

# On the Transformation of Aliphatic Terpenes into Monocyclic Terpenes-A Synthesis of Menthol.

By

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The transformation of aliphatic or olefinic terpenes of the formulae  $C_{10}H_{16}O$  &  $C_{10}H_{18}O$  into their isomeric monocyclic terpenes is very interesting from the stand points of synthetic chemistry on the one hand, and, on the other of biochemistry.

Citral, the principal constituent of oil of lemon and of lemon-grass was employed to prepare by cyclisation of its derivatives, the ionones which are used as a synthetic substitute for the odorous principle of the violet.<sup>1</sup> Monocyclic terpene, isopulegol or menthone had been obtained from the olefinic terpenes of citronellal and rhodinal respectively by the action of acetic anhydride,<sup>2</sup> and the very close relationship between the cyclic terpenes and the open chain ones show that these compounds exhibit among themselves a certain similarity in structure, and this relationship has been used for the confirmation of the structure of citronellal.<sup>3</sup> The cyclisation of the olefinic terpenes, especially of citronellal, awakes the interest of certain chemists among whom F. Tiemann & R. Schmidt<sup>4</sup> were the first who attempted the transformation of the aldehyde

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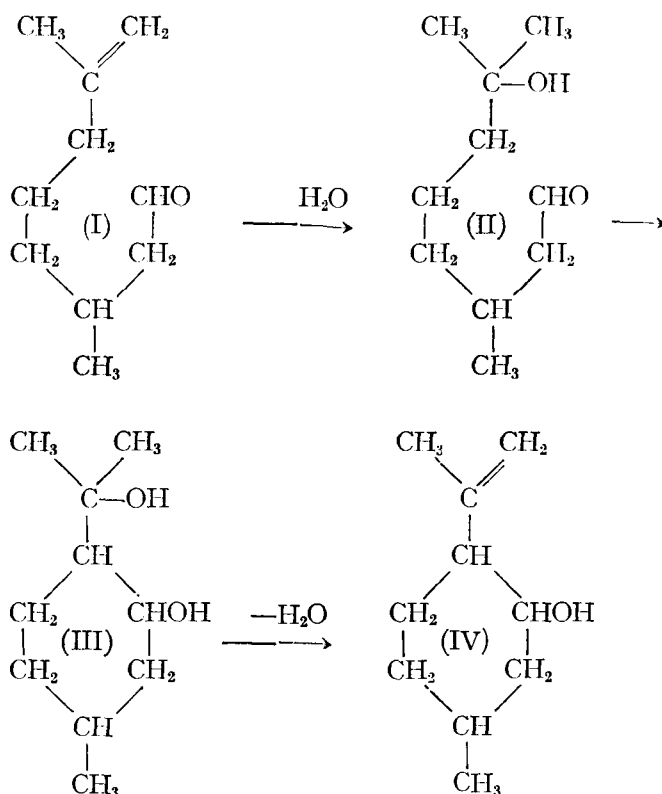
1 F. Tiemann: Ber. D. Chem. Ges., **26**, 2675 (1893).

2 F. Tiemann & Schmidt: *Ibid.*, **30**, 38 (1897).

3 F. Tiemann & R. Schmidt: *Loc. cit.*, P. Barbier & G. Leser: C. R., **124** 1308 (1897); C. Harries & G. Roeder: Ber. D. Chem. Ges., **32** 3357 (1899)  
*Loc. Cit.*,

by heating with acetic anhydride and anhydrous sodium acetate in a sealed tube at  $180^{\circ}$ – $200^{\circ}$  for 10–12 hours, and acetate of isopulegol was isolated.

P. Barbier & G. Leser,<sup>1</sup> however, have succeeded in transforming citronellal by the action of a 5% sulphuric acid into isopulegol, menthogycol or menthanediol (3:8) and a compound of the formula  $C_{20}H_{34}O$  of ethereal character, and in this reaction they stated that citronellal (I) is probably first transformed by the addition of water into hydroxycitronellal (II) and then ring formation occurs with the production of menthogycol (III) which then turns by the removal of water to isopulegol (IV) as represented in the following:

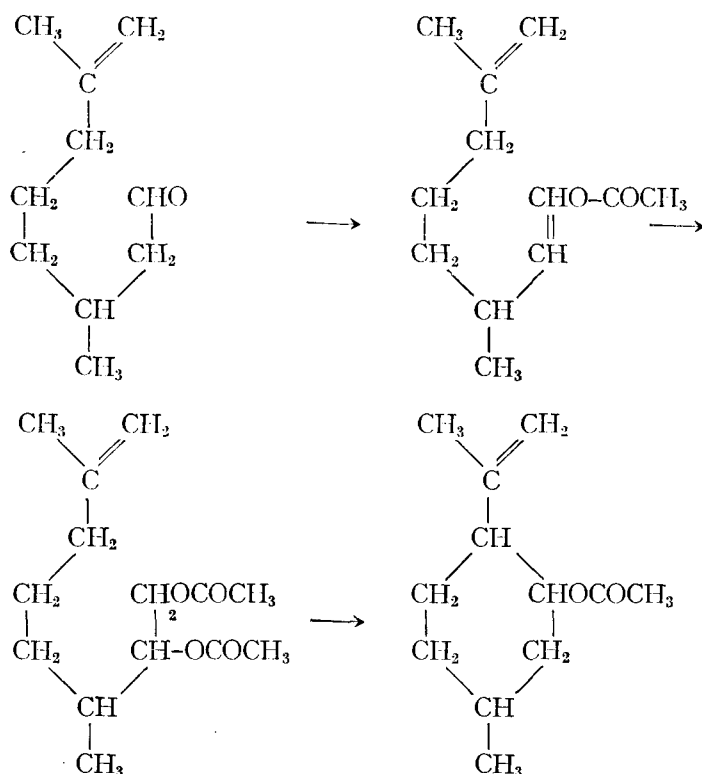


The latter phase of the reactions, the formation of isopulegol was demonstrated by them with an experiment in which monoacetate of

<sup>1</sup> Loc. Cit.

menthoglycol was converted by treating with sodium acetate into acetate of isopulegol.

With regard to the mechanism of the cyclisation of the olefinic terpene, F. W. Semmler<sup>1</sup> has proposed another view that aldehydes of the types  $RCH=CHO$  or  $RCH_2CHO$  are converted to the enolic forms by acetic anhydride and that in the case of citronellal this change precedes ring formation; enol monoacetate and enol di-acetate of citronellal have resulted by the action of acetic acid and sodium acetate on citronellal and the process for the transformation of citronellal into the cyclic terpenes has been represented by the scheme shown below since the enol monoacetate can be converted into isopulegol acetate by heating with acetic anhydride for 20 hours.

