# VINEGAR.

By A. H. Allen and C. G. Moor.

(*Read at the Dublin Meeting, July 18th*, 1893.)

Recent events, well known to the members of this society, have compelled public analysts to give more attention to the chemistry and manufacture of vinegar than the majority of them had previously done. In a recent number of The Analyst there appeared an abstract of a paper by us in which we gave a number of definitions of "vinegar" which we had collated from various sources. Some of these definitions were not drawn by their authors with the expectation of their being quoted in judicial proceedings, and are not unnaturally wanting in the requisite precision on the one hand and the necessary elasticity on the other. Before making an attempt ourselves to formulate a more satisfactory definition of "vinegar," we propose to review shortly the chief processes by which the various products commercially posing as vinegar are manufactured.

No naturalist has any difficulty in classifying a *cow* as an animal and a *cabbage* as a vegetable; but in the case of some of the lower forms of life the biologist is at a loss how to regard the specimen. So it is with vinegar, some commercial products almost defying classification.

The so-called vinegars of commerce may be broadly divided into two classes: those which are the product of the consecutive alcoholic and acetous fermentations, and those which are not. The view is pretty general amongst public analysts that products of the former class have alone the right to be called "vinegar," unless some adjectival prefix be used, such as "wood-vinegar."

Of course the original vinegar was made from wine, as the derivation of the word shows; but in this country wine-vinegar has been almost wholly superseded by malt-vinegar. This again has been superseded, so far as a product made from malt only is concerned; for, just as the beer-brewer has discovered that the substitution of unmalted barley for a portion of the malt is distinctly advantageous, so the vinegar-brewer invariably uses more or less unmalted grain in admixture with the malt. But the beer-brewer has, since the abolition of the duty on malt, largely replaced the malted and unmalted barley by maize and rice, or the "glucose" prepared therefrom by the action of dilute acid; and the vinegar-manufacturer has not been slow to follow suit, and to use sugar and molasses in addition. So general has this practice become that the vinegar-manufacturers who still brew from malted and unmalted barley only might be counted on the fingers of one hand (without reckoning the thumb). Under these circumstances, it is evident that the term "malt-vinegar" is a misnomer, and it behoves public analysts to consider how far they will be justified in permitting the sale of products of mixed origin under the title of "malt-vinegar." There is undoubtedly a popular preference for, or prejudice in favour of,

malt-vinegar; but while manufacturers are quite ready to pander to this preference, whether it be justified or not, they do not always supply an article to which the name "malt-vinegar" can be properly applied, even when used in the extended sense of a product brewed from a mixture of malted and unmalted grain. The contention that by such a term a vinegar merely *flavoured* with malt is to be understood will scarcely bear investigation. Take the case of jam. Are we to understand by "raspberry-jam" an article composed chiefly of apples or turnips, and containing only enough raspberry to give it the characteristic flavour? Or under the title of "malt-whisky" are we to admit a spirit made not only from unmalted barley, but also from rice, maize, dari, potatoes, sugar, molasses, etc.? It would undoubtedly prevent much heartburning, and greatly simplify the question at issue, if the term "malt-vinegar" were definitely abolished.

But the substitution of other fermentable materials for barley is not the only trade-practice the legitimacy of which calls for consideration. The albuminoids present in malt-wort and other vegetable infusions have a prejudicial effect on the keeping properties of the vinegar produced therefrom, especially in the case of the weaker qualities, and it is the object of the scientific vinegar-manufacturer to reduce these to a minimum. Hence it is the practice of some manufacturers to distil a portion of their product—which, contrary to the general impression, can be done very cheaply—reserve the stronger portion of the distillate for sale as "distilled vinegar," and add the weaker fractions to some of the undistilled article. Distilled malt-vinegar is not, as is sometimes erroneously assumed, merely dilute acetic acid. On the contrary, it contains quite appreciable quantities of alcohol, acetal, acetic ether (and probably other esters), furfurol, aldehyde, etc.; and has a highly characteristic taste and odour which appear to be greatly appreciated in Scotland, where distilled vinegar is seen more frequently than the coloured article.

We have obtained the following figures by the analysis of distilled *vinegar* (not mere acetic acid) manufactured by some of the leading vinegar-brewers:

| | A. | B. | C. |
|---|---|---|---|
| Specific gravity ... ... ... | 1·0077 | 1·0080 | 1·0055 |
| Acetic Acid (grammes per 100 c.c.) | 5·16 | 5·80 | 3·88 |
| Total solids ,, ,, | 0·006 | 0·013 | 0·032 |
| Ash ,, ,, | None. | None. | None. |

It is evident that the addition of either of the above distilled vinegars to an undistilled product would tend to alter materially the proportions of certain of the constituents of most value to the analyst in judging of the origin and mode of manufacture of a sample of vinegar. In fact, the manufacturer who practises the addition of a distilled vinegar to his undistilled product runs considerable risk of having his article certified to contain added acetic acid.

