SOME CONDITIONS AFFECTING THE ETHER VALUE OF BRANDY.

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Some little while ago we analysed a brandy which showed an ether value* of 98·8, the alcoholic strength of the sample was 54·2. This sample, we were informed, was unreduced, and had been drawn direct from bond. At the same time we examined a sample which was stated to be the same brandy from duty paid stock, and reduced in strength to 44·5. To our surprise, the ether value of the latter was found to be only 66·5. At first we were inclined to doubt whether the two samples actually represented the same brandy originally, but our subsequent investigations lead us to say that we believe this to have really been the case. We were further informed that the spirit had been "broken down" with New River main water, the object of using this instead of distilled water being, according to our informants, to avoid the slightly mawkish taste that distilled water occasionally imparts to brandy. The cellar operations, which consist substantially in pumping the spirit into a vat, reducing therein with water, with subsequent filtration through paper pulp, and finally bottling, were carried out in the presence of one of us, and samples were drawn at various stages in order to ascertain, if possible, whether any of the operations or vessels were responsible for the falling off of the ether value recorded.

* Expressed in grams per 100 litres of absolute alcohol. In order to avoid needless repetition, we may say that throughout this paper secondary products will be expressed in those terms, and alcoholic strength in per cent. by volume.

As a result, we found that none of the operations or vessels—apart from the "breaking down" with New River tap water, and disregarding for the moment the condition of the bottles—had any material influence in this direction. An examination of the influence of the reducing medium, however, afforded evidence that this factor must be taken into serious consideration by shippers and merchants. In addition, we are satisfied that the condition, or, rather, quality, of the glass bottles employed in bottling is a question deserving the serious attention of those interested. We propose briefly to allude to the latter point first.

The bottles examined by us were of clear white glass, stated to be of excellent quality, and guaranteed to be well cleaned before delivery. Half a dozen of these bottles were filled by us with distilled water, and a few drops of phenolphthalein solution were then added to the contents of each. In two cases a very pronounced pink coloration was produced at the point of contact of the fluid with the glass, but on shaking up this disappeared. After standing, however, for a few days,* the two bottles were observed to have developed a distinct pink colour throughout the liquid. After ten days the contents of the various bottles were titrated with $\frac{N}{10}$ acid, using methyl orange as indicator. The two bottles affected required 1·2 c.c. each for neutralization, the others only 0·3 to 0·4 c.c. It is fairly obvious, therefore, that bottles which display the slightest alkaline reaction should be rejected.

With regard to the influence of the nature of the water used for reducing, we were able to obtain direct evidence that the ether value is seriously affected thereby. The results of the experiments were as follows :

Number of Sample.	Alcoholic Strength.	Alcoholic Strength of Original.	Water Used for Dilution.	Ether Value.	Ether Value of Original.	Time in Days.
1.	44·37	55·46	New River main	66·9	78·2	7
Same as 1.	45·40	do.	do.	67·0	do.	do.
3.	39·14	55·88	do.	87·4	100·6	12
Same as 3.	39·09	do.	distilled	98·4	do.	do.
5.	33·15	55·60	New River main	55·2	69·3	2
Same as 5.	33·12	do.	distilled	62·7	do.	do.
7.	24·13	48·27	New River main	51·7	57·3	4
Same as 7.	23·62	do.	distilled	57·3	do.	do.

N.B.—The *time* refers to the number of days the mixtures of brandy and water were allowed to stand before being analysed.

From the above it will be seen that distilled water exercises very little, if any, influence on the ether value, but that an undistilled water (of otherwise excellent quality) may cause a falling off of nearly 15 per cent., if not more. The figures given at the commencement of this paper indicate that a loss of as much as 30 per cent. may arise from this cause.

We found also, as might have been expected, that the use of New River tap water appreciably affected the acid value of brandies. The following results illustrate the differences obtained in this regard, using distilled and tap water respectively as diluents.

* We need scarcely say that all the bottles were kept tightly corked and completely filled throughout.

No.	Water Used.	Total Acid.
3.	[Original brandy] ...	128·8
	Distilled water ...	125·0
	New River main water	80·6
4.	[Original brandy] ...	46·6
	Distilled water ...	58·6
	New River main water ...	32·5
5.	[Original brandy	43·7
	Distilled water	55·3
	New River main water ...	13·3

We further observed that the use of tap water influenced the colour of the spirit to a much greater extent than does distilled water.

Having obtained these results, it seemed to us to be of interest to ascertain whether any other conditions, more particularly the blending of different brandies, materially affected the ether or other values. With this end in view, we made a number of blends, consisting of two brandies, each of which had been previously analysed. After blending, the samples were analysed at once, and in a number of cases were re-examined at the end of three weeks. For the sake of convenience we think it best to give the results for the total acid, non-volatile acid, and ethers in separate tables.

TOTAL ACID.

