was added with vigorous stirring to 85 g. of benzoic peracid in 1000 cc. of ethyl acetate at 0°. The temperature was never allowed to rise above 8°. After four hours, when the consumption of the peracid had ceased, the aqueous layer was separated and with additional aqueous extracts again extracted with chloroform. After clarification and concentration to 500 cc., analysis by Goebel's method showed 59.9 g. of aldopentose.[14]

The above solution was evaporated to a sirup which was then mixed with 25 cc. of methyl alcohol, 240 cc. of absolute alcohol and 40 cc. of ether. After twenty-four hours 6 g. of crystallized *l*-arabinose was removed and recrystallized, giving the properties in VI of the table. The filtrate containing the *l*-ribose was combined with a similar one (previously prepared by the oxidation of 9 g. of *l*-arabinal, followed by the removal of 1 g. of crystalline *l*-arabinose). These combined filtrates were again reduced to a sirup, which crystallized spontaneously after three weeks, giving 28 g. of *l*-ribose. The remaining sugar in the mother liquor formed the *p*-bromophenylhydrazone of *l*-ribose, which was recrystallized from alcohol by the addition of ether to 35.5 g., with m. p. 170–172° and $[\alpha]^{25}_{D}$ $-10.67°$, in absolute alcohol. The corresponding derivative, prepared from pure *l*-arabinose, melted at 161–162°, had $[\alpha]^{20-25}_{D}$ $+10.23°$ in absolute alcohol, and was much less soluble in the solvents of purification. The decomposition of the above derivative of *l*-ribose by the method of van Ekenstein and Blanksma[15] with benzaldehyde afforded 8.7 g. more of crystalline *l*-ribose. None of the *l*-ribose exhibited mutarotation at 20°, although Phelps, Isbell and Pigman[16] have more recently observed the unusual mutarotation of this sugar at 1°. It was recrystallized from absolute alcohol to a product of the properties given in the table.

These studies were supported in part by a Grant-in-Aid from the National Research Council. Thanks are expressed to Dr. C. S. Hudson, of the National Institute of Health, Washington, D. C., for his interest and valuable suggestions.

Summary

Improved directions have been given for the preparation of *l*-ribose by the Bergmann reaction, involving the preparation of *l*-arabinal and its oxidation to a product containing approximately five parts of *l*-ribose to one part of *l*-arabinose. By this reaction *l*-ribose has been prepared in pure crystalline form from *l*-arabinose with a yield of nearly 10%.

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[14] Goebel, *J. Biol. Chem.*, **72**, 801 (1927).

[15] Van Ekenstein and Blanksma, *Chem. Weekblad*, **22**, 373 (1909).

[16] Phelps, Isbell and Pigman, THIS JOURNAL, **56**, 747 (1934).

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, LOYOLA UNIVERSITY SCHOOL OF MEDICINE]

The Preparation of Two New Crystalline Aldohexoses, *l*-Allose and *l*-Altrose, from *l*-Ribose by the Cyanohydrin Reaction[1,2,3]

BY W. C. AUSTIN AND FRED L. HUMOLLER

After having announced the preparation of crystalline *l*-ribose by improved methods, the authors[3] reported the preparation of crystalline *l*-allonolactone, calcium *l*-altronate and *β*-*l*-allose. To these preparations have now been added the sirupy *l*-altronolactone and crystalline *β*-*l*-altrose, and the authors describe herewith in more detail their studies of the substances made from *l*-ribose after the cyanohydrin reaction. These investigations have been guided, in large measure, by the valuable contribution of Levene and Jacobs,[4] who prepared from *d*-ribose the corresponding enantiomorphous substances and obtained the *d*-allose and *d*-altrose as uncrystallizable sirups.

The *β*-*l*-allose and *β*-*l*-altrose complete the list of the sixteen theoretically possible aldohexoses which have been prepared, although they are only the seventh and eighth which have been crystallized.[5] The reactions of preparation, with structures, of the new substances from *l*-ribose are indicated in the configurations I–V. Under each configuration is given also the percentage yield obtained by the authors in the preparation of each substance from the preceding one.

