# Constitution of Two New Terpenes, Menogene and Menogerene ($C_{10}H_{16}$ and $C_{10}H_{14}$).—The Mechanism of Cyclisation of Citronellal and Citral.

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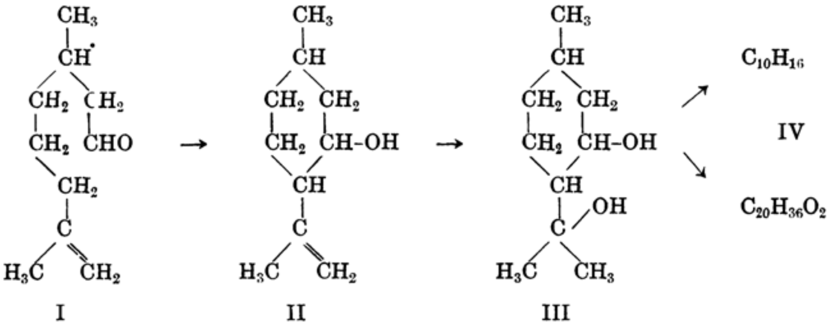
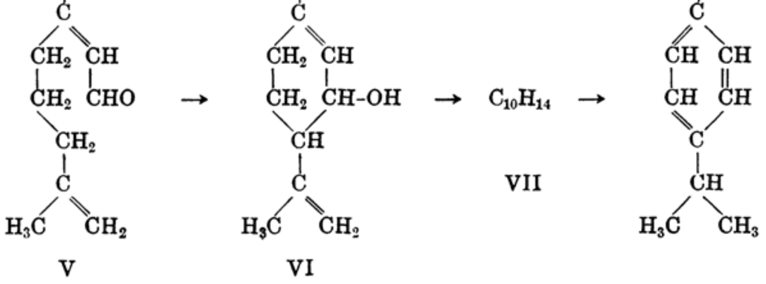
One of the writers⁽¹⁾ has studied the cyclisation-mechanism of olefinic terpenes, citral, $C_{10}H_{16}O$, and citronellal, $C_{10}H_{18}O$, into isomeric monoterpenes, and proved the formation of menthoglycol (III) from citronellal (I) through isopulegol (II), opposing to the theories of P. Barbier and G. Leser,⁽²⁾ F. W. Semmler⁽³⁾ and F. Tiemann.⁽⁴⁾ A new terpene, $C_{10}H_{16}$ (IV), has been isolated in the reaction and named as citronellat-terpene, the scheme being as follows:



Although the cyclisation-mechanism of citral has not been proved, *p*-cymene and a new terpene, $C_{10}H_{14}$, which is named citral-terpene (VII), corresponding to citronellal-terpene, are formed in the cyclisation reaction, the mechanism is, therefore, supposed to be as follows:



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(1) Horiuchi, *Mem. Col. Sci. Kyoto*, **11** (1928), 171.

(2) P. Barbier and G. Leser, *Compt rend.*, **124** (1897), 1308.

(3) F. W. Semmler, *Ber.*, **42** (1909), 2015.

(4) F. Tiemann, *ibid.*, **32** (1899), 107.

When the constitutions of these terpenes have been elucidated, we may have a deeper insight into the proposed cyclisation-mechanisms of citral and citronellal and an explanation may be afforded of the biosynthesis and isomerisation *in vivo* of olefinic terpenes.

**Menogene, $C_{10}H_{16}$.** J. Dœuvre(5) obtained a mixture of unknown terpenes by the dehydration of menthoglycol, supposing to be a mixture of $\Delta^{2:4(8)}$-menthadiene and $\Delta^{3:8(9)}$-menthadiene. Then W. J. Grubb and J. Read(6) isolated a terpene by dehydrating and reducing pulegone and supposed it to be $\Delta^{3:8(9)}$-menthadiene identical with citronellal-terpene obtained by Horiuchi. J. Dœuvre and H. Perret(7) repeated the experiment of Grubb and Read, without obtaining any concrete conclusion.

