PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXXIX.—*On the Products of the Decomposition of Castor Oil. No. 3. On the Decomposition by Excess of Alkaline Hydrate.*

By E. Neison.

By the distillation of castor oil with excess of alkaline hydrate, Bouis (*Compt. rend.*, xxxiii, 143) in 1851 obtained a volatile oil, which he regarded as octylic alcohol.

From the first, however, the exact products of this reaction have been uncertain, and there exists much discrepancy between the results of different investigators. Bouis, as above stated, first regarded the product as octylic alcohol, and after having been for a short time inclined to consider it as heptylic alcohol, returned, on further investigation, to his previous opinion. Bouis published no description of the method of purification adopted by himself; and the next three investigators, by simply fractionating the crude product, obtained a moist substance of variable nature. On this account, although Moschin in 1852 (*Ann. Chem. Pharm.*, lxxxvii, 3) obtained results indicating that the substance was octylic alcohol, Railton (*Chem. Soc. J.*, vi, 205) and Wills (*Chem. Soc. J.*, vi, 307) in 1853 found the reactions and analyses of their products inconsistent with this view; and were led to regard it as heptylic alcohol. Towards the end of 1853, Bouis (*Compt. rend.*, xxxviii, 935) published the method of purification adopted by himself, and gave results supporting the view that it was octylic alcohol. This view met with further confirmation from the researches of Squire (*Chem. Soc. J.*, vii, 108) and Cahours (*Compt. rend.*, xxxix, 259) in the course of the following year.

In 1855 Limpricht, who had turned his attention to the subject, threw new light on the question, by declaring (*Ann. Chem. Pharm.*, xciii, 242) that, in the reaction neither octylic nor heptylic alcohol was produced, but octylic aldehyde. In the same year Bouis (*Compt. rend.*, xli, 603) for the first time published the full details of his own method of preparation; and maintained that while usually nearly pure octylic alcohol is produced, yet under certain modifications octylic aldehyde might also be formed. Here for a short time the question rested as apparently solved.

Two years later, in 1857, Städeler (*J. pr. Chem.*, lxxii, 241) published a more thorough investigation of the products of the reaction, and stated that there was formed neither octylic alcohol nor aldehyde, but a mixture of heptylic alcohol and methyl-hexyl ketone (methyl-œnanthol), which latter had been mistaken for its isomeride, octylic aldehyde. Dachauer in the following year, 1858 (*Ann. Chem. Pharm.*, cvi, 269), obtained results showing that the product contained, as Städeler stated, methyl-hexyl ketone; but maintained that the alcohol produced was octylic and not heptylic. Petersen, however, in 1861 (*Ann. Chem. Pharm.*, cviii, 69) obtained results confirmatory of the view that the alcohol produced was heptylic and not octylic. After a short rest, the question was again taken up by Chapman in 1865 (*Chem. Soc. J.*, xviii, 290), who obtained results indicating that whilst

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not also be varied. And this appeared the more probable, as by this means it is known that members of either the heptyl or octyl group can be produced at pleasure as heptyl aldehyde or methyl-hexyl ketone.

It was now also possible to undertake the further elucidation of the question, from a different basis, namely by the reduction of the substances under examination to known bodies of well established constitution; and this appeared a more favourable plan than the older method, inasmuch as the differences in composition to be determined by analysis were small, and readily influenced by the presence of mere traces of the accompanying products. The progress of chemical research of late years enables this method to be readily executed, as many terms of the then unknown heptyl series have been discovered and their properties well established, mainly through the researches of Schorlemmer, Grimshaw, Franchimont, &c.

From the known properties of the heptyl group, it was evident that the only member of the possible alcohols of this series that could possess a boiling-point as high as 170°—180°, would be a primary one, yielding a heptylic acid on oxidation.

It would also appear, from the boiling point of normal octylic alcohol being as high as 196°—197° (Renesse), that an alcohol of this series boiling between 175°—185°, could not be a primary alcohol, and would yield a ketone and acids of lower series on oxidation.

