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GRAPE SUGAR AND GLUCOSE.

By O. LUTHY.

THE MANUFACTURE OF GLUCOSE AND GRAPE SUGAR.

GRAPE sugar was first manufactured in France, in the year 1809, from grape juice. During the time of the notorious continental blockade, ordered by Napoleon, the prices of sugar (of which only one kind, namely: colonial or cane sugar, then was known, commercially,) went up so high, that cheap substitutes were eagerly looked out for. The grape juice was neutralized by powdered chalk, and rapidly boiled down to a thin syrup of 20° B. It was then cooled and filtered to free it from the lime salts it had deposited, and further evaporated to 32° B., in which state, as it is said, it was used extensively, especially in hospitals instead of sugar. Boiled down to 45° B., this syrup will, on cooling, deposit large quantities of granular grape sugar, which may be separated from the adhering syrupy fruit sugar, by draining in sugar moulds, or better by centrifugal machines: 1,000 parts of grapes yield 800 parts of must, 200 parts of syrup, 140 parts of raw grape sugar, 60 to 70 parts of pure grape sugar.

About the same time, Kirchhoff, a chemist in St. Petersburg, found that starch by boiling with water and a little sulphuric acid was changed into sugar. This discovery created a great sensation, because it was believed that this starch sugar would replace cane sugar. It was soon experienced, however, that there was a great difference between the two, starch-sugar being less sweet and less soluble than colonial sugar, and its manufacture didn't become so important as was anticipated; so much the less, as in the same period and by the same cause (the continental decree), the beet-sugar industry got a great impulse and gradually ripened to its present success.

As a substitute, however, for Indian syrup (colonial molasses) the starch syrup, prepared either by the acid or malt process, became favored and was manufactured in large quantities (best molasses because of its bitter and salty taste is not well fit for the table; it is turned into alcohol.) By the time, also, the solid starch sugar which was found to be identical with grape sugar came into use, especially for the improvement of wine-must in bad seasons. It then was employed also in making fruit wines, and at last in manufacturing wine wholly artificial. In beer-brewing it is also largely used as a substitute for barley. In the year 1874, in Germany, 47 factories turned out over 11,000 tons of starch or grape sugar, and nearly 15,000 tons of starch-syrup or glucose (Wagner's Jahresbericht.) From other countries no statistics were obtained; no doubt, the amount would be doubled, if France, Belgium and Holland were included in the report.

The process, by means of which glucose and grape sugar are manufactured nowadays from starch, is not quite so plain as it might first appear. When we add to a boiling hot thin starch-paste a small quantity (about two per cent. of the starch) of sulphuric acid (oil of vitriol), previously diluted with water, it becomes at once liquid; the starch is rendered soluble, changed into *amiduline*, as this new body is called, By further boiling this is gradually converted in *starch-gum* or *dextrine*, a substance which, when dry, resembles gum arabic, and which is applied in the arts in a great many ways as a substitute for that substance. If the boiling continues sufficiently long, the solution becomes sweet, the gum dextrine by degrees is turned into a new body again, and at last, when the conversion is complete, we find nothing else in the solution besides a sweet body, which behaves exactly like grape-sugar, and the original amount of sulphuric acid which has remained unchanged. On the time spent in boiling, and on the quantity of acid used, it depends whether the conversion is more or less complete; whether the starch is turned wholly into grape sugar or only partially, in which case more or less gum dextrine, and even amiduline (soluble starch merely) is left mixed with the sugar. If we apply from one to two per cent. of acid only, and boil but for a few hours, the result is a product which is still rich in gum dextrine, preventing, by its viscous properties, the admixed grape sugar from crystallizing, and which product consequently refuses to become solid. It is what is commercially called *glucose*. If we, however, raise the amount of acid to two-and-a-half or more, even four per cent., and boil for eight or ten hours, the final result will be a fine granular *solid grape sugar*.

When the conversion of the starch into glucose or grape sugar is brought to the desired degree, we next have to extract and remove the acid. This is done by means of powdered chalk or slacked lime. The sulphuric acid combines with the lime, forming sulphate of lime, which deposits, leaving the solution sweet. After subsiding the liquor is filtered and the water boiled away, until glucose or sugar is left in the proper finished state. We see from these outlines that the manufacture of glucose and grape sugar is divided in three principal processes, namely: conversion, neutralization and evaporation.

