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NOTE ON THE SUGARS OF CONCENTRATED MALT EXTRACT.

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IN the course of an investigation on commercial malt extract we have analysed a number of samples prepared, under conditions which have been communicated to us by the manufacturers, from malts of known origin. We believe the results we have obtained, more especially with respect to the carbohydrate composition of the extracts, are of sufficient interest to warrant us in submitting them to the Society. Thus, we found that the malt extracts contained a considerable proportion of dextrose, which we were able to estimate gravimetrically, with a fair amount of accuracy, as glucosazone, employing the method recently described by Davis and Ling (*Journ. Chem. Soc. Trans.*, 1904, lxxxiv., 24). Having also examined a few of the well-known brands of malt extract on the market, and in every case obtained similar results, we have arrived at the conclusion that dextrose is an invariable constituent.

It is remarkable how very little work has been published on the composition of concentrated malt extract. We believe, however, that most chemists would have regarded the presence of dextrose in this product as evidence of adulteration. Among the few papers on the subject we have been able to find is one published in 1896 by P. Korn (*B. d. Deutsch. pharm. Ges.*, vi., 349), and from an abstract of this paper in the *Wochenschrift für Brauerei* we find that he gives the following mean carbohydrate composition of nine samples of malt extract which he examined:

Maltose ...	...	...	...	between 41·43 and 60·43.
Dextrose ...	...	...	...	„ 0·47 „ 6·24.
Cane-sugar ...	...	...	...	„ 0·33 „ 3·60.
Dextrin ...	...	...	...	„ 11·70 „ 22·70.

As will be seen, the amounts of dextrose found by us are much higher than those recorded by Korn. Indeed, the highest percentage of dextrose which Korn finds is only about half our lowest percentage.

The methods adopted by Korn were to mix the extract with ignited sand and absolute alcohol, and to extract the mass with absolute alcohol. In this way it is contended that the sugars pass into solution in the alcohol, whilst the dextrin remains behind with the sand, and is estimated by lixiviating the dried mass with water and determining the total solids in the aqueous solution. This value, corrected for ash, is taken as the percentage of dextrin. The maltose, dextrose, and cane-sugar are estimated after distilling the alcohol from the alcoholic extract, the residue being taken up with water and its cupric reducing power (towards Ost's solution) determined before and after hydrolysis with hydrochloric acid and with invertase respectively.

In an attempt to make something like a complete analysis of certain samples of malt extract, we found that it was not possible to determine the sugars in terms of apparent maltose and dextrin by the copper method in conjunction with the polarimeter. This will be seen by the results obtained with Samples I. and II., which

samples we shall deal with more fully further on. These gave 58.9 and 60.5 per cent. of apparent maltose—*i.e.*, cupric-reducing power towards Fehling's solution expressed in terms of maltose—whilst the rotatory powers of the 10 per cent. solutions in a 200 millimetre tube for sodium light were 14.2° and 13.9° respectively. The above amounts of maltose, however, require rotations of 16.2° and 16.7° respectively. It is therefore evident that the malt extracts contained either a lævoro-rotatory compound or a sugar having a much smaller dextro-rotatory power than maltose. We are aware that malt extract contains asparagine and other similar compounds, but we do not think the amount of these is sufficient to account for the above differences, the more so as we assured ourselves that the extracts in question contained carbohydrates of higher rotatory power than maltose—*e.g.*, dextrans (malto-dextrans).

This led us, therefore, to examine the behaviour of the malt extracts towards phenylhydrazine, and, as a result of this, we had no difficulty in isolating glucosazone in a practically pure state, when twice crystallised from alcohol it melted at 204° .

The ratios of the carbohydrates in the malt extracts being somewhat different from those in the starch conversions of Davis and Ling, we therefore determined the yield of glucosazone in artificial mixtures of dextrose, maltose, and dextrans (malto-dextrin - *a* was employed), and we found that with approximately equal quantities of these three carbohydrates the yield of glucosazone under the conditions described by Davis and Ling was 0.0731 gramme from 0.1 gramme of dextrose.

