CHAPTER IV

TRANSFORMATION PRODUCTS OF CITRAL
SUMMARY

Conjugate addition of lithium dimethyl-copper
\((\text{LiMe}_2\text{Cu})\) to citral furnishes methyl citronellal (II) which
has been reduced with sodium borohydride to methyl
citronellol (III), a pleasant smelling liquid. Perfumery
grade citronellol can be conveniently prepared by reduction
of citral with iron and 50% acetic acid in presence of nickel
chloride. Reduction of citral (mixture of isomers 'a' and 'b')
with \(\text{NaBH}_4\) in ethanol furnishes a mixture of geraniol and
nerol, free from citronellol. Oxidation of geraniol with
dichloro dicyanobenzquinone (DDQ) furnishes citral.

Methyl heptenone has been treated with allyl
magnesium chloride, phenyl magnesium bromide and benzyl
magnesium chloride; the resulting tertiary alcohols have been
characterised.
Citral (I) occurs as the major constituent in the oil of lemongrass. This oil is obtained from the two botanical species (i) Cymbopogon Flexuosus and (ii) Cymbopogon Citratus, by steam distillation. These species are cultivated in various parts of the world, and in India chiefly in Travancore. According to Arctander\(^1\), the lemon-grass oil is one of the first ten largest essential oils in the world in respect of volume produced annually. The oil is mainly valued for its citral content. India is one of the leading producers of the oil and as the Indian variety is very rich in citral (more than 70%), it has a great demand in perfumery market. Citral finds use in perfumes and flavours and also as a starting material in the production of \(\beta\)-ionone, an intermediate in the synthesis of Vitamin A. Citral is also used in the synthesis of highly valued perfumes such as irones and methyl ionone.

In our present work we have studied some reactions of citral with a view to find a suitable outlet for the Indian lemon-grass oil and also with a view to prepare such perfumery compounds whose production in India is at present dependent on imported essential oils.

**Citral to methyl citronellal**

It is well-known that the reduction of the conjugated double bond of citral furnishes citronellal which is a more pleasant smelling liquid than citral itself. This difference in odour may probably be attributed to the saturation of the
conjugated double bond. It is also known that in some cases the introduction of an additional methyl group in perfumery compounds often leads to products having a better odour value. Thus for instance, methyl ionones and irones are better perfumes than ionones themselves. It was therefore considered of some interest to see whether by some means we could saturate the conjugated double bond of citral and at the same time introduce a methyl group at one end of the double bond so as to produce a new compound, methyl citronellal. This compound, if produced, would be important from the commercial point of view since it might probably have a modified odour and also it would be much stabler than citral itself. Being a new compound it would also be interesting from the academic point of view.

At this stage we came across a paper by House and co-workers\(^2\) who have given a method that proved helpful to us in achieving our objective. The action of a methyl Grignard or methyl lithium on a conjugated carbonyl compound is known to proceed mainly through the normal addition (1,2 addition) and to a certain extent through the conjugate addition (1,4 addition). It was however first noted by Kharasch\(^3\) that catalytic amounts of copper compounds diverted the reaction from the normal course to the conjugate addition and the yields obtained via the latter were quite substantial. This work was then systematically studied by House and co-workers and they confirmed the findings of Kharasch. They
CHART No. 1

\[ \text{CH}_3 \text{C} = \text{C} \left( \text{CH}_3 \right) \text{C} - \left( \text{CH}_3 \right)_2 \text{C} - \text{CH}_3 + \text{CH}_3 - \text{Li} \]

\[ \text{H}_3 \text{C} = \text{C} \left( \text{CH}_3 \right) \text{C} - \left( \text{CH}_3 \right)_2 \text{C} - \text{CH}_3 + \left( \text{CH}_3 \right)_2 - \text{CH} - \text{CH} = \text{C} - \text{CH}_3 \]

\[ \text{H}_3 \text{C} = \text{C} \left( \text{CH}_3 \right) \text{C} - \left( \text{CH}_3 \right)_2 \text{C} - \text{OH} + \left( \text{CH}_3 \right)_2 - \text{CH} - \text{CH}_2 - \text{C} - \text{CH}_3 \]

\[ \text{H}_2 \text{O} \]

\[ \text{NH}_4 \text{Cl} \]

\[ \text{CH}_3 \text{C} = \text{C} \left( \text{CH}_3 \right) \text{C} - \left( \text{CH}_3 \right)_2 \text{C} - \text{CH}_3 + \left( \text{CH}_3 \right)_2 - \text{CH} - \text{CH}_2 - \text{C} - \text{CH}_3 \]
found that if the conjugated ketone, trans-3-penten-2-one (A) is allowed to react with methyl lithium, the products (B) and (C) are obtained as intermediates by normal and conjugate addition respectively (vide Chart No. 1). On working up the reaction mixture, these intermediates are converted to (B) and (C). The proportion of the conjugate addition intermediate (C) and hence of the final product (C) is quite small in comparison with the products (B) and (B). But if methyl lithium is first treated with trace amounts of cuprous salts and then allowed to react with the conjugated ketone (A), the reaction proceeds to form almost exclusively the conjugate addition intermediate (C) so that after working up, the reaction product contains (C) as almost the sole component in which the conjugated double bond of the starting ketone is saturated and a methyl group is introduced in \(\beta\)-position of the double bond. This is exactly the reaction that we intended to have in the case of citral in order to produce methyl citronellal (II).