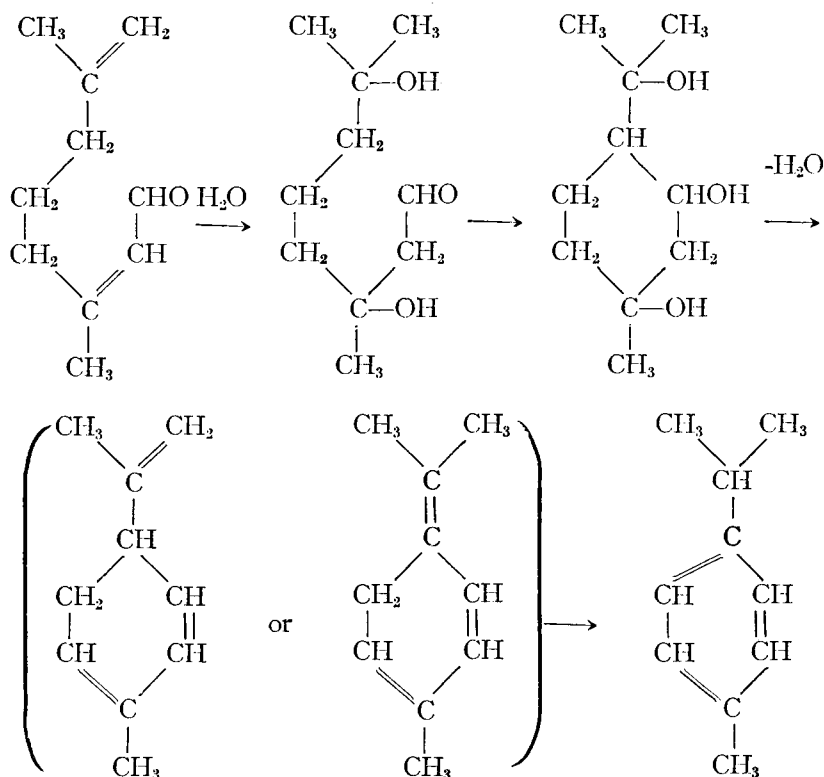


The fact that citral yields, by the action of acetic acid & sodium acetate, enol monoacetate and enol di-acetate of citral and that cymene

<sup>1</sup> Ber. D. Chem. Ges. **42**, 2015 (1909).

was formed from citral by the action of potassium hydrogen sulphate and also from enol acetate citral by treating with acetic acid,<sup>1</sup> were regarded by Semmler to be favourable examples of his view of the cyclisation of open chain-terpenes.

According to F. Tiemann<sup>2</sup>, the cause of the formation of cymene from citral by the action of a 10% sulphuric acid should be attributed, as Barbier and Leser had explained the formation of isopulegol from



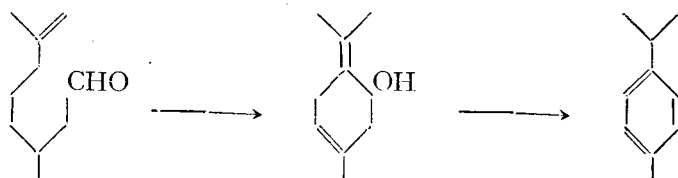
citronellal, to the intervention of water which is alternately added and removed. The above views illustrated by Tiemann, Semmler and Barbier show how difficult it is to explain the formation of dehydro-isopulegol or methyl isopropene cyclohexanol from citral, which, according to A. Verley,<sup>3</sup> was produced from citral by the action of a 50% sulphuric acid

1 F. W. Semmler & Schossberger: Ber. D. Chem. Ges., **44**, 991 (1911).

2 Ibid., **32**, 107 (1899).

3 Bull. Soc. Chim., **21**, 408 (1899).

in an ethyl acetate solution, and by the action of dehydrating agents it gives rise to cymene :



The writer holds an opinion somewhat different from the views above mentioned, for the explanation of the cyclisation of the olefinic terpenes, ascribing the cause of the reaction to the direct condensation between the  $=\text{CH}-\text{CH}_2-$  and the  $\text{CHO}-\text{CH}_2-$  groups which occur in the molecule, and he considers that the keto-enolic change of the  $\text{CHO}-\text{CH}_2-$  group was not the primary cause of the reaction. To confirm the above hypothesis, citral and citronellal were subjected to the action of sulphuric acid of various concentrations and of potassium hydrogen sulphate and acetic acid, and the reaction products surveyed with meticulous care.

d-Citronellal isolated in pure state from the Java citronella oil,<sup>1</sup> B.p.  $97^{\circ}-98^{\circ}$  at 20 mm.;  $d_{15}^{15} = 0.8563$ ;  $n_D^{20} = 1.449$ ;  $\alpha = +10^{\circ}.9'$ , when treated with 5% sulphuric acid at ordinary temperature, yields isopulegol, menthoglycol and a compound of the formula  $\text{C}_{20}\text{H}_{36}\text{O}_2$  of ethereal nature, and the experimental results agree with those of Barbier & Leser<sup>2</sup> except for the formation of the last compound of which having the physical constants, B.p. ( $196^{\circ}-198^{\circ}$ ) 18mm;  $d_4^{20} = 0.9295$ ;  $n_D^{20} = 1.4805$ , and appears to be different from the bispulegone obtained by Harries & Roeder by reducing pulegone with an aluminium amalgam.<sup>3</sup>

Yield			
conc. $\text{SO}_4\text{H}_2$	Isopulegol	Menthoglycol	Ether
5%	7%	75%	3%
20%	9%	39%	21%

<sup>1</sup> H. Finckmore: The essential oils (1926) 118.

<sup>2</sup> Loc. cit.,

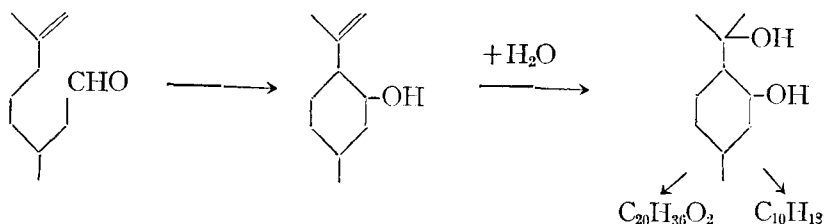
<sup>3</sup> Ber. D. Chem. Ges., **32**, 3357 (1899), and refer V. Paolini: J. Chem. Soc., **118**, 171 (1920).

The yield of the glycol as will be seen in the table, will be increased in inverse proportion to that of the ethereal compound, while isopulegol was formed with a greater yield in the higher concentration of the acid, used as a condensing agent. It seems, therefore, that the isopulegol formed directly from citronellal by the action of the condensing agent was converted into menthoglycol by the addition of water, on the one hand, and on the other, by the removal of water it turns to the other-compound.

As a matter of fact, isopulegol when treated with a 20% sulphuric acid, yields menthoglycol, while the latter substance under the same treatment remains unchanged. Moreover, citronellal, subjected to the action of a 50% sulphuric acid, resulted in forming a new terpene  $C_{10}H_{16}$ ; B.p. ( $60^{\circ}$ — $90^{\circ}$ ) 14mm;  $d_4^{20} = 0.8535$ ;  $n_D^{20} = 1.4875$  and the ether  $C_{20}H_{36}O_2$  instead of forming either the glycol or isopulegol, and both the terpene and ether are also produced, in different proportions, from isopulegol and menthoglycol respectively by treating with strong sulphuric acid, referring to the fact that the terpene is predominant in the reaction product from the glycol while the ether occurs abundantly in that from the isopulegol, and also to the investigation by Senderens<sup>1</sup> of the

Material	Yield	
	Terpene	Ether
Isopulegol	20%	36%
Menthoglycol	44%	18%
Citronellal	14%	32%

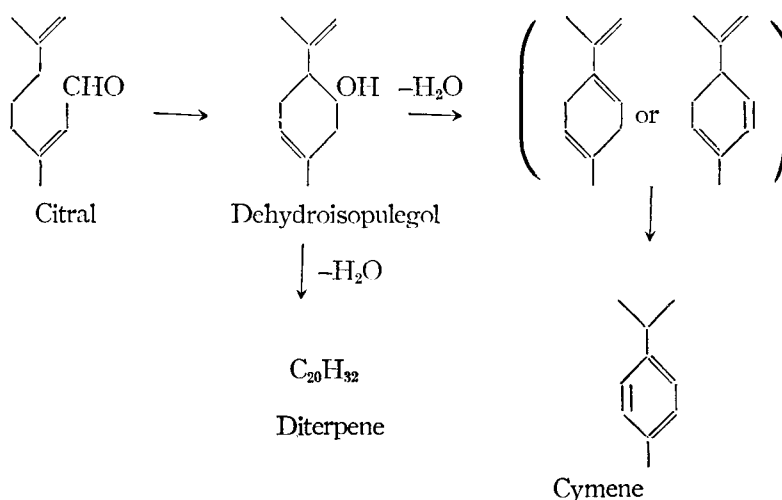
action of sulphuric acid on the polymethylene alcohols and by Wallach<sup>2</sup> on menthenols, the writer has proposed the view on the transformation of citronellal into cyclic terpenes, which is indicated in the following scheme :



<sup>1</sup> C.R., **177**, 1183 (1923).

