without change in k_3/k_2 or k_5/k_4. Between the earlier work,[1] Series 3, $A = 5 \times 10^{-14}$, and Series 5, $A = 1 \times 10^{-14}$, the double front window of the reaction cell was dismantled and the remaining inner window heated to softness.

The data of this Laboratory are, therefore, in complete accord with an energy chain mechanism for the photochemical decomposition of ozone in which (1) the surface acts as an inhibitor, (2) the chain carriers, oxygen atoms and excited oxygen molecules, have an average lifetime of the same order of magnitude as the time between collisions at our pressures and temperatures, and (3) the chain propagating reactions have a positive energy of activation (k_4/k_5 is less than unity).

The author is most grateful to Professor George Shannon Forbes for supplying the materials, apparatus and facilities of his laboratory for this research while the author was associated with him in the pursuit of other problems in photochemistry.

Summary

Initially pure dry ozone at 177 and 390 mm. was photolyzed at λλ 208, 254 and 313 mμ to complete decomposition.

Quantum yields, ϕ, referred to ozone molecules decomposed per quantum absorbed, were found approximately equivalent at 208 and 313 mμ.

The ten-degree temperature coefficient for the photolysis was found to be 1.15 ± 0.02 over the range 0 to 60° after ϕ was corrected for the dark reaction between pressure readings before and after photolysis. The coefficient is apparently independent of the mole fraction of ozone in oxygen and of the temperature interval, even when the dark rate was 20% of the total decomposition. In no case was there an observable after effect.

The ten-degree temperature coefficient for the dark rate over the range 20 to 60° was found to be 3 ± 0.1 for small mole fractions of ozone in oxygen.

Within the limits of experimental error, plots of $1/\phi$ against $p_{O_2}(p_{O_2} + p_{O_3})/p_{O_3}$ fall on smooth curves for which $1/\phi$ increases with this ratio. The decrease in ϕ with increase in light intensity and extinction kp_{O_3} as it varies with wave length at λλ 208, 254 and 280 mμ is secondary. At λ 313 mμ no such dependence of ϕ upon light intensity was observable.

Results, $\phi_{\text{max.}} > 4$ at all wave lengths, are quantitatively accounted for by the mechanism $O_3 + h\nu \longrightarrow O_2' + O$; $O + O_3 \longrightarrow 2O_2'$; $O + O_2 + M \longrightarrow O_3 + M$; $O + S \longrightarrow {}^1/_2\, O_2 + S$; $O_2' + O_3 \longrightarrow 2O_2 + O$; $O_2' + M \longrightarrow O_2 + M$, where M is any energy acceptor including the surface, S.

CAMBRIDGE, MASS. RECEIVED JANUARY 9, 1935

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Rearrangement of Sugar Acetates by Aluminum Chloride. Further Studies on Neolactose and *d*-Altrose[1]

BY NELSON K. RICHTMYER AND C. S. HUDSON

In 1926, Kunz and Hudson,[2] by the action of aluminum chloride on a chloroform solution of lactose octaacetate, obtained the acetochloro derivative of a new disaccharide which they named neolactose. From acetochloroneolactose they prepared the neolactose α- and β-octaacetate; the free sugar was obtained in sirupy form by deacetylation of the α-octaacetate, and the equilibrium specific rotation[3] of neolactose in water was found to be approximately +35°. The structure of neolactose as *d*-galactosido-*d*-altrose was established by acid hydrolysis of the disaccharide and of its oxidation product, neolactobionic acid; the *d*-galactose was readily isolated in crystalline form, while the sirupy *d*-altrose portion was identified (1) through its phenylosazone, (2) through the brucine salt of *d*-altronic acid, and (3) by nitric acid oxidation to crystalline *d*-talomucic acid. It was found that the equimolecular mixture of *d*-galactose and *d*-altrose that results from the acid hydrolysis of neolactose rotates −8.95° in water, from which it follows, since *d*-galactose shows +80°, that the

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. Presented in part before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society, April 22, 1935.