No. of Experiment.	Acid in Each Sample before Blending.	Theoretical Mean.	Found in Blend.	Increase or Decrease Per Cent.
1.	40·9 / 69·6	55·25	45·4	−17·8
2.	35·1 / 43·1	39·1	40·0	+ 2·3
3.	109·7 / 43·7	76·7	90·5	+15·2
4.	66·9 / 49·6	58·25	62·7	+ 7·0
5.	19·2 / 128·8	74·0	61·2	−17·2
6.	144·1 / 19·2	81·6	81·4	− 0·24
6*a**.	do.	do.	103·1	+20·8
7.	19·2 / 55·0	27·1	41·9	+35·3
8.	55·0 / 128·8	91·9	78·0	−15·1
8*a***.	do.	do.	89·6	− 2·3
9.	55·0 / 144·1	99·5	99·1	− 0·4
9*a**.	do.	do.	112·0	+11·1
10.	44·7 / 128·8	86·75	64·9	−25·1
10*a***.	do.	do.	66·0	−23·9
11.	44·7 / 62·4	53·55	50·0	− 6·6
11*a**.	do.	do.	52·7	− 1·5
12.	57·2 / 33·9	45·5	47·2	
12*a**.	do.	do.	47·2	+ 3·7

* Same sample after three weeks.

Looking at the above figures, it is clear that the total acid in a blend is by no means necessarily equivalent to the theoretical mean of the constituents. It also seems that time plays a not unimportant rôle in the changes that take place—that is to say, time quite apart from any actual maturing—as the above samples were kept in glass bottles full to the neck.

The deviation from the mean in the case of the non-volatile acid is not so marked as with the total acid, if we restrict this remark to the figures obtained immediately after blending, for in several cases very remarkable differences were observed after the lapse of three weeks—differences which we certainly cannot explain at present. Omitting the general table, which, as we have indicated, is of no particular interest, we subjoin figures in this connection which we believe to be worthy of attention:

NON-VOLATILE ACID.

No. of Experiment.	Acid in Each Sample before Blending.	Theoretical Mean.	Found in Blend.	Increase or Decrease Per Cent.
6.	63·0 / 4·2	33·6	36·7	+9·1
6*a**.	do.	do.	51·6	+34·8
8.	12·5 / 36·8	24·65	28·5	+15·6
8*a**.	do.	do.	44·7	+80·9
9.	12·5 / 63·0	37·7	33·7	−13·3
9*a**.	do.	do.	64·6	+71·3

With regard to the ethers, the deviations from the mean produced by blending were in a few cases found to be appreciable, and certainly larger than we have found the experimental error to be. At the same time, the results in this regard are not as striking as in the case of the acids. The following figures show the maximum deviations observed:

No. of Experiment.	Ethers in each Sample before Blending.	Theoretical Mean.	Found in Blend.	Increase or Decrease Per Cent.
3.	177·6 / 57·3	117·45	124·4	+ 5·8
8.	58·9 / 100·6	79·7	73·0	− 8·5
8*a**.	do.	do.	70·9	−11·0
11.	135·4 / 47·9	91·6	99·6	+ 8·7
11*a**.	do.	do.	93·5	+ 2·0
12.	47·0 / 106·3	76·65	82·5	+ 7·5
12*a**.	do.	do.	87·0	+13·5

* After three weeks.

Discussion.

The President (Mr. Bevan), referring to the alteration in acidity which accompanied the use of New River water, said that this would obviously be accounted for by the fact that that water was alkaline. It was remarkable, however, that the ethers also should have decreased on the addition of water, unless, indeed, the water contained a good deal of carbonate of soda. He had made one or two small experiments in this direction by mixing with alcohol small quantities of ethyl acetate and adding water containing in one case sodium bicarbonate and in another case calcium bicarbonate. Contrary, however, to the author's experience, he had not found any alteration to take place after several days. Obviously, a man might use any reasonable water-supply that he chose, and if in some cases the ether content was reduced, a very grave question was opened for the magisterial mind to consider.

Mr. Fisher said that he had recently had a sample of strong spirit from the Midi, which was said to be pure grape spirit, and which contained a high proportion of ethers, and it had occurred to him that if such a spirit were mixed with distilled water some of the ethers would hydrolyse, and that, in view of this possibility, it would be desirable to ascertain whether the acidity of the spirit was altered. Accordingly, he had diluted it with an equal volume of distilled water and redistilled the mixture, but had found that the acidity that came over was entirely unaffected; so that apparently there had been no hydrolysis that could be attributed to the addition of distilled water and subsequent distillation. That, in so far, was rather against the authors' conclusions.