<sup>2</sup> Liebig Ann., **360**, 82 (1908).

By the action of the 20% & 50% solutions of sulphuric acid on citral, a new terpene  $C_{10}H_{14}$ , b.p.  $183^{\circ}$ — $186^{\circ}$ ,  $d_4^{20} = 0.8880$ ;  $n_D^{20} = 1.5092$  and p-cymene were respectively isolated from the reaction products, and a diterpene  $C_{20}H_{32}$ , b.p. ( $194^{\circ}$ — $199^{\circ}$ ) 17mm.,  $d_4^{20} = 0.9494$ ;  $n_D^{20} = 1.5303$ , and cymene were formed to occur in the product from citral by the action of potassium acid sulphate, and these compounds should be derived from the dehydro isopulegol which was supposed to be formed from citral as an intermediate product, and previously isolated by Verley.<sup>1</sup>



When citronellal is treated with potassium hydrogen sulphate, a violent reaction takes place suddenly when the temperature has risen to  $140^{\circ}$  and isopulegol and the ether  $C_{20}H_{36}O$ , B.p. ( $185^{\circ}$ ) 12mm.,  $d_4^{20} =$

$0.9120$ ;  $n_D^{20} = 1.4835$  are obtained and the latter substance is identical in property with di-isopulegol ether prepared by Verley. The ether was actually prepared from isopulegol, and also from menthoglycol, by the action of potassium hydrogen sulphate, and in the latter case a terpene is found to occur with the ether in the reaction product.

When, however, acetic anhydride and sodium acetate were used as the condensation agent, citronellal tended to yield as reported by Semmler, isopulegol-acetate, enol monoacetate and enol di-acetate of citronellal

<sup>1</sup> Loc. Cit.

in a molecular proportion of 20:34:30. On the contrary, isopulegol acetate and enol di-acetate of citronellal, and isopulegol and isopulegol acetate were found to be formed when acetic anhydride and acetic acid were used respectively as the condensing catalyst.

As will be seen in the above statements, the cyclisation of citronellal is favourable in case acetic acid or acetic anhydride was used, and citral, in a like manner, by the action of acetic anhydride and acetic acid was converted partly into enol acetate of citral and cymene respectively.

According to the experiments carried out by the writer, the diacetate of enol-citronellal yields by the action of acetic acid neither isopulegol nor its derivative, while according to Semmler, the mono acetate of the enol compound by means of acetic acid converted into isopulegol acetate, and therefore the cyclisation of the olefinic terpenes should be ascribed to the inner condensation between the atomic groups  $\text{CHO}-\text{CH}_2-$  and  $-\text{CH}=\text{CH}-$  in the molecule, but not to the enolisation of the group  $-\text{CH}_2-\text{CHO}$  as stated by Semmler.

The fact that the conversion of the olefinic terpenes into isomeric monocyclic terpenes, no matter what may be the correct theory by which the explanation of this transformation was made, still awakens the writer's interest in connection with the origin of the monocyclic terpenes in plants, in getting a clear understanding of the manner of occurrence of these compounds.

On turning our attention of the natural essential oils, we noticed that pulegones and isopulegones occur in nature associated with menthone, oil of pennyroyal, (*Mentha Pulegium*<sup>1</sup>), contains limonene, pulegone with menthol, and in American hedema oil contains about 24 to 30 per cent of pulegone with 50 per cent of menthones.<sup>2</sup>

On the biochemical connection of these cyclic terpenes and olefinic terpenes, in peppermint oil, R. E. Kremers<sup>3</sup> has made the following observation: "pulegone (& possibly piperitone) is found by Schimmel & Co. in Japanese peppermint oil and was regard as a mother of menthol, and it is suggested that menthenone is first formed from citronellal and that menthol and menthone are formed from its reduction."

Therefore, the reduction of pulegones or pulegols to menthols seems to take an important place in the biochemical connection between the

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<sup>1</sup> Tetry: Bull. Soc. Chim., **27**, 186 (1902).

<sup>2</sup> Finncmore: The essential oils, P. 798 and refer: V. Grignard & I. Savard: C. R., **182**, 422 (1926); V. D. Roberts: J. Chem. Soc., **107**, 1465 (1915).

<sup>3</sup> J. Biol Chem., **50**, 31 (1922).



olefinic and the monocyclic terpenes in nature. However, the reduction of pulegone and pulegol and their isomeric compounds in vitro was stated by Tiemann and Schmidt<sup>1</sup> in the following words:

"Pulegon und Pulegol lassen sich durch Natrium und Alkohol unschwer zu Menthol redugieren; die directe Umwandlung von Isopulegon und Isopulegol in Menthol auf gleichem Wege ist dagegen trotz häufig wiederholter Versuche bis lang nicht gelungen—."

No one could reduced isopulegone or isopulegol into menthol, while the former substance on treatment with baryta undergoes isomeric change to pulegone.<sup>1</sup>

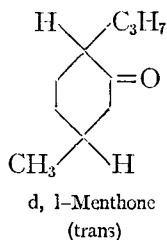
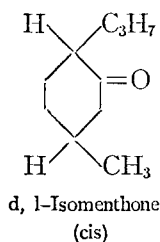
The writer, however, has succeeded in reducing isopulegol which was isolated from isopulegol acetate by hydrolysis and boils at (91.5) 13 mm.;  $d_4^{20} = 0.9162$ ;  $n_D^{20} = 1.4710$ ;  $\alpha = -30'$ , yield by reduction with hydrogen in the presence of platinum block, menthols, of the following constants:

B.p. (103.5—105.5) 18. mm; m.p. 1°—10.°

$d_4^{25} = 0.8944$ ;  $n_D^{25} = 1.458$ ;  $[\alpha]_D = -16.^\circ 77'$ .

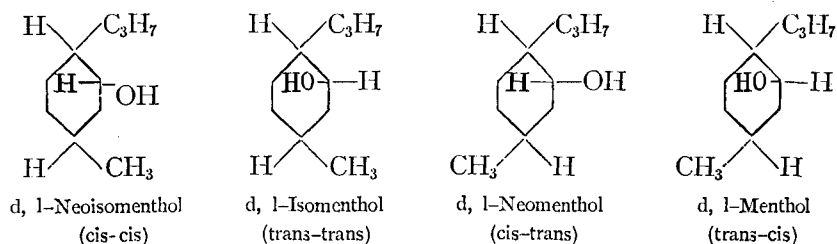
It was fractionated several times under reduced and ordinary pressure, and the fraction B.p. 210°—211°, M.p. 33°—34°,  $[\alpha]_D = -44.^\circ 92$  was isolated, which was assumed to be pure l-menthol.

In theory, there should exist 8 isomers in menthol and 4 isomers in menthone, and the relationship between menthones & menthols with respect to the special configuration, according to the view proposed by S. Komatsu & M. Kurata<sup>2</sup> is as follows:



<sup>1</sup> Ber. D. Chem. Ges., **25**, 32 (1897).