[2] Kunz and Hudson, THIS JOURNAL, **48**, 1978, 2435 (1926).

[3] Throughout the article the rotations are specific rotations at 20° for sodium light.

value of *d*-altrose under such conditions of production of the sugar, is approximately −98° in water.

Last year Austin and Humoller[4] prepared crystalline *l*-altrose from *l*-ribose by the cyanohydrin synthesis, the hexose being generated by the reduction of *l*-altronic lactone with sodium amalgam in cold weakly acid solution, and found the equilibrium specific rotation in water to be −32.3° for *l*-altrose, corresponding to +32.3° for *d*-altrose. The results of these researches were thus in complete disagreement on the specific rotation of *d*-altrose. The following work, in which the crystallization both of neolactose and of *d*-altrose was attained, establishes the cause of the disagreement and brings the results into full accord.

The preparation of α-acetochloroneolactose from lactose octaacetate has been improved by using a mixture of aluminum chloride and phosphorus pentachloride; yields up to 45% have been secured. Removal of the chlorine atom by shaking acetochloroneolactose with silver carbonate in aqueous acetone leads to the formation of the heptaacetate, of which two modifications were obtained. Neolactose β-heptaacetate crystallizes in square prisms melting at 135–136° and shows upward mutarotation in chloroform, the specific rotation changing from +10.0 to +21.0° in the course of several days (Fig. 1); it is converted by acetic anhydride and pyridine to the pure β-octaacetate. The second, the so-called "α"-heptaacetate, crystallizes in clusters of large flakes melting not sharply at 85–95°, and shows downward mutarotation in chloroform, the value changing from +23.3 to +21.0° in the course of twenty-four hours (Fig. 1). It is apparently a double compound composed of the β-heptaacetate and the true α-heptaacetate in a 1:1 ratio, since on cautious acetylation it yields a mixture of the two known octaacetates in approximately that ratio. The two heptaacetate modifications are readily interconvertible.

Deacetylation of the heptaacetate by barium methylate solution led to the crystallization of the parent disaccharide. Neolactose separates from methyl alcohol in large prisms melting with decomposition at 190°, and in water rotates +34.6° changing to +35.5°.

Acid hydrolysis of pure neolactose yielded a mixture of *d*-galactose and *d*-altrose from which the former was removed by fermentation with yeast. The *d*-altrose sirup which remained had a high negative specific rotation in accord with the value −98° estimated in the earlier work. No attempt was made to crystallize the sugar at this stage, but instead it was converted to the crystalline mercaptal by treatment with benzyl mercaptan and concentrated hydrochloric acid.

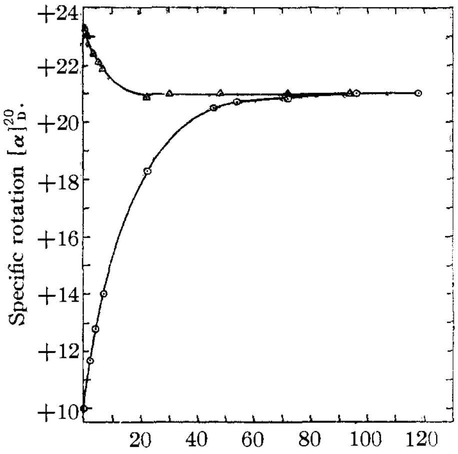

Fig. 1.—Mutarotation of neolactose heptaacetates in $CHCl_3$ at 20°: △, "α"-heptaacetate; ⊙, β-heptaacetate.

d-Altrose benzyl mercaptal melts at 121–122° and rotates +39.4° in pyridine, in close agreement with the melting point 121–122° and rotation −39.2° for the *l*-altrose benzyl mercaptal which was prepared from a small quantity of *l*-altrose placed at our disposal through the kindness of Dr. W. C. Austin. Pure *d*-altrose benzyl mercaptal was then treated under carefully controlled conditions with mercuric chloride and cadmium carbonate, and from the resulting mixture by suitable manipulations the free sugar was crystallized readily. *d*-Altrose thus becomes the eleventh of the sixteen aldohexoses to be secured in crystalline form.[5] In the small sample so far prepared no mutarotation was observed, but the rotation in water (+32.6°) agrees with the equilibrium rotation (−32.3°) reported by Austin and Humoller for *l*-altrose; they also report a small mutarotation of 3.6°.

