

mixtures of previously known arsenicals—which are actually formed in place of Steinkopf's new types—can be separated. Steinkopf reinvestigated only two of the six reactions and merely waives his claim to the discovery of the new compounds which he originally thought had been formed in the four other reactions.

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THE CALCIUM CHLORIDE MODIFICATIONS OF MANNOSE AND GULOSE

Sir:

The writer previously reported [*J. Bur. Standards*, **8**, 615 (1932)] that α - and β -*d*-mannose, on oxidation with bromine in the presence of barium carbonate yield δ -lactones, which indicates that these sugars have 1,5 ring structures. Application by the writer of the same method to the labile calcium chloride compound of mannose reported by Dale [THIS JOURNAL, **51**, 2225 (1929)] shows that this substance gives largely mannonic γ -lactone. This is evidence that *d*-mannose·CaCl₂·4H₂O has a 1,4 ring structure rather than a normal 1,5 ring.

A quantitative oxidation of the labile mannose compound is not possible because, in solution with water, it is converted rapidly into normal α -*d*-mannose. If the oxidation period is short the oxidation product is largely γ -lactone, but with longer periods considerable δ -lactone is formed. Presumably the γ -lactone is derived from the original product, while the δ -lactone arises from normal α -*d*-mannose, formed by the mutarotation reaction.

A 0.025-mole sample of crystalline mannose·CaCl₂·4H₂O was added to 100 cc. of ice water containing 5 cc. of bromine and 15 g. of barium carbonate. After five minutes the reaction was stopped by shaking with olive oil. The aqueous solution contained 0.0127 mole of unoxidized sugar and 0.0123 equivalent of lactone (estimated by titration). Hence the oxidation was 49% complete. The specific rotation of the product based on the above analysis, after eighteen minutes, was +42.6°; (60 min.), +37.9°; (180 min.), +35.2°; (48 hrs.), +26.7°. Since the rotation of the δ -lactone is +111°, the γ -lactone +52°, and that of the unoxidized sugar about +20°, changing to +14.7°, it is estimated that the oxidation product contained 76% γ -lactone and 24% δ -lactone.

The writer is applying his Barium Carbonate Oxidation Method to the sugars and their solutions to obtain data as to the isomeric changes accompanying mutarotation and the effect of salts on the equilibrium existing in solutions. It was previously shown [*Bur. Standards Jour. Res.*, **5**, 748 (1930)] that the equilibrium between the various forms of gulose in solution may be altered by the addition of calcium chloride. The experiments

on mannose indicate that the changes in the compositions of the solutions may involve changes in the proportions of the ring isomers. Rapid measurements at 0° of the optical rotations of α -*d*-gulose \cdot CaCl $_2$ \cdot H $_2$ O show that the mutarotation previously reported is preceded by a short period in which the change in rotation is less rapid than later on. This is evidence that the mutarotation is more complex than the reversible interconversion of only two isomers. It is noted that a new gulose calcium chloride compound has been separated. It corresponds to the formula (C $_6$ H $_{12}$ O $_6$) $_2$ CaCl $_2$, and gives $[\alpha]_D^{20} +34^\circ$ (1.4 minutes after solution in water), constant -167° (3.3292 g./100 cc.).

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CONCENTRATION OF THE HEAVY HYDROGEN ISOTOPE

Sir:

In connection with investigations on some commercial chromium plating baths, the writers have determined the specific gravities of the water contained therein.

The waters from nine baths give specific gravities varying from 1.00002 to 1.00064. These baths have been operated for varying periods of time, the maximum being about three years.

Increases in specific gravity on prolonged electrolysis of water have been reported by Washburn and Urey [*Proc. Nat. Acad. Sci.*, **18**, 496 (1932)] and Lewis [THIS JOURNAL, **55**, 1297 (1933)] and by them attributed to the concentrating of the heavier isotopes of hydrogen. On this basis the highest specific gravity (1.00064) observed by us indicates the presence of about 0.6% of water containing the heavier hydrogen isotope in one of the samples examined.

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THE PREPARATION OF CRYSTALLINE β -*l*-ALLOSE, A NEW ALDOHEXOSE, FROM *l*-RIBOSE BY THE CYANOHYDRIN REACTION

Sir:

In the extension of our studies with *l*-ribose, the synthesis of which from *l*-arabinose through *l*-arabinal was recently announced [THIS JOURNAL, **54**, 4749 (1932)], we have undertaken the preparation of the unknown aldohexoses, *l*-altrose and *l*-allose, by the cyanohydrin reaction. Our investigations have been guided in large measure by the valuable contribution of Levene and Jacobs [*Ber.*, **43**, 3141 (1910)], who prepared the crystalline