to the usual rotatory value for invert sugar, but a peculiar series of rotation changes lasting through many hours was observed, though the final rotation was that of invert sugar. The quantitative interpretation of these rotatory changes shows that the substances which are initially liberated from cane sugar by invertase are α -glucose, specific rotation 109°, and a new form of fructose, α -fructose, specific rotation 17°. The inversion of cane sugar by invertase thus follows the order

 α -fructose $\implies \beta$ -fructose

Cane sugar

,

 α -glucose $\implies \beta$ -glucose

The experiments show that the rotatory power of cane sugar (66°) is equal to the sum of those of its constituent sugars, α -glucose (109°) and α -fructose (17°); in similar manner the rotation of raffinose (124°) is equal to the sum of those of its constituents, α -melibiose (171°) and α -fructose (17°). If the symbol < denote the free carbonyl group of the aldehyde and ketone sugars the constitution of cane sugar and of raffinose can be written, cane sugar = α -glucose <> α -fructose, and raffinose = galactose < α -glucose <> α -fructose. It is not known yet whether the first member of raffinose is α - or β -galactose, though it is probable from the fact that the enzyme emulsin splits raffinose to give galactose and cane sugar, that the member is β -galactose.

Lastly, it is shown that brewers' yeast attacks the α - and β -forms of glucose at very nearly the same rate, though there is an indication that the α -form is fermented slightly more rapidly.

SOME ORGANIC TUNGSTATES.

By John B. EKELEY. Received March 29, 1909.

Freshly prepared tungstic acid, H_2WO_4 , dissolves readily in aqueous solutions of most aliphatic amines, with the formation of substituted ammonium tungstates. From the resulting solutions, the salts crystallize out on evaporation, except in some cases where it is first necessary to evaporate to dryness, drive off the excess of amine at about ro5°, and then crystallize. Of the salts described in this paper, all but two are readily soluble in water. Ethylenediammonium tungstate is difficultly soluble after it has once crystallized out. Diamylammonium tungstate dissolves with difficulty in water, but readily in methyl alcohol.

If any of these salts are heated slowly, the amine is driven off and at the same time the tungstic acid is partially reduced to the blue oxide, which, on further heating, glows and quickly changes to the yellow WO_{g} .

664

In all cases the tungstic acid was prepared by boiling finely powdered sodium tungstate with concentrated hydrochloric acid, and washing the yellow precipitate by decantation until free from chlorides. Salts of the following bases were prepared: methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, propylamine, dipropylamine, diamylamine, and ethylenediamine. The water of crystallization in the salts was determined by drying at 110° to constant weight, and the WO_3 by heating to constant weight at a low redness.

Methylammonium Tungstate, $(CH_3NH_3)_6W_7O_{24}.6H_2O.$ —Tungstic acid was dissolved in a slight excess of 33 1/3 per cent. methylamine solution, evaporated to dryness on the water bath, heated at 105° until there was no odor of methylamine, dissolved in water, and recrystallized. Colorless prisms, which begin to lose their water of crystallization as soon as they are dry.

$$(CH_{3}NH_{3})_{6}W_{7}O_{24}.6H_{2}O \begin{cases} Calculated: H_{2}O, 5.46; WO_{3}, 82.34. \\ Found: H_{2}O, 5.10; WO_{3}, 82.38. \end{cases}$$

Dimethylammonium Tungstate, $((CH_3)_2NH_2)_{10}W_{12}O_{41}.I_3H_2O_{--}$ Tungstic acid was dissolved in a slight excess of 33 I/3 per cent. dimethylamine solution, evaporated on the water bath, and allowed to crystallize. Colorless truncated octahedra, which retain their water of crystallization fairly well.

$$[(CH_3)_2NH_2]_{10}W_{12}O_{41}I_3H_2O \begin{cases} Calculated: H_2O, 6.58; WO_3, 78.24. \\ Found: H_2O, 6.66; WO_3, 78.28. \end{cases}$$

Trimethylammonium Tungstate, $((CH_3)_3NH)_2W_4O_{13}$. H_2O .—Tungstic acid was dissolved in a slight excess of a 33 1/3 per cent. trimethylamine solution, evaporated on the water bath, and allowed to crystallize. Colorless needles and plates.

$$[(CH_{a})_{a}NH]_{2}W_{4}O_{1a}H_{2}O \begin{cases} Calculated: H_{2}O, 1.65; WO_{3}, 85.76. \\ Found: H_{2}O, 1.50; WO_{3}, 85.61. \end{cases}$$

