186. *An Infra-red Spectroscopic Investigation of Double-bond Structure in Simple Acyclic Terpenes and Derivatives thereof.*

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The infra-red spectra of twenty-five purified acyclic monoterpene compounds are described and discussed with particular reference to the position and configuration of the double bonds. A semi-quantitative method for the infra-red detection of *iso*propenyl end-groups is outlined, and the present experimental results as well as those recorded by Thompson and Whiffen are interpreted on this basis. Very strong evidence is obtained that naturally occurring acyclic monoterpenes as a class possess the homogeneous *iso*propylidene end-group structure. In every purified sample examined by us, the proportion of the compound in the *iso*propenyl form never exceeded 3% and was usually very much less or possibly nil. Classical oxidative degradations afford indecisive conclusions in this field.

Some of the characteristic vibration frequencies of alcohol, ether, and vinyl groupings are shown to be modified if they occur in an allylic environment.

The nature of " geranyl chloride " as an anionotropic mixture of primary with some tertiary halide has been established by infra-red analysis of the partly resolved fractions resulting from low-pressure distillation.

A simple unresolved structural problem in organic chemistry is the question of the position of the double bond in the terminal *iso*propylidene (I) or *iso*propenyl (II) groups of acyclic monoterpenes and related substances (cf. Simonsen and Owen, " The Terpenes," Cambridge, 1947; *Endeavour*, 1949, **8**, 26). On oxidative degradation, such compounds generally behave as if they were mixtures of (I) with a smaller and variable proportion of (II), but there is other evidence suggesting that the terpenes are structurally homogeneous and that the ambiguous results of oxidation must be attributed to partial rearrangement. *E.g.*, Kuhn and Roth (*Ber.*, 1932, **65**, 1285) found that the ultra-violet absorption curves of the two crystalline *cis-trans*-isomeric dehydrogeranic acids (III) were incompatible with the presence of some 30% of the less highly conjugated *iso*propenyl form (IV) which is required by ozonolytic evidence (Cahn, Penfold, and Simonsen, *J.*, 1931, 3134; Kuhn and Roth, *loc. cit.*). Recent chemical work on the two crystalline *cis-trans*-isomeric geranamides (V; $X = CO{\cdot}NH_2$) (Caldwell and Jones, *J.*, 1946, 599), and the *X*-ray crystal-structure analysis of geranylamine hydrochloride (VI; $X = NH_3Cl$) (Jeffrey, *Proc. Roy. Soc.*, 1945, *A*, **183**, 388; cf. Sutton, *J.*, 1944, 306) also support the view that these crystalline acyclic terpene derivatives are homogeneous *iso*propylidene compounds, and that much of the older chemical work purporting to prove the presence of *iso*propenyl (II) as well as *iso*propylidene (I) end-groups is of doubtful value.

$CMe_2{:}CHR$ (I.)

$CH_2{:}CMe{\cdot}CH_2R$ (II.)

$CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CO_2H$ (III.)

$CH_2{:}CMe{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CO_2H$ (IV.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHX$ (V.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2X$ (VI.)

Quite generally, the use of oxidative degradation as an unequivocal method of detailed structure diagnosis has become increasingly suspect during recent years (see, *e.g.*, Clemo and Macdonald, *J.*, 1935, 1294; Karrer and Bretscher, *Helv. Chim. Acta*, 1943, **26**, 1758; Caldwell and Jones, *loc. cit.*; Young, McKinnis, Webb, and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 293). Accordingly, physical methods of structure analysis are desirable, and the present paper is the outcome of work initiated five years ago after a study of crystalline geranylamine hydrochloride. The methods and conclusions are set out in detail below. Very strong evidence has been obtained for the absence of *iso*propenyl end-groups (II) from the structure of simple acyclic terpenoid compounds. At the same time, useful information has become available about the allylic isomerism of the second double bond in molecules such as geranyl chloride and its derivatives.

Earlier Spectroscopic Work.—Unconjugated acyclic terpenes do not display characteristic high-intensity absorption in the range 2000—4000 A. (cf. Bateman and Koch, *J.*, 1944, 600). Little significance can therefore be attached to the work of Savard (*Bull. Soc. chim.*, 1929, [iv], **45**, 398) who examined citronellol, rhodinol, and geraniol in this spectral region where the low-intensity absorption is non-selective and excessively sensitive to traces of chromophoric impurities. On the other hand, Kuhn and Roth's interpretation of the high-intensity ultra-violet absorption curves of the fully conjugated dehydrogeranic acids (*loc. cit.*), based on measurements by Hausser and Smakula, appears to be sound. Ultra-violet spectroscopical analysis of the structure of terpenes is restricted to the few special cases where conjugation occurs, and even there the sensitivity of the method is relatively limited. The application of Raman spectroscopy was discussed and adversely criticised by Angus (*Indian Acad. Sci.*, Raman Jubilee Vol., 1935, 529); at that time instrumentation and physical accuracy were sometimes still imperfect, few if any pure standards were available, and the purity of the investigated terpene samples was not always rigorously controlled before and during irradiation, but the usefulness and reliability of Raman data have now been firmly established (cf. Fenske *et al.*, *Ind. Eng. Chem. Anal.*, 1947, **19**, 700; *Analyt. Chem.*, 1949, **21**, 12). At the same time, infra-red absorption probably offers advantages over the Raman method of vibrational spectroscopy in resolving the *iso*propenyl–*iso*propylidene controversy. As a result of an enquiry from Sir John Simonsen, Thompson and Whiffen (*J.*, 1948, 1412) thus examined various samples of acyclic terpenes and concluded that "in general, the compounds examined appear to be mixtures of the two forms containing terminal *iso*propenyl and *iso*propylidene groups" and that "the proportions of the two forms vary in different cases, but it may be significant that in the majority the *iso*propylidene type is predominant." No physical constants or other preparative details of their compounds were given, and the purity of some of their samples was known to be questionable. Thompson and Whiffen's conclusions must therefore be regarded as preliminary and the authors themselves were aware of this limitation in concluding their paper with the remarks: "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." With the aid of approximate extinction coefficients, it will be shown that both their and our results are in fact incompatible with the conclusion that most of the compounds contained *appreciable* amounts (15—50%) of *iso*propenyl end-groups as required by the evidence of oxidative degradation.