<sup>2</sup> These Memoirs A. **8**, 251 (1925) & refer I. Read: Chem. Ind., **46**, 873 (1927).



For identification of the writer's sample, it was oxidized by the usual method to menthone which was confirmed by referring to its physical and chemical properties and also by converting it into the oxime, to be laevomenthone. The mother substance which by oxidation yields l-menthone, according to the theory proposed by S. Komatsu and M. Kurata, should be either laevomenthol or neomenthol.

Referring to the literature concerning the properties of menthols we have learned that the present writer's menthol would be composed mostly of laevo-menthol which occurs in nature as a principal constituent of Japanese peppermint oil, and neomenthol is usually obtained by synthesis.

Brunel<sup>1</sup> has claimed that  $\alpha$  &  $\beta$  thymomenthols were synthesized from thymol by reducing by Sabatier's method, and the  $\alpha$ -compound was identical with neomenthol, and  $\beta$  one was r-menthol.<sup>2</sup> By the hydrogenation of pulegone,<sup>2</sup> in a manner similar to that of thymol, Haller and Martine<sup>3</sup> obtained two menthols which evidently are identical with leavo-menthol and dextroneomenthol and the same results were obtained by V. Paoline<sup>4</sup> by reducing pulegone by means of sodium and alcohol. According to Smith & Read,<sup>5</sup> however, d, l or r-piperitone by catalytic reduction in the presence of reduced nickel or colloidal palladium yielded isomenthones, and by means of sodium and alcohol yielded a product which appeared to consist essentially of isomenthol.

So far as concerns the reduction of thymol, piperitone or menthone

<sup>1</sup> C.R., **140**, 252 (1905).

<sup>2</sup> J. prac. Chem., **55**, 14 (1897); and refer Kondaknow: Ibid., **72**, 185 (1905). Urban & Kreemers: Bull. Soc. chim., **12**, 1439 (1894); Pichard and Littlebury: J. Chem. Soc., **101**, 109 (1912).

<sup>3</sup> C.R., **140**, 1298 (1905).

<sup>4</sup> J. Chem. Soc., **118**, 171 (1920).

<sup>5</sup> Ibid., **123**, 2916 (1923) and refer J. Read: Chem. & Ind., **46**, 873 (1927).

it would seem that the reaction will proceed to form neomenthol.<sup>1</sup>

Piperitone, menthone and pulegone, when submitted to reduction, should theoretically yield an equimolecular mixture of menthol and neomenthol or of isomenthol and neoisomenthol, actually in practice produces only one of the isomers, and this fact would be explained plainly by the theory of asymmetric synthesis; the starting materials for the synthesis of menthol are of optically active substances to which by the operation a new radical is added in such a way as to form a new asymmetric carbon atom, and consequently the original asymmetric nucleus has governed the progress of the reaction to such an extent as to preclude the formation of one isomer.

However, in the writer's synthesis of menthol, it is quite different, in the stereochemical relation of the resulting substances from the above cases; by hydrogenation of the isopulegol molecule, no asymmetric carbon atom was formed; but the relative magnitude of the masses of the carbon radicals attached to the asymmetric carbon atoms already present in the molecule will be changed by this treatment, and there should be a corresponding change in rotatory power of the substance as required by the theory of Guye and Crum Brown.

In the reaction of the formation of active isopulegol by the condensation of citronellal a similar operation is probably carried out in the natural synthesis of l-menthol in plants, which will be fully explained by taking the principle of asymmetric synthesis into consideration.

In tracing back the reactions for the synthesis of laevomenthol, step by step, menthol to isopulegol, isopulegol to citronellal, and citronellal to valeraldehyde, the operations which take place in the plant tissues seem evidently to be imitated in the laboratory.

## Experiment.

### 1. CITRONELLAL.

#### 1. Action of 5% Sulphuric Acid on Citronellal.

Citronellal isolation from the Java citronella oil and purified by means of sodium hydrogensulphite and by distillation shows the following constants:

B.p.  $97^{\circ}$ - $98^{\circ}$  at 20 mm.,  $d_{15}^{15} = 0.8563$ ,  $n_D^{20} = 1.4490$ ;  $[\alpha]_D = +10^{\circ} 9'$

It was treated with 10 times by weight of 5% sulphuric acid at  $25^{\circ}$ - $30^{\circ}$  for 12 hours, following the direction put forward by P. Barbier

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<sup>1</sup> G. Vavon & A. Conderc. C. R., **179**, 405 (1924); P. Beds: Bull. Soc. Chim., **29**, 674 (1926).

& G. Leser,<sup>1</sup> and the reaction product separated from the acidic solution, washed with water, dried with anhydrous sodium sulphate and then subjected to fractional distillation under 18 mm.

	Fraction	Yield Wt. %	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$
1	80°—100°	7	0.9123	1.4692	—
2	100°—145°	trace	—	1.4710	—
3	145°—160°	7	0.9687	1.4730	—
4	160°—175°	76	0.9751	1.4730	—
5	175°—185°	3	0.9699	1.4726	—
6	185°—191°	2	0.9540	1.4740	—
7	191°—195°	5	0.9408	1.4769	-4° 48'

### Isopulegol.

The first fraction was found to be composed of isopulegol by repeated distillation, which show the following physical constants.

B.p. 202°—207°;  $d_4^{20}$  = 0.9087;  $n_D^{20}$  = 1.4672;  
 $[\alpha]_D$  = + 5° 4'; M.R. = 47.1; 47.2 for  $C_{10}H_{18}O$ .

For confirmation, it was oxidized with chromic acid to isopulegone which yields an oxime of m.p. 121°.

### Menthoglycol.

The fourth fraction which composed the main part of the reaction product, was analysed:

0.1027 grm. gave 9.2619 grm.  $CO_2$  & 0.1079 grm.  $H_2O$ , found  
 C = 69.6; H = 11.7; theory requires C = 69.8; H = 11.6 for  $C_{10}H_{18}O_2$ .  
 M.R. = 49.5; theory M.R. = 49.2 for  $C_{10}H_{18}O_2$ .

It was fractionated under 15 mm. pressure and was divided into three portions which were ascertained to be composed mostly of menthoglycol by referring to their properties as follows:

	Fraction	%	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$	M.P.
1	147.5°	34	0.9833	1.4710	+ 37'	62°
2	148°—151°	26	0.9833	1.4710	+ 5° 23'	liquid
3	151°—152°	40	0.9797	1.4700	0	"

### An Ethereal Compound.

The 7th fraction which was assumed to be composed of an unsaturated compound of ethereal nature, and its acetic acid solution

<sup>1</sup> Loc. cit.,

was reduced with hydrogen in the presence of platinum black and the product shows the constants:

$$d_4^{20} = 0.9180; \quad n_D^{20} = 1.4640.$$

## 2. Action of 20% Sulphuric Acid on Citronellal.

The citronellal was treated with 20% sulphuric acid in the manner described above and the reaction product was fractionated under 16 mm. pressure into the following 6 portions:

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$
1	75—110°	9%	0.9181	1.4730
2	110—140°	3%	0.9283	1.4700
3	140—160°	40%	0.9654	1.4729
4	160—185°	3%	0.9581	1.4731
5	185—195°	42%	0.9287	1.4770
6	195—225°	3%	0.9456	1.4790
7	Residue	trace	—	—

### Isopulegol.

The first fraction was ascertained to be composed mostly of isopulegol which was isolated by fractional distillation, showing the constants:

B.p. 100°—102°, 22 mm.;  $d_4^{20} = 0.9077$ ;  $n_D^{20} = 1.4690$ ;  $[a]_D = +3^\circ 26'$

### Menthoglycol.

The third fraction which was assumed to be composed of glycol on dividing by distillation into the three portions gave the following figures:

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$	$[a]_D$
1	145°—146° 15mm.	10%	0.9772	1.4714	$+7^\circ 30'$
2	146°—151° "	45 "	0.9771	1.4710	$+3^\circ 17'$
3	151°—152° "	45 "	0.9748	1.4710	$\pm 0$

### An Ethereal Compound.

The fifth fraction which was distilled on metallic sodium under 20 mm. pressure, shows B.p. 191.5° at 16 mm.;  $d_4^{20} = 0.9341$ ;  $n_D^{20} = 1.4760$ ;  $[a]_D = -5^\circ 30'$ .