Two samples of still-residues from the manufacture of distilled vinegar have been examined by us. They were brown, and of the consistence of treacle. On analysis they yielded the following figures:

| | A. | | B | |
|---|---|---|---|---|
| Total solids | 43·20 | per cent. | 72·30 | per cent. |
| Ash | 8·38 | ,, | 9·21 | ,, |
| Alkalinity of Ash ($K_2O$) | 2·07 | ,, | 1·40 | ,, |
| Phosphoric Acid | 2·67 | ,, | 0·24 | ,, |
| Nitrogen | 2·63 | ,, | 2·63 | ,, |

A was a residue from a true barley vinegar. B was derived from a vinegar brewed with a considerable proportion of rice.

Under the name of "Essig Sprit," or "spirit-vinegar," there is now sold considerable quantities of an article of foreign origin, which is manufactured by subjecting previously distilled potato-spirit to the acetous fermentation. The product has many of the characters of English brewed vinegar, and of course contains those peculiar secondary products of the growth of *Mycoderma aceti* which give vinegar certain of its valued characters. It is usual to add a certain proportion of malt-wort to the spirit, or of malt-vinegar to the fermented product. *Essig Sprit*, as imported, contains about 13 per cent. of acetic acid, and a notable proportion of acetic ether; but the colouring matter is added in England, whereby the article is imported as "acetic acid," and escapes the duty payable on "vinegar." The following figures show the composition of "Essig Sprit" in its concentrated form, and of the "spirit vinegar" of commerce obtained by diluting and colouring it:

| Grammes per 100 c.c. | Essig Sprit. | "Vinegar." | | | |
|---|---|---|---|---|---|
| | | A. | B. | C. | D. |
| Specific gravity ... | 1·0152 | 1·0095 | 1·0086 | 1·0068 | 1·0096 |
| Acetic acid ... ... | 11·26 | 4·68 | 4·50 | 3·75 | 4·80 |
| Total solids... ... | ·64 | 0·79 | 0·50 | 0·40 | 0·65 |
| Ash ... ... ... | ·06 | 0·04 | 0·05 | 0·03 | 0·06 |
| Alkalinity of ash ... | — | Trace | Trace | Trace | 0·01 |
| Phosphoric acid ... | Trace | 0·002 | None | None | Trace |
| Nitrogen ... ... | 0·014 | 0·0084 | 0·0098 | 0·0110 | 0·013 |
| = Albuminoids | 0·089 | 0·053 | 0·062 | 0·069 | 0·082 |

Another product of German manufacture, which finds its way into English commerce to a considerable extent, is prepared by fermenting potato-spirit with *Mycoderma aceti*, neutralising the dilute acetic acid so obtained with "pure lime," and distilling the resultant calcium acetate with an acid. Another manufacturer neutralises the acid with soda instead of lime. By this means a very concentrated acetic acid is obtainable, the strength of which ranges from 40 to close upon 90 per cent. When suitably coloured and flavoured, such acid is extensively sold under such names as "malt acid," "vinegar essence," "vinegar extract," etc., from which a factitious vinegar can be prepared by simple dilution with water. The following figures were obtained by us some time since by the analysis of samples of this so-called "malt acid" and the "vinegar" obtained by its dilution.

| Grammes per 100 c.c. | "Malt Acid." | | "Vinegar." | |
|---|---|---|---|---|
| Specific gravity ... ... | 1·0825 | 1·0977 | 1·0191 | 1·0125 |
| Acetic acid ... ... ... | 88·02 | 45·4 | 3·84 | 8·11 (*sic*) |
| Total solids ... ... ... | 2·77 | 12·14 | 2·00 | 0·27 |
| Phosphoric acid ($P_2O_5$) ... | — | 0·017 | Present. | — |
| Ash ... ... ... ... | 0·15 | 0·180 | 0·04 | — |
| Nitrogen ... ... ... | — | 0·113 | — | — |
| = Albuminoids ... ... | — | 0·70 | — | — |
| Sulphuric acid (free) ... | — | 0·74 | 0·063 | — |