Similarly many other methods appeared open to determine whether a mixture of two alcohols might not be produced by certain of the modifications of Bouis' original process, which had been employed by Städeler, Petersen, &c., who had obtained an alcohol giving on analysis numbers in accordance with those of the heptylic series, and not with those of the octylic series.

The method of preparing the mixture of castor oil, sodium hydrate, and water that was employed throughout was as follows:—The sodium hydrate, roughly powdered, was well mixed with the castor oil, and then, after adding the water, the whole was gently heated, stirring constantly until it solidified. As thus obtained, the mixture consisted of a hard yellow mass, with a smooth surface and fracture. It was distilled in quantities of from one to two hundred grams from a copper flask, by means of a Bunsen burner.

A. To determine the properties of the crude oil a mixture made from

The second and third portions gave gelatinous precipitates with sodium acid sulphite, and the last portion completely solidified with it.

B. For comparison with this result, a mixture made with only one-fourth the amount of water was distilled, at first gently, and subsequently at a higher temperature. The resulting oil was exactly like the last in appearance, and 130 grams were distilled. It separated into 2 per cent. boiling below 140°, into one-sixth boiling between 140°—165°, nearly one-third boiling at 172°—177°, and not quite one-half boiling between 177°—185°. The two products thus appear identical. The fractions of the last were re-distilled, and the portions of each boiling above its upper limit, added to the next fraction above. Fraction 140°—165°, separated into one-sixth boiling below 140°, and one-third boiling between 162°—167°, the remainder boiling above. Fraction 168°—177° gave a mere trace below 168°, and three-fourths between 173°—178°, but chiefly at 176°—177°. Fraction 177°—185° gave a few drops below 170°, two-fifths between 176°—178°, two-fifths between 180°—182°, and the remainder boiling above 185°.

The two chief portions, therefore, came over between 176°—178° and 180°—182°, the former being the largest, and the two constituting three-fourths of the crude oil. From both portions nearly solidifying with acid sodium sulphite, it was evident that the portion boiling at 176°—178° must be a mixture, as the boiling point of methyl-hexyl ketone is only 172°. A portion was distilled from potassium hydrate to destroy the ketone by Bouis' method. It separated into one-fifth boiling at 167°—173°, evidently consisting chiefly of methyl-hexyl ketone, one-tenth between 175°—177°, apparently unaltered, and two-fifths boiling between 179°—184°. The residue was the brown resinous mass produced by the polymerisation of the ketone by the potassium hydrate. From this, then, it would appear that, of the portion boiling between 176°—178°, three-fifths was ketone and two-fifths alcohol.

C. A mixture of 5 parts of sodium hydrate, 4½ parts of castor oil, and 1 part of water, was converted into a soap by the method already described, and distilled as quickly as possible by a powerful heat. The oil presented exactly the same properties as the last, and 220 grams were distilled.

Below 140° some 5 grams came over, chiefly at about 125°, and between 140°—168° about the same quantity also distilled, chiefly near 160°; between 170°—175° one-twelfth came over, and between 175°—177° a similar quantity. After steadily boiling between 177°—179° until more than one-half had passed over, it rose to 180°, between which and 182° one-sixth distilled, finally rising slowly to 200°, nearly one-sixth more distilling over.

In this case it was noteworthy that the fraction boiling at the first distillation below 170° was very small, the whole seeming to boil at higher temperatures. Each fraction was then re-distilled on the same system as before. Portion 140°—168° separated into one-sixth boiling below 160°, and one-sixth boiling between 165°—168°, the rest, of course, boiling above. Portion 168°—177° separated into two-fifths boiling at 176°—177°, and one-fifth boiling 170°—175°. Portion 178°—182° separated into a few drops boiling below 170°, about 5 per cent. boiling between 171°—175°, and three-fifths between 176°—178°. Portion 182°—200° gave one-half boiling at 176°—178°, and the rest boiling between 179°—182°. Finally, of the crude product over three-fifths boiled between 176°—178°, and one-fifth between 179°—183°. The resulting oily liquids appearing identical with the corresponding fraction in series B, the two were mixed.