It was analysed with the following results :

0.1110 gm. gave 0.3194 gm.  $\text{CO}_2$  and 0.118 gm.  $\text{H}_2\text{O}$ ,  
 $\text{C}=78.5$ ;  $\text{H}=11.9$ ; theory requires  $\text{C}=77.9$ ;  $\text{H}=11.7$   
 for  $\text{C}_{20}\text{H}_{36}\text{O}_2$ . or  $\text{C}=78.4$ ;  $\text{H}=11.1$  for  $\text{C}_{20}\text{H}_{34}\text{O}_2$ .

It yields neither phenyl urethane nor any oxime, and was reduced by means of hydrogen and platinum black to a hydrogenated compound:

$$d_4^{20}=0.9155; n_D^{20}=1.4635; [\alpha]_D = -2^\circ 52'.$$

M.R.=93.4, theory 93.4 for  $\text{C}_{20}\text{H}_{38}\text{O}_2$ .

### 3. Action of 50% Sulphuric Acid on Citronellal.

The reaction product formed by the interaction between citronellal & 50% sulphuric acid under conditions similar to the above cases, was fractionated under 14 mm. pressure into 5 fractions :

	Fraction	Yield
1	60°—90°	14%
2	90°—130°	1 "
3	130°—175°	1 "
4	175°—195°	62 "
5	195°—205°	17 "
6	Residue	5 "

#### Citronellal-terpene, $\text{C}_{10}\text{H}_{16}$ .

The first fraction which differs from isopulegol in its physical & chemical characters, was analysed after distilling on metallic sodium :

	Fraction	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$
1	173°—177°	0.8434	1.4840	+33° 30'
2	177°—181°	0.8506	1.4915	+36° 54'
3	181°—185°	0.8637	1.4980	+49° 11'

0.1054 gm. gave 0.3413 gm.  $\text{CO}_2$  & 0.1093 gm.  $\text{H}_2\text{O}$ ,  
 $\text{C}=88.3$ ;  $\text{H}=11.5$ ; theory  $\text{C}=88.2$ ;  $\text{H}=11.8$  for  $\text{C}_{10}\text{H}_{16}$

The physial cconstants  $d_4^{20}=0.8535$ ;  $n_D^{25}=1.4875$ ; M. R.=45.9,

agree well with those of monocyclic terpene with two double bonds in its molecule, and was named citronellal-terpene by the writer on account of its properties which gave neither hydrochloride nor nitross chloride and do not agree with those of known terpenes in the literature

**Ethereal Compound,  $C_{20}H_{36}O_2$ .**

The two fractions, B.p. ( $175^{\circ}$ – $195^{\circ}$ ) 14 mm. & B.p. ( $195^{\circ}$ – $205^{\circ}$ ) 14 mm. combined together and distilled again and divided into 3 fractions :

	Fraction	$d_4^{20}$	$n_D^{20}$	$[\alpha]$
1	$196^{\circ}$ – $198^{\circ}$ 19mm.	0.9295	1.4805	$-5^{\circ} 48'$
2	$198^{\circ}$ – $199^{\circ}$ "	0.9262	1.4800	$-2^{\circ} 5'$
3	$201^{\circ}$ 23mm.	0.9312	1.4820	$-9^{\circ} 3'$

It was indicated in the above physical constants indicate that these fractions would be a mixture of a principal constituent and some others differing in their proportions, and also that the main constituent to each fraction was ascertained from the analysis, to be an ethereal compound and the chemical nature of the first fraction :

0.1319 gm. gave 0.3806 gm.  $CO_2$  and 0.1386 gm.  $H_2O$ ,  
 $C=78.7$  ;  $H=11.7$  ; theory requires  $C=78.8$  ;  $H=11.7$  for  
 $C_{20}H_{36}O_2$ .

**4. Action of Potassium Hydrogen Sulphate on Citronellal.**

Citronellal was heated with twice its weight of powdered potassium hydrogen sulphate on an oil bath, when the temperature of the bath had reached  $140^{\circ}$  a violent reaction took place, separating a water layer, and the reaction product washed with water and then subjected to fractional distillation proved to be :

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$
1	$-90^{\circ}$ 15mm.	3%	0.8840	1.4670
2	$90^{\circ}$ – $92^{\circ}$ "	3 "	0.9035	1.4714
3	$92^{\circ}$ – $92.5^{\circ}$ "	5 "	0.9104	1.4720
4	$92.5^{\circ}$ – $100^{\circ}$ "	1 "	0.9137	1.4726
5	$100^{\circ}$ – $130^{\circ}$ "	1 "	0.9190	1.4730
6	$130^{\circ}$ – $180^{\circ}$ "	0.5 "	0.9212	1.4775
7	$180^{\circ}$ – $190^{\circ}$ "	3 "	0.9162	1.4840
8	$190^{\circ}$ – $191^{\circ}$ "	1.5 "	0.9150	1.4832
9	$191^{\circ}$ – $193^{\circ}$ "	64 "	0.9137	1.4837
10	$193^{\circ}$ – $195^{\circ}$ "	8.5 "	0.9171	1.4841

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$
11	195°—197° "	4.5 %	0.9202	1.4852
12	Residue	5 "	—	—

### Isopulegol.

Second and third fractions combined together and distilled again and the fraction B.p. 92°—92.5° at 15 mm.;  $d_4^{20}=0.9105$ ;  $n_D^{20}=1.4720$ ;  $[\alpha]_D=+6^\circ 10'$ , was confirmed to be composed of isopulegol by oxidizing it into isopulegone which yields an oxime with m.p. 121°.

### Di-isopulegol Ether, $C_{20}H_{34}O$ .

Two fractions, B.p. 191°—193°; B.p. 193°—195°, combined together and distilled, and the fraction B.p. (185°) 12.5 mm. pressure, shows:

$d_4^{20}=0.9120$ ;  $n_D^{20}=1.4835$ ;  $[\alpha]_D=12^\circ 15'$ , and on analysis. 0.1205 gm. gave 0.3642 gm.  $CO_2$  and 0.1271 gm.  $H_2O$ ;  $C=82.4$ ;  $H=11.7$ , theory  $C=82.9$ ;  $H=11.7$  for  $C_{20}H_{34}O$ .

It gave no phenyl urethane, oximes or semicarbazide, and 1 gm. of the substance absorbed 162 cc. of hydrogen in presence of platinum black. Molecular refractive power of the substance being 90.0, agrees with the theoretical value 90.9 which was calculated for the molecular formula  $C_{20}H_{34}O$  containing two double bonds in the molecule.