1. *Conversion.*—The boiling of the starch with the acid water is effected on a small scale in a copper kettle on a naked fire, or in extensive factories in large wooden tubs by means of a large copper steam coil. The proper quantity of water is first heated to boiling, then the requisite amount of sulphuric acid (oil of vitriol), previously mixed with three to five times its weight of water, is added; and whilst the liquid is kept boiling continuously, the starch, which has been mixed with water to a milky consistency, is gradually poured in. The flow of the starch milk is so regulated that the liquor in the tub never cools below boiling, and never becomes cloggy or pasty.

To every 100 pounds of dry starch take 40 gallons of water in all, and 1 to 2 pounds sulphuric acid for glucose, and from 2½ to 4 for grape sugar. When all the starch is added, the boiling is continued until the desired degree of conversion has taken place. Glucose will require about 2½ or 3 hours, grape sugar from 5 to 9 hours. From time to time a sample is drawn to be tested. This is done at first by means of a solution of iodine (prepared by dissolving equal parts of potassium iodide and iodine, in enough water to get a coffee brown colored solution,) and afterwards by strong alcohol. When the proof ceases to turn violet or red on the addition of a few drops of the iodine solution, the starch is converted into gum dextrine and grape sugar, and the boiling may now be discontinued if glucose is to be prepared. If solid grape sugar is intended, the boiling must go on until the alcohol test is satisfactory. A spoonful of the liquor is poured into a test tube, and shaken up with about five times its bulk of strong alcohol. The gum dextrine being insoluble in alcohol will render the mixture turbid if present, whilst grape sugar alone will remain dissolved on the addition of alcohol, the mixture thus being clear; therefore the boiling is continued until all dextrine is completely converted into grape sugar, when the alcohol test will not become milky any longer.

Instead of an open kettle or tub for boiling the acid starch mixture, a closed "converter" is used in many large factories. This is a strong cylindrical vessel of boiler iron, lined with lead inside, and provided with a perforated steam coil for heating, with pressure guage, thermometer, safety valve, etc. Water, acid and starch are introduced and heated as before; but after all the starch is in, the converter is closed, and then by means of high-pressure steam the heat is raised to 320°, when the pressure inside will be about 90 pounds. This temperature is kept up until conversion is complete. It is claimed for this process that the conversion is done in less than half the time of the old way, and that it is more entire, the resulting grape sugar being free of gum, and of a purer, finer taste.

2. *Neutralization or Separation of the Sulphuric Acid from the Sugar Solution.*—When by a sufficiently long boiling the desired degree of conversion into either glucose or grape sugar is accomplished, the sulphuric acid must be removed from the liquor. This end is reached by the addition of carbonate of lime (or technically, powdered chalk, marble or limestone). This is decomposed by the acid, which combines with the lime and expels the carbonic acid gas, which causes the liquor to foam. Chalk or marble must be ground to the finest degree possible, and must be added in small quantities (handfuls) only at a time, in order to prevent overflowing, the liquor being constantly stirred until the last addition causes no more effervescence or bubbling. For every pound of oil of vitriol applied, one pound of carbonate of lime is required, but since chalk, marble or limestone are not pure carbonate of lime, and an excess of them is of no harm, rather more, say 1¼ pounds to every pound of acid applied, may be taken. The chalk or marble powder is best stirred up in water to a milk before it is poured into the liquor.

As a neutralizing agent slaked lime has also been recommended and used. It has two advantages over chalk: it is cheaper, and can easily be made into the finest milk. Its application is somewhat difficult, however, and dangerous to the resulting sugar, as it is not very easy to ascertain when just enough is added, and the least excess of it will color the sugar yellow or brown. Another quite serious trouble with lime is caused by the large quantities of magnesia it often contains—25 to 35 per cent. are quite usual in the different kinds of lime made and sold in the United States along the Atlantic coast. Lime combines with sulphuric acid to make sulphate of lime, which is almost insoluble, and subsides nicely from the liquor on standing. Magnesia, however, forms sulphate of magnesia, or Epsom salts, which, as everybody knows, has a bitter taste. As this salt is very soluble, it does not deposit but remains in the liquor, and will give the resulting glucose or grape sugar that bitter aftertaste so often noticed.

After the neutralization of the liquor is effected, it is drawn off from the converting vat or kettle into a tub or tank below, and allowed to settle for 24 hours. This tank should be surrounded by a bad conductor, and well covered, in order to prevent the cooling of the liquor, as fermentation will otherwise soon set in and turn it sour. When the sediment has pretty well subsided, the clear liquor is drawn off and boiled down (or evaporated, as chemists express themselves more elegantly). The sediment or mud is poured into filtering bags, which, after draining, are subjected to pressure.