The role played by copper in the reaction is supposed to be through the formation of its complex with methyl lithium (or methyl Grignard) and the ether used as solvent. Methyl lithium (or methyl Grignard) in ether first reacts with the cuprous salt to form the methyl copper as an insoluble and apparently polymeric solid. This insoluble methyl copper then reacts with a second molar equivalent of methyl lithium.
(or methyl Grignard) and ether to form a pale yellow or colourless solution. The solution is supposed to contain the derivative (D) of dimethyl copper complex with ether.

\[
\text{CH}_3\cdot M + \text{Cu}^+ \rightarrow (\text{CH}_3\text{Cu})_n + M^+
\]

Methyl copper

\[M = \text{Li}^+ \text{ or MgX}\]

\[
(\text{CH}_3\cdot\text{Cu})_n + \text{CH}_3\cdot M \overset{\text{Et}_2\text{O}}{\rightleftharpoons} (\text{CH}_3)_2\text{Cu}^-\text{(OEt}_2)_2 M^+
\]

(D)

Methyl copper or the derivative (D) have the ability to react very rapidly with the conjugated carbon-carbon double bond while at the same they are inert to carbon-oxygen double bond. Methyl copper or its derivative can thus be safely used to add on selectively to the conjugated carbon-carbon double bond of a conjugated ketone while unprotected ketone, ester or carboxylic acid functions are present in the same molecule. The exact mechanism of conjugate addition is still a matter of speculation and is yet not known with a degree of certainty. However, a broad outline of the reaction course can be depicted stepwise as shown in the Chart No.2.

As only catalytic amounts of copper salts are used in the reaction, the copper complex formed is small in
CHART No. 2

1) \[ \text{CH}_3\text{M} + \text{Cu}^+ \rightarrow (\text{CH}_3\text{Cu})_n + \text{M}^+ \quad (\text{M}^+ = \text{Li}^+ \text{ or } \text{Mg}^+) \]

2) \[ (\text{CH}_3\text{Cu})_n + \text{CH}_3\text{C} = \text{C} = \text{CH} + \text{CH}_3 \rightarrow (\text{CH}_3)_2\text{CH} = \text{C} = \text{CH}_3 \]

3) \[ (\text{CH}_3)_2\text{C} = \text{C} = \text{CH} + \text{M}^+ \rightarrow (\text{CH}_3)_2\text{C} = \text{C} = \text{CH} + \text{Cu}^+ \]

4) \[ (\text{CH}_3)_2\text{C} = \text{C} = \text{CH} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{C} = \text{C} = \text{CH} + \text{OH} \]

\[ \text{Ketonisation} \]

\[ (\text{CH}_3)_2\text{C} = \text{C} = \text{CH} \rightarrow (\text{CH}_3)_2\text{C} = \text{C} = \text{CH} \]

\[ (\text{CH}_3)_2\text{C} = \text{C} = \text{CH} \rightarrow (\text{CH}_3)_2\text{C} = \text{C} = \text{CH} \]
comparison with the total amount of methyl lithium employed. The reaction mixture thus contains two competing species (methyl lithium and methyl copper) which can react with the conjugated ketone in two ways:

(a) methyl lithium predominantly leading to 1,2 addition and to some extent 1,4 addition
(b) methyl copper leading to 1,4 addition only.

House and co-workers found that the action of methyl copper is about one thousand times as fast as that of methyl lithium so that the course of the reaction is dictated in the direction of 1,4 addition. Also the copper(ous) regenerated (as shown in step 3 in the Chart 2) becomes available for producing more methyl copper complex which is then used up in the reaction again. This cycle involving steps 1 to 3 repeats itself several times and far more rapidly than the action of methyl lithium on the conjugated ketone. Thus methyl copper can compete successfully with methyl lithium in its reaction with the conjugated carbonyl compound and only trace amounts of copper salts are sufficient for this purpose. The overall effect of the methyl copper reaction is that the conjugated double bond of an \( \alpha - \beta \) unsaturated carbonyl compound is saturated and a methyl group is introduced in \( \beta \) position of the double bond.

We then decided to take advantage of this reaction and when it was employed in the case of citral (I), we got methyl citronellal (II) quite in accordance with our
expectation. The product gave a single peak in the VPC analysis indicating it to be a single compound. Its IR spectrum (IR-1) also gave bands at 2717 and 1727 cm\(^{-1}\) (non-conjugated aldehyde) indicating that the conjugation had vanished. A band at 833 cm\(^{-1}\) (trisubstituted double bond) was also noticed. A further proof for the disappearance of the conjugation came from the absence of absorption near about 237.5 \(\mu m\) in the ultraviolet spectrum. Finally, the structure (II) assigned to the compound was well supported by the NMR spectrum (NMR-1) which gave signals at \(\nu\): 8.93 (6H, gem dimethyl); 8.39, 8.32 (6H, methyls of isopropylidene group); 4.94 (1H, olefinic proton); -0.05 (triplet, 1H, aldehyde proton).

Methyl citronellal thus produced had a distinctly different odour from that of citral or citronellal but it was not remarkably pleasant.