The specific rotation for crystalline *d*-altrose (+32.6°) is in strong contrast with the value for

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(4) Austin and Humoller, THIS JOURNAL, **56**, 1153 (1934).

(5) The five aldohexoses which have not yet been crystallized are the *d*- and *l*-forms of gulose and idose, and *l*-talose, respectively. A crystalline compound of *d*-gulose with calcium chloride has been reported by Isbell [*Bur. Stand. J. Res.*, **5**, 742 (1930)]. Crystalline *d*-talose has been prepared by Levene and Tipson [*J. Biol. Chem.*, **93**, 631 (1931)], and by Bosshard [*Helv. Chim. Acta*, **18**, 482 (1935)].

the *d*-altrose sirup obtained by acid hydrolysis of neolactose (−98°), but the problem becomes clearer when the crystalline hexose is heated with acid. Thus, *d*-altrose when heated with hydrochloric acid under the same conditions as were used in the hydrolysis of neolactose, changed from +34 to −98°. Similarly, a small sample of *l*-altrose changed from −35 to +98°. This large change in rotation is intimately linked with a very considerable fall in the reducing power of the altrose solution, the mixture reaching an equilibrium at about 43% of the original value. The striking similarity in the behavior of *d*- and *l*-altrose is shown in Fig. 2, in which the changes in reducing power have been plotted on the same curve. The loss in reducing power is presumably due to elimination of the glycosidic hydroxyl through formation of an anhydroaltrose because such an occurrence under similar conditions is known in the case of sedoheptose, recently identified as *d*-altroheptulose,[6] and thus identical in configuration below the carbonyl group, with *d*-altrose. Sedoheptose is weakly dextro-rotatory and is reducing; crystalline anhydrosedoheptose rotates −146° and is non-reducing.[7] From the rotation for *d*-altrose (+32°) and the value −98° for the equilibrium mixture containing 43% *d*-altrose, the specific rotation of the assumed anhydro-*d*-altrose may be estimated as −220°.

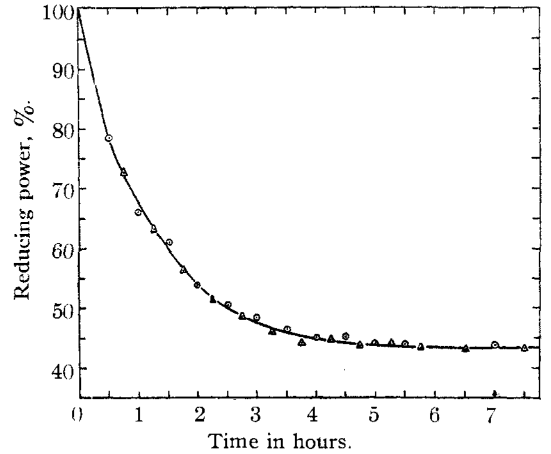

Fig. 2.—Altrose in 0.1 normal HCl at 100°: △, *d*-altrose; ⊙, *l*-altrose.

CHO
HOCH
HCOH
HCOH
HCOH
CH_2OH
d-Altrose

CH_2OH
CO
HOCH
HCOH
HCOH
HCOH
CH_2OH
Sedoheptose
(*d*-Altroheptulose)

It is now seen that the rotation of *d*-altrose found by Austin and Humoller is the rotation that pertains to the sugar itself; in their work the altrose was never subjected to sufficiently acid conditions to generate its anhydro derivative. The rotation −98° found by Kunz and Hudson refers to the equilibrium mixture of *d*-altrose and its anhydro form that results from sufficiently strong acid conditions, such as they necessarily used in order to hydrolyze neolactose.