D. Equal weights of sodium hydrate and castor oil with one-fourth the weight of oil of water, were converted into a soap and distilled as quickly as possible at a high temperature. The resulting oil was nearly colourless.

Equal weights of sodium hydrate and castor oil with one-fifth of the weight of oil of water, were converted into a soap and distilled gently at first, the heat being somewhat increased toward the end.

Twelve parts of sodium hydrate, 15 of castor oil, and 2 of water were converted into a soap and distilled at a moderate temperature.

The oil from each of these series of experiments, on being examined, appeared to possess the same properties, all solidified with acid sodium sulphite, and all contained an alcohol besides the ketone; the three crude oils were, therefore, mixed, and 240 grams of them distilled.

Below 140°, chiefly about 125°, one-twentieth; between 140°—170°, one-twenty-fifth; between 170°—178°, chiefly at 176°—177°, nearly two-fifths; and between 178°—184° one-half came over. The last two portions were re-distilled separately. Portion 170°—178°, a few drops below 170°, one-half between 176°—180°, and the rest between 178°—181°. Portion 178°—184°, nearly two-fifths between 176°—178°, and three-fifths between 179°—183°, but chiefly at 179°—181°. These two portions, comprising 85 per cent. of the crude oil, were added to the similar portions from series B and C, as they all consisted of a mixture of a ketone and alcohol, apparently the same in each.

It was evident that, by this means, the process of determining the products would be considerably shortened; as if the resulting oil could be shown to consist merely of one ketone and one alcohol, variations made in the method of conducting the reactions and in the proportions of oil, water and sodium hydrate could exert no influence upon the nature of the product. The results of these fractional distillations show that the proportions of the two are certainly varied by these means.

It now remained to separate the ketone from the alcohol in the mixture obtained from the three series of experiments. Forty grams of oil, boiling at 173°—178°, was shaken up with sodium acid sulphite. The whole solidified to a white crystalline mass, which was collected, washed well with cold water, pressed between filter paper, and the mass decomposed by a solution of sodium carbonate. The layer of oil floating on the surface was separated, dried over calcium chloride, and distilled; 85 per cent. came over between 174°—176°, and was marked methyl-hexyl ketone β, while the residue consisted of a mixture of the ketone and alcohol. Repeated crystallisation with acid sodium sulphite failed to free the ketone β from some trace of alcohol.

For the purpose of preparing some pure methyl-hexyl ketone, a quantity of the crude oil was acted on by a bichromate oxidising solution ("Schorlemmer's," consisting of potassium bichromate, 2 parts; sulphuric acid, 3 parts; and water, 10 parts); and after standing for some time, the whole was distilled. The layer of oil on the distillate was separated, washed with a solution of sodium carbonate, and then with water, dried over calcium chloride, and fractionated. Between 170°—174°, three-fifths only distilled, the rest coming over between 174°—176°, owing to the presence of a trace of alcohol. A second portion of the crude oil was now treated in a similar manner, and three-fourths of the oily distillate came over between 170°—174°. The two portions boiling between 170°—174° were again fractionated, and the portion distilling between 171°—172°, amounting to nearly nine-tenths of the whole, collected; it was found to consist of pure methyl-hexyl ketone (marked δ).

Before destroying the ketone in the mixed distillates by treatment with potassium hydrate after Bouis' system, it was necessary to ascertain that, by so doing, no new compound was formed that could interfere with the results. Twenty-five grams of the pure methyl-hexyl ketone (δ) were accordingly placed in a flask with inverted condenser attached, and heated over potassium hydrate for two hours, the whole turning dark-red brown. It was then fractionated, and only one-tenth distilled between 160°—180°, and rather more than a tenth between 180°—260°, the remainder consisting of a dark reddish-brown resinous mass. The distillates, on treatment with more potassium hydrate, were similarly converted into a resinous substance. It was evident, therefore, that the effect of the treatment with solid potassium hydrate was simply to remove the ketone without introducing anything else.