The remainder in the bags is good for manure.

3. *Evaporation and Purification of the Liquor.*—The thin liquor has next to be boiled down to a syrup. This may be accomplished in a shallow copper kettle over a low fire, or better by means of a steam jacket or coil. Modern demands as to color and flavor, however, are so great that a vacuum pan can hardly be dispensed with. The evaporation is carried on to about 25 or 30° B.=45 or 55 saccharometer per cent., when the solution has acquired the consistency of a thin syrup, and is now quite turbid again by the separation of sulphate of lime, which had been dissolved. To get rid of this the syrup is drawn off again into subsiding tubs, and allowed to settle for a few days, or it is filtered through a layer of sand. To remove the last trace of dimness and color, bone charcoal filters are provided. They consist in cylindrical tanks, rather high, with sieve bottom, spread with a cloth and filled with granular bone-black.

In large establishments these filters are of sheet or cast iron, from 2 to 6 feet wide and more, and from 10 to 30 feet high. For small manufacture wooden ones, such as old whiskey barrels, will answer for the purpose right well; one head is removed, and the other provided with a number of small holes to serve as false bottom. It is covered with a suitable blanket, and filled with bone charcoal of the same quality as used in sugar refining in general. The thin liquor is poured upon, and, slowly and evenly passing through the animal charcoal, leaves all color and mud behind, and runs off white and clear, the bone charcoal absorbing impurities and coloring-matter. When its power is exhausted, it is washed with boiling hot water, dried and reburnt, and may then be used over again for a great many times.

The clear decolored thin syrup is drawn back into the vacuum pan and boiled down. If the conversion was done with a view of making starch-syrup or glucose, the boiling is continued till the syrup gauges hot 40° B, when the product is ready for the market. On cooling it will form a very heavy (45°) thick syrup, clear and colorless, or almost so, of an agreeable pure taste, sweet and mucilaginous at once. It should not deposit any crystals on standing, and shouldn't turn sour or mouldy.

In the other case, if grape sugar is intended, the boiling is discontinued when the contents of the pan gauge 38° or 40°. They are then also drawn off in crystallizing tanks, and allowed to cool and congeal. The resulting crystalline mass is freed from syrup by strong pressure, after which it is remelted and cast into moulds; or, if a less pure article is desired, the syrup is evaporated in the pan (to about 44°) till on cooling it hardens completely. It is run into packing boxes directly, and, while cooling, stirred occasionally to promote the formation of a uniform grain.

The manufacture of grape sugar from *pulp* (the waste of starch manufacture), *saw-dust, rags, etc.*, which is sometimes spoken of, has never acquired any practical shape. Not only is the required amount of acid a very large one (one pound and more to every pound of rags), but the resulting product is so impure that it could never be used for sweetening purposes. It might be put to fermentation, and by distilling turned into alcohol—if we hadn't purer and cheaper raw materials for the same product.

MANUFACTURE OF GLUCOSE BY MEANS OF MALT.

During the germination of grains in the process of malting, a peculiar body (or mixture of bodies) is formed, named *diastase*, which has the mysterious power (simular to sulphuric acid) to turn starch into grape sugar and dextrine gum, at a temperature of 140° to 165°. Such grains, which have been made to germinate by soaking in water and spreading in thin layers on floors for from six to fourteen days, and then were dried to interrupt growing, are known everywhere by the name of *malt*, and used extensively in brewing and distilling, for the conversion of the starch into sugar in the process of *mashing*.

For the conversion of every 100 parts of starch, from 5 to 10 parts bruised malt are required, with 350 to 400 water. Water and malt are heated to 140° to 155° F.; then the starch added, previously stirred up with water, and with constant stirring the temperature is raised to 160° and 165°, and kept there for some time to increase the amount of sugar. When the conversion is complete the heat is raised to boiling, the wort skimmed and filtered and then boiled down. The resulting syrup is very gummy, light-brown colored, and has a peculiar taste, by no means disagreeable, resembling that of malt. However, it is subject to souring and moulding, and very much so; when, instead of starch, corn meal directly is applied.

It remains to say something of the different uses of glucose and grape sugar. The largest quantity of grape sugar is probably consumed for the purpose of improving wines. This is done on the following principles:

When the proportion between the chief constituents of the must, sugar, acid, and water are such that no good wine would result on fermentation, these proportions are altered and improved by the addition of grape sugar. When in a bad season the must is poorer in sugar but richer in acid than in a good one, by the addition of the proper quantity of grape sugar and water the equilibrium is restored.

