Summary.

TABLE I.—SUBSTANCES ACTUALLY ISOLATED FROM THE OXIDATION PRODUCTS OF MALTOSE, PER 100 G. OF MALTOSE HYDRATE.

	Maltose and H_2O_2. Grams.	Maltose and air. Grams.
Formic acid	43.30	8.94
Glucosido acids	37.0	15.56
d-Glucose	19.22	9.98
d-Erythronic lactone	1.40	0.32
d-Arabonic phenylhydrazid	2.96	1.94
Simple acids	13.0	63.06
Calcium glycollate	1.66	6.68
Calcium oxalate	0.14	...
Quinine *l*-glycerate	...	3.34
C_4-Saccharinic phenylhydrazid	...	1.54
Calcium *d*-arabonate	1.16	...
d-Arabonic phenylhydrazid	...	3.78

A study of the preparation and properties of maltobionic acid, its calcium, brucine, strychnine, quinine and cinchonine salts and its phenylhydrazid is also reported.

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE ISOMERIC TETRACETATES OF *l*-ARABINOSE AND BETA-TRIACETYL-METHYL-*l*-ARABINOSIDE.

BY C. S. HUDSON AND J. K. DALE.

Received March 25, 1918.

The possibility of the existence of 2 isomeric tetracetates of arabinose has been foreshadowed by the preparation of an isomeric pair of completely acetylated derivatives of most of the other naturally occurring mono- and disaccharides. Stone[1] acetylated arabinose by heating it with acetic anhydride and sodium acetate for one hour at 105°, but he obtained only a sirup. By shaking a solution of bromoacetyl-arabinose in acetic acid with silver carbonate, Chavanne[2] obtained crystals melting at 80° which he supposed were tetracetyl-arabinose but the quantity was too small for analysis.

Although the form of arabinose tetracetate that can be obtained directly by the acetylation of arabinose crystallizes readily when nearly pure, its preparation caused us great difficulty because there was formed at the same time a large proportion of sirupy material which interfered with its crystallization. With the aid of crystals that were produced by the method of Chavanne, the sirups that resulted from the acetylation of ara-

[1] *Am. Chem. J.*, **15**, 653 (1893).

[2] *Compt. rend.*, **134**, 661 (1902).

binose with acetic anhydride and sodium acetate could be brought to crystallization but even under the best conditions the yield was small. The pure compound, which will be named *α-l-arabinose tetracetate*, had a specific rotation in chloroform of $+42.5°$. When a solution of it in acetic anhydride containing a little zinc chloride was warmed on the steam bath the specific rotation gradually increased and became constant about 70° higher than the initial value. From this transformed solution a second crystalline tetracetate of arabinose was obtained, having a specific rotation in chloroform of $+147.2°$. It will be designated *β-l-arabinose tetracetate*. This naming of the two isomers is in accordance with the fact that they are derivatives of the *l*-form of arabinose, and hence the one of more positive specific rotation is named beta.[1]

It has been shown in previous articles[2] that considerations of molecular structure lead to the conclusion that the difference in molecular rotation between the α- and β-forms of the fully acetylated aldose sugars should be equal. The experimental evidence in support of this relationship is collected in the accompanying table which includes the molecular rotations in chloroform at 20° of all the previously described pairs of completely acetylated aldose sugars with the addition of those of the arabinose tetracetates that are described in this article.

Substance.	Molecular rotation of α-form.	Molecular rotation of β-form.	Difference.
d-Glucose pentacetate	+39,600	+ 1,500	+38,100
d-Lactose octacetate	+36,500	— 2,900	+39,400
d-Maltose octacetate	+83,000	+42,500	+40,500
d-Cellose octacetate	+27,800	—10,200	+38,000
d-Glucosamine pentacetate	+36,400	+ 470	+35,930
d-Chondrosamine pentacetate[3]	+39,500	+ 4,100	+35,400
d-Gentiobiose octacetate	+35,500	— 3,600	+39,100
d-α-Glucoheptose hexacetate	+40,200	+ 2,200	+38,000
d-Mannose pentacetate	+21,400	— 9,800	+31,200
d-Galactose pentacetate	+41,600	+ 8,900	+32,700
d-Xylose tetracetate	+28,300	— 7,900	+36,200
l-Arabinose tetracetate	+13,400	+46,800	—33,400[4]

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

[2] THIS JOURNAL, **37**, 1270, 1276, 1280, 2748 (1915); **38**, 1431, 1575 (1916); **39**, 1272 (1917); *J. Ind. Eng. Chem.*, **8**, 379 (1916).