This new compound, methyl citronellal, was then reduced with sodium borohydride in ethanol and the corresponding alcohol, methyl citronellol (III) was obtained. The reduction product gave a single peak in the VPC analysis and its IR spectrum (IR-2) showed the presence of a hydroxy function (3500, 1050 cm\(^{-1}\)) and a trisubstituted double bond (837 cm\(^{-1}\)). As anticipated, this alcohol was found to have a pleasant odour but different from that of citronellol.
Citral to citronellol

Although citral by itself has no value as a perfume, citronellal which can be obtained from it, is a fragrant smelling liquid and the corresponding alcohol, citronellol (IV) is still better in this respect. This alcohol is at present technically prepared by catalytic hydrogenation of citronellal and since the latter is obtained mainly from the imported Java citronella oil, this method of preparing citronellol is uneconomical for Indian market. We therefore thought it desirable to use citral as the starting material since it is available in abundant quantities from the indigenous oil of lemon grass. For bringing about the conversion of citral to citronellol two methods were considered as practicable (i) catalytic hydrogenation with Raney nickel (ii) chemical reduction with iron and acetic acid.

The former method has a distinct advantage that unlike the chemical method it is clean and easy to handle. However, it is not without drawbacks; some byproducts are formed which are difficult to remove and citronellol formed is contaminated with impurities. In either case, the first attack is mainly on the conjugated double bond, leading to the formation of citronellal and subsequently the aldehyde group is reduced to a hydroxy group, furnishing citronellol. However, in the catalytic method, the selectivity of attack is not restricted to the conjugated double bond; a further
and simultaneous attack also proceeds on the isolated double bond and 3,7-dimethyl octanol (V) is produced as a byproduct which is difficult to remove from citronellol. Obviously this means that in the catalytic method a rigorous control has got to be kept on the amount of hydrogen absorbed, and the reaction interrupted at the proper stage. But it has been further noted that even after keeping a proper control, some amount of dimethyl octanol is inevitably formed and the catalytic method thus becomes unsuitable where pure citronellol, free from dimethyl octanol is required. This drawback is totally absent in the chemical method since the isolated double bond is almost inert to chemical reduction.

We carried out the chemical reduction of citral by heating it with iron powder and 50% acetic acid on a water bath at 70°C and under stirring. A small amount of nickel chloride was added to catalyse the reaction. The reaction was over in three hours and the product distilled under vacuum. IR spectrum of the distillate gave strong absorption bands at 3300 and 1050 cm⁻¹ (hydroxy group) and weak absorption bands at 1250 and 1725 cm⁻¹ indicating that probably some acetate was also formed. It was therefore saponified and totally distilled. The distillate now did not show any of the above acetate bands in the IR spectrum and it was subjected to fractional distillation under vacuum.
A low boiling product was obtained as the first fraction, though in small amounts. Most of the remaining material distilled over at 117-119°/17 mm and it was found to be the pleasant smelling citronellol. Its IR spectrum was identical with that of authentic citronellol and in the UV spectrum there was no absorption near about 237.5 μ indicating it to be free from citral. The VPC analysis (neat and mixed with authentic citronellol) gave a single peak showing it to be pure citronellol. Although the low-boiling product mentioned above was obtained as an impurity, it could be removed easily by fractional distillation and citronellol thus obtained was quite pure. The chemical reduction thus furnishes an easy and economical method of obtaining pure citronellol from citral.

The nature of the low-boiling fraction was then investigated. The IR spectrum of this fraction showed complete absence of a carbonyl function but it indicated the presence of at least some traces of a hydroxy compound. It was therefore chromatographed over alumina (Grade II) and the fraction eluted with pet. ether accounted for most of the material loaded for chromatography. But the IR spectrum of this chromatographed material now gave no indication for a hydroxy compound and it was tentatively presumed to be a hydrocarbon probably having the structure (VI). This presumption was further substantiated by the micro analytical
results. However, the VPC analysis (6 ft., polyester on firebrick, 110°, hydrogen flow rate 60 ml/min.) gave two peaks (retention time 2 min., 30 sec. and 3 min., 45 sec.) so that it was further necessary to suppose that the product was a mixture of two geometric isomers, 2,6-dimethyl-2, trans-6-octadiene (VI) and 2,6-dimethyl-2, cis-6-octadiene (VII). If this presumption about the nature of the low-boiling fraction were correct, it would give levulinic acid (VIII) as one of the products of ozonolysis. Actually when the low-boiling fraction was subjected to ozonolysis and the resulting acid treated with diazomethane, a methyl ester was obtained. A distilled sample of the methyl ester gave a single peak in the VPC analysis and it also formed a 2,4-DNP derivative identical in all respects with the 2,4-DNP derivative prepared from an authentic sample of methyl levulinate. These results gave a clear and confirmatory proof to the presumption that the low-boiling fraction obtained above was a mixture of the hydrocarbons (VI) and (VII).

In order to account for the formation of these hydrocarbons it was necessary to revise our previous idea, at least to some extent, about the sequence of attack in the acid-metal reduction of citral. Instead of supposing the attack to be taking place entirely on the conjugated double bond first, it was necessary to consider that some amount of

*This mode of 'cis' and 'trans' nomenclature is in accordance with the convention given in the text book 'Organic Chemistry' by D.J. Cram and G.S. Hammond, page 120-21, 1959 edition, McGraw-Hill publication.
citral underwent an attack at the carbonyl group first
to produce a mixture of two allylic alcohols, geranial and
nerol corresponding to citral 'a' and citral 'b'. This
transformation from aldehyde to alcohol group must have
rendered the double bond in allylic position less vulnerable
to attack, and by a continued reduction, the allylic alcohols
underwent hydrogenolysis, giving rise to the hydrocarbons
(VI) and (VII). This point was borne out by subjecting an
authentic mixture of geranial and nerol to the action of iron and
acetic acid, when a small amount of a mixture of hydrocarbons
was obtained which was shown by the VPC analysis and
IR spectra to be identical with the low boiling fraction
obtained in the acid-metal reduction of citral above.