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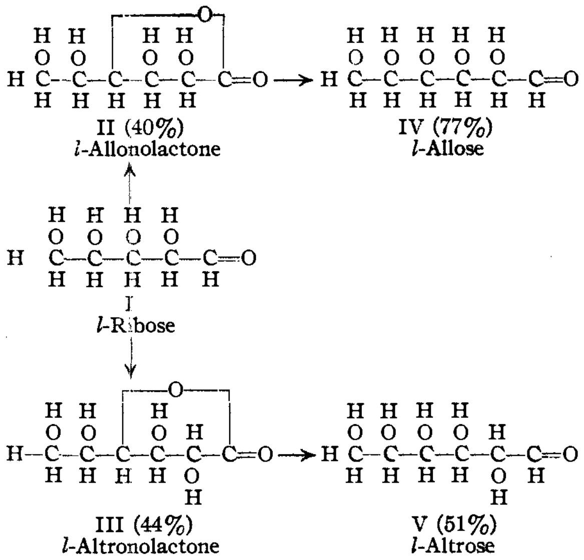
[1] Through the coöperation of Dr. F. C. Koch, Professor of Physiological Chemistry and Pharmacology at the University of Chicago, this investigation will constitute a portion of the thesis of Mr. Humoller in partial fulfilment of the requirements for the degree of Doctor of Philosophy from the Division of the Biological Sciences of the University of Chicago.

[2] The progress of this investigation was greatly aided by the technical assistance of Mr. B. J. Gregory.

[3] Austin and Humoller, THIS JOURNAL, **54**, 4749 (1932); **55**, 2167 (1933); **56**, 1152 (1934).

[4] Levene and Jacobs, *Ber.*, **43**, 3141 (1910).

[5] In the short communication by Austin and Humoller[3] the *β*-*l*-allose was termed the sixth crystalline aldohexose, *l*-mannose having been omitted from the list. The authors have since received a personal communication from Professor J. J. Blanksma, calling their attention to the description in *Chem. Zentr.*, II, 1265 (1914), of his synthesis of crystalline *l*-mannose. The authors take this opportunity to express their regret at the unintentional omission and make the necessary correction. The previously crystallized aldohexoses are *d*- and *l*-glucose, mannose and galactose.



II (40%) *l*-Allonolactone

IV (77%) *l*-Allose

I *l*-Ribose

III (44%) *l*-Altronolactone

V (51%) *l*-Altrose

Both of the two new sugars are faintly sweet, soluble in water, less soluble in methyl alcohol and still less soluble in ethyl alcohol. The β-*l*-allose crystallizes from ethyl alcohol in the form of rosets of slender prisms, while the β-*l*-altrose crystallizes from the same solvent in more stout and pointed prisms. Microcolorimetric tests have shown that the reducing powers of the *l*-allose and *l*-altrose are, respectively, 23 and 80% of that of *d*-glucose. The two new aldohexoses formed identical phenylosazones, melting singly or mixed at 165°. Some of the remaining properties of these two sugars and their corresponding lactones, together with those of their derivatives, are grouped in Table I. The rotations are given for 4% aqueous solutions of the hexoses at 20°, and the initial values have been calculated from the data of the observed mutarotations.

A consideration of the direction of the changes of mutarotation, in connection with the nomenclature of Hudson,[6] discloses that the crystalline forms of these sugars are β-*l*-allose and β-*l*-altrose. At equilibrium, in 4% aqueous solutions, the alpha modifications of the *l*-allose and *l*-altrose comprised only 15 and 4%, respectively, of the two systems, the remaining 85 and 96% existing as unchanged β-*l*-allose and β-*l*-altrose.

Experimental

***l*-Allonic Acid and *l*-Altronic Acid from *l*-Ribose.**—A solution of 30 g. of *l*-ribose and 10 g. of calcium cyanide[7] in 300 cc. of water lost its reducing power in twenty-four hours at 10°. Successive treatments with barium hydroxide, oxalic acid and calcium hydroxide removed ammonia, hydrogen cyanide and interfering ions, and led to a solution which was concentrated to give 16.5 g. of calcium *l*-altronate, recrystallized from water. The mother liquor was freed from calcium with oxalic acid and evaporated to a sirup which formed *l*-allonolactone, recrystallized from absolute alcohol to 13.5 g. Small additional quantities of the two new compounds were obtained by retreatment of the mother liquors.