[3] Since Levene (*J. Biol. Chem.*, **31**, 609 (1917)) has shown that chondrosamine belongs in the *d*-series of sugars, he having synthesized it from *d*-xylose, the naming of its α- and β-pentacetates must be changed from that which we used in a former article (THIS JOURNAL, **38**, 1431 (1916)) and the more levorotatory form designated as beta.

[4] The negative sign of this value follows from the system of nomenclature of α- and β-forms because the sugar belongs to the *l*-series. The difference for *d*-arabinose tetracetates would be +33,400, conforming in sign to the values for the other *d*-sugars of the table.

Experimental.

Preparation of Bromoacetyl-*l*-arabinose.—Chavanne[1] has prepared bromoacetyl-arabinose by the action of acetyl bromide upon the sugar. One of us[2] has prepared the bromoacetyl derivatives of a number of the sugars by the action of a saturated solution of hydrobromic acid in acetic anhydride in place of acetyl bromide. This method was also found applicable for the preparation of bromoacetyl-arabinose. Twenty-five g. of finely powdered *l*-arabinose was treated in an Erlenmeyer flask at room temperature with 150 cc. of a saturated solution of hydrobromic acid in acetic anhydride. A vigorous reaction followed. The resulting straw-colored sirup was cooled, mixed with 400 cc. of chloroform and the solution shaken with ice water, sodium bicarbonate solution and again with ice water. After drying with calcium chloride the solution was evaporated under diminished pressure to a thick sirup, which crystallized in the flask. The crystals were washed out of the flask with a little ether, dried on a Büchner funnel and then recrystallized from ether. Eight g. of the pure compound was obtained.

Conversion of Bromoacetyl-*l*-arabinose into α-Tetracetyl-*l*-arabinose.—Eight g. of pure bromoacetyl-*l*-arabinose was dissolved in 200 cc. of glacial acetic acid and shaken with 10 g. of silver acetate until a few drops gave no test for halogen with silver nitrate. The silver salt was then filtered off and the filtrate was diluted with water, neutralized with sodium bicarbonate and extracted with an equal volume of chloroform. The chloroform extract was dried with calcium chloride and evaporated to a thick sirup which was then dissolved out of the flask with a little warm ether. This solution on evaporation in a current of air deposited beautiful plate-like crystals. After filtering and washing on a Büchner funnel 4.0 g. was obtained. The melting point of this product was 94 to 96° and the specific rotation in chloroform $[\alpha]_D^{23} = +45.4°$, values which are very near the ones found for pure α-tetracetyl-*l*-arabinose, now to be described.

Preparation of α-Tetracetyl-*l*-arabinose by Direct Acetylation of *l*-Arabinose.—To a boiling solution of 5 g. of anhydrous sodium acetate in 40 cc. of acetic anhydride 10 g. of *l*-arabinose was gradually added, and the solution was boiled a few minutes, cooled and poured into about 800 cc. of cold water. A sirup immediately separated and settled to the bottom of the flask. The supernatant acid liquid was poured off and the sirup washed with a little cold water, after which it was dissolved in a small amount of alcohol, decolorized with carbon and then evaporated to a thick sirup. This sirup was seeded with tetracetate crystals obtained as previously described from the bromoacetyl compound and after a few days it had partially crystallized. The crystalline material was easily separated from

[1] *Compt. rend.*, 134, 661 (1902).

[2] Dale, THIS JOURNAL, 37, 2745 (1915); 38, 2187 (1916).

the large amount of sirupy mother liquor by thinning out with ether and filtering on a Büchner funnel. A small amount of the same substance was also crystallized from the acid solution which had been decanted from the original sirupy material. It was neutralized with sodium bicarbonate, filtered and extracted with chloroform. The extract was dried with calcium chloride and evaporated to a thick sirup, which slowly deposited crystals of arabinose tetracetate. From 50 g. of arabinose there was obtained by this method 11.0 g. of the nearly pure tetracetate. It was recrystallized from water until its specific rotation became constant. The melting point of the pure substance, *α-tetracetyl-l-arabinose*, was 97° (corr.).

