

LXXXIII.—*The Preparation of Active Amyl Alcohol and Active Valeric acid from Fusel Oil.*

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AMONG the substances which Professor Thorpe was desirous of examining with a view of determining their physical constants was the optically active constituent of fusel oil, and at his request I undertook the separation of this substance from the purified fusel oil of commerce.

The oil used (obtained from Messrs. Hopkin and Williams) was of German origin; it boiled from 125° to 133° , and had an average rotatory power of -2° in a 200 mm. tube.

Two methods have been employed in preparing active primary amyl alcohol; that of Pasteur, in which the fusel oil is converted into hydrogen amyl sulphate, the more soluble barium salt being then

separated from the less soluble compound, and the alcohol regenerated by hydrolysis with dilute sulphuric acid (*Compt. rend.*, **41**, 296); and that of Le Bel, in which hydrogen chloride is passed into fusel oil heated to the boiling point; the latter method depending on the fact that of the two constituents, the active alcohol is less readily converted into chloride under these conditions, and, therefore, accumulates in the material which escapes attack (*Compt. rend.*, **77**, 1021). Preliminary experiments were made by both methods, but as Le Bel's process was the less laborious, it was decided to employ it in preference to Pasteur's. The operation was at first conducted in the form of apparatus described by Just (*Annalen*, **220**, 149), but it was found that a reduction in volume of nine-tenths only led to the doubling of the rotatory power; 3 litres of purified fusel oil yielding 310 c.c. of an alcohol rotating -4° in a 200 mm. tube.

This result was disappointing in view of Le Bel's statement that in a similar manner, by a like reduction in volume, he obtained an alcohol exhibiting a rotatory power of -9° in a 200 mm. tube; but it is in fair accord with Just's observation that by the treatment of 15 litres of fusel oil rotating -2.43° , 950 c.c. of an alcohol rotating -4.6° in a 200 mm. tube were obtained, further treatment failing to increase the rotatory power.

At this stage of the work I learned from Professor Thorpe that far better results had been obtained by Professor Odling and Mr. J. E. Marsh by a modification of Le Bel's method, and my thanks are due to these gentlemen not only for furnishing details of their process, but also for permitting me to publish an account of my work in which their method has been exclusively employed.

The method consists in heating fusel oil in sealed tubes with twice its volume of fuming hydrochloric acid (sp. gr. 1.2) during about three hours at 100° . The tubes employed were about 5 ft. long, and of an average internal diameter of 1 in.; they were heated in iron tubes through which a current of steam was passed. Each tube contained from 130 to 150 c.c. of fusel oil, being filled about three parts full of the mixture of fusel oil and fuming acid, and could be employed five or six times without danger. When mixed together, the fusel oil dissolved in the acid, but after heating at 100° during three hours, three layers were always noticed in the tube, the middle layer, however, being sometimes narrow and hardly discernible. The top layer was found to consist almost entirely of amylic chloride, the middle layer of about equal proportions of amylic chloride and alcohol, together with a little acid, and the bottom layer of acid containing alcohol in solution, but free from amylic chloride.

The top layer was fractionally distilled and was found to boil at $95-100^{\circ}$, excepting a small quantity which came over towards the

end, when the temperature rose to 160° or higher. This high boiling liquid was collected separately.

The strongly acid middle layer was treated with excess of potassium carbonate, the oily layer separated from the alkaline solution, and afterwards fractionally distilled to separate the amylic chloride from the unattacked alcohol.

On diluting the bottom layer with water, some of the dissolved alcohol usually separated and was removed by means of a funnel. The strongly acid solution was then distilled, when the remainder of the alcohol came over with the first portion of the distillate.

As a rule about one-third of the alcohol originally taken was recovered in this way, and the effect of the treatment was to increase the rotatory power by about $1^{\circ} 30'$.

The product of the first treatment with fuming acid was then submitted to a second treatment. In this manner the process was continued, using, however, equal bulks of acid and alcohol, until no further increase in the rotatory power was produced.