Citral to geranial and nerol by the action of NaBH₄

Reduction of citral to geranial and nerol is known
since long time. However, since this reduction requires
retention of the conjugated double bond, only a limited
number of methods are available for that purpose. Tiemann⁵
prepared geranial by reducing citral 'a' with sodium amalgam
in alcohol in presence of acetic acid. It has also been
obtained⁶ from citral 'a' by reduction with aluminium iso-
propoxide. We have now brought about the reduction of a
mixture of citral 'a' and citral 'b' to geranial and nerol
with sodium borohydride in ethanol. IR spectrum of the
product formed showed complete absence of a carbonyl function
but it indicated the presence of a hydroxy group (bands at
Raman and 1080 cm\(^{-1}\)). VPC analysis of the product gave two peaks superimposable with the two peaks of an authentic mixture of geraniol and nerol but no trace of citronellol was detected.

As from the point of odour value, the above mixture of geraniol and nerol was found to be much better than the one obtained through aluminium isopropoxide reduction.

**Citral from geraniol by the action of DDQ**

Just as citral can be reduced to geraniol, the latter can also be oxidised back to citral by choosing a suitable reagent. Slemmer\(^7\) used potassium dichromate and sulphuric acid as the oxidising agent whereas catalytic oxidation\(^8\) in presence of copper at elevated temperature has also been reported. Manganese dioxide in particular is used for the oxidation of allylic alcohols and it is actually in use for converting geraniol to citral. In our work we tried the reagent 2,3-dichloro-5,6-dicyanobenzquinone (DDQ) (IX) as the oxidising agent in benzene solution and converted geraniol to citral. This conversion of geraniol to citral is of little practical value for Indian market since citral is already available in plenty from Indian resources. However, we have studied the action of DDQ simply by way of academic curiosity.

Quinones have been known since long to act as dehydrogenating agents. Abstraction of hydride ions and proton
elimination is the primary reaction of quinones. This ability to abstract hydride ions is markedly influenced by the nature of substituents in the quinone nucleus, electron-withdrawing substituents enhancing this tendency. DDQ has all the four substituents two chloro and two cyano as electron withdrawing groups so that the dehydrogenating ability of DDQ is much more than that of quinone itself. This reagent although prepared in 1906, was not much in use but from 1960 onwards it found considerable application in steroid field. The peculiar feature of the reagent is that like manganese dioxide it also selectively oxidises allylic alcohols to \( \alpha-\beta \) unsaturated aldehydes and ketones but its real advantage is that as it is considerably soluble in solvents like benzene, tetrahydrofuran, the reaction mixture forms a homogeneous phase so that the oxidation is smooth and reproducible. This advantage is lacking in the case of manganese dioxide as it forms a heterogeneous phase with the reaction mixture. By using a solution of DDQ in benzene we oxidised geraniol to citral and the latter gave IR spectrum identical with that of authentic citral.

Uptill now almost all reactions of DDQ reported in literature have been found to be mainly restricted to steroid field and so far only one paper has appeared dealing with the action of DDQ on four non-steroidal allylic alcohols. On this background the above action of DDQ on geraniol that we have studied is important since it is probably the first
instance of a non-steroidal allylic alcohol belonging to terpene series.

**Grignard reactions with methyl heptenone**

As has been mentioned earlier, large quantities of citral are being used in the synthesis of β-ionone which is ultimately used for the production of Vitamin A. During the conversion of citral to β-ionone, methyl heptenone (X) is obtained as one of the byproducts. Since methyl heptenone itself has no value as a perfume it was our aim to find out some outlets for this byproduct.

In 1953 Normant\textsuperscript{12} found that methyl heptenone reacted with vinyl magnesium bromide to give the sweet smelling natural perfume, linalool (XI), and since that time this has become a convenient method for getting synthetic linalool. Although no correlation has been established between odour and structure of compounds, we thought that compounds closely related to linalool might possess a pleasant perfumery property like linalool. We thought that instead of using vinyl halide in the above reaction, if the corresponding dihydro halide (ethyl halide) be used, the product produced would be dihydro linalool i.e. 3,7-dimethyl-6-octen-3-ol (XII). Similarly if allyl halide which is a higher homologue of vinyl halide were used, the product of the reaction would be 4,8 dimethyl-1,7-nona dien-4-ol (XIII). Actually when methyl heptenone was allowed to react with ethyl magnesium iodide and allyl magnesium chloride, the compounds (XII) and
(XIII) were obtained respectively, quite in conformity with our expectation. These products gave single peaks in their VPC analyses and their IR spectra (IR-3 and IR-4) bands at 3333, 1050 cm\(^{-1}\) and 3450, 1072 cm\(^{-1}\) indicating the presence of a hydroxy group. The structures of these compounds were finally confirmed by the NMR spectral data.