All terpenes produced by the direct dehydration of isopulegol and menthoglycol will be represented by the following three formulas:


VIII


IX


X

VIII and IX are to be produced from both isopulegol and menthoglycol, but X from only menthoglycol. VIII has been synthesised by W. H. Perkin(8) and his coworkers and IX has been discovered by Henry and Paget;(9) the properties of these compounds are therefore known. Among these three, IX has no rotatory power.

Citronellal is treated with 50% sulphuric acid according to Horiuchi's(1) method, a terpene part is separated from the product and fractionated by repeated distillation, physical properties of the main part being as follows:

| B. p. (764.5 mm. Hg) | $d_4^{20}$ | $n_D^{20}$ | $[\alpha]_D^{17}$ | $[RL]_D$ | Ex. |
|---|---|---|---|---|---|
| 184 – 186° | 0.8624 | 1.5026 | +49.11° | 46.59* | 1.35 |

* Calculated for $C_{10}H_{16}\vDash_2$: $[RL]_D$, 45.24.

Analysis

Found: C, 87.82; H, 12.16. Calculated for $C_{10}H_{16}$: C, 88.2; H. 11.8%.

The analytical result shows that the formula of the compound is $C_{10}H_{16}$, but the specific gravity and the refractive index are extremely high

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(5) J. Dœuvre, *Bull. soc. chim.* [4], **53** (1933), 27.
(6) W. J. Grubb and J. Read, *J. Chem. Soc.*, **1934**, 242.
(7) J. Dœuvre and H. Perret, *Bull. soc. chim.* [5], **55** (1935), 2985.
(8) W. H. Perkin, *J. Chem. Soc.*, **1906**, 848; **1911**, 537.
(9) Henry and Paget, *J. Chem. Soc.*, **1921**, 1714.

compared with those of the formerly known terpenes. When $C_{10}H_{16}\vDash_2$ is adopted, the exaltation is 1.35 and the presence of conjugated double bonds is supposed, favouring the adoption of formula X.

The terpene was dissoved in petroleum ether and shaken with an aqueous solution of sodium nitrite and crystals were obtained, which were recrystallised out as colourless scales from a mixture of methanol and chloroform, melting at 154.5 – 155°. The melting point of a mixture of the nitrosite and $\alpha$-terpinene nitrosite was lower by about 30°. The terpene is therefore not identical with any known terpene, but is a new one.

The nitrosite has large specific rotation: $[\alpha]_D^{20}, -174.06°$; and the elementary analysis gives the following data:

Found: C, 56.41; H, 7.70; N, 13.29. Calculated for $C_{10}H_{16}N_2O_3$:
C, 56.58; H, 7.61; N, 13.20%.

When reduced with hydrogen, using palladium oxide as a catalyst in an alcoholic solution, the terpene absorbs two moles of hydrogen. The main fraction of the reduced product absorbs no bromine and has the following constants, which show good agreement with those of *p*-menthane; the terpene is therefore identical with *p*-menthadiene.

| B. p. (756.5 mm. Hg) | $d_4^{20}$ | $n_D^{20}$ | $[\alpha]_D^{25}$ |
|---|---|---|---|
| 168 – 171° | 0.8102 | 1.4490 | ± 0 |

The terpene absorbs one mole of bromine in its amyl alcohol ether or glacial acetic acid solution, but white fume is evolved by further addition of bromine to the solution. So the terpene should have conjugate double bonds in it. To prove this, the writers utilised the diene synthesis:⁽¹⁰⁾ a solid is obtained by warming a benzene or ether solution of the terpene and an equivalent amount of maleic anhydride, its melting point being 205 – 208° and $[\alpha]_D^{25} - 18.76°$ in an acetone solution. By neutralising the compound with 30% potassium hydroxide solution, white crystalline powder is produced, its melting point being 228 – 230°. This powder absorbs bromine equivalent to one double bond; the bromide melts at 282 – 285°. Thus combining with maleic anhydride the terpene in question gave a dibasic acid anhydride having one double bond. It is therefore concluded that the terpene has conjugated double bonds.