Physical Basis of the Present Analytical Method.—It has been amply established in recent years that the infra-red absorption spectra of olefinic hydrocarbon compounds are sharply differentiated according to the number and relative position (symmetrical or unsymmetrical, *cis* or *trans*) of one or more hydrogen atoms directly attached to the unsaturated carbon atoms (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246; Rasmussen and Brattain, *J. Chem. Physics*, 1947, **15**, 120, 131, 135; Kilpatrick and Pitzer, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 191; Sheppard and Sutherland, *J.*, 1947, 1540; *Proc. Roy. Soc.*, 1949, *A*, **196**, 195; Amer. Petroleum Inst., "Catalog of Infra-Red Spectrograms," 1949). The following *strong* bands due to out-of-plane deformational modes of vibration of the olefinic hydrogen atoms always occur at or near the frequencies indicated, whenever the requisite structural groupings are present (R = alkyl or substituted alkyl):

$CHR{:}CR'R''$	800—840 cm.$^{-1}$	$CH_2{:}CRR'$	890 cm.$^{-1}$
cis-$CHR{:}CHR'$	690 ,,	$CH_2{:}CHR$	910 and 990 cm.$^{-1}$
trans-$CHR{:}CHR'$	965 ,,		

No exception to these correlation rules has yet been found, although the A.P.I. catalogue alone lists some eighty unsaturated hydrocarbons. Failure to absorb at any of the given characteristic frequencies is therefore proof that the corresponding grouping is absent; in particular, the presence of *iso*propenyl groups may be safely discounted when no absorption occurs close to 890 cm.$^{-1}$ (at suitable path length). On the other hand, the appearance of bands at or near the given frequency positions does not necessarily indicate the presence of any of the above types of double bond, since other vibrations of the molecular framework often happen to give rise to absorption in this spectral region. For example, *n*-octane, 3-ethylhexane, 3-methyl-3-ethylpentane (A.P.I., *op. cit.*), and crystalline geranylamine hydrochloride (see below) display a marked absorption near 890 cm.$^{-1}$, although the $CH_2{:}CRR'$ grouping is certainly absent in these compounds. In many cases, the suspected presence of a given type of olefinic structure can be confirmed by reference to the C=C stretching frequency near 1660 cm.$^{-1}$ (Sheppard and Sutherland, *loc. cit.*, 1947; Thompson and Whiffen, *loc. cit.*); $CHR{:}CR'R''$ gives rise to an infra-red band near 1670 cm.$^{-1}$, but $CH_2{:}CRR'$ and $CH_2{:}CHR$ absorb around 1645 cm.$^{-1}$. Here again, however, some caution must be exercised in the assignment of weak bands which may occasionally represent overtones or combinations of lower frequencies; both *cis*- and *trans*-3-methylpent-2-ene, for instance, exhibit absorption between 1620 and 1660 cm.$^{-1}$, although they do not contain a terminal methylene group (A.P.I., *op. cit.*). The position may be summarised by stating that *the* absence *of a particular double-bond structure in a hydrocarbon residue can be inferred with complete confidence from the absence of the characteristic infra-red frequencies at suitable path length, whereas additional evidence is sometimes required to prove the* presence *of a suspected grouping.*

In order to estimate the composition of isomeric mixtures and to fix an upper analytical limit of detection for the infra-red method, we must know the molecular extinction coefficients of the characteristic olefinic bands. It has been pointed out elsewhere (Sheppard and Sutherland, *loc. cit.*, 1947) that both the characteristic hydrogen deformation and the bouble-bond stretching frequencies of $CH_2{:}CRR'$ (*e.g.*, *iso*propenyl) groupings exhibit relatively much greater absorption intensities than do the corresponding frequencies of $CHR{:}CR'R''$ (*e.g.*, *iso*propylidene) groups in the pure compounds. The sensitivity of the infra-red method of detecting the very strongly absorbing *iso*propenyl groups can be estimated from the approximate molar decadic extinction coefficients of a representative number of pure compounds which have now been determined in dilute solution and are listed in the table below.

Approximate infra-red extinction coefficients of iso*propenyl and* iso*propylidene groups.*

Compound.	Type.	Frequency (cm.$^{-1}$).	ε (litres.g.-mol.$^{-1}$ cm.$^{-1}$).
Geraniolene (mainly V; X = H)	*iso*Propenyl	890	120 (in CCl_4)
α-Lupene [1]	,,	885	150 ,,
Lupeol [2]	,,	883	200 (in CS_2)
2-Methylpent-1-en-4-one	,,	895 [3]	160 [3] ,,
2 : 3 : 3-Trimethylbut-1-ene	,,	890	155 (in CCl_4)
2 : 4 : 4-Trimethylpent-1-ene	,,	890	155 ,,
2-Methylpent-1-en-4-one	,,	1650 [3]	24 [3] ,,
2 : 3 : 3-Trimethylbut-1-ene	,,	1640	20 (in C_6H_{12})
2-Methylpent-2-ene	*iso*Propylidene	830	38 (in CS_2)
2-Methylbut-2-ene	,,	1680	$1 < \varepsilon < 10$ [4] (neat)

[1] A pentacyclic triterpene hydrocarbon, $C_{30}H_{50}$, of known structure (see Experimental). [2] A pentacyclic triterpene alcohol, $C_{30}H_{50}O$, of known structure (see Experimental). [3] Taken from A.P.I. spectrogram (*loc. cit.*, serial no. 634). [4] Estimated from one single spectral run. According to Kletz and Sumner (*J.*, 1948, 1456), the extinction coefficient of the *iso*propylidene C=C stretching frequency band in 2 : 4 : 4-trimethylpent-2-ene is about 0·35 times that of the corresponding *iso*propenyl absorption in 2 : 4 : 4-trimethylpent-1-ene.

Clearly, the extinction coefficient of the 890-cm.$^{-1}$ band of the *iso*propenyl group is much greater than that of either of the two characteristic *iso*propylidene bands or the 1645-cm.$^{-1}$ C=C stretching frequency of the *iso*propenyl double bond. The relatively low value of ε observed in geraniolene can almost certainly be ascribed to the presence of structural isomers in this hydrocarbon (cf. Simonsen and Owen, *op. cit.*; Naylor, *J.*, 1947, 1532), and the anomalously high value obtained for lupeol may not be reliable owing to the use of a different cell in this case (see Experimental). Whether or not the 890-cm.$^{-1}$ band extinction coefficient of the *iso*propenyl group remains *strictly* constant in different compounds (cf. Thompson and Whiffen, *loc. cit.*; Anderson and Seyfried, *Analyt. Chem.*, 1948, **20**, 998), it is evidently always high, and quite small amounts of *iso*propenyl groups could not escape detection by the infra-red method. As little as 1% of the hypothetical *iso*propenyl form of a simple terpene, for instance, would give rise to about 10% absorption in a 0·05-mm. path-length of the isomeric mixture.

According to the evidence of chemical oxidations provided by Grignard and his school, most acyclic monoterpenes contain 15—50% of the *iso*propenyl isomer admixed with an excess of the *iso*propylidene form (see Simonsen and Owen, *op. cit.*). On the basis of the above extinction coefficients, more than 70% absorption should then be displayed at the 890-cm.$^{-1}$ band when the spectrum is examined through a conventional path-length of 0·05 mm. of the liquid monoterpene. In actual fact, however, the absorption generally appears to be at most 10% of this, both in our own purified samples and in those examined by Thompson and Whiffen (particularly their citronellol " B," geranamide, citral, linalool, and dihydromyrcene " A "). Contrary to first impressions, therefore, Thompson and Whiffen's published data also indicate that the chemical evidence is in many instances altogether unreliable, and that many of the acyclic terpenes are almost, if not completely, homogeneous *iso*propylidene structures.

EXPERIMENTAL.