The application of the aluminum chloride rearrangement to other sugar acetates is now being studied. If *d*-altronic acid or a salt of *d*-altronic acid, such as the crystalline calcium *d*-altronate,[8] can be made readily available through this reaction it may furnish the best way for the preparation, by degradation, of *d*-ribose, the most needed of the pentoses for biochemical studies and at present one of the least accessible.

Experimental

Acetochloroneolactose.—The modified procedure is as follows. To a solution of 50 g. of recrystallized lactose β-octaacetate in 350 cc. of alcohol-free dry chloroform in a one-liter flask is added 100 g. of powdered commercial aluminum chloride and 50 g. of powdered phosphorus pentachloride. The flask is shaken for a minute or two to ensure thorough mixing; then, as the contents become warm and a small amount of hydrogen chloride is evolved, it is connected with a reflux condenser and heated for twenty minutes in a bath at 55–58°. The mixture is cooled, the chloroform layer poured on ice, and the residue, sometimes granular and sometimes a hard gum, carefully decomposed with ice and water. The combined chloroform extracts are washed in succession with ice water, cold aqueous sodium bicarbonate and ice water, dried with calcium chloride, and concentrated *in vacuo* to a thick sirup. This is dissolved at once in 100 cc. of dry ether, and an additional 300 cc. of dry ether added as the acetochloroneolactose begins to crystallize in small prisms. The flask is kept in the refrigerator for a week to complete crystallization. The mixed acetochloro derivatives of neolactose and lactose weigh about 40 g., from which the needles of acetochlorolactose are readily dissolved by cold ethyl acetate. The crude acetochloroneolactose remaining weighs 16–22 g. (33–45% yield). It is pure after one recrystallization from a mixture of chloroform and ether.

A few variations of the procedure may be noted. The action of aluminum chloride alone produced a 4% yield of acetochloroneolactose; that of phosphorus pentachloride alone caused no chlorination and 92% of the lactose octaacetate was recovered unchanged. With carbon tetrachloride in place of chloroform as the medium a 9% yield of the neo compound was obtained. The substitu-

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(6) Ettel, *Coll. Czech. Chem. Comm.*, **4**, 513 (1932).

(7) LaForge and Hudson, *J. Biol. Chem.*, **30**, 61 (1917).

(8) Levene and Jacobs, *Ber.*, **43**, 3143 (1910).

tion of thionyl chloride, phosphorus trichloride, and phosphorus oxychloride for phosphorus pentachloride produced yields, respectively, of 3, 16 and 23%. Contrary to expectations from a statement in the first paper, the action of aluminum and phosphorus chlorides on acetochlorolactose failed to rearrange it to the neo compound.

Neolactose β-Heptaacetate.—The chlorine atom is replaced by a hydroxyl group upon shaking at room temperature 50 g. of acetochloroneolactose with 25 g. of silver carbonate in 500 cc. of acetone and 25 cc. of water until the solution no longer gives a test for halogen (about twelve hours); one hour's boiling accomplishes the same result. The mixture is filtered, and the clear solution concentrated *in vacuo* at 25° to a sirup from which the heptaacetate crystallizes upon addition of ether. The yield is practically quantitative. The heptaacetate is best recrystallized by dissolving in acetone containing 5% of water, concentrating to a sirup, and adding ether cautiously. The square flat prisms apparently contain water of crystallization which they lose upon standing in air, and completely in a vacuum desiccator overnight. The compound is readily soluble in acetone, chloroform and ethyl acetate, moderately soluble in warm methyl and ethyl alcohols and in hot water, and sparingly soluble in ether. The specific rotation became constant after three recrystallizations; after the sixth recrystallization it was +10.0° in U. S. P. chloroform (*c*, 4 to 8), changing in the course of three or four days at 20° to +21.0° (Table I and Fig. 1). The melting point is 135–136°.

