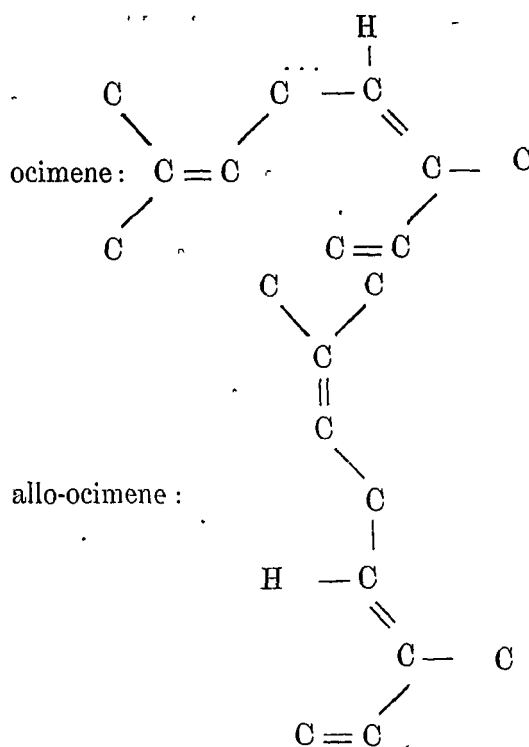


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I am still engaged with this geometrical isomerism and the other substances described. I soon hope to make a further communication about the alcohols formed from these terpenes.

Of late, after this research had already been partly finished, SABATIER and SENDRENS have made some valuable additions to our methods of research of the unsaturated compounds. I am engaged in applying the same to the aliphatic terpene group and to the sesquiterpenes. Dihydro-ocimene, which cannot be further hydrogenised by sodium and alcohol, eagerly absorbs hydrogen at 180°

under the influence of reduced nickel; a nearly odourless liquid is formed which boils at a considerably lower temperature and contains only traces of the original product. It consists, probably, of dimethyl-2.6.octane, the as yet unknown foundation of the aliphatic terpene group. The aliphatic terpene-alcohol, geraniol, also reacts with nickel and hydrogen; the reaction product is a liquid, possessing a particular odour; it contains, besides some water, a hydrocarbon, which probably is identical with the hydrocarbon, obtained from dihydroacimene and a substance of a higher boiling point, which I suppose to be the saturated alcohol, corresponding with geraniol.

Chemistry. — “*On some aliphatic terpene alcohols.*” By DR. C. J. ENKLAAR. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of January 27, 1906).

According to the process of BERTRAM and WALBAUM¹⁾ terpene alcohols may be obtained from terpenes by digesting their solution in glacial acetic acid for some hours with dilute sulphuric acid at 50°—60°. The aliphatic terpene ocimene, discovered by VAN ROMBURGH

¹⁾ D. R. Pat. No. 80711, Journ. f. Prakt. Chem. 49. 1. Also compare WALLACH and WALKER, Ann. 271, 285, and POWER and KLEBER, Pharm. Rundschau (N.-York) 1895, No. 3.

and investigated by myself¹⁾, was treated by me in this way²⁾. The greater half of the ocimene operated upon was recovered unaltered while a small portion underwent polymerisation. At the same time an alcohol was formed, the quantity of which was about 10% of the ocimene used. This alcohol was an agreeably smelling liquid, which gave the following constants:

sp. gr. ₁₅	nd ₁₅	B.p. at 10 mm.	Mol. Refraction (M.R.)
0.901	1.4900	97°	49.22
(calculated for $C_{10}H_{18}O$ is: MR = 48.86)			

The analysis had given the composition $C_{10}H_{18}O$.

This alcohol, probably an aliphatic terpene alcohol is, therefore, formed by the addition of the elements of water to ocimene. In properties it does not correspond with any of the already known aliphatic terpene alcohols, as is shown by the following table:

	sp. gr. ₁₅	nd	B.p. at 10 mm.
geraniol:	0.882	1.477	116°
nerol ³⁾ :	0.8814		112°
myrcenol (BARBIER):	0.901	1.477	99°
linalool:	0.870	1.464	86°

On account of its formation from ocimene, I call this new alcohol ocimenol. The investigation of this ocimenol is still of a provisional character.