For structure (XII), \(J\) values: (NMR-2)

- 9.12 (3H, triplet, \(J = 7\) cps, primary methyl)
- 8.88 (3H, s, CH\(_3\) attached to C\(_3\))
- 8.37 (3H, s, CH\(_3\) attached to C\(_7\))
- 8.32 (3H, s, CH\(_3\) attached to C\(_7\))
- 4.9 (1H, m, olefinic proton at C\(_6\))

For structure (XIII), \(J\) values: (NMR-3)

- 8.88 (3H, s, CH\(_3\) attached to C\(_4\))
- 8.38 (3H, s, CH\(_3\) attached to C\(_8\))
- 8.34 (3H, s, CH\(_3\) attached to C\(_8\))
- 4-5.25 (4H, m, olefinic protons at C\(_1\), C\(_2\) and C\(_7\))

Methyl heptenone was then treated with two aryl magnesium halides with a view to see whether any perfumery compounds could be produced. Sometimes the introduction of an aryl group at a suitable site in an organic molecule gives a new compound which has better perfumery value than the original compound itself. As for instance, ethyl alcohol and allyl alcohol have no value as a perfume. But if a phenyl radical is somehow brought in to join on to the \(\beta\) carbon of ethyl alcohol or to the \(\gamma\) carbon of allyl alcohol,
NMR-2 3,7-DIMETHYL-6-OCTENE-3-OL (XII)
(IN CC\(_4\))
the resultant products are β-phenyl ethyl alcohol and cinnamyl alcohol respectively and these resulting compounds are quite pleasant smelling. A similar entry of an aryl group in methyl heptenone could be brought about by the action of an aryl Grignard but with a slight difference that the carbonyl carbon would be involved in the reaction. We were interested in testing the perfumery properties of such compounds. Actually when methyl heptenone was allowed to react with phenyl magnesium bromide and benzyl magnesium chloride, the anticipated products 2 phenyl-6-methyl-5 hepten-2-ol (XIV) and 2-benzyl-6 methyl-5 hepten-2-ol (XV) were produced respectively. The VPC analyses of these products gave single peaks and their IR spectra (IR-5 and IR-6) gave bands at 3401, 1029 cm⁻¹ and 3400, 1033 cm⁻¹, indicating the presence of a hydroxy group. The NMR spectral data finally confirmed the structures (XIV) and (XV) assigned to these alcohols.

For structure (XIV), J values: (NMR-4)

8.52 (3H, s, CH₃ attached to C₂)
8.37 (3H, s, CH₃ attached to C₆)
8.2 (3H, s, CH₃ attached to C₆)
4.95 (1H, m, olefinic proton at C₅)
2.72 (5H, m, aromatic protons of phenyl group)
NMR 4. 2-PHENYL-6-METHYL-5-HEPTEN-2-OL (XIV)

IN CC(4)
For structure (XV), J values:

8.92 (3H, s, CH₃ attached to C₂)
8.37 (5H, s, CH₃ attached to C₆)
8.32 (3H, s, CH₃ attached to C₆)
7.3 (2H, s, benzyl CH₂)
4.88 (1H, m, olefinic proton at C₅)
2.8 (5H, s, aromatic protons of phenyl group)

Although the preparation of the four alcohols (XII), (XIII), (XIV) and (XV) was attempted with a view to study their perfumery properties, none of them excepting dihydro-linalool (XII) was found to have any remarkable pleasant odour.
EXPERIMENTAL

Citral used in the reactions was obtained by fractionating the oil of lemon-grass over a Vigreaux column. The fraction distilling over at 117-19°/20 mm was the proper fraction with $n^2_D$ 1.4847 and its IR spectrum was identical with that of the authentic sample of citral. Similarly the stock sample of methyl heptenone was distilled and the fraction distilling over at 108°/20 mm was used as the pure methyl heptenone. It gave $n^2_D$ 1.4417 and a single peak in the VPC analysis and its identity was confirmed through its NMR spectrum.

Lithium dimethyl copper(-ous) reagent

This reagent was prepared from methyl lithium and cuprous iodide in ethereal medium at 0°.

Methyl lithium was prepared by the usual procedure from lithium (1.68 g., 0.24 atoms) and methyl iodide (26 g, 0.18 mol.) in dry ether (250 ml). The solution was cooled to 0° and dry cuprous iodide (11.4 g, 0.06 mol) was added in small instalments to the above solution under stirring while the temp. was maintained throughout at 0°. Most of the cuprous iodide went into solution which ultimately became pale tan.

Methyl citronellal (II)

To the above ethereal solution of lithium dimethyl copper kept stirring at 0°, a solution of citral (4.56 g,
0.03 mol) in dry ether (200 ml) was added dropwise, care being taken that the temp. did not rise above 0°. After the addition was over, stirring was continued for 45 minutes and then the reaction mixture was poured into a cold aqueous saturated solution of ammonium chloride. The solution was allowed to stand for 1/2 hr. and the organic layer separated out. The aqueous phase was extracted three times with ether (3 x 75 ml). The ether extracts and the previously separated organic layer were pooled together and dried over anhydrous sodium sulphate. Ether was removed by distillation and the pale yellow residue subjected to fractional distillation under vacuum (5 mm). The first fraction (4.32 g) distilled over at 100-105°/5 mm (bath temp.). The IR spectrum of this fraction showed it to be mainly composed of a non-conjugated aldehyde with traces of an alcohol while the UV spectrum gave no absorption near 237.5 μ (absence of citral).

