

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

calcium salt of *d*-altronic acid and the crystalline lactone of *d*-allonic acid after the addition of hydrogen cyanide to *d*-ribose. After formation and reduction of the sirupy lactone of *d*-altronic acid and the crystalline lactone of *d*-allonic acid, Levene and Jacobs obtained sirups which were shown to contain *d*-altrose and *d*-allose.

After applying the cyanohydrin reaction to 30 g. of *l*-ribose we were able to isolate 17 g. of the crystalline calcium salt of *l*-altronic acid and 14.5 g. of the crystalline lactone of *l*-allonic acid. The recrystallization of the lactone of *l*-allonic acid to constant properties gave 13 g. with m. p. 130° and $[\alpha]_D^{25} +6.3^\circ$, in water. Levene and Jacobs found $[\alpha]_D^{20} -6.8^\circ$ for *d*-allonolactone.

The reduction of the 13 g. of *l*-allonolactone was accomplished in the usual manner with sodium amalgam. After evaporation of the solution, removal of sodium sulfate by precipitation in hot 85% alcohol, and evaporation of the filtrate, the unchanged *l*-allonolactone was removed by conversion to the barium salt of *l*-allonic acid and precipitation of the latter from hot 90–95% alcohol. During the evaporation, under reduced pressure, of the final alcoholic filtrate the *l*-allose began to crystallize in rosetts of very slender prisms. These crystals were filtered out and combined with other portions of the sugar, obtained by further evaporation, to give 9.2 g. of white crystalline *l*-allose. By one recrystallization of this quantity of *l*-allose from 93% alcohol there was obtained 7.2 g. of the purified sugar, with m. p. 128–129°. A 4% aqueous solution of the *l*-allose gave the following values of $[\alpha]_D^{20}$: -2.88° , four minutes after solution; -8.13° , thirty-four minutes after solution; and -13.88° (constant), twenty hours after solution. By the usual unimolecular equation $1/t \log [(r_0 - r_\infty)/(r - r_\infty)] = k_1 + k_2$ we have determined that the velocity coefficient at 20° of the mutarotation, $(k_1 + k_2)$, is 0.0094 (minutes and decimal logarithms), and that the calculated $[\alpha]_D^{20}$ value at zero time is -1.9° . This crystalline form of the sugar is to be designated β -*l*-allose according to the nomenclature proposed by Hudson [THIS JOURNAL, 31, 66 (1909)], since it is the less levorotatory form of a sugar of the levo configurational series. Crystalline *l*-allose is the sixth crystalline aldehydohexose of the sixteen possible stereoisomers in the series of aldohexoses. The other known crystalline aldohexoses are *d*- and *l*-glucose and galactose, and *d*-mannose.

These investigations, which were facilitated by a Grant-in-Aid from the National Research Council, will be extended to the reduction of the *l*-altronolactone and more fully described in a future publication in THIS JOURNAL. Thanks are expressed to Dr. C. S. Hudson, of the National Institute of Health, Washington, D. C., for his interest and valuable suggestions.

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