Anal. Calcd. for $C_{26}H_{36}O_{18}$: C, 49.03; H, 5.70; acetyl, 11.00 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 48.84; H, 5.85; acetyl, 10.74 cc.

In the absence of sufficient water the heptaacetate may crystallize in fine needles melting at 53–54°; this indicates acetone of crystallization, since the liquid resolidifies and then melts at 135–136°. After standing in a desiccator over granular calcium chloride for two months a sample showed only the higher melting point.

Acetylation of Neolactose β-Heptaacetate.—A mixture of 5 cc. of acetic anhydride and 30 cc. of pyridine, cooled to −10° was added to 5.0 g. of pure β-heptaacetate also at −10°. The acetate dissolved rapidly and the solution was kept in the refrigerator for three days. The octaacetate crystallized readily when the solution was poured into ice and water. After one recrystallization from alcohol the product weighed 5.0 g., melted at 148–149°, and in chloroform rotated −6.3°, which compares favorably with the m. p. 148° and rotation −7.1° for neolactose β-octaacetate after twenty-one recrystallizations by Kunz and Hudson.

The So-called Neolactose "α"-Heptaacetate.—During the preliminary study of the β-heptaacetate it became evident that in some preparations a second type of crystal was separating from the mother liquors; this new compound may be obtained readily by dissolving the β-heptaacetate in acetone, evaporating on a hot plate to a thick sirup, redissolving in a very small amount of acetone and then adding ether and petroleum ether. The product separates in clusters of flaky prisms which are transparent but become translucent when removed from contact with the mother liquor. It is considerably more soluble than the β-heptaacetate in the same solvents. It melts between 85 and 95° to a liquid containing air bubbles which make the exact melting point range uncertain. In chloroform solution it mutarotates downward, hence is called the "α"-heptaacetate; the rotation changed from +23.3 to +21.0° as shown in Table I and Fig. 1. For analysis the sample was dried *in vacuo* at 56° to constant weight.

Anal. Calcd. for $C_{26}H_{36}O_{18}$: C, 49.03; H, 5.70; acetyl, 11.00 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 49.01; H, 5.81; acetyl, 10.82 cc.

The "α"-heptaacetate may be reconverted to the β-heptaacetate by recrystallization from hot water.

Acetylation of Neolactose "α"-Heptaacetate.—The so-called "α"-heptaacetate was treated with acetic anhydride and pyridine in the same manner as was the β-heptaacetate. The product obtained by pouring into ice water was filtered, washed thoroughly with water, and dried *in vacuo* at 56°. It melted at 135–145°, indicating a mixture of α- and β-octaacetates. In chloroform it rotated +21.7°, which would correspond to a mixture containing 47.7% α-octaacetate and 52.3% β-octaacetate, as estimated from the known rotations of the two octaacetates. That the product was a mixture of the α- and β-octaacetates was established by crystallizing it slowly from alcohol, and then separating the crystals mechanically into two fractions. The one, recrystallized once from alcohol, formed the typical rhombohedral prisms of the β-octaacetate, melted at 144–147°, and at 146–148° when mixed with an authentic specimen. The other and less soluble fraction was recrystallized twice from alcohol, and then showed m. p. 176–178°, and rotation +49.6° in chloroform. Recrystallized further, to a constant rotation, it melted at 178–179°, and rotated +53.3°, in agreement with the m. p. 178° and rotation +53.4° found by Kunz and Hudson.

