edges of the hole. The ends of the copper wires are made fast to binding posts, screwed into a narrow strip of wood upon the front of the battery of water-baths.

One heater is required for each four-holed water-bath, and the heaters are connected in parallel. The length of the iron wire in one heater is seventy feet, and its resistance when hot is twenty-six ohms. The potential difference across the ends of the heating coils is fifty-two volts, thus using two amperes of current and 104 watts per heater. The heat generated is sufficient to keep the water in the bath at 65° C., and the ether in the extraction apparatus falls from the condenser at the rate of twenty or twenty-five drops per minute. The currents from a storage battery and from a 125-volt dynamo have been used to run this apparatus with perfect success, and with little attention and no risk of fire.
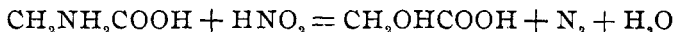
September 25, 1898.

GLYCOLLIC ACID: ONE OF THE ACIDS OF SUGAR-CANE.

BY EDMUND C. SHOREY.

IN continuing work on organic non-sugar in sugar-cane, indicated in a paper[1] "On the Principal Amid of Sugar-Cane," glycollic acid was prepared from the sugar-cane amid by the action of nitrous acid,

$$CH_2NH_2COOH + HNO_2 = CH_2OHCOOH + N_2 + H_2O$$

and the acid so obtained compared in chemical and physical properties with glycollic acid obtained from other sources, monochloracetic acid, hippuric acid, etc. The samples of glycollic acid obtained in various ways were found to be identical in every respect with that obtained from the sugar-cane amid.

The presence of glycollic acid as such in sugar-cane was, in a sense, discovered by accident, and its isolation and identification are of considerable interest to the sugar manufacturer, the analyst, and the student of plant physiology. It was noted that on adding a few drops of strong nitric acid to a sample of cane juice, clarified for the polariscope in the usual way, with a slight excess of lead subacetate, a white crystalline precipitate was thrown down. This, on examination, was found to contain

[1] This Journal, 19, 11.

lead, and on decomposing with hydrogen sulphide gave an acid solution, which, on evaporation to a sirup, deposited needle-shaped crystals, generally grouped in radiating clusters. These crystals were exactly the same in appearance as those of glycollic acid, which had been prepared from various sources, and were found to possess the same chemical and physical properties. To further verify the identity of the various preparations with glycollic acid, this acid was prepared by still another method ; *viz.*, by the action of caustic potash on sulphonic acetic acid,

$$CH_2\diagup^{SO_2OH}_{\diagdown COOH} + KOH = CH_2\diagup^{OH}_{\diagdown COOH} + KHSO_3.$$
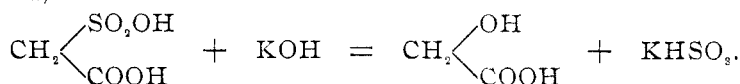
The glycollic acid formed in this case was the same in every respect as that which had already been prepared by other methods.

The crystalline precipitate thrown down by nitric acid appears to be a mixture of normal and basic lead glycollates, containing from sixty to seventy per cent. of lead. The isolation of glycollic acid from cane juice in this way is open to the objection that it may have been formed from glycocoll by the action of some nitrous acid in the nitric acid, and may not occur as such in the cane. To remove this objection, advantage was taken of the sparing solubility of the copper salt, and the acid has been isolated from cane juice in quite large quantities by the following method :

The fresh cane juice was treated with an excess of freshly precipitated cupric hydroxide, washed thoroughly with cold water by decantation, and the precipitate treated with hydrogen sulphide, filtered from cupric sulphide, and the resulting acid solution evaporated until crystals began to form, when, on cooling, a solid mass of crystals was obtained. By this method glycollic acid equivalent to from seventy-five to eighty per cent. of the total acidity of the juice has been obtained ; but its value as a quantitative method has not been established. Glycollic acid prepared in the various ways mentioned has been obtained in four-sided needle-shaped crystals generally arranged in tufts, soluble in water, alcohol, and ether, with a purely sour taste not unlike that of tartaric acid. If great care be taken not to carry

the evaporation of the solution too far, the crystals are quickly formed, are completely soluble in water again, are unchanged in the air, melt, turn brown, and decompose below 100° C., and give precipitates in neutral solution with lead acetate, mercuric nitrate, and cupric sulphate.

The most notable characteristic of glycollic acid is the ready formation of the anhydride. If the water solution be evaporated to dryness stopping short of the formation of brown color, the mass of crystals presents the same appearance as that obtained by careful evaporation noted above; but it rapidly deliquesces in the air, and on treating with water a portion is found to be insoluble as white flocks or as a white powder. This insoluble portion is the anhydride, part of which is dissolved by the acid remaining, resulting, if not too dilute, in a thick solution not unlike vaseline, from which needles of glycollic acid are slowly deposited. If the free acid be neutralized with caustic soda the whole of the anhydride is precipitated.

In some respects glycollic acid resembles malic acid, and might, in some cases, be confounded with it, but it differs at the following points :

1. Glycollic acid is more readily obtained in crystalline form.

2. It is optically inactive : natural malic acid appears to be always optically active, being right- or left-handed as it is more or less concentrated.

3. The lead precipitate obtained from neutral solution of glycollic acid is soluble in acetic acid and insoluble in strong ammonia.

4. On heating, glycollic acid chars and suffers decomposition, the chief product of which is formic acid. Malic acid decomposes into maleic and fumaric acids, which can readily be identified.