The production of a liquid containing more than 14 to 15 per cent. of acetic acid by the acetous fermentation is simply impossible, and the practical limit is reached in Essig Sprit with about 13 per cent. But vinegar-brewers do not, as a rule, aim at producing an article containing more than 6 per cent. at the outside. Hence the mere fact of a liquid having an acidity corresponding to 80 or even to 40 per cent. of acetic acid is absolute proof that it is not a product of fermentation, whatever the manufacturer may declare. Nor can a vinegar resulting from fermentation be, in practice, materially concentrated by evaporation, although absolute acetic acid has a boiling-point somewhat above that of water. Thus, on distilling a sample of commercial malt vinegar, containing 4·17 grammes of acetic acid per 100 c.c. to half its bulk, we found the distillate to contain 2·87 grammes of acetic acid per 100 c.c., while the liquid remaining in the retort contained 4·38 per 100 c.c. On reducing 500 c.c. of the same vinegar to 15 c.c. by distillation, without the use of any fractionating arrangement, the residual liquid contained only 10·1 per cent. of acetic acid. A similar experiment made on a mixture of malt vinegar and acetic acid B. P., containing before distillation 14·16 grammes of $C_2H_4O_2$ per 100 c.c., yielded a distillate containing 10·92 of acetic acid, while the half remaining in the retort retained 17·4 grammes of acid per 100 c.c.

We have recently met with as many as ten samples of vinegar containing a notable quantity of free sulphuric acid, though it is right to add that there is reason to believe these were all supplied to the retailers by the same "vinegar maker." This article was stated to be made by adding to the vinegar brewed from 2 cwt. of malt and 1 cwt. of molasses 25 gallons of "wood-vinegar," and sufficient water to reduce the strength of the mixture to a little over 4 per cent. of acetic acid. From these data we calculate that the product would contain about 8 per cent of true fermentation-vinegar. On analysis it has given the following figures :

| | | |
|---|---|---|
| | Specific gravity ... ... ... | 1·0130 to 1·0138 |
| Grammes per 100 c.c. | Acetic acid ... ... ... ... | 4·0 ,, 4·2 |
| | Total solids ... ... ... ... | 1·6 ,, 1·7 |
| | Ash ... ... ... ... | 0·06 ,, 0·09 |
| | Phosphoric acid ... ... ... | Trace. |
| | Sulphuric acid (free) ... ... ... | 0·22 ,, 0·30 |
| | Nitrogen ... ... ... ... | 0·016 ,, 0·020 |

The residues obtained by the evaporation of these vinegars were quite black.

The solicitor who defended the vendors of this article, the casks containing which were labelled by the manufacturer "pure malt vinegar," stated that its manufacture cost as much as true malt vinegar. Taking the price of 25 per cent. acetic acid at 7s. per cwt. (as per list in the *Chemical Trade Journal*), it follows that a 4 per cent. "vinegar" could be made therefrom for a trifle over 1½d. per gallon.

We have tried to compare the taste of dilute acetic acid with that of sulphuric acid, and find the latter to leave a sourness on the palate equal to an acetic acid of fully four times the strength. Hence 0·25 per cent. of sulphuric acid is palatably equivalent to about 1·0 per cent. of acetic acid, and the manufacturer who adds it can reduce his bill for the latter by 25 per cent. Arsenic-free sulphuric acid of 1·725 specific gravity is quoted at 26s. per ton; whence it follows that a dilute acid

equal in sour taste to a vinegar containing 4 per cent. of acetic acid can be manufactured for 2d. per 100 gallons!

We may here express our opinion that the use of the term "pyroligneous acid," to express the quality of wood acetic acid used in the production of factitious vinegar, is misleading. By pyroligneous acid is commonly understood an acid obtained by the distillation of wood. By conversion into a calcium or sodium salt it can be readily purified to a much greater extent than if neutralization be omitted, and when recovered from its salt by distillation with a mineral acid it is technically known as "acetic acid." Although the term pyroligneous acid is very convenient for indicating the origin of an acetic acid, it implies the presence of tarry matters, which, in our experience, do not exist in the acetic acid employed for manufacturing factitious vinegar.

In order to obtain more reliable information respecting the composition and range of variation of vinegar prepared from different materials, we have obtained samples of representative vinegars from most of the leading vinegar-brewers, and have analysed these samples in some detail. The actual figures obtained we reserve for the present. Our analyses have included the determination of specific gravity, total acid in terms of acetic acid, total solids, ash, the alkalinity of the ash in terms of $K_2O$, the phosphoric acid, the nitrogen by Kjeldahl's process, free sulphuric acid when present, tests for heavy metals, and qualitative tests for alcohol, furfurol, aldehyde, acetic ether, etc.

With regard to phosphoric acid, the importance of which as an indication of the origin of vinegar was pointed out in "Commercial Organic Analysis," vol. i., p. 389, and has since been insisted on by Hehner (ANALYST, xvi., 81), its value as a quantitative method is seriously discounted by the influence on the composition of the wort produced by the use of hard water. As, however, any precipitation of phosphate of calcium thus occasioned is more than counterbalanced by the formation of a corresponding soluble salt, the proportion of total ash is not reduced thereby.