A solution consisting of 0.6679 g. of the tetracetate made up to 25 cc. with chloroform (*Chloroformum purificatum*, U. S. P.) rotated 2.27 circular degrees to the right in a 200 mm. tube, using sodium light, hence $[\alpha]_D^{22} = +42.5°$.

Acetyl determinations, made by boiling in a quartz flask with a reflux condenser 0.3 g. substance with 100 cc. 0.1 *N* H_2SO_4 during 4 hours, gave 75.80 and 75.65% acetic acid, which agree with the theoretical value for arabinose tetracetate, 75.48%.

Calc. for $C_{13}H_{18}O_9$: C, 49.03; H, 5.70. Found: C, 48.86; H, 5.74.

Transformation of α-Tetracetyl-*l*-arabinose to the Isomeric β-Form.—Twelve g. of *α-l*-arabinose tetracetate was dissolved in 25 cc. of acetic anhydride containing one g. of zinc chloride and the solution heated on the steam bath until the specific rotation reached a constant value, which was found to be about 70° higher than the initial reading. When this solution was poured into 700 cc. of ice water an insoluble phase separated and soon crystallized. The yield was 2 g. The filtrate from this crystalline material was neutralized with sodium bicarbonate and extracted with chloroform. The extract was dried with calcium chloride and evaporated to a thick sirup, which crystallized after being stirred with successive portions of cold water and the crystals were recrystallized once from water with a yield of 2 g. These two products had nearly the same specific rotation and melting point. By this method 12 g. of this substance was prepared and it was found to be a tetracetate of arabinose, isomeric with the arabinose tetracetate which from it was prepared. It was purified by recrystallization from water until its specific rotation became constant. The pure substance melted at 86° (corr.). Since it is more dextrorotary than its isomer it is to be named *β-tetracetyl-l-arabinose*, its isomer of m. p. 97° being the *α*-form.

A chloroform solution (*Chloroformum purificatum*, U. S. P.) containing 1.2047 g. of the substance in 25 cc. solution rotated to the right, 14.19 circular degrees, in a 200 mm. tube, using sodium light, hence $[\alpha]_D^{21} = +147.2°$.

Acetyl determinations made by boiling in a quartz flask with a reflux condenser 0.3 g. substance with 100 cc. 0.1 *N* H_2SO_4 during 4 hours gave 75.57 and 75.34% acetic acid, which agree with the theoretical value for arabinose tetracetate, 75.48%.

Calc. for $C_{13}H_{18}O_9$: C, 49.03; H, 5.70. Found: C, 48.98; H, 5.76.

Preparation of β-Triacetyl-methyl-*l*-arabinoside.—It had been hoped

that both the α- and β-forms of triacetylmethyl-arabinoside might be prepared in a crystalline form, but though the β-form crystallized readily all attempts so far to obtain the α-form in a crystalline state have failed. By shaking bromoacetyl-*l*-arabinose with methyl alcohol and silver carbonate and also by acetylating α-methyl-*l*-arabinoside with acetic anhydride and sodium acetate only clear, colorless sirups have been obtained. When β-methyl-*l*-arabinoside was acetylated the product crystallized almost immediately.

Four g. of fused sodium acetate was dissolved in 40 cc. of boiling acetic anhydride and to this solution was gradually added 10 g. of β-methyl-*l*-arabinoside, of m. p. 170° and $[\alpha]_D^{20} = +246°$. The solution was then boiled 2 or 3 minutes, cooled and poured into 800 cc. of cold water. A sirupy phase separated which on stirring soon crystallized. After recrystallization from water there was obtained 11 g. with $[\alpha]_D^{22} = +182.2°$. Another recrystallization from water was made.

A chloroform (*Chloroformum purificatum*, U. S. P.) solution containing 1.1042 g. substance in 25 cc. solution rotated 16.08 circular degrees to the right in a 200 mm. tube, using sodium light, hence $[\alpha]_D^{23} = +182.0$. The melting point of the pure substance, *β-triacetylmethyl-l-arabinoside*, was 85° (corr.).