A cooled glacial acetic acid solution of the terpene is mixed with ethyl nitrite, to which hydrochloric acid is added drop by drop. No nitroso-chloride is obtained but the product remains in a liquid state. At low temperature, the product is of deep blue colour, and the colour changes gradually to green, yellow, deep red, reddish brown, and deep brown, according to the elevation of temperature of the liquid. The

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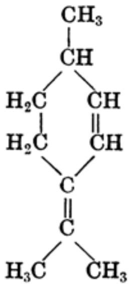
(10) Diels and Alder, *Ann.*, **460** (1928), 98; **478** (1930), 139.

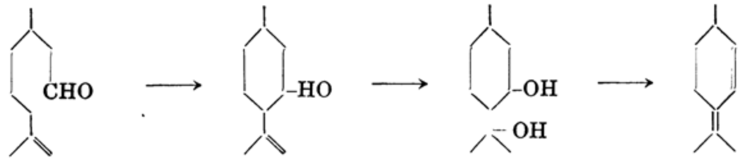
same phenomena had been observed by A. Baeyer(11) as a characteristic property of tertiary-tertiary ethylene bond, >C = C <. From these facts the terpene is assumed to have a semicyclic structure.

A mixture of the terpene and metallic sodium becomes orange yellow and the colour changes to deep red by heating. When distilled, small amounts of liquid are obtained at 55−75° and at 100−130° and then the main fraction of the terpene follows. The former has an odour of acetone and gives feathery crystals of golden colour, melting at 148 − 148.5°, by reacting with *p*-nitrophenyl-hydrazine. A mixture of the obtained hydrazone and acetone-*p*-nitrophenyl-hydrazone shows no depression of the melting point. The acetone should be the product of the split of the semicyclic part of the terpene. Wallach(12) obtained acetone by the decomposition of pulegone and A. Pfau(13) from atlantone. The terpene should therefore have double bonds between 4- and 8-carbon atoms and 2- and 3- or 5- and 6-carbon atoms; and the structure of the so-called citronellal-terpene is as shown below.

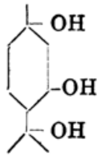
Among fourteen isomers of $C_{10}H_{16}$ terpenes, two of them have not yet been reported, and now one of the two has been clearly and definitely identified. It is not a derivative of isopulegol, but that of menthoglycol, it is therefore named menogene. The cyclisation mechanism of citronellal proposed by one of the writers(1) has been proved by the above facts as follows, contrary to the theories proposed by Barbier(2) Semmler(3) Tiemann(4) and Dœuvre(5):



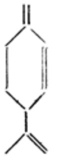
Menogene



**Menogerene, $C_{10}H_{14}$.** As one of the writers(1) has reported, citral-terpene has the formula $C_{10}H_{14}$ and is an isomer of *p*-cymene, if it has the skeleton of *p*-menthane; but none of supposed twelve isomers has not yet been definitely identified. As discussed above, menogene derived from citronellal is produced by dehydration of menthoglycol, citral-terpene should therefore be derived by dehydration of menthoglycerol and their isomers may be represented by the following seven formulas:



Menthoglycerol



XI

XII

XIII

XIV

XV

XVI

XVII

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(11) A. Baeyer, *Ber.*, **27** (1894), 436.
(12) Wallach, *Ann.*, **365** (1909), 243.
(13) A. Pfau, *Helv. Chim. Acta*, **17** (1934), 129.