In countries wherein the grape juice acid is always in excess, certainly this method of improvement (called after its inventor, Gall's method), is generally taken advantage of. Another way of using grape sugar in preparing wine was taught by Petiot. The husks of the grapes, after expressing the juice, still contains enough extractive matter (acids, salts, etc.) to make a tolerable good wine when fermented together with a solution of sugar of proper strength.

Gall's method is almost always applied in making wines from fruits, as currant, gooseberry, etc., wine, the acid predominating always in these fruits. Also in the manufacture of artificial wine (of which a very large quantity is consumed in this country) grape sugar plays an important part. In beer-brewing also an enormous quantity of this sugar is worked up. We state on the authority of Prof. Wagner, in Wurzburg, Bavaria, that to every three cwt. of malt one cwt. of potato-sugar is employed. A large quantity also of this sugar by heating is turned into "sugar coloring," originally used for coloring cordials, etc., then to imitate rum or cognac, and to give whiskey its proper much esteemed color; and where the erring of taste has gone far enough, also lager beer receives its dark color by burnt sugar. That glucose and grape sugar are also largely employed in fruit preserving, confectionery, etc., I hardly need to mention here.

As with commercial cane sugars, so also with glucose and grape sugar; there is a great difference in quality, and no easy way of establishing their real value. Pure taste, absence of color, perfect transparency, and great density are the points by which glucose may be judged. Pure grape sugar should be perfectly white, opaque, of a dry large grain, and, like glucose, have a pleasant taste.

There seems to prevail quite a popular prejudgment that neither strong glucose nor hard grape sugar can be made from corn starch, but that potato starch is required, and that corn, containing an oil, produces a disagreeable flavor. A more unfounded superstition than this is hardly possible, for there is as much difference between the "potato sugars" of different European manufacturers as there is between "potato sugar" on one hand and "corn sugar" on the other; and as to the corn oil, I am of the opinion that it is pretty well removed during the preparation of the starch. The potato sugar manufacturer has quite a similar foe to battle with. During the conversion of potato starch, such an unpleasant odor is disengaged with the steam that (as Otto reports) a starch-sugar factory in Braunschweig, Germany, had to be removed out of town as a public nuisance.

By looking to a complete conversion, a most careful separation of the acid, and a proper use of bonecharcoal, the difficulties in manufacturing glucose and grape sugar are overcome.

CHRYSOLIN, A NEW YELLOW DYE DERIVED FROM RESORCIN.

By F. REVERDIN.

THE coloring matter of which we are about to speak, and which we have prepared since March this year at the works of MM. P. Monnet & Co., at Geneva, is formed by the simultaneous action of phthalic and sulphuric acid upon benzyl-resorcin.

Benzyl-resorcin is obtained very readily either by causing the chloride of benzyl to act upon resorcin in presence of a small quantity of zinc-powder, or by heating an alkaline and alcoholic solution of resorcin with chloride of benzyl, or, lastly, by heating to about 150° in the oil-bath, a mixture of 1 molecule of resorcin and of 2 molecules of chloride of benzyl.

The most simple manner of preparation consists in adding the chloride of benzyl, little by little, to the melted resorcin; a large quantity of hydrochloric acid escapes, and the mass becomes a reddish-brown. When all the chloride of benzyl has been introduced it is heated to 150° in the oil-bath in a flask fitted with an ascending condenser until the escape of hydrochloric acid is at an end. The product of the reaction is poured into water, boiled to expel the last traces of chloride of benzyl, let settle, and decanted.

The compound thus obtained is a strongly-colored oil, very thick, insoluble in water, in which it sinks; it distils at a very elevated temperature, with partial decomposition. It dissolves in alcohol with a yellow color; the solution has a decided green fluorescence. Benzyl-resorcin is soluble also with a yellow color in benzol, chloroform, and ether.

Preparation of Chrysolin.—The following method dispenses with the previous preparation of benzyl-resorcin: We heat in the oil-bath to 130° to 140° in a retort of enamelled cast-iron.

Sulphuric acid	460 grms.
Common phthalic acid	1 kilo.

The letter substance is transformed, in this operation, into phthalic anhydride. We then introduced into the retort:

Resorcin	1 kilo.
Sulphuric acid	460 grms.
Chloride of benzyl	1 kilo.