Eighty-five grams of the oil, boiling between 170°—175°, were treated with solid potassium hydrate; the liquid turned pale yellow, gradually darkening to a deep red after twenty-four hours. It was distilled from potassium hydrate, and separated into one-tenth boiling between 140°—148°, one-third between 173°—180°, and one-fourth between 180°—190°, the remainder not coming over. The three fractions were all allowed to stand for some days over solid potassium hydrate, which turned them all yellow, and were then mixed and re-distilled; one-fifth came over below 170°, one-fifth between 170°—180°, and one-half between 180°—187°. The last two fractions again allowed to stand over potassium hydrate still turned yellow, they were again distilled from potassium hydrate, two-fifths coming over between 170°—178°, and a like amount between 178°—184°. Of the original oil, however, over one-half had been resinised by the potassium hydrate.

The greater portion of the oil distilling between 178°—184° (series B, C, D), was allowed to stand over potassium hydrate, and the resulting deep red liquid distilled from fresh portions of hydrate. Between 160°—170°, only a trace came over; between 173°—178°, one-fifth; and between 179°—185°, nearly one-half. The last two portions were still acted on by potassium hydrate, and on being mixed and again rectified from potassium hydrate, separated into two-fifths coming over between 173°—178°, and three-fifths between 178°—185°. Of the crude oil, however, two-fifths had been resinised by the potassium hydrate. By similar treatment, the portion boiling between 140°—168° of the three series (B, C, D), was separated by three distillations from potassium hydrate into nearly one-half boiling between 120°—168°; one-eighth boiling between 173°—178°; and one-fourth boiling between 178°—185°, the rest having been resinised.

The corresponding fractions of each of these three portions that had been thus acted on by potassium hydrate, were now mixed. The portion boiling between 178°—185° was allowed to stand for some days over potassium hydrate, which still turned it slightly yellow, and was rectified over potassium hydrate. Between 174°—178°, one-third came over, two-fifths between 179°—186°, and one-tenth below 200°, some being still polymerised. After being again treated with, and rectified over potassium hydrate, it was finally separated into one-seventh boiling between 174°—178°, and six-sevenths between 179°—182°. Potassium hydrate had no longer any action on this latter portion, which was, therefore, Bouis and Schorlemmer's octylic alcohol, and was marked α.

An examination of the above percentages shows that of the oil boiling between 170°—178°, about one-fifth, and of the oil boiling between 178°—185°, about one-half, was octylic alcohol, nine-tenths of the rest being the ketone. It was also apparent that only by five or six distillations from potassium hydrate could the ketone be removed, a circumstance having important bearings on previous investigations.

There could be no doubt that the alcohol obtained as above was what Bouis and Schorlemmer have shown to be octylic alcohol; it was, however, carefully analysed by combustion with cupric oxide and oxygen gas.

For	Theory.	Found.
C_8	73·84	73·69
H_{18}	13·84	13·67
O_4	12·32	12·64
	100·00	

Although this gave direct evidence that only one alcohol, and that octylic, existed in the crude product, it was judged best to make a direct search for Städeler's and Petersen's heptylic alcohol by a method based on their own processes.

Fifty grams of the oil, distilling between 173°—178°, was shaken up with acid sodium sulphite solution, and after standing for 24 hours the white crystalline mass obtained was washed with water and ether, and squeezed in muslin, moistening well with ether. The resulting crystalline mass was decomposed by hot water, the oil which rises to the surface, and amounting to half that used, was collected, dried, and distilled. Between 174°—178° one-seventh came over, and five-sixths between 178°—180°. This last portion was again treated with acid sodium sulphite, after washing with water, moistening with ether, and squeezing between folds of muslin. On decomposing this purified crystalline mass with hot water, about one-third of the oil employed was obtained, and distilled between 173°—178°. The ether from the last obtained ethereal washings was distilled off, and one-half of the weight of oil employed obtained, two-thirds of which boiled between 178°—180°, but instantly solidifying with acid sodium sulphite solution. It was evident that by this means the ketone could not be obtained pure.