Pearl and Dehn⁽¹⁴⁾ obtained a terpene, $C_{10}H_{14}$, by treating camphor with phosphoric acid, which is presumed to be $\Delta^{3:5:8(9)}$ -*p*-menthatriene. from its rotatory property, and moreover to be identical with the citral-terpene obtained by Horiuchi.⁽¹⁾

By repeating fractional distillation of citral-terpene obtained by treating citral with 20% sulphuric acid as reported by Horiuchi,⁽¹⁾ the following four fractions were obtained, none of them having rotatory power:

| Fraction | B. p. (769 mm. Hg) | Weight (g.) | $d_4^{20}$ | $n_D^{20}$ | $\alpha_D$ | $[RL]_D$ |
|---|---|---|---|---|---|---|
| A | 80 – 82° | 5.5 | 0 8209 | 1.4095 | ± 0 | |
| B | 110 – 111° | 9.6 | 0.8451 | 1.4783 | ± 0 | |
| C | 175 – 176° | 27.5 | 0.8595 | 1.4916 | ± 0 | |
| D | 180 - 181° | 50.5 | 0.8672 | 1.5005 | ± 0 | 45.66* |

* Calculated for $C_{10}H_{14}F_3$: $[RL]_D$, 44.78.

Below 80° a small fraction was obtained, which was proved to be acetone by the identification of *p*-nitrophenylhydrazone, m.p. 148 – 148.5°. Fraction A may be isopropyl alcohol as its phenylurethane melts at 88 – 89°.

Fraction B has toluene-like odour and is unstable in air quickly producing a syrup and explosively decomposes by distillation. From the easy polymerisation of $\Delta^{1:3}$-*l*-methylcyclohexadiene and easy formation of peroxide of cyclohexene and of general methylcyclohexenes, some peroxide should be produced also in this case. By oxidising with potassium permanganate as usual, it gives succinic acid, m.p. 180 – 182°. When hydrogenated on palladium oxide, it absorbs two moles of hydrogen exactly. Fraction B is therefore a new compound, 1-methyl-$\Delta^{1:5}$ -cyclohexadiene, i.e., 3,4-dihydrotoluene. The analytical results are as follows and the other constants are described above:

Found: C, 89.06; H, 10.31. Calculated for $C_7H_{10}$: C, 89.14; H, 10.71%.

Fraction C is *p*-cymene, as it gives *p*-hydroxyisopropyl benzoic acid, m.p. 157 – 158°, by oxidising with potassium permanganate as usual.

Fraction D is the so-called citral-terpene and has the constants described above. The elementary analysis of the compound gives the following results:

Found: C, 89.96; H, 10.90. Calculated for $C_{10}H_{14}$: C, 89.48; H, 10.52%.

In a glacial acetic acid solution, the terpene absorbs one mole of bromine, producing a dibromide, m.p. 114.5 – 115°; a mixture of the dibromide and terpinolene tetrabromide melts lower by about 10°.

The terpene is unstable. By distillation after long standing, one part of the terpene changes into *p*-cymene. By treating with 20% sul-

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(14) Pearl and Dehn, this Bulletin, **12** (1937), 493.

phuric acid, it changes also into *p*-cymene; it contains, therefore, *p*-cymene skeleton in it. The terpene is therefore the intermediate compound in the changing course of citral into *p*-cymene by treatment with sulphuric acid.

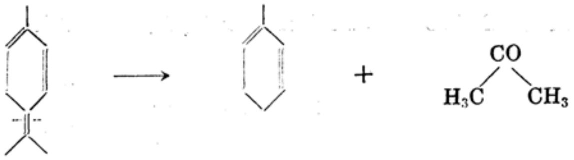
A nitroso-chloride of the terpene is not isolated as crystals and gives special colour reaction as in the case of menogene. The terpene has a semicyclic structure having a tertiary-tertiary ethylene bond. When distilled with metallic sodium the terpene gives acetone. The structure of the terpene should therefore be XII or XV among seven isomers given above.

In a pure methanol solution, the terpene absorbs one mole of hydrogen in the presence of palladium oxide and then the absorption-velocity of hydrogen is extremely small. The product gives the following two main fractions, (a) and (b) by fractional distillation.