The following table (p. 1133) is a summary of the results obtained. It will be seen that 16.2 litres of purified fusel oil gave 250 c.c. of an alcohol rotating $-8^{\circ} 30'$ per 200 mm., beyond which value it was not found possible to increase the rotatory power by this method.

It may be noted that the alcohol thus separated has a slightly higher rotatory power than that obtained by Pasteur (*Compt. rend.*, **41**, 296), but a lower rotatory power than that of Le Bel, unless of course the values given by these chemists are the specific rotatory powers of the alcohols obtained by them.

There is no guarantee that the alcohol thus obtained is a uniform substance; it may very well be a mixture of the active and inactive constituents of fusel oil, in such proportions that hydrogen chloride acts to an equal extent on each of them, and that consequently further treatment with acid does not lead to any increase in the rotatory power.

The active amyl alcohol was dried over fused potassium carbonate, and finally allowed to remain over anhydrous copper sulphate during about two months; on being then redistilled, it was found to boil at 128.35° to 129.15° under a pressure of 768 mm. Its density at $22^{\circ}/22^{\circ}$ was 0.818, and its rotatory power per 200 mm. at 22° , determined in a Laurent and also in a Duboseq polarimeter, was found to be $-8^{\circ} 30'$, using sodium light; thus giving as the specific rotatory power at 22° the value -5.2° . The alcohol had a more pleasant and less pungent odour than the ordinary amyl alcohol.

The conversion of active amyl alcohol, isolated by Pasteur's method, into valeric acid has been effected by Pedler (*J. Chem. Soc.*, 1868, **21**, 74) and Ley (*Ber.*, **6**, 1367). As the active amyl alcohol isolated by

AND ACTIVE VALERIC ACID FROM FUSEL OIL.

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Treat- ment.	Volume of alcohol used.	Average rota- tion in 200 mm. tube.	Volume of acid used.	Volume of alcohol recovered.	Rotation of recovered alcohol in 200 mm. tube.	Boiling point and rotation of chloride pro- duced.	Approximate volume of material boiling between 100° and 180°.
1	16,200 c.c.	-2°	Twice the bulk	5400 c.c.	-3° 30'	{ 97-101° + 6'	380 c.c.
2	5,400 c.c.	-3° 30'	"	1800 c.c.	-5° 15'	{ 96-100° + 12'	80 c.c.
3	1,800 c.c.	-5° 15'	Equal quantity	900 c.c.	-6° 30'	{ 95-99° + 20'	30 c.c.
4	900 c.c.	-6° 30'	"	450 c.c.	-8° 6'	{ 95-99° + 25'	20 c.c.
5	450 c.c.	-8 6'	"	250 c.c.	-8° 30'	{ 95-99° + 30'	8 c.c.
6	80 c.c.	-8° 30'	"	52 c.c.	-8° 30'	{ 95-99° + 30'	1 c.c.

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Le Bel's method has not seemingly been converted into valeric acid, and its primary nature established beyond question, it seemed desirable to submit a portion of this product to oxidation. After various trials, the following method was found to give the best results.

A solution of 40 grams of potassium dichromate in 150 c.c. of water was heated nearly to boiling in a reflux apparatus, and 10 grams of the alcohol allowed to pass slowly into the hot liquid by means of a stoppered funnel dipping to the bottom of the flask. The addition of the alcohol was completed in about 30 minutes. The contents of the flask were afterwards heated to incipient boiling during about six hours until all signs of action ceased. During the action carbonic anhydride was evolved, and towards the end a tarry-like substance separated. After standing during 24 hours in the cold, the contents of the flask were distilled, but only a small quantity of valeric acid passed over, the greater portion remaining, apparently as a chromium salt, in the tarry residue. This material was insoluble in water, but soluble in alcohol, from which it could be precipitated by the addition of water. When purified by fractional precipitation, it yielded 24.4 per cent. of chromium sesquioxide on ignition. When distilled with dilute sulphuric acid (1 to 1), it was slowly decomposed, valeric acid and water passing over into the receiver, five-sixths of the total yield of valeric acid being isolated in this way. The distillates were then rendered alkaline with sodium carbonate, and the oily layer consisting of amylic valerate (analysis gave C, 69.12; H, 11.7) having been separated, the solution of sodium valerate was evaporated and, when sufficiently concentrated, distilled with dilute sulphuric acid (1 : 1). The distillate was dried over calcium chloride and afterwards distilled. By this method 40 grams of the alcohol were found to yield 19 grams of valeric acid.