From the ethereal washings of the first treatment with acid sodium sulphite, the ether was distilled off, and the resulting oil obtained, 25 grams in amount, was fractionated, when one-tenth came over between 174°—179°, and nine-tenths between 179°—184°, but both portions still contained ketone, as they combined with acid sodium sulphite. They were therefore mixed, and the oil from the ethereal washings of the second treatment with acid sodium sulphite added, and the whole again treated with the sulphite. The resulting semi-solid mass was again pressed through folds of muslin, when two-thirds of the oil easily separated, and on treating this portion again with acid sodium sulphite, only a mere trace combined. The oil separated from this was then washed, dried, and distilled, and the portion coming over between 178°—180°, amounting to nine-tenths of the whole, was collected. As this was obtained in the same manner as Städeler's heptylic alcohol, it was so called. Petersen, who prepared his in the same manner, gave his alcohol a final rectification over potassium hydrate. A portion of this was therefore similarly treated, little apparent action taking place, and the resulting alcohol still distilled between 178°—180°. This was termed Petersen's heptylic alcohol. Further examination of these products was deferred.

E. It was also necessary to examine the products of the methods of Bouis and Schorlemner. A soap was prepared from 7 parts of castor oil, 6 of sodium hydrate, and 2 of water, and distilled by means of a powerful heat as quickly as possible. The pale yellow oil, amounting to one-fifth of the weight of castor oil employed, was allowed to stand over, and then rectified from, potassium hydrate, 80 grams being taken. Between 140°—170° about one-twentieth came over; between 170°—178°, one-half; between 178°—185°, one-tenth; and between 185°—200°, one-sixth. The fractions 140°—185° were redistilled from potassium hydrate; one-tenth came over below 170°, and three-fourths between 170°—180°. This latter portion was again distilled from potassium hydrate, when one-half came over between 173°—182°, and two-fifths between 182°—200°. The former portion was rectified once more from potassium hydrate, when one-tenth came over below 170°, one-third between 173°—180°, and the rest between 180°—186°; but the potassium hydrate had now no longer any action on the oil, which remained perfectly colourless. The various portions boiling above 180° were now mixed and rectified over potassium hydrate, which remained throughout perfectly unaffected, and the oil distilled between 181° and 183°. The amount obtained was one-half of the crude product, the remainder, consisting of one-twentieth, distilling between 173°—178°, about twice as much distilling below 150°, and one-third which had been destroyed by the action of the potassium hydrate.

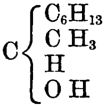
This is Bouis and Schorlemmer's octylic alcohol, and was marked β, and it was evident that any heptylic alcohol that might have been formed must be contained in the small portion boiling between 173°—178°, which was unaffected by potassium hydrate.

F. A soap was made from equal parts of sodium hydrate and castor oil, with a quantity of water equal to one-fourth of the weight of oil, and was distilled at a medium temperature, the resulting oil being allowed to stand over potassium hydrate for a long time. Eighty grams of the dark-red thick oil obtained was then rectified repeatedly over potassium hydrate, in the same manner as the last, until the hydrate remained without action on the oil. By this means the crude oil was separated into one-thirtieth distilling below 165°, one-twentieth distilling between 170°—180°, and one-third of its weight of pure octylic alcohol, boiling between 181°—184°, which was added to the last, while more than one-half had been destroyed by the action of the potassium hydrate. Comparison of this result with the last shows that the percentage of ketone increases as the temperature is lowered.

After having been again rectified, the octylic alcohol (β) boiled constantly between 181° and 183°, and had a specific gravity of 0·823 at 16° C. It gave on analysis the following very accordant numbers :—

For	Theory.	Found.	
C_8	73·84	73·76	73·70
H_{18}..........	13·84	13·76	13·75
O_4	12·32	12·48	12·55
	100·00		

This was, therefore, a pure octylic alcohol, and obviously, from its boiling point, a secondary alcohol, at least; and according to Schorlemmer it was the secondary alcohol methyl-hexyl carbinol—



$$C\left\{\begin{array}{l} C_6H_{13} \\ C\,H_3 \\ H \\ O\,H \end{array}\right.$$

On oxidation this gives, of course, a mixture of caproic and acetic acids, as was found by Schorlemmer. It was necessary, however, to redetermine this point for the alcohol in question.