The physical constants of the reduced compound was determined to be:

$$d_4^{20}=0.8932; n_D^{20}=1.4678; [\alpha]_D=+6^\circ 1'$$

$$M.R.=91.5; \text{theory } 91.8 \text{ for } C_{20}H_{34}O.$$

### 5. Action of Acetic Anhydride & Sodium Acetate on Citronellal.

In order to learn the behavior of the aldehydes toward acetic anhydride and sodium acetate, a mixture of acetic anhydride and sodium acetate was heated with citronellal on an oil-bath at 150° for 15 hours, according to the directions put forward by F. Tiemann & R. Schmidt.<sup>1</sup> The reaction product which shows the ester value 316.0, was fractionated:

<sup>1</sup> Ber. D. Chem. Ges., **29**, 913 (1896); and refer: F.W. Semmler: Ibid **42**, 2015 (1909).



	Fraction	Yield	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$	E.V.
1	106°—110° 12.5mm	20%	0.9200	1.4566	— 37'	288.2
2	112°—116° "	65 "	0.9082	1.4572	—4° 30'	300.6
3	116°—120° "	34 "	0.9054	1.4582	—7° 9'	302.9
4	147.5°—150.5° "	30 "	0.9747	1.4460	+1° 14'	439.5

It was ascertained from their physical constants and ester values (E.V) that the first, third and forth fractions were composed of isopulegol acetate, enol monoacetate of citronellal, and enol diacetate of citronellal respectively, and the second fraction was assumed to be a mixture of isopulegol acetate and enol acetate of citronellal.

### 6. Action of Acetic Anhydride on Citronellal.

Citronellal was heated with acetic anhydride on an oil-bath at 150°, for 15 hours, and the reaction product, treated with hydrogen sodium sulphite to remove an unchanged aldehyde, and remaining oil showed:

$d_4^{20}=0.8504$ ;  $n_D^{20}=1.4490$ ;  $\alpha_D=+10.35'$  and ester value 323, was subjected to fractional distillation:

	Fraction	Yield
1	90°—100° 9mm.	13%
2	100°—105° "	46 "
3	105°—110° "	6 "
4	110°—140° "	7 "
5	140°—150° "	20 "
6	150°—160° "	4 "
7	Residue	4 "

The main fractions (1,2 and 5) by further distillation under 12.5 mm. pressure, were divided into the two portions with the following constants:

	Fraction	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$	E.V.
1	102°—106°	0.9396	1.4590	—1° 45'	284
2	147.5°—150.5°	0.9780	1.4475	+2° 36'	—

### Isopulegol Acetate.

The first fraction was assumed to be composed of isopulegol acetate

from its physical constants and ester value. In confirmation the free alcohol was isolated by saponification of the ester, which was found to be possessed of the following properties B.p.  $92.5^{\circ}$ — $93.5^{\circ}$  at 14 mm.  $d_4^{20}=0.9150$ ;  $n_D^{20}=1.4723$ ;  $[\alpha]_D=+4^{\circ} 10'$  and these constants agree well with those of isopulegol.

### 7. Action of Glacial Acetic Acid on Citronellal.

By the interaction of citronellal and glacial acetic acid at  $150^{\circ}$  for 15 hours, isopulegol and its acetate were obtained from the reaction product which was fractionated after being separated from the unchanged citronellal.

	Fraction	Yield
1	$65^{\circ}$ — $100^{\circ}$ 16mm.	5%
2	$100^{\circ}$ — $110^{\circ}$ "	46 "
3	$110^{\circ}$ — $151^{\circ}$ "	6 "
4	$151^{\circ}$ — $181^{\circ}$ "	6 "
5	$181^{\circ}$ — $203^{\circ}$ "	37 "

The first two fractions B.p.  $65^{\circ}$ — $100^{\circ}$ , B.p.  $100^{\circ}$ — $110^{\circ}$ , by repeating the distillation were divided into two portions:

	Fraction	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$	E.V.
1	$100^{\circ}$ — $105^{\circ}$ 15.5mm,	0.9254	1.4617	$+1^{\circ} 40'$	180
2	$105^{\circ}$ — $110^{\circ}$ "	0.9367	1.4586	$-1^{\circ} 10'$	260

The two fractions when hydrolysed yielded equally isopulegol B.p. ( $100^{\circ}$ — $101^{\circ}$ ) 20mm.  $d_4^{20}=0.9143$   $n_D^{20}=1.4720$ ;  $[\alpha]_D=+4^{\circ} 41'$  and also yielded by further acetylation with acetic anhydride & sodium acetate isopulegol acetate B.p. ( $94^{\circ}$ — $97^{\circ}$ ) 8mm.  $d_4^{20}=0.9394$ ;  $n_D^{20}=1.4572$   $[\alpha]_D=-1^{\circ} 10'$ .

From the other fractions no definite compound could be obtained by distillation.

## II. Citral.

### 8. Action of 5% Sulphuric Acid on Citral.

The citral used in the experiment was obtained from the East

Indian lemon-grass oil by distillation and was purified by the sulphite method.

B.p.  $112.5^{\circ}$ — $115^{\circ}$  at 17mm pressure,  $d_4^{20}=0.8886$ ;  $n_D^{20}=1.4901$ ;  
 $[\alpha]_D=0^{\circ} 10'$ .

It was treated according to the directions suggested by F. Tiemann<sup>1</sup>, with 10 times the quantity of 5% sulphuric acid at  $27^{\circ}$  for 12 hours. The product estimated to contain 86% free citral by the sulphite method, was fractionated under 20 mm. pressure after the unchanged citral had been removed.

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$
1	to $100^{\circ}$	1.5	0.9723	1.4995
2	$100^{\circ}$ — $115^{\circ}$	6.5	0.9320	1.4950
3	$115^{\circ}$ — $118^{\circ}$	73	0.9085	1.4914
4	$118^{\circ}$ — $140^{\circ}$	4.5	0.9214	1.4920
5	Residue	14.5	—	—

The third fraction by repeated fractional distillation shows the constants:  $d_4^{20}=0.9080$ ;  $n_D^{20}=1.4902$ ;  $\alpha_D=\pm 0$  which differ from those of citral. However; it yields  $\alpha$ -citryl- $\beta$ -naphthio-cincomenic acid with a melting point of  $197^{\circ}$ .

### 9. Action of 20% Sulphuric Acid on Citral.

By the interaction of citral with 10 times the quantum of 20% sulphuric acid at  $25^{\circ}$  for 12 hours, besides resinous substance, some cyclic terpenes were obtained. The product was fractionated under 22 mm. pressure:

	Fraction	Yield
1	to $80^{\circ}$	23%
2	$80^{\circ}$ — $100^{\circ}$	10 "
3	$100^{\circ}$ — $196^{\circ}$	5 "
4	$196^{\circ}$ — $199^{\circ}$	27 "
5	Residue	35 "

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<sup>1</sup> Ber. D. Chem. Ges., **32**, 114 (1899).

The first and second fractions combined together and subjected to distillation over metallic sodium under ordinary pressure; and the fraction, B.p.  $183^{\circ}$ – $186^{\circ}$ ,  $d_4^{20}=0.8886$ ;  $n_D^{20}=1.5092$ , was analysed with the following results:

0.1187 gm., gave 0.3883 gm.  $\text{CO}_2$  and 0.1115 gm.  $\text{H}_2\text{O}$ ,

$\text{C}=89.2$ ;  $\text{H}=10.5$ ; theory requires  $\text{C}=89.5$ ;  $\text{H}=10.5$  for  $\text{C}_{10}\text{H}_{14}$ .

Chemical properties and physical constants M.R. = 45.1, theory requires 44.8 for  $\text{C}_{10}\text{H}_{14}\text{F}_3$ , of the fraction indicates the occurrence of a new terpene in it, which was named by the writer citral terpene.