The second fraction (0.41 g) showed b.p.110-15°/1 mm (bath temp.). Its IR spectrum indicated it to be mainly an alcohol and further work was not carried out on this fraction.

The first fraction (4.32 g) was chromatographed over alumina (neutral, grade II, 1:30). The pet.ether-benzene (50:50) fraction accounted for the major quantity of the material (4.1 g) and was shown by IR to be an aldehyde free from alcohol. The benzene-ether (80:20) fraction was a mixture of alcohol(s) and aldehyde(s) in which the former predominated.
The material (4.1 g) eluted with pet. ether-benzene (50:50) was redistilled and pure methyl citronellal (I) (3.83 g, 0.029 mol) was obtained.

b.p. 125-30° (bath temp.); \( n^D_27 \) 1.4475

**Analysis**

Found: C, 78.64; H, 11.87
Calculated for \( C_{11}H_{20}O \) : C, 78.51; H, 11.98%.

IR bands (IR-1) at 2899, 2717, 1727, 1464, 1449, 1376, 1339, 1292, 1259, 1232, 1208, 1171, 1131, 1105, 1060, 1021, 990, 917, 833, 740 cm\(^{-1}\).

Vapour phase chromatographic analysis (6 ft., polyester on fire brick, 180°, hydrogen flow rate 67 ml/min,) showed it to be only one compound (retention time 2 min., 29 sec.)

**Methyl citronellol (III)**

To a solution of sodium borohydride (0.38 g, 0.01 mol) in ethanol (10 ml), a solution of methyl citronellal (1.68 g, 0.01 mol) in ethanol (10 ml) was added dropwise, the temp. being maintained at 5-10°. The mixture was allowed to stand overnight at room temp. and after adding water (10 ml) to it, cold dil. hydrochloric acid was added gradually till the solution became acidic. The mixture was further diluted with water (50 ml) and extracted three times with ether (3 x 50 ml). The ether extracts were pooled together, washed successively with water, sodium carbonate solution and finally with water and dried over anhydrous sodium sulphate.
Ether was removed by distillation and the crude residue (1.5 g) chromatographed over alumina (neutral, grade II, 1:30). The pet. ether and benzene fractions were free from alcohol as indicated by the IR spectrum. But the material eluted with benzene-ether (80:20) gave an alcohol (1.38 g) which on distillation under vacuum yielded pure methyl citronellol (1.12 g; 0.007 mol).

b.p. 140°/6 mm (bath temp.)

Analysis

Found: C, 77.96; H, 13.02.
Calculated for C_{11}H_{22}O: C, 77.58; H, 13.12%

IR bands (IR-2) at 3500, 2907, 1460, 1442, 1776, 1362, 1339, 1250, 1126, 1110, 1050, 990, 926, 837, 741 cm^{-1}.

Vapour phase chromatographic analysis (6 ft., polyester on firebrick, 174°, hydrogen flow rate 67 ml/min.) showed it to be composed of only one compound (retention time 7 min., 11 sec.)

Reduction of citral with iron and acetic acid

A mixture of citral (30.4 g, 0.2 mol), iron dust (90 g, 1.6 mol), glacial acetic acid (150 ml, 2.6 mol) diluted with an equal volume of water, and NiCl₂ 6H₂O (1 g) was stirred in a three necked flask on a water-bath at 70°. Condensors were fitted to ensure that no volatile matter escaped. After a period of three hrs., the reaction mixture formed a thick slurry which was subjected to steam distillation.
The distillate (2 litres) collected was allowed to stand for 2 hrs. The oily layer (26.8 g) which separated was saponified by refluxing with a mixture of potassium hydroxide (15 g) in ethanol (100 ml) for 3 hrs. The reaction mixture was cooled, diluted with water (400 ml) and extracted three times with ether (3 x 150 ml). The ether extracts were dried over anhydrous sodium sulphate and ether removed by distillation when the oily material free from acetate was obtained. The oily material (25.2 g) was fractionally distilled under vacuum (17 mm). A low-boiling product (60-65°/17 mm) which was obviously not citronellol was collected as the first fraction (0.85 g). Further fractions were collected at different intervals and those distilling over in the range 115-20°/17 mm were found to be mainly composed of citronellol with some impurities as indicated by the VPC analysis. These enriched fractions were pooled together and refractionated to furnish a major fraction (21.4 g, 0.14 mol) distilling over at 117-19°/17 mm and this was identified as citronellol.

IR spectrum of this product was identical with that of an authentic sample of citronellol.

b.p. 117-19°/17 mm ; (literature, b.p. 115°/17 mm)

n_D^27 1.4538 (literature, n_D^20 1.4566)

VPC analysis, neat and mixed, (6 ft., polyester on fire brick, 184°, hydrogen flow rate 67 ml/min.) gave a single peak with the retention time (3 min., 48 sec.) indicating it to be a single compound. Similarly the VPC analysis, neat and mixed, (6 ft., carbowax on firebrick, 172°, hydrogen flow rate
70 ml/min.) gave a single peak with the retention time (6 min., 1 sec.) and indicated it to be a single compound.