Dr. J. T. Hewitt said that he was very glad this matter had been brought forward, because there were several things that must affect the ether value to a certain extent. For his own part, he was rather surprised that, on breaking down the brandy with a high ether value, so slight a diminution in the ether content had resulted. He should like to ask whether the authors had made any attempt to ascertain whether any constant value was obtainable for such an expression as—

$$\frac{\text{Number of molecules of ethers} \times \text{number of molecules of water}}{\text{Number of molecules of acid} \times \text{number of molecules of alcohol.}}$$

He had been wondering whether the authors were going to say anything about the flasks in which the estimations were made. This was really a very important point, and if thoroughly reliable flasks were not available, the only thing was to make a control determination, either beforehand or afterwards, with the same materials. He should also like to ask whether the author's ether estimations were made on the original samples or on the spirit after the removal of aldehydes. The latter mode of procedure was perhaps the more scientifically correct, but, as far as one could judge, most of the published results were obtained on the original samples, and any potash used in resinifying or effecting any other changes in the aldehydes had always been counted as ethers, so that for his own part he was rather inclined to take the total value obtained by working on the original sample. Moreover, it was difficult to effect the removal of the aldehydes satisfactorily, because nearly all the reagents available for the purpose were of such a nature that one could not quite say whether they would or would not have any effect on the ethers. One had to take into account

the presence of hydrogen or hydroxyl ions which might affect the saponification and cause a low ether value to be obtained; and, again, certain reagents might act on the ethers and keep back part of their acids in the form of anilides or similarly constituted compounds.

Dr. DYER suggested that these changes might conceivably be due to some biological influence, if the water were used straight from the tap and not filtered through a Pasteur filter.

Mr. CHAPMAN said that Dr. and Mrs. Veley had some years ago described an organism which was capable of living and developing in tolerably strong rum, and it was not impossible that something of the same sort might occur, as Dr. Dyer had suggested, in the case of brandy. The question of the composition of the glass of the distilling flasks, which had been raised by Dr. Hewitt, was, however, a matter of much greater importance, and in his own laboratory he was in the habit of using carefully selected Jena glass for the purpose. The results which Dr. Schidrowitz had brought before them that evening were exceedingly interesting and curious, but he (Mr. Chapman) must confess that he would have liked to have seen a greater number of results with other kinds of water, such, for example, as the soft alkaline waters from the chalk underlying the London clay, and also with artificially prepared waters. Owing to its practical bearing, the statement made by Dr. Schidrowitz was a serious one, and it was obviously very desirable that further experiments should be made. He was rather surprised to hear that any spirit-merchant employed New River water for the purpose of breaking down brandy, as he should have thought that turbidity would have resulted.

Mr. CRIBB said that he was somewhat inclined to question the possibility of these changes being entirely accounted for by the saponifying action of New River water. New River water contained about 18 parts per 100,000 of calcium carbonate, and, supposing a brandy to be diluted with half its volume of New River water, about a third of that amount, or 6 parts of calcium carbonate per 100,000, would be available for first neutralizing the acidity and then saponifying the esters. That would represent 12 parts of calcium carbonate per 100,000 parts of alcohol if the brandy contained 50 per cent. of absolute alcohol, and the quantity of acetic acid it could neutralize would only be a trifle greater. As the average amount of acidity was far greater than this, the possibility of the esters being attacked at all seemed to him to be very remote.

Mr. W. T. BURGESS inquired whether the artificial waters used by the President were made up so that they contained what might be termed an excess of carbonic acid—for instance, by putting sodium carbonate or calcium carbonate into the water and passing carbon dioxide through it.

The PRESIDENT said that he had taken a saturated solution of sodium bicarbonate, estimated the soda, and diluted it down; and had then used a rather large quantity, representing about 70 parts of sodium carbonate per 100,000. In the case of the calcium carbonate he had simply passed an excess of carbon dioxide through water containing calcium carbonate in suspension. He did not, however, lay much stress on these experiments.

Dr. DYER observed that one could not argue necessarily from ethyl acetate to the esters in brandy. The esters were calculated in terms of ethyl acetate, but that

might under some circumstances be a very stable thing, whereas some esters might be very unstable.

The PRESIDENT said that it had merely occurred to him that, if there were any action, it would serve as confirmatory evidence. It did not, of course, follow that because there was no action on ethyl acetate there would be none in the case of actual brandy.

Dr. SCHIDROWITZ, in reply, said that, although it might be anticipated that the acidity should be diminished somewhat on the addition of New River water, it was remarkable that there should be such a diminution in mixed brandies. They had not as yet found any constant of the nature mentioned by Dr. Hewitt. He quite agreed with what had been said in reference in flasks. They were very careful as to this, and the experiments had been practically all made in the same flasks and under the same conditions. The aldehydes had not been removed previous to the estimation of the ethers. He had found in practice that the difference in the results due to the removal of aldehydes was, practically speaking, inappreciable. They had used the New River tap-water direct from the main, as it had been used in the case in question. With regard to Mr. Cribb's remarks, he could only say that the results of their experiments were purely matters of fact, and he might point out that they had not advanced the theory that the changes recorded were due to the alkalinity of the water. Possibly the explanation suggested by Dr. Dyer might be the correct one.

The PRESIDENT asked, as bearing on Dr. Dyer's suggestion, how long the blended brandies had been left to stand.

Dr. SCHIDROWITZ said that the mixed samples were examined immediately, and the same brandies were then left to stand for periods of three weeks, when the examination was repeated. In the experiments with water, the examinations were made after periods of two to twelve days had elapsed subsequent to the dilution.