Most of the infra-red spectra were measured with one of two Hilger D 209 spectrometers: one at Cambridge was employed under double-beam conditions (cf. Sheppard and Sutherland, *loc. cit.*, 1947), and the other at Welwyn was employed as a single-beam instrument in an exhaustively dried atmosphere (humidity below 5%). Interference by water-vapour absorption in the 1640—1670-cm.$^{-1}$ region was therefore rendered insignificant. The spectra of a few samples, and most of the extinction coefficients given in the above table, were determined on a Grubb–Parsons single-beam instrument as described elsewhere (Barnard, Fabian, and Koch, *J.*, 1949, 2442). The effective slit widths employed were 3—5 cm.$^{-1}$ at 890 cm.$^{-1}$, and 7—10 cm.$^{-1}$ at 1650 cm.$^{-1}$. A fixed absorption cell (within a very small tolerance 0·1 mm. thick) was used for all extinction measurements, except in the case of lupeol which was investigated in a 0·25-mm. cell at higher molar dilution. The liquid terpene samples were studied as films from

0·05 to 0·1 mm. thick between sodium chloride plates, and the crystalline samples in suspension in "Nujol" as well as in solution as indicated. The commercial samples of the various terpenes were purchased from Messrs. Boake Roberts & Co., except when otherwise specified. All liquid compounds were freshly distilled and either examined immediately or kept sealed *in vacuo* between distillation and spectrographic examination.

Compounds used for Extinction-coefficient Measurements.—The sample of geraniolene (mainly V; X = H) was that described by Dr. R. F. Naylor elsewhere (*loc. cit.*). α-Lupene and lupeol were pure crystalline samples given to us by Professor E. R. H. Jones (cf. Heilbron, Kennedy, and Spring, *J.*, 1938, 329; Jones and Meakins, *J.*, 1941, 757). Pure 2 : 3 : 3-trimethylbut-1-ene was prepared by Dr. J. L. Bolland by dehydration of 2 : 3 : 3-trimethylbutan-2-ol obtained from *tert.*-butylmagnesium chloride and acetone, and 2 : 4 : 4-trimethylpent-1-ene was a specially distilled sample obtained from Imperial Chemical Industries, Limited, through Dr. A. G. Evans. Dehydration of 2-methylpentan-2-ol with iodine afforded a mixture of 2-methylpent-2-ene with 2-methylpent-1-ene which gave the following fractions after distillation through a column packed with Dixon copper gauze (23 theoretical plates) : (i) b. p. 64·3—66·0°/754 mm. (70 g.) (25% of 2-methylpent-1-ene); (ii) b. p. 66·0—66·4°/754 mm. (70 g.) (10% of 2-methylpent-1-ene); (iii) b. p. 66·5—66·6°/751 mm. (37 g.) (3% of 2-methylpent-1-ene); (iv) b. p. 66·6°/751 mm. (3·5 g.) (0·2% of 2-methylpent-1-ene). Fraction (iv) was used (the isomer contents in this preparation, which was made by Dr. J. I. Cunneen, were established by infra-red analysis). 2-Methylbut-2-ene was similarly prepared by Dr. A. W. Kenchington from 2-methylbutan-2-ol, and had $n_D^{15\cdot5}$ 1·3908 (2-methylbut-1-ene content, 0·1%).

2-*Methylhept*-2-*en*-6-*one* (VII). A commercial sample from Messrs. Boake Roberts & Co. afforded a solid semicarbazone only with considerable difficulty, even after fractionation (boiling range 59—70°/12 mm; refractive index range $n_D^{11\cdot5}$ 1·4562—1·4430). A similar sample from Messrs. Hopkin and Williams Ltd. distilled over a much smaller range (55—57°/12 mm.; $n_D^{11\cdot5}$ 1·4625) and gave a good yield of solid semicarbazone from aqueous alcohol. The pure derivative was obtained in the form of colourless needles, m. p. 135·5—136° (lit., *ca.* 135°), after repeated crystallisation from benzene–light petroleum (b. p. 60—80°). Spectroscopically and otherwise identical ketone samples were obtained by regeneration from this semicarbazone by (*a*) steam-distillation with phthalic anhydride, or (*b*) prolonged cold treatment with 2N-sulphuric acid and light petroleum (b. p. 40—60°). Pure 2-methylhept-2-en-6-one has b. p. 58°/12 mm., $n_D^{12\cdot5}$ 1·4414 (we are indebted to Mr. A. L. Morris for these preparations). Another specimen was obtained directly by alkaline cleavage of citral (commercial grade), followed by simple fractionation (b. p. 66—66·5°/16 mm.; n_D^{12} 1·4420); it exhibited a spectrum indistinguishable from that of the products obtained as above from the pure semicarbazone.

(±)-2-*Methylhept*-2-*en*-6-*ol* (VIII). The above ketone was reduced with aluminium *iso*propoxide in *iso*propyl alcohol to give the corresponding alcohol as a colourless, slightly viscous liquid, b. p. 76·5—77°/14 mm., $n_D^{11\cdot5}$ 1·4515, n_D^{20} 1·4481.

Citronellol (3 : 7-*dimethyloct*-6-*en*-1-*ol*) (IX). Commercial citronellol ("C" and "Q" grades) is a complex mixture. On fractionation through a 15-plate column under reduced pressure, "C" grade was found to consist largely of material possessing almost exactly the b. p. (113·8—114·2°/14 mm.) and refractive index (n_D^{21} 1·4561) attributed to pure citronellol (Simonsen and Owen, *op. cit.*). "Q" Grade appears to be more heterogeneous. After neglecting a small fore-run, the following fractions were collected in approximately equal proportions : (i) b. p. 109—112°/17 mm., n_D^{21} 1·4498; (ii) b. p. 112—113·5°/17 mm., n_D^{21} 1·4535; (iii) b. p. 113·5—115°/17 mm., n_D^{21} 1·4598; (iv) a dark residue, n_D^{21} 1·4680.

Rhodinol (IX). The main bulk of a commercial sample had b. p. 117—118°/20 mm., n_D^{20} 1·4660.

Citronellal (3 : 7-*dimethyloct*-6-*en*-1-*al*) (X; X = O). Fractionation of the commercial product yielded a considerable amount of low-boiling material and a main fraction, b. p. 89·0—89·5/17 mm., n_D^{20} 1·4500.

Citronellal semicarbazone (X; X = $N{\cdot}NH{\cdot}CO{\cdot}NH_2$). This was prepared from the above purified aldehyde according to the directions of Tiemann and Schmidt (*Ber.*, 1897, **30**, 34) and had m. p. 82·5° [after three crystallisations from light petroleum (b. p. 60—80°)].

Geraniol (3 : 7-*dimethylocta*-trans-2 : 6-*dien*-1-*ol*) (VI; X = OH). A commercial sample, purified *via* the calcium chloride adduct, had b. p. 114°/13 mm., n_D^{14} 1·4782. Another sample was specially prepared from the crystalline diphenylurethane (see below) which was decomposed in the usual manner, the last traces of admixed diphenylamine being removed chromatographically on alumina (geraniol was more strongly adsorbed). This specimen distilled at 110°/12 mm., and had n_D^{11} 1·4806 (free from diphenylamine according to the ultra-violet light absorption test). The two geraniol samples displayed identical infra-red spectra.

