylhydrazone had f. p. 89—90°, and after one crystallization m. p. 91·2°.

Linaloöl from Bois de Rose Oil.—After saponification with alcoholic potassium hydroxide the separated oil was fractionated in a vacuum. A fraction having n_D^{20} 1·4632 and d_4^{20} 0·8670 (commerical linaloöl) was obtained, and this was further fractionated to produce pure linaloöl (*N*), n_D^{20} 1·4630, d_4^{20} 0·8670. The phenylurethane was obtained in nearly quantitative yield, f. p. 60—61°, which after one crystallization had m. p. 62·5°.

iso*Pulegol.*—Citronellal (*C*) was refluxed with acetic anhydride for 24 hours, the product hydrolysed with alcoholic potassium hydroxide, and the oil distilled. The alcohol (*D*) obtained in good yield had n_D^{20} 1·4727 and d_4^{20} 0·9130.

Citronellal from Hydroxycitronellal.—The hydroxy-aldehyde (Verley, *Bull. Soc. chim.*, 1928, [iv], **43**, 846) was dehydrated by heating it with 0·1% *m*-xylenesulphonic acid under a short column at 90°/1 mm., so that citronellal distilled off as it was formed. A yield of 35% of citronellal of 94% purity was obtained, and this gave the pure product (*G*) (100% as citronellal) in good yield after sodium hydrogen sulphite treatment, having n_D^{20} 1·4450, d_4^{20} 0·8501, α_D^{20} 9·5°. The semicarbazone, obtained in theoretical yield, had f. p. 58°. This was not quite homogeneous, as after repeated crystallizations the m. p. was 65°. A mixed m. p. with the semicarbazone of (*C*) gave a maximum depression of 7°.

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