The "alkalinity" of the ash when obtained is also a useful indication, but we have not found the results very concordant. A better plan is undoubtedly to determine the actual potash, as is practised by R. R. Tatlock. It is very difficult to obtain a fairly white ash by the combustion of vinegar-residues, and if the temperature be too high, or the ignition very prolonged, there is a serious danger of losing some of the more volatile salts. In our later experiments, therefore, we have adopted the practice of sulphating the ash. This does not interfere with the determination of potassium by direct precipitation with platinic chloride in the portion of the ash soluble in water. In practice we find it convenient to take 5 c.c. for the determination of the extract, and having weighed the total solids, to add another 20 c.c. of the same vinegar, and again evaporate. When reduced to the consistency of a syrup, a few drops of strong sulphuric acid are added, the evaporation completed, and the residue ignited at a low red heat. By these means a perfectly white and practically infusible ash is readily obtained. As a rule, 115 to 120 parts of the sulphated ash represent 100 parts of unsulphated ash, the extreme limits hitherto observed being 106 and 130. Of course the ratio will vary with the composition of the ash, and

consequently with the origin of the vinegar, and may in the future afford very valuable information.

With regard to the determination of nitrogen, we find it convenient to operate on 20 c.c. of the vinegar, though a smaller quantity will suffice. When concentrated to a syrup, we employ Gunning's modification of the Kjeldahl process. We have also obtained very good results by Stock's oxide of manganese process.

For the determination of free acetic acid in vinegar we employ 10 or 20 c.c. of the sample, which we titrate in a weighed porcelain dish with caustic soda, using phenol-phthalein as an indicator. There is not the least difficulty in noting the end of the reaction, without diluting the vinegar or taking any other precaution. The neutralized liquid is distilled, and the distillate tested for the volatile constituents of vinegar. Alcohol is readily recognised by the iodoform test, and aldehyde by the rosaniline sulphite reaction. Acetic ether can be determined by Berthelot's method, similar to Koettstorfer's process for oils. Furfurol, we at first thought might be indicative of acetic acid derived from wood, especially as the ordinary acetic acid of commerce gives abundant evidence of the presence of furfurol when tested by the aniline acetate reagent. Unfortunately there is either furfurol or a body giving a similar reaction produced when sugar is caramelised. On treating the resulting caramel with water, distilling, and testing the distillate with the aniline acetate reagent, a strong furfurol reaction is obtained.

We have attempted to find some compound which would be directly indicative of a brewed vinegar as distinguished from the various forms of distilled acetic acid. Alcohol is only practically valuable for this purpose in special cases, and the objections to relying implicitly on the natural presumption from its presence are obvious. Glycerin, another constant product of the alcoholic fermentation, is very difficult to determine in the presence of some of the other constituents of vinegar. We have attempted, therefore, to determine the succinic acid, which substance the experiments of Pasteur showed to be a constant product of the alcoholic fermentation. There are great difficulties in its accurate determination under the conditions with which analysts have to deal in practice, but our experiments in this direction are not complete, and we are not hopeless that we may be able to devise a practicable method of dealing with it.

In interpreting the results obtained by the analysis of vinegar, it is important to eliminate the variations due to differences of dilution. This may be effected to some extent by expressing all the items per 100 parts of acetic acid, but a far preferable plan is to adopt the principle suggested by Hehner (ANALYST, xvi., 82), who calculates the amount of phosphoric acid, ash, etc., per 100 parts of the original solids of the vinegar. These are deduced from the fact that 180 parts of glucose yield theoretically 120 parts (or two-thirds of its weight) of acetic acid. Hence, by multiplying the acetic acid found in the vinegar by 1·5, and adding to the product the percentage of total solids still existing in the vinegar, the "original solids" are obtained. In practice, the actual yield of acetic acid is rarely more than two-thirds of the theoretical amount, so that a more accurate expression of the original solids of the wort would be obtained by multiplying the percentage of acetic acid by 9/4 (= 2·25), and adding the extract to the product.

We purposely leave any discussion of the deductions from the foregoing analytical data for the present, as also the actual figures we have obtained by the analysis of the numerous samples of typical vinegar, with which we have been kindly furnished by a number of the leading vinegar-brewers of the kingdom. We may, however, conveniently give here the results of the analysis of two special vinegars. One of these was manufactured on the large scale from locust-beans; the other was a domestic product, obtained simply by fermenting a solution of brown sugar with brewers' yeast, and allowing the liquid to stand in a loosely-covered vessel:

| Grammes per 100 c.c. | Locust-bean Vinegar. | Sugar Vinegar. |
|---|---|---|
| Specific gravity | 1.0217 | 1·0284 |
| Acetic acid | 7.26 | 6·90 |
| Total solids | 2.47 | 4·69 |
| Ash | 0.31 | 0·46 |
| Alkalinity ($K_2O$) | 0.11 | — |
| Phosphoric acid | trace | trace |
| Nitrogen | 0·03 | 0·046 |
| = Albuminoids | 0·189 | 2·290 |