It has been shown by Pedler, and also by Ley, that acetic acid is a product of the oxidation of active amyl alcohol; my results confirm this conclusion, inasmuch as a noteworthy quantity of acetic acid was found in the aqueous distillate accompanying the valeric acid, and was isolated as the silver salt.

The active valeric acid thus obtained was found to boil at 174.5° to 175.3° under 768 mm. pressure; its density at $22^{\circ}/22^{\circ}$ was 0.936; its rotatory power at 22° , as determined in a Duboscq polarimeter, was found to be $+26^{\circ}$ in a 200 mm. tube, using sodium light, giving therefore 13.9° as the specific rotatory power.

For purposes of comparison, some of the fusel oil, rotating -2° per 200 mm., was oxidised by the method just described; approximately, the same percentage yields of valeric acid and amylic valerate were obtained, and the product was found to boil at 174.7° to 175.5° under 768 mm. pressure; its density was 0.928 at $22^{\circ}/22^{\circ}$; and its

rotatory power was $+5^{\circ} 52'$ per 200 mm. This result is noteworthy, inasmuch as a comparison of the rotatory powers of the active alcohol and acid with the rotatory powers of the fusel oil and acid derived from it, shows that the increase of rotatory power is in both cases in approximately the same proportion.

Since this work was completed, a paper by Guye and Chavanne has appeared in the *Compt. rend.*, **116**, 1454, in which it is stated that, using an alcohol of which the rotatory power was $[\alpha]_D -4.40^{\circ}$, an active valeric acid was obtained, having a rotatory power $[\alpha]_D = +13.64^{\circ}$, the density of which was 0.938 at 22° , and the boiling point $173-174^{\circ}$ under 730 mm. pressure, results corresponding very closely with mine.

The liquid boiling between 100° and 180° , isolated during the preparation of the amylic alcohol from the amylic chloride, was examined, by first shaking repeatedly with water to remove any alcohol which might be present, drying over calcium chloride, and afterwards fractionating in a Glynsky apparatus to remove amylic chloride. After repeated fractionation, the product amounted to 59 grams from 380 c.c. of the chloride obtained in the first treatments with hydrogen chloride, and was found to boil at $166.9-167.9^{\circ}$ under a pressure of 758 mm. An analysis gave figures showing that its composition corresponds with that of diamylic ether, $(C_5H_{11})_2O$.

0.2627 gave 0.3367 H_2O and 0.7278 CO_2 . C = 75.95; H = 13.93.

$(C_5H_{11})_2O$ requires C = 75.92; H = 14.24 per cent.

To check this result, two vapour density determinations were made in Professor Thorpe's modification of Hofmann's apparatus (*J. Chem. Soc.*, 1880, **37**, 147), and these gave 80 (heated in the vapour of turpentine) and 77.7 (heated in steam), as against 79, the calculated density for diamylic ether.

Diamylic ether appears to be a constant product of the action of fuming hydrochloric acid on amylic alcohol, the amount formed, however, being small. Attempts to prepare it by heating amylic alcohol with amylic chloride, in varying proportions, at 100° in sealed tubes during several hours were fruitless, and hence, probably, the presence of hydrogen chloride is necessary to effect the condensation.

In conclusion, I beg to tender my heartiest thanks to Dr. W. P. Wynne for aid given during the progress of the work.

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