TABLE I

MUTAROTATION OF NEOLACTOSE HEPTAACETATES IN CHLOROFORM (*c*, 8) AT 20°

Time, hours	"α"-Heptaacetate $[\alpha]^{20}_D$	Time, hours	β-Heptaacetate $[\alpha]^{20}_D$
0.15	+23.3°	0.1	+10.0°
1	23.1	2	11.7
3	22.4	4	12.8
5	22.1	7	14.0
6.25	21.9	22	18.3
22	20.9	46	20.5
30	21.0	54	20.7
48	21.0	72	20.8
72	21.0	96	21.0
94	21.0	118	21.0

Crystallization of Neolactose.—Deacetylation was effected by dissolving 30 g. of the well-dried "α" or β-heptaacetate in 600 cc. of absolute methyl alcohol, chilling in ice and salt, and then adding 25 cc. of about 0.5 *N* barium methylate solution.[9] A gelatinous precipitate soon formed. The mixture was kept in the refrigerator overnight, then treated with the exact amount of 0.5 *N* sulfuric acid necessary to precipitate all the barium as sul-

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(9) Weltzien and Singer, *Ann.*, **443**, 104 (1925); Zemplén, *Ber.*, **59**, 1258 (1926); Zemplén and Pacsu, *ibid.*, **62**, 1613 (1929); *cf.* Fischer and Bergmann, *ibid.*, **52**, 852 (1919); Isbell, *Bur. Stand. J. Res.*, **5**, 1185 (1930).

fate, filtered, and concentrated *in vacuo* to a thick sirup. The sirup was taken up in 200 cc. of dry methyl alcohol and seeded, the first crystals having been obtained by rubbing a small portion of the sirup with acetone and alcohol. Neolactose crystallizes in small prisms which grow to form a very hard cake on the bottom and sides of the flask. The yield was nearly quantitative. Neolactose melts at 190° with decomposition. In 8% aqueous solution at 20° a small mutarotation was always observed, the specific rotation changing in the course of twenty minutes from +34.6 to +35.5 ± 0.2°.

Anal. Calcd. for $C_{12}H_{22}O_{11}$: C, 42.08; H, 6.48. Found: C, 41.86, 41.78; H, 6.59, 6.69.

Hydrolysis of Neolactose and Removal of Galactose.—The cleavage of neolactose into equal parts of *d*-galactose and *d*-altrose was carried out by boiling 10 g. of the disaccharide with 100 cc. of 1 *N* hydrochloric acid for two and one-half hours. The chloride was removed by shaking with silver carbonate, and the soluble silver ions removed by precipitation with hydrogen sulfide. The clear, colorless, neutral solution obtained by filtering through a layer of activated carbon was concentrated *in vacuo* to 100 cc. before removing the galactose by fermentation. To the above solution was added 2 g. of calcium carbonate, 1 g. of dibasic ammonium phosphate, 5 g. of fresh, washed brewer's yeast, 10 g. of glucose (to activate the yeast) and water to make the volume 250 cc. Fermentation of the glucose and galactose was complete in two days at room temperature as judged by the cessation of evolution of carbon dioxide, the settling of the yeast, and the reading on a Brix spindle. The mixture was filtered through a layer of activated carbon and filter-cel to remove the yeast, treated with lead acetate as long as a precipitate was formed, to remove substances derived from the yeast, and the excess lead precipitated with hydrogen sulfide. The solution then showed a specific rotation of −91°, assuming *d*-altrose solely present in theoretical amount, which agrees very well with the −98° obtained elsewhere, considering the number and nature of the manipulations here involved.

***d*-Altrose Benzyl Mercaptal.**—The *d*-altrose solution obtained above was concentrated *in vacuo* to a thick sirup, a small amount of water added, and the process repeated several times to remove most of the acetic acid (from the lead acetate treatment). The residue was dissolved in 10 cc. of concd. hydrochloric acid, 7.0 g. of benzyl mercaptan added, and the mixture shaken in a small glass-stoppered flask. At the end of eight hours there were still two layers. Ice water was added, and the product crystallized spontaneously in the course of a few hours. After one recrystallization from alcohol there was obtained 3.2 g. of mercaptal melting at 120–121° and 1.0 g. of less pure material, a yield of 35%.

d-Altrose benzyl mercaptal crystallizes from hot alcohol in felted needles, from hot water in fine long needles. It is readily soluble in acetone, sparingly soluble in ether, alcohol and hot water, and nearly insoluble in cold water. It melts at 121–122°. The specific rotation, constant after three recrystallizations from alcohol, was +39.4° in pyridine (*c*, 3).