Pure octylic alcohol, as prepared by each of the preceding methods, was oxidised by Schorlemmer's bichromate solution as long as any action took place, and the whole distilled. The aqueous distillate separated from the ketone which formed was neutralised with sodium carbonate, evaporated to dryness, and after being completely decomposed by dilute sulphuric acid, distilled.

The distillate consisted of an oily acid floating on an aqueous layer, consisting of acetic acid holding a little of the oily acid in suspension. To determine the nature of the oily acid it was washed cautiously and converted into the barium and silver salts, which were analysed.

For $Ba\{C_6H_{11}O_2\}_2$,	Ba per cent.	Theory 37·31.	Found 37·58
For $AgC_6H_{11}O_2$,	Ag per cent.	Theory 48·43.	Found 48·37
For $AgC_6H_{11}O_2$,	Ag per cent.	Theory 48·43.	Found 48·47

It was, therefore, caproic acid, and consequently the octylic alcohol is the same as Schorlemmer's methyl-hexyl carbinol.

The ketone found floating on the aqueous distillate was dried after washing, and distilled, coming over between 170°—172°, and was evidently methyl-hexyl ketone.

G. For the purpose of still further examining the alcohol, a number of its derivatives were prepared, the olefine being first taken.

A portion of the alcohol was rectified twice from fused zinc chloride, and fractionated after drying over calcium chloride and potassium carbonate. Between 120°—125° only a few drops distilled, then three-fourths came over between 125°—128°, and one-fifth more below 130°. After removing the last traces of moisture by a second rectification, the pure olefine was obtained, boiling between 126°—128°, and having a sp. gr. of 0·714 at 22°. This was evidently octylene, which Bouis found to boil at 125°, and to have a sp. gr. of 0·723 at 16°, as a heptylene would have boiled below 123°. The alcohol therefore must have been entirely free from any heptyl alcohol.

The octylene thus obtained combined energetically with bromine to a pale yellow, heavy, oil, distilling, with decomposition, at about 200°, and slowly losing bromine at 100°. It could not be perfectly purified, but was merely well washed with dilute potassium hydrate and water, and dried. On analysis it gave—

For $C_8H_{16}Br_2$.	Theory.	Found.
Br per cent.	58·8	57·6

On passing a current of chlorine through octylene, it is entirely absorbed, the whole becomes hot and turns thick and green, and after a time evolves hydrochloric acid gas. The current is then stopped, and the heavy oil is well washed with water and dilute sodium carbonate, dried, and rectified. Nine-tenths comes over between 197°—240°, while the rest blackens and decomposes at that temperature. After washing and drying the distillate, it distils nearly entirely between 206°—210°, and forms a heavy oily liquid, with a peculiar strong aromatic odour, On analysis, it gave the following results, showing it to be octylene dichloride:—

For $C_8H_{16}Cl_2$.	Theory.	Found.
Cl per cent.	38·8	38·2

If the current of chlorine is continued merely for a short time, so as to convert only a portion of the octylene into chloride, it is separated, on careful fractionation, into octylene dichloride boiling between 205°—210°, and unaltered octylene boiling at 128°—135°.

Pure octylic alcohol was treated with bromine and phosphorus, and the thick, heavy, red oil obtained was well washed with dilute potassium hydrate and water, and dried. Pale yellow oil, possessing a slight pleasant odour, decomposing slightly when kept, and decomposing at 190° before distilling. On analysis it gave the following numbers:—

For $C_8H_{17}Br$.	Theory.	Found.
Br per cent.	41·45	41·28

By acting on octylic alcohol with phosphorus pentachloride as long as any hydrochloric acid gas was liberated, washing the resulting pink oil with water and dilute potassium hydrate, and carefully fractionating, a colourless thin mobile liquid, with a faint odour not unlike oranges, was obtained. This boiled between 168°—174°, and gave, on analysis, numbers showing it to be *octylic chloride.*

For $C_8H_{17}Cl$.	Theory.	Found.
Cl per cent.	23·90	24·31

If prepared by Groves' method, by the simultaneous action of zinc chloride and hydrochloric acid, it is readily obtained, but mixed with a small quantity of octylene.