Ozonolysis of the low-boiling fraction

A purified sample (0.5 g) of the low-boiling fraction in the previous expt. was ozonised in ethyl acetate (20 ml) below 10° till the issuing gas gave a positive test with starch iodide paper. The solvent was removed under reduced pressure by heating to 40°. The ozonide was treated with 30% H₂O₂ (4 ml) and carefully heated with water (10 ml) on a water-bath for 4 hrs; 10% Na₂CO₃ solution (10 ml) was added to the above solution and the mixture extracted with ether to remove non-acidic organic material. From the aqueous phase containing the sodium salts, the organic acids were regenerated by addition of hydrochloric acid till the solution was acidic to Congo red. Levulinic acid being water soluble, its extraction with organic solvents was difficult. The solution was therefore subjected to distillation under reduced pressure (60 mm) so that water, excess hydrochloric acid, and acetic acid were removed. Last traces of water from the residue were removed by treatment with dry benzene followed by azeotropic distillation. Finally the residue was taken in ether and dried over sodium sulphate. Ether was removed by distillation leaving behind the crude acid (0.34 g).

Methyl ester of the acid

The above crude acid (0.3 g) in dry ether (10 ml) was treated under cooling (ice-salt bath) with a solution
of diazomethane in ether till the mixture became yellow. The mixture was left aside in cold for 2 hrs. and at room temp. for 2 hrs. Excess of diazomethane was decomposed by addition of acetic acid and the solution was washed successively with water, Na₂CO₃ solution, water and dried over sodium sulphate. Removal of ether by distillation left behind a crude liquid which on vacuum distillation gave the pure methyl ester (0.25 g).

VPC analysis of the methyl ester (6 ft., polyester on firebrick, 173° hydrogen flow rate 60 ml/min.) gave a single peak (retention time 5 min., 56 sec.) indicating it to be only one compound.

2,4-DNP derivative of methyl levulinate

2,4-Dinitrophenylhydrazine (0.5 g) mixed with conc. hydrochloric acid (1 ml) was taken in alcohol (5 ml). To this solution, a solution of the above methyl ester (0.2 g) in alcohol (5 ml) was added and the mixture heated just to boiling. On cooling to room temp., an orange red compound crystallised out. It was filtered, washed with water, cold alcohol and recrystallised from alcohol to give the pure 2,4-dinitrophenylhydrazone of methyl levulinate (0.362 g).

m.p. and mixed m.p. 140° (literature m.p. 141.2°)

Analysis

Found: C, 46.54; H, 4.63; N, 18.01
Calculated for C₁₂H₁₄N₄O₆: C, 46.45; H, 4.55; N, 18.06%.
The IR spectrum of this DNP derivative was found to be exactly superimposable with that of the DNP derivative prepared from the authentic methyl levulinate.

**Reduction of citral with sodium borohydride**

To a solution of sodium borohydride (0.76 g, 0.02 mol) in ethanol (25 ml), a solution of citral (3 g, 0.02 mol) in ethanol (10 ml) was added gradually at a temp. 5-10°C. The mixture was allowed to stand overnight at room temp. and then after dilution with water (10 ml), it was treated with cold dilute hydrochloric acid till the solution became acidic. After a further dilution with water (100 ml), the solution was extracted three times with ether (3 x 50 ml). The ether extracts were pooled together and washed successively with water, sodium carbonate solution and finally with water. The ethereal solution was dried over anhydrous sodium sulphate and ether removed by distillation to furnish a residue (2.82 g) whose IR spectrum showed it to be free from aldehyde (citral). It was distilled under vacuum when the distillate was obtained as a mixture of geraniol and nerol (2.64 g, 0.017 mol).

b.p. 133°C/25 mm. \( n^D_{20} \) 1.4709

The VPC analysis (6 ft., polyester on fire-brick, 180°C, hydrogen flow rate 85 ml/min.) gave two peaks (retention time 4 min. 50 sec., and 5 min. 22 sec.) exactly coinciding with those of an authentic mixture of geraniol and nerol.
DPQ oxidation of geraniol and nerol

A pure sample of DDQ (5 g, 0.022 mol) was dissolved in benzene (30 ml). To this solution, a freshly distilled mixture of geraniol and nerol (2.31 g, 0.015 mol) in benzene (10 ml) was added and the entire mixture refluxed over water-bath for 4 hrs. On cooling to room temp., a substantial amount of a solid (dichloro-dicyano-hydroquinone) separated out and was removed by filtration. The filtrate was distilled on a water-bath under a fractionating column when almost the entire amount of benzene was removed. The residue was chromatographed over alumina (neutral, grade II, 1:30). The pet. ether and pet. ether-benzene (80:20) fractions gave an aldehyde (1.92 g) as indicated by the IR spectrum. Further fractions eluted with benzene and benzene-ether were composed chiefly of the unreacted alcohol and was rejected.

The crude aldehyde (1.92 g) was distilled under vacuum to give pure citral (1.81 g, 0.011 mol).

b.p. 117°/20 mm (literature b.p. 119°/20 mm)

n^27_D 1.4847 (literature n^20_D 1.4975)

The IR spectrum of the reaction product was exactly superimposable with that of the authentic sample of citral.

The vapour phase chromatographic analysis (6 ft., polyester on fire brick, 165°, hydrogen flow rate 67 ml/min.) gave two peaks (retention time 6 min., 34 sec. and 7 min., 49 sec.) exactly coinciding with the two peaks of an authentic sample of citral.
3,7-Dimethyl-6-octen-3-ol or Dihydroinalcool (XII)

The Grignard, ethyl magnesium iodide was prepared from magnesium ribbon (2.64 g., 0.11 atom), freshly distilled ethyl iodide (15.6 g., 0.1 mol) and dry ether (100 ml).