In the following analyses the dextrose was determined as glucosazone, the maltose being calculated from the reducing power, less that due to the amount of dextrose found, whilst the dextrin was calculated from the rotatory power after deducting that due to the dextrose and maltose. We have ignored the small amount of cane-sugar which, according to Korn, is present.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Specific gravity : 15.5° C. / 15.5° C. } 1395.70 1395.12 — — — — 1408.43 1377.82 —									
Maltose (apparent) %	31.1	30.9	24.8	27.4	23.0	25.9	34.2	25.2	33.0
Dextrose - - - %	17.2	18.2	22.0	19.1	19.4	16.5	12.5	20.0	16.9
Dextrin (apparent) %	9.8	8.6	10.0	9.8	13.5	12.3	9.9	6.7	7.8
Unfermentable matter (expressed as dextrin) - - -	4.5	3.5	8.9	5.8	4.1	—	—	—	—
Ash - - - - -	1.45	1.49	1.58	1.64	1.68	1.21	1.34	1.64	1.33
Water - - - - -	24.30	24.67	27.36	24.84	24.82	25.20	24.38	29.52	24.20
Diastatic power (Lintner) - -	30.8	27.2	32.3	25.6	32.2	28.0	39.2	46.5	61.7
Specific rotatory power $[\alpha]_D$ -	91.8°	90.5°	84.2°	86.8°	88.0°	89.6°	94.5°	81.1°	90.7°

Of these extracts, Samples I. to VI. were prepared under known conditions from low-dried English malt. We are not at liberty to state what were the precise mashing conditions adopted in the preparation of these samples; but the first two were not raised in the tun at any time during the mashing process to a temperature above 145° F., whilst Nos. II. to VI. were mashed a few degrees lower.

The values given under "unfermentable matter expressed as dextrin" were obtained as follows: 25 grammes of the extract were dissolved in water (150 c.c.), and the solution boiled to destroy the diastase. After cooling, the solution was pitched with yeast at 70° F., and allowed to ferment at that temperature. When fermentation was complete, a little moist alumina was added and the liquid made up to 250 c.c. It was then shaken and filtered through a dry filter, the rotation of the clear filtrate being observed and calculated as dextrin. The yeast used in the above experiments was a Yorkshire stone square yeast. It is interesting to note that the values for apparent dextrin, calculated from the rotatory power, less that due to dextrose and apparent maltose, differ from the values for dextrin calculated from the rotatory power of the unfermentable residue. Not only this, but the two sets of values do not exhibit a constant difference. This is, however, by no means surprising when we bear in mind the fact that the dextrans (maltodextrans) are all reducing compounds, and that their fermentability probably differs inversely as their reducing power. The nature of these dextrans or maltodextrans, other things being equal, will vary according to the diastatic power of the malt.

The malt used for the first two samples had a diastatic power of 60.6 on Lintner's scale.

In seeking for an explanation of the production of glucose, there is the possibility that it may be due to the presence of the enzyme maltase in the malt. This enzyme is seldom found even in low-dried malt, and an extract of the malt from which the first two samples were prepared was incapable of hydrolyzing maltose, so that it was not present. The glucose might also be formed as a result of restricting the diastase in the manner shown by Ling and Davis (*Journ. Fed. Inst. of Brewing*, 1902, viii., 475, and *Journ. Chem. Soc., loc. cit.*). We find, however, that when the malt in question is mashed in the ordinary laboratory manner, but at a temperature of 145° F. for two hours, the amount of glucose in the wort is only 0.39 per cent., calculated on the malt. Now, there is certainly more dextrose (or invert sugar) existing ready formed in the malt than this; but we have some data showing that during mashing this ready-formed dextrose disappears, laboratory worts from ordinary brewer's malt giving, as a rule, no glucosazone whatever. This is what we might expect from the recent observations of Davis and Ling (*loc. cit.*).

One of us has shown (British Association Report, 1903, and *Journ. Fed. Inst. Brewing*, 1903, ix., 450) that when any of the products of the incomplete hydrolysis of starch by diastase are isolated, and submitted to the further action of the enzyme, even at a temperature of 131° F., glucose is invariably formed. Now, in the preparation of malt extract there are two distinct stages: first the mashing process, and secondly the evaporation. The hydrolysis of the starch is never carried to its final point in the mash-tun, and after the mashing process, the reaction is temporarily stopped. It commences again, however, during the evaporation, which in the case

of the first six extracts was conducted at a temperature of 115° F. It is probable that any reaction which occurs during this stage would be quite distinct from that which takes place in the mash-tun, not only on account of the lower temperature and the different concentration, which gradually increases up to the point at which further diastatic action is impossible, but also because the diastase is not acting on starch during this second stage, but on the hydrolytic products of starch formed during the first stage. Under these circumstances, we might expect glucose to be formed, although we must leave the exact explanation of this to future experiment.