Ethylammonium Tungstate, $(C_2H_5NH_3)_6W_7O_{24}.5H_2O.$ —Tungstic acid was treated with a slight excess of 33 1/3 per cent. ethylamine solution and allowed to evaporate spontaneously. Colorless prisms were obtained, which do not lose their water of crystallization so easily as the corresponding salt from methylamine.

$$(C_{2}H_{\delta}NH_{2})_{\delta}W_{7}O_{24}.5H_{2}O \begin{cases} Calculated: H_{2}O, 4.40; WO_{3}, 79.68. \\ Found: H_{2}O, 4.38; WO_{3}, 80.04. \end{cases}$$

Diethylammonium Tungstate, $((C_2H_5)_2NH_2)_2W_4O_{18}$, $3H_2O$.—Tungstic acid was treated with diethylamine and water and warmed. After the solution had stood a day, a white residue was filtered off. The filtrate was partially evaporated on the water bath and then allowed to evaporate spontaneously. After several days the liquid became thick, showing a few minute crystals throughout the mass. The colloid could be drawn out into threads. The whole mass was then evaporated again on the water bath, but it held moisture tenaciously. On drying at 105° until there was no further odor of the amine, the mass became brittle. It was dissolved in water and allowed to stand. After a day, large, pale, strawcolored crystals formed, which become opaque shortly after being removed from the mother liquor. The crystals are truncated octahedra and prisms, which, when dry, melt to a viscous blue liquid on being heated.

$$[(C_{2}H_{5})_{2}NH_{2}]_{2}W_{4}O_{13} \cdot 3H_{2}O \begin{cases} Calculated: H_{2}O, 4.79; WO_{3}, 79.94. \\ Found: H_{2}O, 4.71; WO_{3}, 80.39. \end{cases}$$

Propylammonium Tungstate, $(C_{3}H_{7}NH_{3})_{10}W_{12}O_{41}.6H_{2}O.--Tungstic acid was warmed with propylamine and water, evaporated on the water bath, and allowed to crystallize. Minute colorless needles.$

$$(C_{3}H_{7}NH_{3})_{10}W_{12}O_{41}.6H_{2}O \begin{cases} Calculated: H_{2}O, 3.02; WO_{3}, 77.91. \\ Found: H_{2}O, 2.96; WO_{3}, 77.97. \end{cases}$$

Dipropylammonium Tungstate, $((C_3H_7)_2NH_2)_2W_4O_{13}$.H₂O.—Tungstic acid dissolves slowly in dipropylamine and water. The solution was evaporated to dryness on the water bath, the residue heated several hours at 105°, and recrystallized from water. Colorless hexagonal plates and short thick prisms, having an appreciable purple color in thick layers, nelt on heating to a blue liquid, giving off amine.

$$[(C_{3}H_{7})_{2}NH_{2}]_{2}W_{4}O_{13}H_{2}O \begin{cases} Calculated: H_{2}O, I.54; WO_{3}, 79.60. \\ Found: H_{2}O, I.33; WO_{3}, 79.59. \end{cases}$$

Diamylammonium Tungstate, $((C_5H_{11})_2NH_2)_2W_5O_{16}$ (anhydrous).—Tungstic acid, on being treated with diamylamine and water, partly dissolves and partly forms a white sticky mass. This was evaporated on the water bath to dryness, and then heated at about 110° until most of the amine odor had disappeared. The residue is only slightly soluble in water, but dissolves in methyl alcohol to a pale straw-colored solution, from which, after standing several days, long, pale, straw-colored needles (sometimes several inches in length and about a square millimeter in cross section) separate. On removing the transparent needles from the mother liquor, they quickly become opaque, losing alcohol of crystallization. It was impossible to obtain checking results as to how much alcohol of crystallization the crystals contained.

$$[(C_{\delta}H_{11})_{2}NH_{2}]_{2}W_{\delta}O_{16} \begin{cases} Calculated: WO_{3}, 77.74. \\ Found: WO_{3}, 77.66. \end{cases}$$

Ethylenediammonium Tungstate, $C_2H_{10}N_2W_2O_7$.—Tungstic acid was dissolved in a slight excess of ethylenediamine solution and heated on the water bath. As the solution increased in concentration white microscopic needles separated, which were soluble in water with difficulty. They contained water of crystallization, but no checking results were obtained in the moisture determinations.

$$C_2H_{10}N_2W_2O_7$$

 $\begin{cases} Calculated: WO_3, 85.61. \\ Found: WO_3, 85.97. \end{cases}$

UNIVERSITY OF COLORADO, March 28, 1909.