Nerol (3 : 7-*dimethylocta*-cis-2 : 6-*dien*-1-*ol*) (VI; X = OH). This alcohol was prepared in a pure state by extensive fractional crystallisation of the diphenylurethane mixture obtained from a commerical sample after 2 treatments with excess of calcium chloride. The final diphenylurethane (see below) was decomposed in the usual manner, and the regenerated alcohol freed from diphenylamine (ultra-violet light absorption test) by distillation and chromatography on alumina. This sample had b. p. 105°/12 mm., n_D^{11} 1·4795 (tetrabromide, silky needles, m. p. 116—118°). Another specimen (n_D^{14} 1·4749), kindly given us by Messrs. CIBA Ltd. of Basle, and said to contain a small proportion of geraniol, exhibited similar infra-red absorption.

Diphenylurethanes of geraniol and nerol (VI; X = $O{\cdot}OC{\cdot}NPh_2$). These well-known derivatives (cf. Simonsen and Owen, *op. cit.*) formed a continuous series of mixed crystals of space group C. 2/c. We are indebted to Dr. G. A. Jeffrey for the following crystallographic data :

		Unit cell dimensions in A.				
Alcohol basis of derivative.	M. p.	[*a*].	[*b*].	[*c*].	*β*.	Vol. in A.^{3}.
Pure geraniol	80·5—81°	30·26	6·31	24·20	116·7°	4126
Mixture M	60—63	30·09	6·37	23·87	117·6	4055
Mixture N	52—55	30·01	6·44	23·67	118·4	4024
Pure nerol	50—51	29·96	6·50	23·55	119·0	4011

Geranamides I *and* II (trans- and cis-V; $X = CO{\cdot}NH_2$). The preparation of these crystalline compounds is fully described elsewhere (Caldwell and Jones, *loc. cit.*; Barnard and Bateman, following paper).

Digeranyl (2 : 6 : 11 : 15-*tetramethylhexadeca*-2 : 6 : 10 : 14-*tetraene*) (XI) *and* iso*digeranyl* (XV) These are described elsewhere (Barnard and Bateman, following paper).

Digeranyl ether (XII) (b. p. 152°/0·1 mm., n_D^{20} 1·4846). This was prepared by Dr. R. F. Naylor (*J.*, 1949, 2724) by interaction of geranyl chloride with the potassium derivative of geraniol in ethereal solution.

Homogeranic acid (VI; $X = CO_2H$) *and* iso*homogeranic acid* (XIV; $X = CO_2H$). These and their respective amides are described elsewhere (Barnard and Bateman, following paper).

Geranylamine hydrochloride (1-*amino*-3 : 7-*dimethylocta*-trans-2 : 6-*diene hydrochloride*) (VI; $X = NH_3Cl$). This compound, m. p. 146°, has been fully described by Sutton (*loc. cit.*) and Jeffrey (*loc. cit.*).

Linalool (3 : 7-*dimethylocta*-1 : 6-*dien*-3-*ol*) (XIV; X = OH). Two commercial samples of different botanical origin (Bois de Rose and Bergamot) yielded on fractionation an identical main constituent, b. p. 86°/14 mm., n_D^{19} 1·4630.

Geranyl chloride (VI and XIV; X = Cl). This was prepared from geraniol as described elsewhere (following paper). A liquid boiling over the range 45—70°/0·2 mm. constituted 90% of the total yield. This was fractionated through a 30-cm. Vigreux column and separated into the following four equal fractions (Calc. for $C_{10}H_{17}Cl$: Cl, 20·56%): (i) b. p. 40—45°/0·2 mm., n_D^{20} 1·4710 (Found: Cl, 20·3%); (ii) b. p. 45—47·5°/0·2 mm., n_D^{20} 1·4738 (Found: Cl, 20·4%); (iii) b. p. 47·5—52°/0·2 mm., n_D^{20} 1·4777 (Found: Cl, 20·5%); (iv) b. p. 52—53°/0·2 mm., n_D^{20} 1·4797 (Found: Cl, 20·5%).

RESULTS AND DISCUSSION.

The infra-red absorption curves of most of the compounds investigated are presented in the accompanying diagrams, and others are more briefly described in the course of the discussion. A summary of the observed group frequencies is also given in tabular form. In comparisons of spectroscopic estimates for the maximum percentage of *iso*propenyl groups with deductions from chemical work, the latter values have been taken from the review by Simonsen and Owen (*op. cit.*).

Group frequencies (cm.$^{-1}$).

(? signifies uncertain structural correlation; w, weak band; —, band absent. The usual CH_2 and CH_3 bands near 1450 and 1375 cm.$^{-1}$ are not shown.)

	Structure.	$CH_2{:}CR_2$.	$CHR{:}CR_2$.	$CH_2{:}CHR$.	CH_2.	C·O or C:O.
Methylheptenone	(VII)	— —	810		735	1720
Methylheptenol	(VIII)	—	832, 1670	?908, ?990, ?1645 w	745	1120
Citronellol (rhodinol)	(IX)	?885 w, ?1645 w	830, 1670		738	1055
Citronellal ...	(X; X = O)	?900, ?1645	825, 1675		738	1720
Citronellal semicarbazone	(X; $X = N{\cdot}NH{\cdot}CO{\cdot}NH_2$)	?900 w	840		740	
Geraniol	(VI; X = OH)	?888 w, —	838, 1670		740	1010
Nerol	(VI; X = OH)	?888 w, —	832, 1670		742	1010
Geranamides (CS_2 solution)	(V; $X = CO{\cdot}NH_2$)	?900 w,	820, 825		745, 750	
Dimethyloctadiene	(VI; X = H)	?888 w, —	820, 1678		740	
Dihydromyrcene	(VI; X = H and XIII)	889, 1650 —	820, 1678		740	
Geraniolene	(V; X = H)	891, 1654	821, 1680		745	
Digeranyl	(XI)	?885 w, —	832, 1670		738	
Digeranyl ether	(XII)	?887 w, —	830, 1668		745	~1080
Homogeranic acid	(VI; $X = CO_2H$)	—	827		740	
Homogeranamide	(VI; $X = CO{\cdot}NH_2$)	?888 w	825		742	
Geranylamine hydrochloride	(VI; $X = NH_3Cl$)	?888	835, 1670		725	
Geranyl chloride {	(VI; X = Cl)	?890 w	845, 1665		745	
	(XIV; X = Cl)	?900 w	830	925, 990, 1415, 1645	745	
Linalool	(XIV; X = OH)	—	835, 1672	925, 997, 1415, 1645	740	1115
*iso*Digeranyl	XV	?885 w	832, 1670	908, 998, 1415, 1642	742	
*iso*Homogeranamide	(XIV; $X = CO{\cdot}NH_2$)	—	835	920, 1005	730	

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$
(VII.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$
(VIII.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$
(IX.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}X$
(X.)

Analysis of iso*Propenyl Groups.*—Methylheptenone (VII) and methylheptenol (VIII) are important degradation products of citral and geraniol respectively, and may be regarded as based on a common end-group structure of many simple acyclic terpenes. The infra-red spectra (Fig. 1) of both these simple compounds showed absence of absorption at 890 cm.$^{-1}$, so that no more than a fractional percentage of *iso*propenyl groups could have been present in the samples examined (see Introduction, p. 917).