Anal. Calcd. for $C_{20}H_{26}O_5S_2$: C, 58.49; H, 6.39; S, 15.63. Found: C, 58.43, 58.34; H, 6.64, 6.68; S, 15.45, 15.42.

***l*-Altrose Benzyl Mercaptal.**—For the purpose of comparing the *d*- and *l*-forms, 0.7 g. of pure *l*-altrose[10] was shaken for several hours with 1.5 cc. of concd. hydrochloric acid and 2 cc. of benzyl mercaptan, and proceeding as above, 0.8 g. of crude mercaptal, m. p. 119–121°, was obtained. It was recrystallized from 800 cc. of hot water containing 1% of ethyl alcohol. The fine needles weighed 0.7 g., melted at 121–122° and rotated −39.2° in pyridine (*c*, 2), in agreement with the properties to be expected for it from those of the *d*-form.

Anal. Calcd. for $C_{20}H_{26}O_5S_2$: C, 58.49; H, 6.39; S, 15.63. Found: C, 58.37, 58.35; H, 6.44, 6.50; S, 15.41.

Crystallization of *d*-Altrose.—In a series of experiments with galactose and galactose benzyl mercaptal[11] we found that mercuric chloride and even cadmium carbonate were capable, apparently, of causing a slow destruction of galactose in hot aqueous solution (80–90°). In order to obtain pure altrose the following adaptation of Wolfrom's method was then applied.[12] A suspension of 5.0 g. of finely powdered *d*-altrose benzyl mercaptal and 10 g. of cadmium carbonate was stirred vigorously with the theoretical amount, 6.617 g., of mercuric chloride in 350 cc. of water at 50°. The reaction proceeded readily, the characteristic crystals of the $C_6H_5CH_2SHgCl$ compound appearing as the mercaptal dissolved. After three hours the solid material was removed by filtration, and the chloride ions removed by shaking with silver carbonate. Excess silver ions, together with the mercury and cadmium, were precipitated with hydrogen sulfide, leaving after filtration through activated carbon covered with a little precipitated aluminum hydroxide, 765 cc. of clear colorless solution. In a 4-dm. tube this showed a specific rotation +30.2 ± 1.5°, assuming the complete conversion to *d*-altrose. To a 10-cc. portion was added 0.1 cc. of concd. hydrochloric acid and the solution heated at 100° for six hours; the specific rotation became −87 ± 6°, thus undergoing the change which is shown later to be characteristic of altrose. The remainder of the solution was concentrated *in vacuo* to a thick sirup, dissolved in a small amount of absolute methyl alcohol and left in a vacuum desiccator over granular calcium chloride for two days. Into the thick sirup was stirred absolute ethyl alcohol until the solution was slightly more than saturated; after five hours crystallization was noticed and solidification was complete by the next morning. The *d*-altrose, filtered, washed with a little methyl alcohol, and dried, weighed 1.2 g. and rotated +32.8° in water (*c*, 4.4). It was recrystallized by dissolving in water, concentrating to a thick sirup, and proceeding as above. The product, tiny prisms, weighed 0.9 g., melted at 103–105°, and rotated +32.6° in water (*c*, 7.6); mutarotation was not observed.

Anal. Calcd. for $C_6H_{12}O_6$: C, 39.98; H, 6.71. Found: C, 39.84; H, 6.61.

The Change in Rotation and Reducing Power of *d*- and *l*-Altrose in Acid Solution.—A small sample of *d*-altrose (0.1059 g.) dissolved in 1 *N* hydrochloric acid in a 10-cc. volumetric flask rotated +34.3°; the solution was then heated for two and one-half hours at 100°, cooled, and

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[10] Kindly supplied by Dr. W. C. Austin.