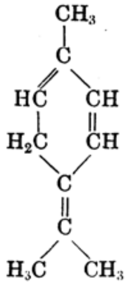
| Fraction | B. p. | Weight (g.) | $d_4^{20}$ | $n_D^{20}$ | $\alpha_D$ |
|---|---|---|---|---|---|
| a | 168 – 170° | 0.3 | 0.8109 | 1.4495 | ± 0 |
| b | 172 – 174° | 5.2 | 0.8440 | 1.4795 | ± 0 |

As fraction (a) does not absorb bromine and is not oxidised with potassium permanganate, it should be *p*-menthane from its physical constants. By treating with maleic acid anhydride, fraction (b) gives a crystalline substance, melting at 126 – 127°; melting point of a mixture of (b)-addition product and *dl*-*α*-phellandrene addition product does not fall. From these results, the terpene gives, by the hydrogenation, *p*-menthane on one side by saturating all double bonds and *dl*-*α*-phellandrene on the other by saturating semicyclic structure. So the positions of the ethylene bonds other than the tertiary-tertiary ethylene bond are between carbon atoms 2 and 3 and carbon atoms 6 and 1.

The terpene is, as stated above, very unstable. Not only it reacts with acids or alkalis, but also it changes during keeping. That acetone and 1-methyl-$\Delta^{1:5}$-cyclohexadiene were produced in the course of fractional distillation of the terpene obtained from citral is due to the breakage of a double bond between carbon atoms 4 and 8. And the production of isopropyl alcohol is due to the reduction of acetone in the course of distillation with metallic sodium.



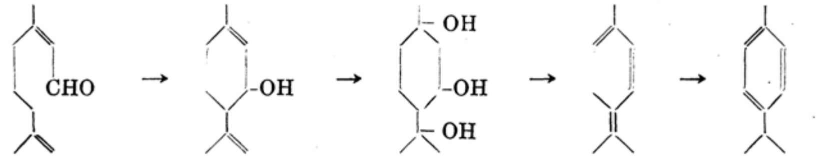
From the above stated facts the terpene should have the following structure. As just like menogene is produced from menthoglycol, the terpene should be produced from the corresponding menthoglycerol, so



Menogerene

the terpene is named menogerene. A terpene, $C_{10}H_{14}$, an isomer of p-cymene is here now definitely identified.

The mechanism of the formation of the new compound by the action of sulphuric acid upon citral should be as follows, as proposed by Horiuchi,(1) presuming the formation of dehydro-isopulegol and menthoglycerol as intermediates. The intermediate between menthoglycerol and p-cymene is, however, menogerene contrary to the presumption by Horiuchi.(1)



**citral** Menogerene *p*-cymene

This explanation of the mechanism is further substantiated by the formation of menogene from citronellal, and the formation-mechanism proposed by A. Verley(15) was proved to be only a supposition.

## Summary.

One of the writers (Horiuchi)(1) has proposed a mechanism of the cyclisation which occurs in treatment of citronellal and citral with sulphuric acid. The constitutions of two new terpenes, $C_{10}H_{16}$ and $C_{10}H_{14}$, produced by the reaction, are cleared up and they are named menogene and menogerene respectively.

The mechanism of cyclisation of citronellal and citral or generally of olefinic terpene aldehydes is largely cleared up. The intermediate state of these compounds in organisms is assumed. Not only the ring formation, but also the formation process of the terpenes is suggested. It is also shown that the semicyclic double bond is unstable and changes its position into the ring, taking the form of *p*-cymene.

Especially these two olefinic terpene aldehydes show the same behavior; that is, water is not needed for the ring formation; the terpenes are formed by dehydration of the hydrate; and the forms and positions of the double bonds are completely corresponding.

Their derivatives, menogene nitrosite and menogerene bromides, and 1-methyl-$\Delta^{1:5}$-cyclohexadiene are formed and their natures are described.

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(15) A. Verley, *Bull. soc. chim.*, [3], **21** (1899), 408.