Two commercial samples of the simplest terpene alcohol, citronellol (IX), were rather impure, but one of them (" C " grade) furnished on distillation a main fraction possessing physical constants identical with those given for the pure carbinol by Simonsen and Owen (*op. cit.*). This purified material, similarly to Thompson and Whiffen's citronellol " B," exhibited (Fig. 1) a weak band at 885 cm.$^{-1}$, accompanied by slight absorption near 1645 cm.$^{-1}$, so that a trivial amount (approximately 2% as estimated from the 885-cm.$^{-1}$ absorption) of the isomer containing the terminal *iso*propenyl double band *may* have been present. It will be shown below, however, that even this low proportion of terminal double bonds (if real) probably originated in some foreign impurity. Chemical evidence suggests that some 18—28% of the citronellol molecules exist in the *iso*propenyl form. A nearly identical spectrum was displayed by rhodinol (citronellol from a different source); a distinct enhancement of the characteristic *iso*propylidene double-bond absorption was almost certainly due to the presence of a small amount of the more highly unsaturated geraniol.

A commercial sample of citronellal (X; X = O) gave a spectrum very similar to that recorded by Thompson and Whiffen. This is compatible with the presence of some 5% of *iso*propenylic isomer or extraneous impurity; oxidative degradation indicates an isomer content of 40%. More significantly, the pure crystalline semicarbazone of this aldehyde (X; X = $N{\cdot}NH{\cdot}CO{\cdot}NH_2$) displayed (Fig. 1) less than 5% absorption between 860 and 910 cm.$^{-1}$ in a path-length affording 30% absorption at the characteristic 840-cm.$^{-1}$ band of the *iso*propylidene group; an approximate calculation on the basis of these figures shows that the semicarbazone contains even less of the *iso*propenyl form than is allowed by the spectrum of purified citronellol (*i.e.*, less than 2%). Far from being an inseparable mixture of appreciable amounts of both *iso*propenyl and *iso*propylidene isomers as may be deduced on chemical grounds (see Simonsen and Owen, *op. cit.*), citronellal semicarbazone evidently exists in the homogeneous *iso*propylidene form (cf. Harries, *Annalen*, 1915, **410**, 1).

Differing from Thompson and Whiffen, we found that geraniol (VI; X = OH), purified in the usual manner *via* its solid adduct with calcium chloride, displayed (Fig. 1) no absorption peak near 1645 cm.$^{-1}$, and only a small band at 890 cm.$^{-1}$ (less than 1% of *iso*propenyl form present). The stereoisomeric nerol, regenerated from the diphenylurethane derivative, was similar in this respect (see Fig. 1). Oxidative data suggest the presence of over 20% of the *iso*propenyl isomers in these alcohols. Infra-red analysis of various chemical derivatives of geraniol, nerol, and the corresponding aldehydes, citral *a* and *b*, also supports the conclusion that the original alcohols are free from *iso*propenyl groups. Thus both the solid and the solution spectra of the two stereoisomeric geranamides (V; X = $CO{\cdot}NH_2$) (see Fig. 2) are incompatible with the presence of more than 3% of this structural grouping. The dimethyloctadiene (VI; X = H), obtained by sodium–liquid ammonia reduction of geraniol, cannot contain as much as 2% of the *iso*propenyl isomer according to the spectrum already reported (Sheppard and Sutherland, *loc. cit.*, 1947; Thompson and Whiffen, *loc. cit.*), and the synthetic " double molecule " digeranyl (XI) has now been found to display closely similar absorption (Fig. 3). Again, the intensity of the band at 887 cm.$^{-1}$ in the spectrum of synthetic digeranyl ether (XII) (see Fig. 3), if attributed to *iso*propenyl structures, limits their proportion to 3% of the total end-groups present.

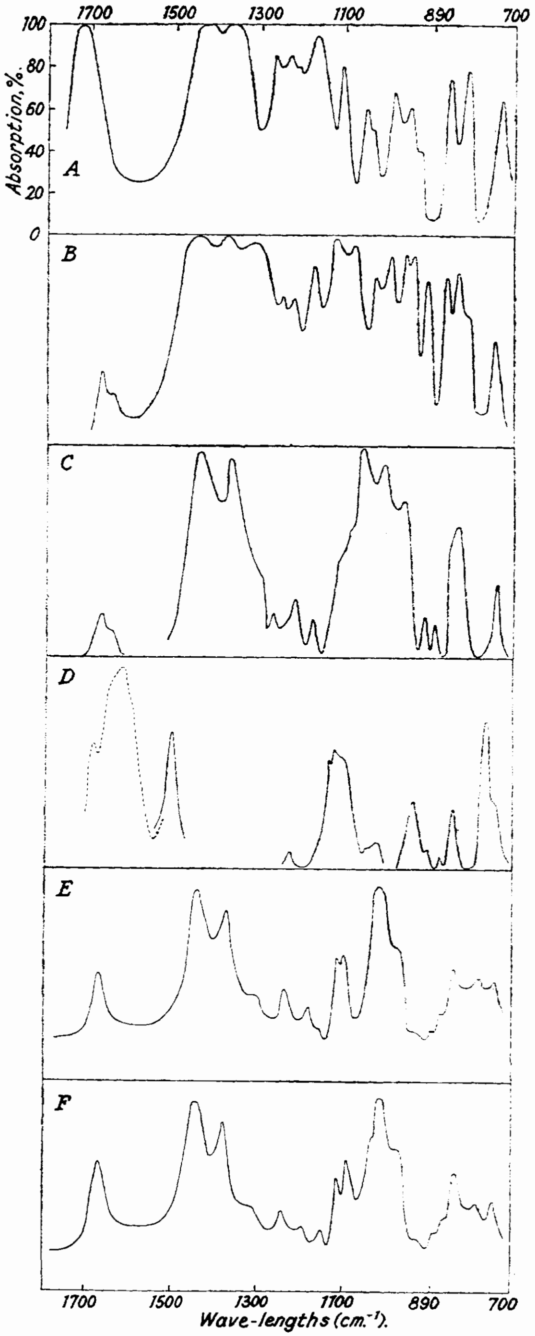
$(CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot})_2$
(XI.)

$(CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot})_2O$
(XII.)

Crystalline geranylamine hydrochloride (VI; X = NH_3Cl) is notable in showing very strong absorption at 888 cm.$^{-1}$ (see Fig. 3) although the presence of the hypothetical *iso*propenyl isomer has been excluded by Jeffrey's (*loc. cit.*) complete *X*-ray structure analysis. The readily crystallised homogeranamide (VI; X = $CO{\cdot}NH_2$) also exhibits a rather large band in this spectral region (see Fig. 2), but this again cannot be attributed to the presence of *iso*propenyl groups since the corresponding liquid acid (VI; X = CO_2H) from which it was made showed no such absorption.