H. It now remained to examine the heptylic alcohols of Städeler and Petersen, and as their alcohols were sensibly identical, a mixture of the two was used for this purpose.

The alcohol was twice rectified over fused zinc chloride, and the distillate dried and fractionated, when three-fourths came over between 123°—127°, chiefly at 125°—126°, and one-fourth more nearly below 130°. The residue, boiling a little above 130, was shaken up with acid sodium sulphite, when it partially solidified, showing the presence of a trace of ketone in the original alcohol; this could not be detected by the acid sodium sulphite. The olefine thus obtained, which possessed the same physical characters as that from octylic alcohol, was shown by its property of boiling at 125°—127° to be not a heptylene, which would have boiled below 100°, but octylene.

From Petersen's heptylic alcohol, treated in a similar manner, was separated a small quantity of the ketone, which, boiling at 170°—172°, was evidently methyl-hexyl ketone.

The supposed heptylic alcohol was, therefore, without doubt, essentially octylic alcohol mixed with a small quantity of methyl-hexyl ketone. The presence of this latter would account for the increased percentage of chlorine found by Petersen in the chlorine-derivative, and is in accordance with the vapour-density, 4·34, obtained by him. For the purpose of comparison with the pure octylic alcohol, this alcohol of Städeler and Petersen was analysed, and gave the following results:—

	Theory.		Theory.	Found.
C_7	72·42	C_8	73·84	73·63
H_{16}	13·79	H_{18}	13·84	13·83
O	13·79	O	12·32	12·54
	100·00		100·00	

The cause of the low percentages obtained by Petersen and Städeler remains undiscovered, but possibly lay in the alcohol retaining a trace of moisture. An octylic alcohol retaining about one and a half per cent. of moisture, would give numbers agreeing with those of Städeler and Petersen; and octylic alcohol, like others of this series, does retain moisture with some persistency.

I. It remained to examine also the small portion of oil boiling between 170°—178°, obtained in the preparation of the octylic alcohol by Bouis and Schorlemmer's process; this was not affected by potassium hydrate. For although a similar liquid obtained by the latter had been shown by him to consist of a mixture of hydrocarbons and octylic alcohol, yet it could not be assumed to be likewise so with this portion.

By the action of phosphorus pentachloride it turned red, and evolved much hydrochloric acid gas from presence of an alcohol. After well washing with dilute sodium carbonate and water, it was dried and rectified repeatedly over potassium carbonate, by which means it was completely separated into two portions, boiling at 170°—175°, and 190°—210°, possessing all the properties of octylic chloride and octylene dichloride, and on analysis gave numbers agreeing with these, although the quantity of each was too small for complete purification.

A second portion was then rectified several times over fused zinc chloride, and on fractionation was resolved into octylene boiling between 123°—128°, and a small trace of oil boiling between 130°—140°, and containing a small quantity of ketone. This oil then, like Schorlemmer's, probably consisted of octylic alcohol, whose boiling point had been lowered by admixture with a small quantity of octylene, and a trace of methyl-hexyl ketone.

J. There was only now a small quantity of oil from the preparation of octylic alcohol, &c., that had not been examined, and this had been merely rectified over potassium hydrate several times. It was twice distilled from fused zinc chloride, and after drying, it was by fractionating resolved into nearly equal volumes of methyl-hexyl ketone boiling at 169°—173°, and octylene boiling at 125°—129°; while a small quantity remained which boiled between 130°—140°, consisting of a mixture of the two.

The octylene obtained by this means was converted into octylene dichloride by the action of a current of chlorine in presence of water, and the resulting chloride, which boiled at 206°—210°, was analysed, with results agreeing fairly with the theoretical numbers.

For $C_8H_{16}Cl_2$.	Theory.	Found.
Cl per cent.	38·8	39·3

This portion, therefore, as might have been expected, consists of a mixture of methyl-hexyl ketone and octylic alcohol.

