

How this compound, which without doubt was an acetone, has been formed I am at a loss to understand. The very small quantity of liquid boiling above 120° consisted chiefly of amylvalerate; at least it had the odour of this ether.

I should have wished to be able to give more definite results, but the preparation of amyl alcohol from petroleum is difficult and requires a very long time. But as the oxidation-products of the different amyl alcohols are being at present investigated by different chemists, I thought it would not be without interest to publish these incomplete results.

V. "On the Constitution of Capryl Alcohol from Castor-oil."

By C. SCHORLEMMER. Communicated by Prof. G. G. STOKES, Sec. R.S. Received May 7, 1868.

There is perhaps no other compound known which has been so often and so fully investigated by different chemists, and yet whose constitution is clouded in so much obscurity, as the alcohol which is obtained by distilling castor-oil soap with caustic alkalies. From the time of its discovery until recently, this compound has been alternately considered by one investigator to be capryl or octyl alcohol, and by another to consist of cœnanthyl or heptyl alcohol. As a proof that it is capryl alcohol, Bouis states that, by the moderate action of nitric acid, a small quantity of caprylic acid is produced, the greater part of the alcohol, however, being oxidized to lower members of the fatty acid series*; and Kolbe concludes, from the formation of these acids, that it is a secondary or isoalcohol, probably

methyl-hexyl carbinol, $C \begin{cases} CH_3 \\ C_6H_{13} \\ H \\ OH \end{cases}$ †. As I shall show in this paper, Kolbe's

view is correct; by moderate oxidation, the alcohol loses two atoms of hydrogen, and is converted into the corresponding acetone, methyl cœnanthol, the same compound which is generally obtained as a byproduct in the preparation of the alcohol. The alcohol which I used was prepared by distilling a mixture of castor-oil soap and caustic soda in a flask of thin copper-sheeting as quickly as possible. The distillate was repeatedly rectified over fused caustic potash, the portion boiling below $200^{\circ} C.$ only being collected. The alcohol was isolated from this liquid by fractional distillation; its corrected boiling-point was $181^{\circ} C.$ The portions having a lower boiling-point consist of hydrocarbons, which combine with bromine, probably members of the olefine series, amongst which octylene, boiling at $125^{\circ} C.$, preponderates. A considerable quantity of liquid distilled above 160° , the boiling-point remaining somewhat constant at $170^{\circ} C.$ Neither

* Ann. de Chim. et de Phys. 3^e Sér. vol. xliv. p. 123.

† Ann. der Chem. und Pharm. vol. cxxii. p. 116.

this fraction nor any other distillate contained an acetone, as none combined with hydrogen-sodium sulphite. According to Chapman, the liquid boiling at 170° consists chiefly of heptyl alcohol*. In order to isolate this alcohol, I acted upon the liquid boiling between 160° – 175° with iodine and phosphorus. The product, subjected to fractional distillation, was found to consist of isoctyl iodide, boiling at 210° – 215° , and of hydrocarbons, distilling below 160° ; the portion which came over between 160° and 210° was very small, and diminished after each further distillation. This shows that no heptyl alcohol was present, and that the original liquid boiling at 170° was a mixture of isoctyl alcohol and hydrocarbons, which could not be separated by simple fractioning.

To obtain the oxidation products of isoctyl alcohol, I acted upon it with a solution consisting of 3 parts of sulphuric acid, 2 parts of potassium bichromate, and 10 parts of water, the reaction being moderated by surrounding the vessel with cold water. As soon as no further action was observed, the liquid was distilled. The distillate consisted of an aqueous liquid, which had a slight acid reaction, and a light oily fluid; it was neutralized with sodium carbonate, and the oil treated again with the oxidizing mixture, which, however, had hardly any action upon it in the cold. This oily liquid is methyl α -nanthol; it has the characteristic odour of that compound, and when shaken with a concentrated solution of hydrogen-sodium sulphite, solidifies to a mass of pearly white crystals. These were dried between blotting-paper, and decomposed by a dilute solution of caustic soda. The oil which separated was dried over calcium chloride; it distilled completely between 170° – 172° , the boiling-point of methyl α -nanthol being 171° .