DISCUSSION

The PRESIDENT (Mr. Fairley) having invited discussion,

Mr. JULIAN L. BAKER said that this paper was especially interesting, because malt extracts of the kind referred to were now beginning to command attention in some of the fermentation industries, notably in the manufacture of alcohol, and also in bread-making. One of the most striking statements the authors had made was the large amount of dextrose which was present in these evaporated malt extracts, and which, they pertinently pointed out, might well be regarded, in the hands of anyone unaccustomed to deal with such extracts, as an indication of adulteration with glucose syrup. Mr. Ling's further investigations concerning the reasons for the presence of this amount of dextrose would be awaited with much interest. It was to be remembered that the extracts were prepared under special conditions. In the first place, the barleys used were inferior small-grain foreign barleys—Californian, Smyrna, Indian, and so forth—which were in themselves highly diastatic as barleys. They were malted under entirely different conditions from the malt which the brewer used, being grown freely and dried off—they could hardly be said to be cured—at a very low temperature, somewhere about 100° to 120° F., whereas brewer's malt would be finished off at about 190° to 200° F. Thus none of the diastase was crippled by the curing process. The mash was made at a low temperature, filtered in a press and evaporated, and there was a pause in the process (during filtration) between the mashing and the evaporation, which, as the authors pointed out, would mark the second stage in the diastatic action. He did not think that analogies could very well be drawn between the action of brewer's malt extract and these highly diastatic ones, because, under the conditions obtaining in the preparation of the latter, it seemed quite possible that the starch hydrolysis would proceed somewhat differently. One other point was that these malt extracts were highly concentrated syrups from a large amount of malt, and he should like to know how much of the dextrose present the authors would put down as being ready-formed in the malt before mashing.

Dr. SCHIDROWITZ said that the fact of the presence of such a considerable amount of dextrose was in his opinion possibly to be put down to the general conditions of enzymic action. He understood the authors to say that in low-dried malts—ordinary brewer's malts, he presumed—they had never found any maltose-splitting enzyme. These malt extracts, however, were evaporated at a temperature very favourable to enzymic action, and the degree of concentration was constantly changing. As a solution became more concentrated there was a tendency towards a reversion of the enzymic action, and he thought it just conceivable that the amount of dextrose found

in the final product might not be a maximum, but that at an intermediate stage a considerably larger quantity might be present, there being a certain amount of reversion as the extract became more concentrated. Of course, this was purely hypothesis; but possibly Mr. Ling had made some experiments in this direction, and if so, his opinions would be of interest.

The PRESIDENT said he had been wondering whether it would be worth while making synthetic experiments, under as definite conditions as possible, with carbohydrates of known composition, so as to study this problem in its simplest form. In complicated mixtures of varying concentration, such as those now under consideration, all sorts of change, and even reverse action, might occur, and he thought that possibly such a matter could be best attacked in detail by studying the carbohydrates themselves, or known mixtures of them.

Mr. SEYLER inquired how the authors had determined the cupric oxide reducing power, which was a matter of some importance in the case of complex mixtures of this kind. The methods generally used seemed to be very largely conventional. For his own part, he was in the habit of relying chiefly on the tables of Soxhlet, Wein, and Allihn. These, however, although they answered very well for pure solutions of dextrose and maltose, were not applicable to mixtures, owing to the different conditions under which each was obtained.

Mr. LING, referring to the President's remarks, said that corresponding determinations had already been made in pure starch conversions, in the course of the investigation which he had recently communicated to the Chemical Society, in conjunction with Mr. Davis. In determining the dextrose as glucosazone, it was most essential always to start with freshly-distilled phenylhydrazine; otherwise the results fluctuated very much. For the gravimetric determination of the cupric oxide reducing power he preferred the method of Brown, Morris, and Millar. In the case of these malt extracts, however, the cupric oxide reducing power had been determined volumetrically. Many chemists stated that the volumetric process lacked sufficient accuracy, but, after many years' experience, he had modified the process, so that in repeated experiments he was able to get almost as great uniformity as with a gravimetric process. His solutions were all standardized with the pure carbohydrates. In cases where no disturbing element occurred the volumetric results were identical with those yielded by the process of Brown, Morris, and Millar. That reversion during evaporation occurred he thought was very likely; in fact, in the experiments made by Mr. Davis and himself it was noticed how much the results fluctuated from day to day, especially the percentage of glucose. The nature of the body produced from glucose was not known. He had suggested at the British Association that it was Lintner's isomaltose. He believed that the body which yielded the osazone with a melting-point of 152° , and which Lintner regarded as one of the products of starch hydrolysis, was a secondary product. He had a number of data on that point, which he hoped to publish sooner or later. He agreed with Mr. Baker that no analogy could be drawn between low-dried and high-dried malts.