The beautifully crystallised phenylurethane, which I could prepare from it in good yield, renders it possible to characterise and readily investigate the alcohol. This urethane, when recrystallised from dilute alcohol, forms white needle-shaped crystals, which melt without decomposition at 72°, whilst according to the analysis, it has the composition $C_{17}H_{23}O_2N$. I am still occupied with the regeneration of ocimenol from its urethane and the closer investigation of these substances; however from the fair yield of this urethane, and the absence of oily by-products, it seems that the product obtained from ocimene is mainly a simple alcohol.

For me, the study of this alcohol was of particular importance as I wanted to compare ocimene in this respect with myrcene. Several investigators have been already occupied with the alcohol,

¹⁾ Compare my previous paper and my dissertation.

²⁾ I worked according to the directions of POWER and KLEBER. 100 parts of terpene were heated with 250 parts of glacial acetic acid and 10 parts of 50% sulphuric acid for three hours at 40°.

³⁾ Nerol is distinguished from geraniol by a more delicate odour of roses, by not combining with calcium chloride and by yielding a diphenylurethane melting at 52°.

which is formed from myrcene in the manner indicated; their statements, however, are often diametrically opposed.

POWER and KLEBER¹⁾, who first prepared it, took it to be linaloöl on account of its odour and the formation of citral on oxidation with chromic acid. BARBIER²⁾ declared it to be a new alcohol; on oxidation, he obtained no citral but another as yet unknown aldehyde. From the results of the oxidations he deduced for this alcohol, which he named myrcenol, a structural formula, which had been given already by TIEMANN and SEMMLER to linaloöl. In a further research on linaloöl, he gave as his opinion³⁾ that it was not a simple alcohol, but a mixture, and also that its main constituent was not optically active, a reason why he rejected the formula of T. and S. SEMMLER⁴⁾, however, looked upon myrcenol as a mixture already partly converted into cyclic products, and upheld his linaloöl formula against BARBIER's objections.

I prepared the myrcenol according to the directions of POWER and KLEBER. The greater part of the myrcene was recovered unaltered (6%), a small portion polymerised whilst the alcohol had formed to the amount of about 20%. For this alcohol distinguished from linaloöl also by its intense, agreeable odour, I obtained the constants attributed to it by BARBIER, who, however, had a much larger quantity of the alcohol at his disposal:

	sp. gr. ₁₅	nd_{15}	Bp. at 10 mM.	Mol. Refr.
myrcenol (<i>E</i>):	0,9032	1.4806	97—99°	48,44
„ (<i>B</i>):	0,9012	1.47787	99°	48,34
MR, calculated for $C_{10}H_{18}O _2 = 48,16$				

My analyses also pointed to the composition $C_{10}H_{18}O$. I do not consider this alcohol to be perfectly pure as it has not got a quite constant boiling point; it seems still to contain a more volatile fraction.

The closer investigation of this substance has, as stated, led to differences of opinion. It seems to me that these have been caused by the different methods used. The formation of citral in the oxidation in acid solution is no reliable test for the presence of linaloöl as it may be yielded also by other alcohols. BARBIER showed, however, that on oxidation of myrcenol with chromic acid an aldehyde was formed, having the same formula as citral, but not identical with the same. He regenerated it, for instance, from its oxime, and obtained a

¹⁾ l. c.

²⁾ Bull. Soc. Chem. [3], 25, 687 (1901).

³⁾ Bull. Soc. Chem. [3], 25, 828 (1901).