In order to oxidize this compound further, it had to be heated with the oxidizing mixture, when a slight evolution of carbon dioxide was observed. The acid distillate was neutralized with sodium carbonate, and the acetone unacted upon treated again as before. The different solutions of the sodium-salts were evaporated, and the solid residue decomposed by diluted sulphuric acid. An oily acid separated, which, after drying, distilled at 198° – 200° , which is the boiling-point of caproic acid, the characteristic odour of which it also exhibited. To place beyond doubt that it was really this compound, a portion of it was neutralized with ammonia and precipitated by silver nitrate. A white curdy precipitate was obtained, which was nearly insoluble in cold water, and only slightly soluble in boiling water. It did not darken either by exposure to the light or to a temperature of 100° . From the hot saturated solution it separated as a crystalline powder; nor could I obtain it in definite crystals by evaporating the solution *in vacuo*.

(1) 0.2407 of this salt gave 0.1170 silver.

(2) 0.3720 gave 0.1810 silver.

* Journ. Chem. Soc. New Ser. vol. iii. p. 295.

Calculated for $C_6H_{11}AgO_2$	Found	
	I.	II.
48·43 per cent. Ag.	48·60 per cent.	48·65 per cent.

Another portion of the acid was converted into the barium-salt, which crystallized from a hot saturated solution in long needles, grouped in stars, the characteristic form of barium caproate.

0·2475 of the barium salt gave ·1318 barium carbonate.

Calculated for $(C_6H_{11}O_2)_2Ba$.	Found.
37·33 per cent. Ba.	37·40 per cent.

I also prepared the ethyl compound, which I found to boil at 160° – 162° ; the boiling-point of ethyl caproate is, according to Fehling, 162° *.

Besides caproic acid, a large quantity of acetic acid was formed, which was isolated by distilling the aqueous liquid from which the caproic acid had been removed. With the first portion of the distillate, oily drops of caproic acid came over; the latter portion, which was collected separately, had the pure odour of acetic acid; it was rectified twice, and the last portion collected, which was boiled with silver carbonate. From the filtered solution silver acetate crystallized on cooling in characteristic long, flat needles.

(1) 0·2140 of this silver-salt gave 0·1373 silver.

(2) 0·5895 of the salt gave 0·3825 silver.

Calculated for $C_2H_3AgO_2$.	Found.	
	I.	II.
64·68 per cent. Ag.	64·20 per cent.	64·88 per cent.

These experiments prove that the capryl alcohol from castor-oil is a secondary or isocetyl alcohol to which, adopting the nomenclature

proposed by Kolbe†, the name methyl hexyl carbinol, $C \begin{cases} CH_3 \\ C_6H_{13} \\ H \\ OH \end{cases}$

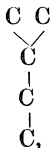
must be given. This alcohol yields, on oxidation, first, the corresponding acetone, methyl ænanthol, $C \begin{cases} CH_3 \\ C_6H_{13} \\ O \end{cases}$, which, under further oxidation, splits up into caproic and acetic acid, exactly as the theory requires.

Another question to be answered was, what is the structure of the group Hexyl C_6H_{13} , contained in this isalcohol? The caproic acid contained in fats and that prepared from amyl cyanide appear to be identical with that which I obtained‡. Now, according to Erlenmeyer, in the amyl compounds the carbon atoms are grouped in the following manner:—

* Ann. der Chem. und Pharm. vol. liii. p. 408.

† Ibid. vol. cxxxii. p. 103.

‡ Caproic acid deviates the plane of the polarized light, whilst that from cocoa-nut-

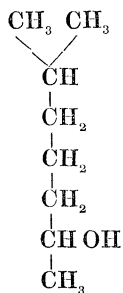


and this grouping must therefore also exist in caproic acid and in isoctyl alcohol. To obtain evidence respecting this question, I converted the alcohol into the corresponding hydride by a very simple method, which is a general one, and by which, with the greatest ease, the corresponding hydrocarbon can be obtained from any alcohol. The alcohol was first converted into the iodide, which was brought together with zinc turnings and diluted hydrochloric acid in a flask which was surrounded with cold water. After a few hours the heavy layer of iodide had disappeared, and a light liquid swam on the top. This consisted almost entirely of the hydrocarbon C_8H_{18} ; traces of iodide and alcohol which still adhered were removed by treating the liquid with sulphuric and nitric acids, and by distilling it over sodium. The pure hydrocarbon boils constantly at 124°C ., and has the specific gravity 9.7083 at $12^\circ.5$.