K. It was noticed that a portion, if not the whole of the methyl-hexyl ketone, whether obtained directly from the crude oil, or by the action of oxydising agents, usually boiled as high as 176°—178°. As this is the boiling point of Limpricht's octylic aldehyde, instead of 172°, the boiling point of methyl-hexyl ketone, it seemed to invite some further examination.

When impure methyl-hexyl ketone, boiling between 170°—178°, separated by simple rectification of the crude oil, is oxidised by repeated distillation with an oxidising solution (Schorlemmer's bichromate) as long as any action occurs, the resulting ketone boils between 170°—178°, but chiefly between 174°—177°. On investigation, however, this was found to be owing to its still retaining obstinately traces of alcohol, not separable by the action of either the oxidising solution, nor by that of acid sodium sulphite. By repeated rectification over zinc chloride this alcohol can be removed, and on distillation the liquid resolved into four-fifths boiling between 170°—173°, and one-eighth boiling at 165°—170°, while the rest came over below 174°, both the latter portions being almost pure ketone. That coming over at 165°—170° may, by careful and repeated fractionation, be separated into octylene boiling at 125°—133°, and methyl-hexyl ketone boiling at 169°—172°. The cause of the higher boiling point is therefore manifest, and explains probably that of Limpricht's supposed aldehyde.

When pure, methyl-hexyl ketone is a colourless, thin, limpid oil, having a peculiar aromatic odour, and hot, bitter taste. It boils constantly between 171° and 172°, and has a specific gravity of 0·811 at 18°. It is oxidised very slowly and partially by the action of potassium bichromate and dilute sulphuric acid, yielding a mixture of caproic and acetic acids. Nitric acid oxidises it energetically, forming nearly all the lower members of the acetic series of acids, together with nitro-compounds, amongst which dinitro-octylene predominates. By the action of phosphorus pentachloride it is slowly converted into chlorinated derivatives, octylene dichloride boiling at 195°—205° being the chief. Bromine acts energetically on the ketone, forming a dark, orange-coloured, thick, heavy oil, boiling, with decomposition, at 190°—210°, and having the characteristic aromatic odour found in both octylene chloride and bromide.

With a solution of acid sodium sulphite, the ketone forms a white crystalline mass, gradually hardening in the air. The compound has a very powerful, peculiar, penetrating, aromatic odour, exerting a strong action upon the eyes, and is but slightly soluble in alcohol or ether. By cold water it is slowly dissolved, with partial separation of the ketone, but by hot water it is rapidly and completely decomposed.

From its reaction there could be no doubt that Städeler, Petersen, and Schorlemmer's view of its constitution is perfectly correct.

L. For the purpose of ascertaining the effect of change of alkaline hydrate upon the products obtained, the oil produced by the distillation of mixtures of potassium hydrate and oil, in the proportion of from three of hydrate to one of castor-oil, to one of hydrate to three of castor-oil, was examined. The resulting products were, however, found to be identical in nature with those already described.

A similar result was also produced by the substitution of soda-lime for sodium hydrate, with the exception that the amount of sebacic acid was somewhat decreased.

M. From the results that have been detailed, it appears, therefore, that the sole product of the decomposition of sodium ricinolate by distillation with excess of sodium hydrate, consists of a secondary octylic alcohol, namely, methyl-hexyl carbinol, and the corresponding ketone, methyl-hexyl ketone, without any heptylic alcohol.

The ratio between the amount of alcohol and ketone appears to depend upon the excess of alkaline hydrate and the temperature employed, and the relatively greater yield of alcohol varies directly as the temperature and excess of alkaline hydrate, within, of course, proper limits.

It would therefore appear that the heptylic alcohol of Railton and Wills was a mixture of octylic alcohol and methyl-hexyl ketone; that of Chapman, a mixture of octylic alcohol with the same ketone and octylene; and in all probability that of Städeler and Petersen was somewhat impure octylic alcohol, not entirely free from moisture.

N. The properties of the pure products obtained by these methods, together with their derivatives, are at present undergoing more detailed investigation.