A solution of pure methyl heptenone (6.3 g, 0.05 mol) in dry ether (50 ml) was added dropwise to the above Grignard at 0°. The mixture was stirred at room temp. for two hrs. and under reflux (IR lamp) for 2 hrs. It was then poured into a cold saturated solution of ammonium chloride and extracted three times with ether (3 x 50 ml). The ether layers were pooled together, washed with water and dried over anhydrous sodium sulphate. Ether was removed by distillation and the residue was distilled under vacuum. The distillate (6.92 g, 0.044 mol) was the expected alcohol (XII).

b.p. 105-70/20 mm; nD

Analysis

Found: C, 76.35; H, 13.29
Calculated for C10H20O: C, 76.86; H, 12.5%.

IR bands (IR-3) at 3333, 2901, 1656, 1445, 1433, 1362, 1328, 1259, 1215, 1172, 1133, 1050, 990, 952, 920, 895, 782, 733 cm⁻¹. Vapour phase chromatographic analysis (6 ft., polyester on fire-brick, 170⁰, hydrogen flow rate 75 ml/min.) indicated the presence of only one compound (retention time 1 min., 35 sec.).
Similarly, for the same product, the vapour phase chromatographic analysis (6 ft., carbowax on fire brick, 172°, hydrogen flow rate 77 ml/min.) showed the presence of only one compound (retention time 2 min., 53 sec.)

4,8-Dimethyl-1,7-nonadien-4-ol (XIII)

Allyl magnesium chloride was prepared from magnesium ribbon (2.88 g, 0.12 atom), allyl chloride (7.65 g, 0.1 mol) and dry ether (100 ml). To this Grignard, a solution of pure methyl heptenone (6.3 g, 0.05 mol) in dry ether (25 ml) was added at 0° and the reaction carried out until the product worked out as in the previous experiment. The product was distilled under vacuum and the distillate (7.96 g, 0.047 mol) was the required alcohol (XIII).

b.p. 98-100°/7 mm; \( n^\text{D}_{25} \) 1.4615

**Analysis**

Found: C, 78.54; H, 11.91

Calculated for \( \text{C}_{11}\text{H}_{20}\text{O} \): C, 78.51; H, 11.97%.

IR bands (IR-4) at 3390, 2950, 1825, 1645, 1451, 1381, 1341, 1295, 1269, 1252, 1182, 1115, 1073, 1002, 917, 885, 848, 807, 781, 746 cm\(^{-1}\).

Vapour phase chromatographic analysis (6 ft., polyester on fire brick, 186°, hydrogen flow rate 75 ml/min.) showed the presence of only one compound (retention time 3 min., 45 sec.)
Phenyl magnesium bromide was prepared from distilled bromobenzene (15.7 g, 0.1 mol), magnesium ribbon (2.64 g, 0.11 atom) and dry ether (100 ml). A solution of methyl heptenone (6.3 g, 0.05 mol) in dry ether (20 ml) was added to the above Grignard at 0° and the reaction conducted as in the previous expt. The crude reaction product on distillation under vacuum gave the pure product (XIV) (3.32 g, 0.04 mol).

b.p. 100-101°/1 mm; n_D 1.5160.

Analysis

Found: C, 82.69; H, 10.02.

Calculated for C_{14}H_{20}O: C, 82.3; H, 9.87%.

IR bands (IR-5) at 3401, 3003, 2915, 1944, 1873, 1802, 1742, 1698, 1600, 1490, 1441, 1372, 1305, 1261, 1211, 1171, 1111, 1067, 1029, 990, 962, 938, 918, 892, 807, 768, 698 cm⁻¹.

Vapour phase chromatographic analysis (6 ft., polyester on fire-brick, 213°, hydrogen flow rate 75 ml/min.) gave a single peak (retention time 6 min.) indicating the presence of only one compound.

2-Benzyl-6-methyl-5-hepten-2-ol (XV)

The Grignard, benzyl magnesium chloride was prepared from benzyl chloride (12.65 g, 0.1 mol), magnesium ribbon (2.88 g, 0.12 atom) and dry ether (100 ml). To this Grignard was added a solution of methyl heptenone (6.3 g,
0.05 mol) in dry ether (20 ml) at 0°C and the reaction carried out and the product worked out as in the previous experiments. The crude product obtained was distilled under reduced pressure when the distillate (8.12 g, 0.037 mol) was obtained as the pure alcohol (XV).

b.p. 122-24°C/1.5 mm; n_D^20 1.5170

Analysis

Found: C, 82.28; H, 10.31
Calculated for C_{15}H_{22}O; C, 82.51; H, 10.16%.

IR bands (IR-6) at 3460, 3030, 2959, 1946, 1876, 1808, 1669, 1605, 1532, 1495, 1453, 1378, 1266, 1244, 1182, 1144, 1112, 1087, 1033, 990, 955, 825, 917, 880, 845, 783, 761, 728, 702 cm⁻¹.

Vapour phase chromatographic analysis (6 ft., polyester on fire-brick, 220°C, hydrogen flow rate 67 ml/min.) showed the presence of only one compound (retention time 7 min., 21 sec.)
IR - 5. 2-PHENYL-6-METHYL-5-HEPTEN-2-OL (XIV)

( LIQUID FILM )
REFERENCES