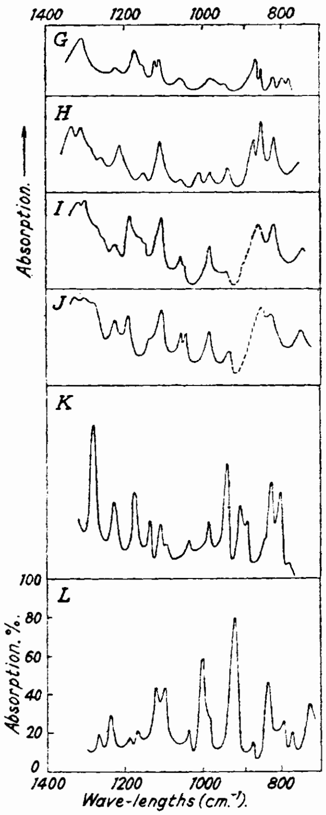
Elimination of the $-CH_2{\cdot}OH$ grouping from geraniol results in the *iso*propenyl structure (V; X = H), which is the main constituent of geraniolene. The intense 890-cm.$^{-1}$ absorption

FIG. 1.



A, *Methylheptenone* (VII) (0·06-*mm. cell*). B, *Methylheptenol* (VIII) (0·06-*mm. cell*). C, *Citronellol* " *C* " (IX) (0·04-*mm. cell*). D, *Citronellal semicarbazone* (X; X = N·NH·CO·NH$_2$) (*in* " *Nujol* "). E, *Geraniol* (trans-VI; X = OH) (0·03-*mm. cell*). F, *Nerol* (cis-VI; X = OH) (0·03-*mm. cell*).

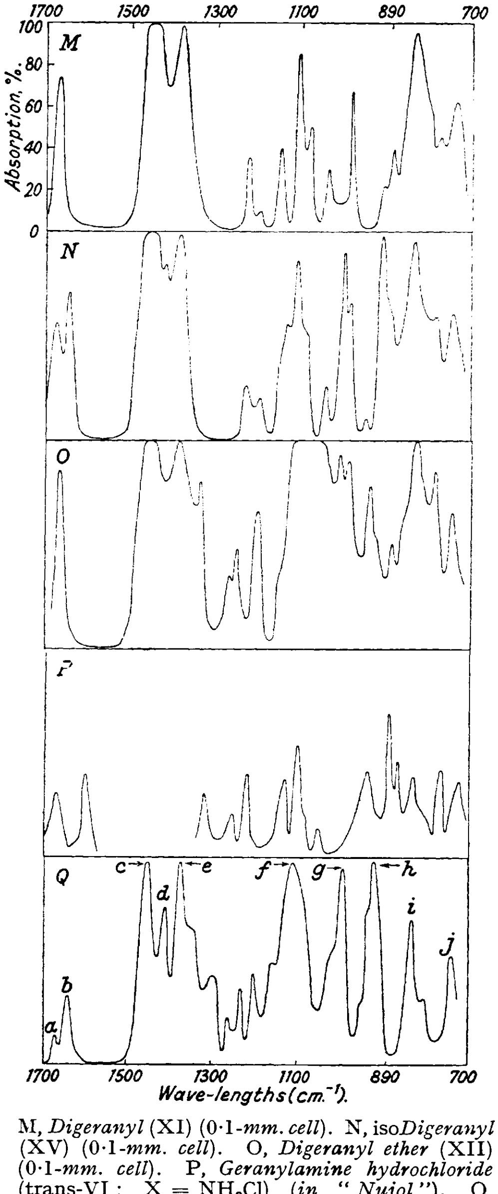
FIG. 2.



G, *Geranamide* I (trans-V; X = CO·NH$_2$) (*in* " *Nujol* "). H, *Geranamide* II (cis-V; X = CO·NH$_2$) (*in* " *Nujol* "). I, *Geranamide* I (20% *in* CS$_2$; 0·25-*mm. cell*). J, *Geranamide* II (20% *in* CS$_2$; 0·25-*mm. cell*). K, *Homogeranamide* (VI; X = CO·NH$_2$) (*solid*; 0·015 *mm. approx.*). L, iso*Homogeranamide* (XIV; X = CO·NH$_2$) (0·015-*mm. cell*).

of this hydrocarbon has already been referred to in the table of extinction coefficients (p. 917), as well as in the earlier paper by Sheppard and Sutherland (*loc. cit.*, 1947). A strong band at 890 cm.$^{-1}$ is also known to occur in the spectrum of " dihydromyrcene " obtained by sodium–ethanol reduction of natural myrcene (Sheppard and Sutherland, *loc. cit.*; Thompson and Whiffen, *loc. cit.*), where it arises from the presence of 2-methyl-6-ethylhepta-2 : 6-diene (XIII) (cf. Simonsen and Owen, *op. cit.*).

FIG. 3.



M, *Digeranyl* (XI) (0·1-*mm. cell*). N, iso*Digeranyl* (XV) (0·1-*mm. cell*). O, *Digeranyl ether* (XII) (0·1-*mm. cell*). P, *Geranylamine hydrochloride* (trans-VI ; X = NH_3Cl) (*in* " *Nujol* "). Q, *Linalool* (XIV ; X = OH) (0·04-*mm. cell*); a $>C{:}CH{\cdot}$; b $:CH_2$; *c* C–H; *d* $:CH_2$; *e* $\cdot CH_3$; *f* $\geqslant C{\cdot}OH$; *g* and *h* $\cdot CH{:}CH_2$; *i* $>C{:}CH{\cdot}$; *j* ·C·C·C·C·C.

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CEt{:}CH_2$
(XIII).

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMeX{\cdot}CH{:}CH_2$
(XIV.)

Finally, we have failed to detect any sign of 890-cm.$^{-1}$ absorption in samples of linalool (XIV; X = OH) from two different natural sources (see Fig. 3) (cf. also Thompson and Whiffen), so that this terpene alcohol is unquestionably more than 99% homogeneous in the *iso*propylidene form.

It is clear from the above approximately quantitative infra-red characterisation of purified samples of methylheptenone, methylheptenol, citronellol, citronellal semicarbazone, geraniol, nerol, linalool, the two stereoisomeric geranamides, and certain other synthetic derivatives of geraniol, that none of these substances could possibly contain more than 2—3% of the hypothetical *iso*propenyl isomers, and some of them certainly contain considerably less. Much of the older chemical evidence indicating the presence of 15—50% of such isomers must therefore be deemed unreliable. Furthermore, since certain authentic non-*iso*propenyl compounds display absorption in the 890-cm.$^{-1}$ spectral region, it would seem reasonable to extrapolate most of the observed maximum permissible isomer percentages to zero, and to conclude that *iso*propenyl end-groups do not occur at all in natural acyclic monoterpenes but are confined to the cyclic series (*e.g.*, limonene) where the different structural conditions can reasonably be expected to stabilise the *iso*propenyl relative to the *iso*propylidene forms.

Analytical Significance of Chemical Purification.—During the preparation or isolation of terpenoid substances for infra-red analysis of the *iso*propenyl isomer content, two interrelated problems arise and will be considered in this section: how far the presence of terminal double-bond absorption at 890 and 1645 cm.$^{-1}$ may be attributed to a foreign impurity other than the *iso*propenylic isomer to be detected; and how far on the other hand the isomer in question may escape detection owing to its previous removal as an " impurity " during a rigorous purification.