The third & fourth fractions show the occurrence of a compound of unstable nature toward heat since the fractions by repeated distillations abundantly yielded resinous matter with the boiling point ranging from  $150^{\circ}$  to  $200^{\circ}$  under 14 mm. pressure, and the main portion B.p.  $194^{\circ}$ – $199^{\circ}$  17 mm.;  $d_4^{20}=0.9494$ ;  $n_D^{20}=1.5303$ ;  $\alpha_D=-0.4^{\circ}$ ; 0.1256 gm. subst. gave 0.4003 gm.  $\text{CO}_2$  and 0.1185 gm.  $\text{H}_2\text{O}$ ,  $\text{C}=86.7$ ;  $\text{H}=10.5$  which shows an unsaturated nature towards chemicals, and was assumed to be a mixture of diterpene and a compound of ethereal nature.

### 10. Action of 50% Sulphuric Acid on Citral.

Citral by the action of 50% sulphuric acid at  $20^{\circ}$ , was converted into a resinous substance, cymene, and substances of unknown nature. For the isolation of these compounds, the reaction product was distilled under 20 mm. pressure.

	Fraction	Yield
1	$70^{\circ}$ – $90^{\circ}$	6%
2	$90^{\circ}$ – $100^{\circ}$	25 "
3	$100^{\circ}$ – $198^{\circ}$	5 "
4	$198^{\circ}$ – $220^{\circ}$	14 "
5	Residue	50 "

The second fraction by distillation over metallic sodium yielded a fraction with a B.p.  $174.5^{\circ}$ – $175^{\circ}$ ,  $d_4^{20}=0.8588$ ;  $n_D^{20}=1.4892$ , which was mostly composed of p-cymene.

The fourth fraction was assumed to be composed mostly of the portion of the properties B.p. ( $189^{\circ}$ – $193^{\circ}$ ) 16mm.  $d_4^{20}=0.9616$ ;

$n_D^{20}$  1.5303; 0.1108 gm. gave 0.3512 gm.  $\text{CO}_2$  & 0.1042 gm.  $\text{H}_2\text{O}$ ,  
C=86.5; H=10.5;

### 11. Action of Potassium Hydrogen Sulphate on Citral.

By the action of potassium hydrogen sulphate on citral at  $140^\circ$  for 30 minutes, p-cymene and a diterpene were obtained from the reaction product which was subjected to fractional distillation under 14 mm. pressure after the usual treatment.

	Fraction	Yield
1	to $70^\circ$	35%
2	$70^\circ-100^\circ$	7 "
3	$100^\circ-180^\circ$	5 "
4	$180^\circ-192^\circ$	14 "
5	$192^\circ-201^\circ$	9 "
6	Residue	30 "

p-Cymene was isolated from the first and second fractions by distillation over metallic sodium, B.p.  $174^\circ-175^\circ$ ,  $d_4^{20}=0.8572$ ;  $n_D^{20}=1.4678$ .

For confirmation, it was oxidized to p-oxyisopropyl-benzoic acid of m.p.  $155^\circ-157^\circ$ .

Other fraction by repeated fractional distillations were found to consist mostly of hydrocarbon of the formula  $\text{C}_{20}\text{H}_{28}$ , which shows the following constants; B.p.  $(190^\circ-194^\circ)$  14mm.;  $d_4^{20}=0.9244$ ;  $n_D^{20}=1.5280$ ; 0.1493 gm. subst. gave 0.4872 gm.  $\text{CO}_2$  & 0.1412 gm.  $\text{H}_2\text{O}$ , C= 89.0; H=10.6.

By reduction with hydrogen and platinum black, 1 gm. of substance absorbs 258 c.c. hydrogen, and the resulting compound;  $d_4^{20}=0.8840$ ;  $n_D^{20}=1.4875$  shows a still unsaturated nature toward an iodine solution.

### 12. Action of Acetic Anhydride on Citral.

When citral came into contact with acetic anhydride at  $23^\circ$ , no reaction could be observed, but when the temperature was raised to  $150^\circ$ , a reaction took place in the formation of a product which was separated

from the unchanged citral (14%) by the sulphite method, and distilled under 19 mm. pressure :

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$
1	to 100°	4%	0.8805	1.4889	—
2	100°—120°	5 "	0.9340	1.4860	—
3	120°—125°	8 "	0.9650	1.4890	—
4	125°—127°	10 "	0.9520	1.4830	—
5	127°—132°	20 "	0.9520	1.4860	—0° 27'
6	132°—135°	8 "	0.9558	1.4905	—
7	135°—140°	6 "	0.9598	1.4909	—
8	Residue	40 "	—	—	—

#### Enol Citral Acetate.

The fourth and fifth fractions were assumed from their physical constants to be equally composed of enol citral acetate, and the analytical results confirm this assumption.

0.1467 grm. gave 0.3959 grm. CO<sub>2</sub> & 0.1270 grm. H<sub>2</sub>O,  
 C=73.6; H=9.6 theory requires  
 C=74.2; H=9.3 for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>.

### 13. Action of Glacial Acetic Acid on Citral.

By the action of glacial acetic acid on citral at 150° for 15 hours, p-cymene could be isolated from the reaction product of an ester value of 44.4, which on distillation gave the following results :

	Fraction	Yield
1	60°—100° 16 mm.	33%
2	100°—130° "	3 "
3	130°—190° "	6 "
4	190°—200° "	18 "
5	200°—203° "	5 "
6	Residue "	—

Cymene was composed of the first fraction, which, isolated by distillation under ordinary pressure, gave the constants :

B.p. 174°—174.5°;  $d_4^{20}$  = 0.8571;  $n_D^{20}$  = 1.4942.

### III. Isopulegol.

#### 14. Action of 20% & 50% Sulphuric Acid on Isopulegol.

Isopulegol which was isolated from isopulegol acetate by hydrolysis gave the constants:

B.p.  $100.9^{\circ}$ – $101^{\circ}$ , 20mm.,  $d_4^{20} = 0.9143$ ;  $n_D^{20} = 1.4720$ ;  $[\alpha]_D = +4^{\circ} 41'$ .

It was treated with 10 times by weight of 20% sulphuric acid at  $15^{\circ}$  for 12 hours, and the product was treated as usual.

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$
1	$86^{\circ}$ — $89^{\circ}$ 10mm.	87%	0.9151	1.4714	$+3^{\circ} 8'$
2	$89^{\circ}$ — $92^{\circ}$ "	44 "	0.9177	1.4712	$+2^{\circ} 57'$
3	$92^{\circ}$ — $100^{\circ}$ "	7 "	—	—	
4	$100^{\circ}$ — $135^{\circ}$ "	5 "	—	—	
5	$135^{\circ}$ — $140^{\circ}$ "	2 "	—	—	
6	$140^{\circ}$ — $142^{\circ}$ "	5 "	0.9640	1.4720	
7	Residue	trace	—		

By this treatment the main part of the isopulegol remained without any reaction from the sulphuric acid and some part was converted into menthoglycol by adding a water molecule, and the latter substance was isolated from the sixth fraction.

When, however, isopulegol was treated with 50% sulphuric acid at  $17^{\circ}\text{C}$ , for 13 hours, a terpene of a nature identical with that of the citronellal terpene above mentioned, and a substance of ethereal nature were isolated from the product by fractional distillation.