Acetyl determinations made by shaking 0.30 g. of the compound with 75 cc. 0.1 *N* NaOH in glass stoppered bottles for 2 and 4 hours gave, respectively, 61.60% and 62.40% acetic acid. Calc. for triacetylmethyl-*l*-arabinoside, 62.07%.

Calc. for $C_{12}H_{18}O_8$: C, 49.63; H, 6.25. Found: C, 49.50; H, 6.35.

In determining whether the crystalline compound just described is the α- or β-isomer, the fact that it was made by direct acetylation of β-methyl-*l*-arabinoside, so named because it is more dextrorotary than α-methyl-*l*-arabinoside, is good evidence for the β-classification. In addition we have the data at hand for a calculation of the rotations of both the α- and β-forms of triacetylmethyl-*l*-arabinoside; it will be seen that the measured specific rotation of the compound that is under investigation, though not agreeing exactly with the calculated value for the β-form, is close enough to it to fully warrant classification in the β-series.

The molecular rotations of the α- and β-triacetylmethyl-*l*-arabinosides may be denoted by $(-A - B)$ and $(A - B)$,[1] respectively, when A denotes the rotation due to the terminal asymmetrical carbon atom and $-B$ that due to the remainder of the structure. The difference between these 2 molecular rotations is $-2A$. Using similar notation the difference between the molecular rotations of the α- and β-tetracetyl-methyl-*d*-glucosides is $2A$, and it has been shown in the last article cited that this value is +53,900, hence $A = 26{,}950$. A value for B can be obtained from the measured molecular rotations of the α- and β-forms of tetraacetyl-*l*-arabinose. Since these compounds differ in structure from the acetylated

[1] For explanation of these terms see THIS JOURNAL, 31, 66 (1909); 37, 1264 (1915).

methyl arabinosides only in respect to the terminal asymmetric carbon atom which has an acetyl instead of a methyl group, the rotation of the 2 forms of the tetracetate may be expressed as $(-A'-B)$ and $(A'-B)$, and their sum, $-2B$, from the values of the molecular rotations of the α- and β-arabinose tetracetates given earlier in this article, is +60,200 or $-B$ = 30,100. Hence, the specific rotation of α-triacetyl-methyl-*l*-arabinoside (M. W. 290) is calculated to be $(-A-B)/290$ = (—26,950 + 30,100)/290 = +11°, and that of the β-form (26,950 + 30,100)/290 = +197°. The calculated value for the β-form, +197°, is near enough to the specific rotation (+182°) of the triacetyl-methyl-*l*-arabinoside that we have described to justify its classification in the β-series.

WASHINGTON, D. C.

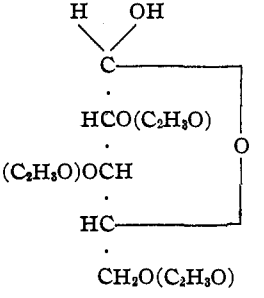
[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

TRIACETYL-*d*-XYLOSE AND ALPHA TRIACETYLMETHYL-*d*-XYLOSIDE.

BY C. S. HUDSON AND J. K. DALE.

Received March 28, 1918.

In a recent article one of the authors[1] described the preparation from *d*-xylose ($[\alpha]_D$ = +19°) of bromoacetyl-*d*-xylose, a crystalline compound which was found to be very similar in its reactions to bromoacetyl-glucose. The bromine atom could be replaced by an oxymethyl or an oxyacetyl group by reactions that are quite analogous to those by which tetracetyl-methyl-glucoside and pentacetyl-glucose are prepared from bromoacetyl-glucose. An incompletely acetylated derivative of glucose, tetracetyl-glucose, can also be prepared from bromoacetyl-glucose by the substitution of an hydroxyl group in place of the bromine atom.[2] In analogy with this reaction a partially acetylated derivative of xylose, *triacetyl-d-xylose*, has been prepared from bromoacetyl-xylose. On the assumption that it is a γ-cyclo derivative its structure is



This triacetate showed mutarotation in both chloroform and water

[1] Dale, THIS JOURNAL, 37, 2745 (1915).

[2] Fischer and Kurt, *Ber.*, 45, 912 (1912).