0.2870 of this liquid gave 0.8840 CO_2 and 0.4150 H_2O .

Calculated.			Found.
C_8	96	84.2	84.0
H_{18}	18	15.8	16.1
	<hr/>	<hr/>	<hr/>
	114	100.0	100.1

As I have shown in my last communication to the Society, a hydrocarbon, having the formula C_8H_{18} and the boiling-point 123° , contains one carbon atom, which is combined with 3 others, or the carbon atoms are grouped in a similar manner as in the amyl compounds. The structure of isoctyl alcohol will therefore most probably be expressed by the following formula:—



oil is inactive. This physical difference is most probably caused by a different arrangement of the molecules, and not by a different grouping of the atoms in the molecule.

By distilling sebacic acid with caustic baryta, Riche* obtained the hydrocarbon C_8H_{18} , which boiled at 127° . Riche, however, did not obtain this compound in a pure state. I prepared this hydrocarbon in the same way, and found that the distillate is a mixture of different compounds, just as is the case when suberic and azelaic acids are distilled with baryta†. The pure hydrocarbon, isolated from this mixture by means of strong acids and so on, boils at 123° – 125° , and has the same specific gravity as that from isotyl alcohol, viz. 0.7083 at $12^\circ.5$. These two hydrocarbons appear, therefore, to be identical, and the carbon atoms in sebacic acid must also be arranged in a similar manner as in isooctyl alcohol.

The secondary amyl and octyl alcohols may be considered to be derived from the tertiary butyl alcohol, in a similar manner as the butyl and amyl alcohols formed by fermentation from the secondary propyl alcohol, viz.—

		Boiling-point.	Difference.
Secondary propyl alcohol,	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{OH} \end{array} $	84°	
			24°
Fermentation butyl alcohol,	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array} $	108°	
			24°
Fermentation amyl alcohol,	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array} $	132°	
Tertiary butyl alcohol,	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{COH} \\ \\ \text{CH}_3 \end{array} $	82°	
			26°

* Ann. der Chem. und Pharm. vol. cxv. p. 111.

† Dale, Journ. Chem. Soc. New Ser. vol. ii. p. 258.

	Boiling-point.	Difference.
		26°
Secondary amyl alcohol,	$ \begin{array}{c} \text{C}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CHOH} \\ \\ \text{CH}_3 \end{array} $	108°
		3 × 24°
Secondary octyl alcohol,	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CHOH} \\ \\ \text{CH}_3 \end{array} $	181°

It is seen that the difference in the boiling-points in both series is about 24° for each increase of CH₂; and further, that the boiling-point of a member of the first series is the same as the boiling-point of that member of the second series which contains CH₂ more.

VI. "Announcement of the intention of the Swedish Government to send out a new Polar Expedition." In a Letter addressed to the President, by Prof. A. E. NORDENSKIÖLD. Communicated by the President. Received May 14, 1868.

Stockholm, May 9, 1868.

DEAR SIR,—Some days ago I had the pleasure of receiving your kind letter of the 12th February, and the same day I was informed that the sum necessary for a new Polar Expedition was furnished by some private gentlemen of Gottenburg. Since then this undertaking has been embraced with great interest by the Swedish Government and the navy, who have granted the new expedition a strong and excellent screw-steamer, which will be supplied with provisions for a year.

The main object of the expedition will be to penetrate northward from Spitzbergen; but several naturalists will also accompany it.

I hope the new undertaking will be embraced by you with the same interest as the former ones, though the measurement of an arc of meridian does not yet make the aim of our enterprise. But I think that during the expedition I shall be able to amend my omission of measuring the hill south of Fairhaven*, which surely will furnish an excellent datum for determining

* Philosophical Transactions, 1824, p. 290.