The brucine *l*-allonate, formed by reaction between 1 g. of *l*-allonolactone and 3 g. of brucine in water on the steam-bath, was recrystallized from 97% alcohol to 2 g. of pure compound, small clusters of needles. From 1 g. of calcium *l*-altronate, by successive treatment with oxalic acid and brucine, there was formed 1.5 g. of brucine *l*-altronate, purified by recrystallization from absolute alcohol and resembling the corresponding derivative of *l*-allonic acid in solubility and crystalline appearance.

By heating 0.5 g. of *l*-allonolactone with 0.6 g. of phenylhydrazine for two hours on the steam-bath there was formed the phenylhydrazide of *l*-allonic acid, recrystallized from 95% alcohol to 0.5 g. of pure substance, light yellow prisms.

The quantitative removal of calcium with oxalic acid from 17.5 g. of calcium *l*-altronate gave a filtrate which was evaporated to 14.19 g. of uncrystallizable sirup. After solution of this sirup in water to 100 cc. for observation of its rotation, the titration of 1.0 cc. with standard base revealed 11.88 g. of *l*-allonolactone.

TABLE I

NEW SUBSTANCES PREPARED AFTER THE CYANOHYDRIN REACTION WITH *l*-RIBOSE

Substance	*l*-Allonolactone	*l*-Altronolactone	*l*-Allose	*l*-Altrose
M. p., °C.	130	Sirup	128–129	107–109.5
$[\alpha]^{20-25}_D$ in water Init.	+6.32°	...	−1.90°	−28.75°
Final	+4.34°	−37.20°	−13.88°	−32.30°
Derivatives— Compound	Brucine *l*-allonate	Brucine *l*-altronate	Phenylosazone	Phenylosazone
M. p., °C.	168–169	171–175	165	165
$[\alpha]^{20-25}_D$ in water	−24.75°	−21.44°	...	...
Compound	*l*-Allonic acid phenylhydrazide	Calcium *l*-altronate	*p*-Bromophenylhydrazone	Benzylphenylhydrazone
M. p., °C.	151–155	...	141–145	147–148
$[\alpha]^{20-25}_D$	...	...	+6.4 (EtOH)	...

Reduction of *l*-Allonolactone and *l*-Altronolactone.—The reduction of 13.0 g. of *l*-allonolactone in 100 cc. of water

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[6] Hudson, THIS JOURNAL, **31**, 66 (1909).

[7] The use of the calcium cyanide here was suggested by a personal communication from Dr. C. S. Hudson prior to his publication with Hartley and Purve in THIS JOURNAL, **56**, 1248 (1934).

at 0° was accomplished in the usual manner with 400 g. of 2.5% sodium amalgam and 20% sulfuric acid. From the product the mercury was removed by decantation, the sodium sulfate by precipitation in hot 80–90% alcohol, and the unreduced lactone as barium *l*-allonate (insoluble in 93% alcohol), leaving an alcoholic solution of the sugar. During the evaporation of this solution under reduced pressure it crystallized, giving 5 g. of *l*-allose. Further evaporation of the mother liquor afforded an additional 4.2 g. of the crystalline hexose.

The reduction of 11.7 g. of *l*-altronolactone, followed by purification as outlined above, afforded an alcoholic solution which was evaporated to a sirup, free from mercury, sodium sulfate and unreduced lactone. After 2.8 g. of this sirup had been used for the formation of derivatives of the sugar the remaining 7–8 g. crystallized three months later in the form of thick pointed prisms. A sirupy impurity, insoluble at 0° in 10 cc. of methyl alcohol and 20 cc. of absolute alcohol, was removed and 3.5 g. of crystalline *l*-altrose was had by the slow evaporation of the solution in absolute alcohol. An additional 1.15 g. of this sugar was obtained from the mother liquors, partly from 3.5 g. of purified benzylphenylhydrazone by the general procedure of Ruff and Ollendorff.[8]

l-Allose and l-Altrose.—The *l*-allose was recrystallized from 93% alcohol to constant rotation and melting point.