Experience with such relatively low-boiling *iso*propylidene–*iso*propenyl mixtures as that of 2-methylpent-2-ene with 2-methylpent-1-ene (see Experimental) shows that even with the use of modern packed laboratory fractionating columns it would be extremely difficult to achieve effective separation of terpenoid isomers of this type in a single distillation. Except for citronellol, all terpene samples for infra-red examination were distilled in ordinary Vigreux or spiral columns, and hence there can be no question of the possible removal of *iso*propenyl forms during distillation. In particular, the methylheptenone obtained directly by alkaline cleavage of commercial citral followed by simple fractionation through a short Vigreux column proved constant-boiling and spectroscopically identical with a special sample regenerated from the pure crystalline semicarbazone. The reported homogeneity of this ketone must therefore refer to the entire bulk of the material prepared from natural sources, and not only to some chemically isolated fraction of it. The same conclusion applies to our samples of linalool which had been ordinarily distilled without passing through a crystalline derivative, and also to geraniol isolated from the calcium chloride adduct; the spectrum of the latter alcohol was identical with that of a special sample regenerated from the crystalline diphenylurethane. The same calcium chloride method had been used in the purification of the geraniol which behaves on oxidation as if it contained some 20% of the *iso*propenyl isomer. Similarly, it is the crystalline citronellal semicarbazone of sharp melting point identical with that of our own homogeneous sample which affords ambiguous results by chemical degradation. There can be no doubt, therefore, that the samples investigated by us are truly representative of the compounds described in the chemical literature.

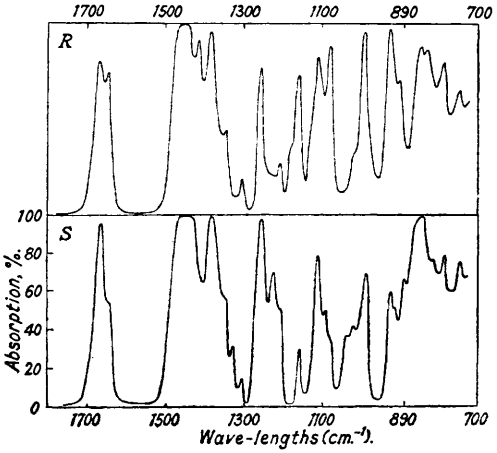
As already indicated, some trouble was experienced in obtaining reasonably pure specimens of citronellol from commercial sources; similar difficulties were evidently encountered by Thompson and Whiffen who have published spectrograms for two different grades of citronellol revealing different absorption intensities at the 890- and 1645-cm.$^{-1}$ bands. In view of the rather wide boiling and refractive index range of our crude samples (which also displayed somewhat strong absorption at these characteristic frequencies), we believe foreign impurities possessing terminal double bonds rather than the *iso*propenyl isomer of citronellol to have been present. The main citronellol fraction selected as a representative sample of the pure compound had very low terminal double-bond absorption and physical constants identical with those given for pure citronellol by Simonsen and Owen (*op. cit.*).

In their specimens of dimethyloctadiene (VI; X = H) obtained by the sodium–liquid ammonia reduction of geraniol, Thompson and Whiffen suspected the presence of an impurity containing vinyl groups, $CHR{:}CH_2$, because variable infra-red absorption occurred at 910, 990, and 1645 cm.$^{-1}$. In our own pure samples of this hydrocarbon (cf. Sheppard and Sutherland, *loc. cit.*, 1947), 910-cm.$^{-1}$ absorption was always small, and there was never any sign of 1645-cm.$^{-1}$ absorption which would be required by the presence of either vinyl or *iso*propenyl groupings. We see no reason to doubt, therefore, that chemically pure dimethyloctadiene from geraniol is a structurally homogeneous compound; on the other hand, it is possible and indeed probable that vinyl groups may be formed on autoxidation, which may account for the variable 910-cm.$^{-1}$ band intensities reported by Thompson and Whiffen.

Terpenoid Compounds containing Vinyl Groups.—The spectra of all the substances hitherto described exhibit certain common characteristic frequencies due to the presence of methyl (1370—1380 cm.$^{-1}$), saturated methylene (1450 and 735—745 cm.$^{-1}$), and *iso*propylidene or other $CHR{:}CR'R''$ (825—845 and 1665—1675 cm.$^{-1}$) groupings. Additional strong bands at 925, 997, 1415, and 1645 cm.$^{-1}$ arise in the spectrum of linalool (XIV; X = OH) (Fig. 3) where a vinyl group is present. The particularly intense 925- and 997-cm.$^{-1}$ absorptions obviously represent the out-of-plane vinyl C–H deformation frequencies which are normally found nearer 910 and 990 cm.$^{-1}$ in hydrocarbons. We have been able to observe similar band displacements in a variety of other allylic functional derivatives of vinyl hydrocarbons (see also below). As a general rule, in a molecule $CH_2{:}CH{\cdot}CRR'X$, where R may be either hydrogen or alkyl, but X represents a functional group, the 908—913-cm.$^{-1}$ hydrocarbon frequency is increased to 918—930 cm.$^{-1}$ (cf. Thompson and Torkington, *Trans. Faraday Soc.*, 1946, **42**, 432; Bateman *et al.*, *J.*, 1950, 936), whereas the 990-cm.$^{-1}$ frequency remains more or less constant when R = R′ = H, but is increased to 995—1005 cm.$^{-1}$, even in hydrocarbons (X = R), when the saturated carbon atom is fully substituted. The latter effect may be explained in terms of increased electron density at the nearer vinyl carbon atom resulting from the extensive substitution (cf. Sheppard and Sutherland, *loc. cit.*, 1949), but the reason for the marked shift in the 910-cm.$^{-1}$ frequency is not at present understood. The 1415- and 1645-cm.$^{-1}$ bands in the linalool spectrum are normal characteristic frequencies of vinyl groups in hydrocarbons, being associated respectively with an in-plane deformation of the terminal methylene group and the stretching of the double bond.

When the hydroxyl group of linalool or geraniol is replaced by halogen, the same halide is formed which is not constant-boiling (cf. Ruzicka, *Helv. Chim. Acta*, 1923, **6**, 499; Sutton, *loc. cit.*) and has frequently been suspected of consisting of an anionotropic mixture of (VI) and (XIV; X = Hal) (cf., *e.g.*, Karrer and Helfenstein, *Helv. Chim. Acta*, 1930, **14**, 78), although positive proof of structure has never been obtained. These compounds are generally referred to simply as " geranyl " halides. In view of the practical and theoretical interest of the structural problem, we have carried out a careful low-pressure fractional distillation (bath temperature $<70°$) of freshly prepared geranyl chloride and subjected the resulting four fractions to immediate infra-red analysis. The experiment clearly shows that geranyl chloride as originally obtained is mainly (VI), with a small proportion of the lower-boiling tertiary form (XIV). Allylic chlorides of this type exemplify those moderately mobile anionotropic systems in which the isomeric constitution of the isolated product is governed both by the nature of the reaction introducing the mobile atom or group and by the facility of isomeric interconvertibility under the conditions of reaction and isolation (Catchpole, Hughes, and Ingold, *J.*, 1948, 8). Comparison with simpler allylic halides (*loc. cit.*) indicates that the linaloyl isomer occurs in ordinarily isolated " geranyl chloride " to considerably greater extent than its thermodynamic equilibrium proportion (*ca.* 1%), and in agreement with this fact prolonged heating at a moderate temperature (*ca.* 60°) gives a more homogeneous product.