⁴⁾ Ber. 34, 3122 (1901).

semicarbazone melting at 197° , whilst citralsemicarbazone melts at 135° . Here we have a difference in the method of research. POWER and KLEBER tested for citral by converting it into citrylnaphthocinchonic acid; in this way a possibly formed ketone — I presume myrcenol is a secondary alcohol — must have escaped their notice, whilst a little citral thus detected may be simply a by-product. On the other hand, semicarbazone, made use of by BARBIER, is according to others unfit for testing for citral. BARBIER may have obtained the semicarbazone from the eventually formed ketone, the main product, whilst a little admixed citral may have given the aldehyde reactions. Moreover BARBIER's oxidations with permanganate in aqueous solutions cannot be taken as decisive for the differentiation of myrcenol and linalool¹⁾.

Instead of investigating the oxidation products of myrcenol, I have prepared from the alcohol itself a crystallised derivative, in the form of a phenyl-urethane, melting at 68° . The analysis again pointed to the composition $C_{17}H_{28}O_2N$. This urethane has been prepared in the same manner as WALBAUM and HUTHIG²⁾ prepared the phenyl-urethane from linalool; the latter melts at 65° . By means of the phenyl-urethane obtained from myrcenol, it could be decided very readily and distinctly, that the alcohols, myrcenol and linalool, were totally different. The mixture of racemic linaloolurethane and myrcenol-urethane melted at 60° — 62° ; the depression of the melting point sufficiently proves the non-identity. The alcohol, which is characterised by the phenyl-urethane melting at 68° , is also the main product of crude myrcenol. I obtained from this a yield of nearly 60 pCt. of crystallised urethane; besides this alcohol, a little linalool may possibly be contained in the myrcenol (the hydration product of myrcene); the formation of some oily urethane in presence of the crystallised substance might even point to this. The facts mentioned render it possible, however, to decide the matter. By regenerating myrcenol from its urethane, the properties of pure myrcenol may be ascertained. I am still engaged with this. Of this alcohol, myrcenol, it may be stated that it is a typical derivative of myrcene; its constants differ from those of ocimenol, in the same manner as those of myrcene do from those of ocimene; the tendency towards polymerisation of myrcenol is still larger than that of myrcene.

For ocimenol and myrcenol I devised provisional structural formulae³⁾, based on their formation from the terpenes ocimene and myrcene.

¹⁾ Compare previous communication.

²⁾ Journ. f. prakt. Chem. **67**, 323 (1903).

³⁾ Dissertation, p. 73.

I have not been able to obtain the above racemic urethane of linalool by mixing *d*- and *l*-linalool and preparing the urethane from this racemic linalool; nothing but an oil was formed, which could not be brought to crystallise. Still, from each oil separately (*d*-coriandrol and *l*-linalool, the latter obtained from SCHIMMEL & Co.) I obtained the urethanes at once crystalline. In order to obtain racemic urethane, I was obliged to mix these urethanes of *d*- and *l*-linalool in the proportion of their optical activity. The latter, however, had not been determined; in fact it was doubtful whether they were optically active at all. WALBAUM and HUTHIG, who desired to prove in this manner the identity of linalool derived from different ethereal oils, have overlooked the fact, that alcohols of such varying optical activity as those found with linalool (from 1° to 35°) could not yield the same phenyl-urethane.

Racemic urethane has generally quite another melting point than the pure optically active substance. I was, therefore, obliged to fill this void in their research. I found that the yield of crystallised urethane, which only amounts to 15%, when one works according to their directions (time of reaction one week), may be increased to 85% increase of the time to three months. The urethanes formed, which all melt at 65° are optically active in proportion with the optical activity of the alcohols started from. They consist of mixtures of racemic urethane (probably a racemic compound) with the optically active component, which in a pure condition shows a rotation of $23^{\circ} 27'$ in a 200 mM. tube and has the m.p. 66° . The rotation of pure optically active linalool under the same conditions may also be calculated from this; it then becomes $35^{\circ} 27'$, whereas the highest observed rotation of the natural substance amounts to $35^{\circ} 14'$. This alcohol appears, therefore, to be very strongly subject to racemisation, even in nature. By the facts stated it has, therefore, been proved that linalool consists of a simple optically active terpene alcohol; the incorrectness of BARBIER's formula for linalool and myrcenol has been demonstrated, whilst the linalool formula of TIEMANN and SEMMLER has received support.