After the observation of the mutarotation at 20° in a freshly prepared 4% aqueous solution the value of the initial rotation at zero time was calculated from the unimolecular equation $k_1 + k_2 = 1/t \log (r_0 - r_\infty)/(r - r_\infty)$. The phenylosazone was prepared by heating 0.9 g. of this sugar with 2 g. of phenylhydrazine in 50 cc. of 5% acetic acid for two hours. It was recrystallized from 50% alcohol to 1.1 g. of pure light yellow crystals. By the procedure of Levene and Jacobs[4] 1 g. of *l*-allose gave 1.2 g. of twice recrystallized *p*-bromophenylhydrazone of *l*-allose, silky plates. By the method of Folin and Wu[9] 0.4 mg. of the *l*-allose showed 23% of the reducing power of an equal weight of *d*-glucose.

The *l*-altrose was recrystallized to purity both from absolute alcohol and glacial acetic acid. The tabulated values of the rotations of this sugar are averages from concordant mutarotations in 2 and 6% aqueous solutions. From 1.8 g. of the sirupy *l*-altrose there was prepared 1.9 g. of the phenylosazone, recrystallized to purity from 50% alcohol. From 1.0 g. of sirupy *l*-altrose, and from 0.18 g. of crystalline *l*-altrose, the same pure benzylphenylhydrazone was made. A sample of 0.3858 mg. of *l*-altrose showed 79.8% of the reducing power of an equal weight of *d*-glucose.

Analytical values obtained on the new substances which have been described are given in Table II.

TABLE II

ANALYSES OF COMPOUNDS PREPARED AFTER THE CYANOHYDRIN REACTION WITH *l*-RIBOSE

Compound	Formula	Analyses, % Calculated	Analyses, % Found
l-Allonolactone	$C_6H_{10}O_6$	C, 40.42; H, 5.66	C, 40.36; H, 5.68
l-Allose	$C_6H_{12}O_6$	C, 39.98; H, 6.72	C, 40.04; H, 6.59
l-Altrose	$C_6H_{12}O_6$	C, 39.98; H, 6.72	C, 39.87; H, 6.79
Phenylhydrazide of *l*-allonic acid	$C_{12}H_{18}O_6N_2$	N, 9.79	N, 10.03
Calcium *l*-altronate	$(C_6H_{11}O_7)_2Ca \cdot 3.5H_2O$	Ca, 8.12	Ca, 8.22
Benzylphenylhydrazone of *l*-altrose	$C_{19}H_{24}O_5N_2$	N, 7.78	N, 7.78
Phenylosazone of *l*-allose	$C_{18}H_{22}O_6N_4$	N, 15.64	N, 14.99 15.77
Phenylosazone of *l*-altrose	$C_{18}H_{22}O_4N_4$	N, 15.64	N, 15.48

These studies were supported in part by a Grant-in-Aid from the National Research Council. Thanks are expressed to Dr. C. S. Hudson, of the National Institute of Health, Washington, D. C., for his interest and valuable suggestions.

Summary

The reduction of the newly prepared crystalline *l*-allonolactone and sirupy *l*-altronolactone has led to the isolation of two new crystalline aldohexoses, *l*-allose and *l*-altrose. These sugars are the seventh and eighth of the sixteen theoretically possible aldohexoses which have been crystallized, and the fifteenth and sixteenth which have been prepared. The directions of the mutarotations of these sugars in aqueous solution have identified their crystalline forms as *β*-*l*-allose and *β*-*l*-altrose, in the nomenclature of Hudson. The constants of these sugars, their corresponding acids and lactones, together with those of their derivatives, have been recorded.

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[8] Ruff and Ollendorff, *Ber.*, **32**, 3234 (1899).

[9] Folin and Wu, *J. Biol. Chem.*, **38**, 81 (1919).