Aconitic acid has often been stated to be present in sugar-cane, and for this reason the glycollic acid in cane juice might be mistaken for it, but they can readily be distinguished by the fact that aconitic acid melts at 140° C., boils at 160° C., decomposing into itaconic acid and carbon dioxide. I have before me, at the present writing, preparations of glycollic acid made in the following ways :

1. By the action of nitrous acid on glycocoll, obtained from hippuric acid.

2. By the action of nitrous acid on glycocoll obtained from sugar-cane.

3. Obtained directly from cane juice by treatment with cupric hydroxide and subsequent decomposition with hydrogen sulphide.

4. By the action of caustic potash on sulphonic acetic acid and isolation as the copper salt, as above.

These four preparations are exactly the same in appearance, and I have not been able to find any physical or chemical test, by which one can be distinguished from another.

To the sugar manufacturer the presence of glycollic acid presents the following points of interest : In evaporating cane juice in multiple-effect evaporators, acid vapors are sometimes given off and the free acid can be found in the condensed vapor from the following drum, or under other conditions the acid is found in this water in combination. In the *Planters' Monthly* (Honolulu), **15**, 8, E. Hartmann has shown that these condensed vapors contain organic acids, chiefly formic, in combination with iron. Hartmann assumes that the formic acid results from the oxidation of sugar in the process of evaporation ; but, as I have already noted, glycollic acid is decomposed below 100° C., giving formic acid as one product of decomposition, and it is quite possible for this decomposition to take place in cane juice under certain conditions.

The formic acid, given off on heating glycollic acid, I have identified by its general physical properties, its action on silver nitrate, and by its conversion into the copper salt, the anhydrous salt containing 41.1 per cent. copper. The exact behaviour and conditions under which free glycollic acid and the calcium salt decompose, or undergo change, when heated in sugar solutions, are not yet determined, and, as subjects of future study, present possible explanation of several hitherto unexplained facts in sugar-house work. Three of these may be briefly noted :

1. It is known that if raw acid cane juice be boiled or evaporated, it becomes less acid, and it is also well known that starting with cane juice exactly neutral, the molasses from the second or third sugar may be quite acid, without any fermentation hav-

ing taken place. The ease with which glycollic acid is converted into the anhydride, which is a neutral body, and the fact that the anhydride, on long boiling with water, is converted into the acid again, have a very probable connection with these facts.

2. The natural coloring-matter of cane juice is quite different from that which results from the processes of sugar manufacture, and which causes largely the dark color of low-grade sugars and molasses. The former can be completely removed by lead subacetate, while the latter, which seems to partake of the nature of caramel, cannot, in many cases be removed by any reagent. The ease with which glycollic acid chars or becomes brown when heated, explains probably the presence of a portion of this coloring-matter in low-grade products of the sugar-house.

3. It is customary to boil low-grade molasses to a certain consistency known as "string proof," and molasses thus boiled is placed in coolers or wagons and allowed to remain until granulation has reached the point when the massecuite can be conveniently and profitably dried in centrifugal machines. It sometimes happens that in a short time, twenty-four to thirty-six hours after this massecuite has been placed in coolers or wagons, considerable frothing or foaming takes place, and a considerable portion of the massecuite runs over on the floor. In Louisiana, where it happens much more commonly than in Hawaii, this foaming is attributed to boiling at too high a temperature, 165° F. being considered the point beyond which it is not safe to go. In Hawaii this rule does not always apply, but when foaming takes place it undoubtedly is due to the decomposition of some body in the slowly cooling mass, and the gas resulting from this decomposition entangled in the viscous mass necessarily causes foaming. The presence of glycollic acid, a body easily decomposed at a comparatively low temperature, is not unlikely to be connected with this phenomenon.

To the sugar chemists the presence of glycollic acid in sugar-cane presents at least two points of interest; First as a possible explanation of the formation of the color of low-grade sugars and molasses which every worker with the polariscope finds so troublesome to remove; and second, as a probable explanation

of the impossibility of accurately estimating ·the total solids in cane juice by evaporating to dryness. When cane juice is evaporated to dryness, even in a vacuum, some of the bodies contained suffer decomposition into gaseous products, giving a residue less than the actual weight of solids originally held in solution ; the decomposition of glycollic acid is no doubt responsible for a portion of this loss.

The presence of glycollic or hydroxyacetic acid, $CH_2OHCOOH$, in sugar-cane is full of suggestions to the physiologist. The principal amid of sugar-cane, glycocoll, CH_2NH_2COOH, is very closely related to this acid ; in what relation do they stand in the plant ? Is one formed from the other or have they each their separate rôle in the plant economy ? Glycollic acid is readily obtained by oxidation of dextrose or levulose and so from cane-sugar ; does it stand in any relation to the building-up of the cane-sugar in the plant ? Glycocoll and glycollic acid are comparatively simple methyl compounds ; how close do they stand to the supposedly simple first product of carbon assimilation ? These and numerous other questions present themselves, —questions, the answers to which extend over the whole realm of plant physiology.

LABORATORY OF KOHALA SUGAR CO.,
    KOHALA, HAWAII, Sept. 8, 1898.

A NEW APPARATUS FOR THE DETERMINATION OF VOLUME.[1]

BY CHAS. F. MCKENNA.

THIS instrument has been devised in order to obviate certain objectionable features of those others, whose type is the Schumann or Candlot Volumenometer. Such objections are :

a. The reading is not delicate, since the caliber of the tube is large. Such instruments are limited in accuracy by our ability to read to 0.01 cc. This is obviously impossible in such tubes.

b. The solid must be introduced through the liquid on the lines where the reading is subsequently made. The slight coating here formed on the walls of the tube tends to increase the difficulty of making this observation correctly.

c. The ground joint by which the tube fits into the flask