[11] This mercaptal has been described by Pacsu and Ticharich, *Ber.*, **62**, 3010 (1929).

[12] Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

the rotation found to be −98.2°. Similarly treated, 0.0566 g. of *l*-altrose[10] in 10 cc. of 1 *N* hydrochloric acid showed a change from −35.5 to +98.1°.

Because of the limited amount of crystalline altroses available, the behavior with acid was most readily followed by noting the loss in reducing power toward a copper solution, using the excellent micro method of Shaffer and Hartmann.[13] The results are shown in Table II, and plotted in Fig. 2. In comparing *d*- and *l*-altrose by this method it was found that *d*-altrose has only about 56% the reducing power of *l*-altrose. This may be due to the fact that the copper carbonate reagent contains an optically active substance, namely, *d*-tartaric acid; the *d*- and *l*-forms of the reducing sugar may behave differently in its presence. This explanation is supported by the further observation that pure *d*-arabinose has only 76% the reducing power of pure *l*-arabinose toward the Shaffer–Hartmann reagent. We hope to make a further study of this problem at a later date. The values given in Table II are therefore based not on the absolute reduction but on the change in percentage reduction as compared with the original solution.

TABLE II

THE CHANGE IN REDUCING POWER OF ALTROSE IN 0.1 *N* HCl AT 100°

Time, hours	Per cent. reduction shown by *l*-Altrose	*d*-Altrose
0	100	100
.5	78.4	
.75		72.7
1.0	66.0	
1.25		63.3
1.5	61.0	
1.75		56.4
2.0	53.8	
2.25		51.4
2.5	50.4	
2.75		48.6
3.0	48.3	
3.25		46.0
3.5	46.4	
3.75		44.2
4.0	45.1	
4.25		44.8
4.5	45.1	
4.75		43.5
5.0	44.2	
5.25		44.2
5.5	43.9	
5.75		43.5
6.5		43.2
7.0	43.9	
7.5		43.2
10.0	44.2	
11.0	44.2	

This work has been materially aided by a grant to one of us (N. K. R.) from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Acetochloroneolactose, now obtainable in 40% yield from lactose octaacetate, has been converted to neolactose heptaacetate, of which two crystalline forms have been isolated.

2. Neolactose has been crystallized by deacetylation of its heptaacetates.

3. The acid hydrolysis of neolactose, followed by removal of the galactose by fermentation, yields a sirupy *d*-altrose, $[\alpha]^{20}_{\mathrm{D}}$ about −98° in water; this was converted to pure *d*-altrose benzyl mercaptal, from which was obtained crystalline *d*-altrose, $[\alpha]^{20}_{\mathrm{D}}$ +32.6° in water (final).

4. Crystalline *d*-altrose is converted by hot hydrochloric acid from $[\alpha]^{20}_{\mathrm{D}}$ +34° to −98°; this is accompanied by partial loss of reducing power, presumably due to the formation of an anhydro-*d*-altrose to the extent of 57% at equilibrium. *l*-Altrose undergoes a similar reaction, changing in rotation from −35 to +98°, and decreasing in reducing power to the same extent as the *d*-form. This unique spontaneous change of an aldose to a non-reducing form under the influence of moderate acidity resembles the similar change of sedoheptose (a ketose) to anhydro-sedoheptose, a similarity which is borne out further by the close relationship of altrose and sedoheptose (*d*-altroheptulose) in stereochemical configuration.

5. *l*-Altrose benzyl mercaptal has been prepared from *l*-altrose.

6. These new results confirm the conclusion of Kunz and Hudson that neolactose is *d*-galactosido-*d*-altrose.

WASHINGTON, D. C.

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(13) Shaffer and Hartmann, *J. Biol. Chem.*, **45**, 377 (1921).