FIG. 4.



R, *Geranyl chloride* (*first fraction*) (VI *and* XIV; X = Cl) (0·1 *mm. cell*). S, *Geranyl chloride* (*last fraction*) (VI *and* XIV; X = Cl) (0·1 *mm. cell*).

The spectra (Fig. 4) of the first and last fractions from the distillation of geranyl chloride are recorded in the figures. The highest-boiling fraction consists essentially of the primary chloride (VI), with strong absorption at 845 and 1665 cm.$^{-1}$, but the small band at 925 cm.$^{-1}$ and the shoulder at 1645 cm.$^{-1}$ indicate the presence of traces of tertiary chloride incorporating a vinyl group in the molecule. In the successively lower-boiling fractions, the 845- and 1665-cm.$^{-1}$-band strengths become gradually reduced, whereas the 925- and 1645-cm.$^{-1}$ bands are greatly intensified; at the same time, existing strong absorption at 988 cm.$^{-1}$ acquires additional intensity, and a new peak appears at 1415 cm.$^{-1}$. The interpretation of these changes in terms of increasing relative amounts of tertiary chloride incorporating the vinyl group is obvious. Other intensity changes occur simultaneously with those of the characteristic bands; in particular, the primary geranyl form appears to be associated with very intense absorption at 1255 cm.$^{-1}$, and the tertiary linaloyl form with a similarly strong band at 1080 cm.$^{-1}$. In view of the markedly different extinction coefficients of vinyl and trialkyl-substituted types of double bond, the spectrum of the lowest-boiling fraction indicates that even here the higher-boiling geranyl form predominates. It may be noted that the usual 910-cm.$^{-1}$ frequency of the vinyl group is again displaced to 925 cm.$^{-1}$; in allyl chloride itself, we observed the characteristic vinyl frequencies at 930, 985, 1415, and 1645 cm.$^{-1}$.

Two structurally isomeric hydrocarbons are produced during the coupling reaction of geranyl chloride over magnesium (Barnard and Bateman, *J.*, 1950, 932). The straight-chain digeranyl (XI) (with a very small band at 908 cm.$^{-1}$ probably due to a trace of the isomer) has already been referred to above; the structure of the branched-chain *iso*digeranyl (XV) is clearly characterised by intense vinyl absorption peaks at 908, 998, and 1642 cm.$^{-1}$, as well as a smaller

$$\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(CH{:}CH_2){\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}$$

(XV.)

band at 1415 cm.$^{-1}$ (Fig. 3). The slight but significant increase in the usual 990-cm.$^{-1}$ frequency of the vinyl group to 998 cm.$^{-1}$ in this hydrocarbon can probably be attributed to the inductive effect of the three alkyl substituents at the adjacent carbon atom, as suggested above. *iso*Homogeranamide (XIV; $X = CO{\cdot}NH_2$) similarly displays vinyl absorption at the displaced frequencies of 920 and 1005 cm.$^{-1}$ (Fig. 2).

Stereoisomerism.—In accordance with certain chemical evidence (Simonsen and Owen, *op. cit.*) and the known structure of the derived amine hydrochloride (Jeffrey, *loc. cit.*), geraniol (VI; $X = OH$) is believed to be the *trans*-isomer * with respect to the ambiguous configuration of the double bond adjacent to the primary alcohol grouping. The stereoisomeric nerol (*cis*-VI; $X = OH$) shows only minor differences of infra-red absorption, as might be expected from the general similarity of the two structures. The same kind of *cis-trans*-isomerism about a trisubstituted ethylenic linkage exists in the two 3-methylpent-2-enes where, again, relatively little, but nevertheless distinct, differentiation of infra-red spectra has been reported (A.P.I., *op. cit.*). We have also observed slight differences of infra-red absorption between the two isomorphous crystalline diphenylurethanes of geraniol and nerol. The *cis-trans*-isomeric geranamides (V; $X = CO{\cdot}NH_2$) were crystallographically distinct from each other (Dr. G. A. Jeffrey, private communication) and the accompanying diagrams show that their infra-red spectra were more highly differentiated for the crystalline substances than they were for solution.

C–O *Frequencies of Terpenoid Alcohols.*—It appears to be generally true that saturated primary, secondary, and tertiary aliphatic alcohols display intense absorption at 1040—1080, 1100—1130, and 1160—1200 cm.$^{-1}$ respectively (cf. A.P.I., *op. cit.*; Sexton and Britton, *J. Amer. Chem. Soc.*, 1948, **70**, 3606), arising from the stretching vibration involving the C–O bond. The strong bands of the primary citronellol (IX) at 1055 cm.$^{-1}$ and of the secondary methylheptenol (VIII) at 1120 cm.$^{-1}$ are in line with this classification, but the characteristic frequencies of the allylic alcohols geraniol and nerol (VI; $X = OH$) at 1010 and of linalool (XIV; $X = OH$) at 1115 cm.$^{-1}$ are below the range assigned to their primary or tertiary class. Since allyl alcohol itself exhibits a similar shift of the alcohol band to 1027 cm.$^{-1}$ (Thompson and Torkington, *loc. cit.*, 1946), these low-frequency displacements appear to arise from the presence of the double bond in the allyl position and may be associated with a lowering of the force constant of the C–O bond in allylic environment. The characteristic ether absorption of digeranyl ether (XII) near 1080 cm.$^{-1}$ likewise occurs below that commonly observed above 1100 cm.$^{-1}$ in saturated primary ethers, and the displacement may again be ascribed to an allylic structural effect (for comparative data, cf. Barnes *et al.*, *Ind. Eng. Chem. Anal.*, 1943, **15**, 659).

The infra-red measurements were initiated at Cambridge, later continued by courtesy of the Directors at the Research Department of Messrs. Imperial Chemical Industries, Ltd. (Plastics Division), where facilities were kindly provided by Mr. H. A. Willis, and finally completed at the B.R.P.R.A. laboratories with valuable assistance from Miss J. M. Fabian. The work described forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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* We have adopted the general convention recently recommended by the Nomenclature Committee of the American Chemical Society (*Chem. Eng. News*, 1949, **27**, 1303), according to which geraniol is derived from *trans*-octadiene and should therefore be correctly formulated as 3 : 7-dimethylocta-*trans*-2 : 6-dien-1-ol. This convention seems both logical and in harmony with the universal practice of describing the two stereoisomeric polyisoprenes rubber and gutta-percha as *cis*- and *trans*-isomers respectively. Unfortunately, some confusion exists in the literature as many authors (*e.g.*, Simonsen and Owen, *op. cit.*; Caldwell and Jones, *loc. cit.*) have rather arbitrarily referred to geraniol and its derivatives as *cis*-isomers.