	Fraction	Yield	$d_4^{20}$	$d_D^{20}$	$[\alpha]_D$	Remark
1	to $86^{\circ}$ 13mm.	22%	0.8582	1.4890	—	Terpene
2	$86^{\circ}$ — $140^{\circ}$ "	10 "				
3	$140^{\circ}$ — $170^{\circ}$ "	13 "				
4	$170^{\circ}$ — $185^{\circ}$ "	10 "				
5	$185^{\circ}$ — $190^{\circ}$ "	36 "	0.9471	1.5011	$-8^{\circ} 9'$	Ethereal
6	Residue "	9 "	—	—	—	compound

#### 15. Action of Potassium Acid Sulphate on Isopulegol.

Isopulegol was treated with potassium hydrogen sulphate under the

same conditions described in the case of citronellal, and the reaction product was distilled under 14.5 mm. pressure, and di-isopulegol ether, which was previously prepared by Verley<sup>1</sup> was isolated as shown in the following table.

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D$	Remark
1	80°—90°	13%	—	—	—	Isopulegol
2	90°—110°	14 "	—	—	—	—
3	110°—189°	3 "	—	—	—	—
4	189°—193°	60 "	0.9110	1.4861	+3° 3'	Ether
5	Residue	10 "	—	—	—	—

When the ether reduced with hydrogen and platinum black, yielded a compound with the following properties  $d_4^{20}=0.8868$ ,  $n_D^{20}=1.4666$ ;  $[\alpha]_D=+24^\circ 29'$ .

#### IV. Menthoglycol.

##### 16. Action of Sulphuric Acid on Menthoglycol.

The menthoglycol used in this experiment shows the constants: B.p. (141°—146°) 13 mm.  $d_4^{20}=0.9806$ ;  $n_D^{20}=1.4730$   $[\alpha]_D=+6^\circ 31'$ .

When menthoglycol was subjected to the action of 20% sulphuric acid at 12° for 12 hours, the main part (80%) of the substance remained in an unchanged state. (B.p. 140°—147°, 13mm.,  $d_4^{20}=0.9784$ ;  $n_D^{20}=1.4720$ ;  $[\alpha]_D=+8^\circ 22'$ .)

By the action of 50% sulphuric acid on menthoglycol at 12°, it was transformed partly into the so-called citronellal terpene (with the following properties, B.p. 175°—181°,  $d_4^{20}=0.8583$ ;  $n_D^{20}=1.4900$ ) which was isolated from the first fraction of the reaction product by distillation.

	Fraction	Yield	$d_4^{20}$	$n_D^{20}$
1	to 95°	10 mm.	44%	—
2	95°—170°	"	trace	—
3	170°—180°	"	22 "	0.0355
4	180°—190°	"	18 "	0.9430
5	Residue	"	16 "	—

<sup>1</sup> Loc. Cit.,



### 17. Action of Potassium Hydrogen Sulphate on Menthoglycol.

By the interaction of the glycol and potassium hydrogen sulphate, the so-called citronellal-terpene and di-isopulegol ether were isolated from the reaction product by distillation under 15-16 mm. pressure.

	Fraction	Yield	$d_4^{29}$	$n_D^{20}$	Remark
1	74°—79°	13%	0.8713	1.4930	Terpene
2	79°—84°	9 "	0.8810	1.4911	—
3	84°—192°	18 "	—	—	—
4	192°—193°	40 "	0.9140	1.4855	Ether
4	193°—196°	13 "	0.9137	1.4867	—
5	Residue	7 "	—	—	—

### V. Menthol.

#### 18. Reduction of Isopulegol., and Formation of l.-Menthol.

Isopulegol prepared from its acetate of B.p. (101.5°—104.5°) 12 mm,  $d_4^{20}=0.9378$ ;  $n_D^{20}=1.4570$ ;  $a_D=-33'$ , by saponification with alcoholic potash, boils at 91.5° under 13 mm. pressure,  $d_4^{20}=0.9162$ ;  $n_D^{20}=1.4710$ ;  $a_D=-30'$ .

When the alcohol was reduced with hydrogen in presence of platinum black in its glacial acetic acid, yields menthol of the following properties:

$d_4^{25}=0.8944$ ;  $n_D^{25}=1.458$ ;  $[a]_D=-16^\circ.77$  grm. of the sample were fractionated under 18 mm. pressure into 4 parts, and the fractions shows the following constants:

	Fraction	Yield	$d_4^{25}$	$[a]_D$
1	87°—100°	2.3 grm.	0.8772	-9°.80
2	101°—103°	16.0 "	0.8922	-11°.77
3	104°—106°	45.0 "	0.8931	-18°.25
4	107°—108°	7.5 "	—	-26°.75
5	Loss	6. "	—	—

The fourth fraction solidified on cooling and the crystals separated were found to melt at  $30^{\circ}$ . By further distillation of the third fraction, the fraction which regarded to consist mostly of menthol was isolated.

#### Laevo Menthol.

The third fraction in the above table was further fractionated under 15 m.m. pressure and two fractions were resulted:

	Fraction	Yield	$d_4^{25}$	$[\alpha]_D$
1	$102^{\circ}-103^{\circ}$	15.2 gm.	0.8924	$-13.22$
2	$105^{\circ}-106^{\circ}$	28.3 "	solid	$-26.06$

The first fraction was then subdivided by distillation under 25 m.m. into 3 portions:

	Fraction	Yield	$[\alpha]_D$	Remark
1	$108^{\circ}-109^{\circ}$	8.3 gm.	$-9.58$	liquid
2	$109^{\circ}-110^{\circ}$	4.2 "	$-16.50$	solid
3	$110^{\circ}-111^{\circ}$	3.0 "	$-23.76$	"

The fractions which mentioned above and show the rotatory power- ( $23^{\circ}\sim 26^{\circ}$ ) combined together, and subjected to distillation in order to isolate pure l-menthol, and finally obtained a compound which possessed the physical constants, M.p.  $33^{\circ}-34^{\circ}$ ;  $[\alpha]_D = -44.92$ , agree well with those of pure l-menthol.

Other fractions which show the low rotatory power, were treated, with phthalic anhydride following the direction by Pickard & Littlebury, and l-menthol hydrogen phthalate of M.p.  $128^{\circ}-131^{\circ}$ ;  $[\alpha]_D = -32.42$  in acetic acid solution, was isolated. Thus, the yield of l-menthol isolated in the free and combined states was amounted to be 26% of the reduction product from isopulegol.

#### Laevo Menthone.

Menthol obtained from isopulegol by catalytic reduction was oxidized with chromic acid following the directions suggested by E. Beckman<sup>2</sup> into menthone which was then converted into its oxime with the following constants: m p.  $54^{\circ}-62^{\circ}$ ;  $[\alpha]_D = -43.21$ . The oxime was purified by converting it into hydrochloride in its ethereal solution, and by repeating the operation pure laevo menthone oxime hydrochloride was isolated as will be seen in the following table:

1 Loc. cit.,

2 Liebig Ann., **250**, 322 (1888).

	First crystallisation	Second "	Third "	Hiraidzumi's sample
m.p.	106°-107°	110°-112°	114°-116°	115°-116°
$[\alpha]_D$	-47°.78	-54°.65	-58°.77	-56°.21
$[\alpha]_{H\alpha}$	-42°.66	-41°.46	-47°.77	-47°.96
$[\alpha]_{H\beta}$	-67°.00	-75°.40	-75°.17	-84°.87
$[\alpha]_{462}$	-74°.23	-87°.45	-84°.96	-94°.30

Beckmann<sup>1</sup> has described M. p. 117°-118°;  $[\alpha]_D = -62^\circ$ . for pure l-menthone oxime hydrochloride, while the pure sample prepared by Dr. T. Hiraidzumi shows the constants mentioned in the table.

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<sup>1</sup> Ber. D. Chem. Ges., **42**, 846 (1909).