glyoxal is oxidized more slowly than the trioses. Pyruvic acid is not oxidized. With the ferrous complex lactic acid is oxidized to pyruvic acid, and isopropyl alcohol to acetone; this does not occur with the ferric complex. There is no indication that, under the experimental conditions described, microörganisms are responsible for the formation of significant amounts of carbon dioxide in the oxidation of glucose.

STANFORD UNIVERSITY, CALIF. RECEIVED JUNE 6, 1934

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

Studies of the Forms of Arabinose[1]

BY EDNA MONTGOMERY AND C. S. HUDSON

Although alpha and beta forms of arabinose are to be expected from analogy with such known forms of many other reducing sugars, only one modification has so far been crystallized; it is designated beta because for *l*-arabinose its initial specific rotation in water is more dextrorotatory than the final value. One can calculate the rotations to be expected for the two forms from the rotations of the alpha and beta methylarabinosides, which are known with fair precision. Thus in the *l*-arabinose series half the sum of the molecular rotations (sodium line) in water of the methyl *l*-arabinosides is 21,550,[2] the value *b* of the isorotation rules. Accepting the value $A_{\text{OH}} = 8500$ from the known rotations of alpha and beta *d*-glucose, the specific rotation of alpha *l*-arabinose (mol. wt. 150) at 20° and with sodium light is calculated to be $(b - A_{\text{OH}})/150$ or +87° and that of its beta-form, $(b + A_{\text{OH}})/150$ or +200°. Hudson and Yanovsky[3] found +175° for the beta modification, though they later raised this value to +186°. Riiber[4] has determined the rotation to be +192°, which is more nearly in agreement with the calculation. While the expected low rotating alpha form has never been obtained crystalline, Austin and Walsh[5] have recently described a crystalline double compound of it with calcium chloride, from the initial rotation of which they obtained a specific rotation of +75° for alpha *l*-arabinose, somewhat lower than the calculated value. We wish now to report the results of our reinvestigation of the rotation of beta arabinose carried out during the past several years and our recent study of Austin and Walsh's calcium chloride compound of alpha arabinose and of Dale's[6] calcium chloride compound of beta arabinose. We have found that the specific rotations of the two forms of the sugar are +202 and +89°, respectively, in excellent agreement with the calculations from the isorotation rules. These rotations are somewhat different from those obtained by Dale (+186°) and by Austin and Walsh (+75°), doubtless due to the fact that special precautions described below are essential to the obtaining of these substances in pure condition.

Experimental[7]

The specific rotations in every case were measured at 20.0 ± 0.5° with sodium light in a 2-dm. tube.

The Preparation of Pure Beta *l*-Arabinose.—The determination of the optical rotation of this substance involves the crystallization of the sugar and observation of its mutarotation, since the initial value can be obtained only by extrapolation. Since some commercial supplies of arabinose contain impurities very difficult to remove by recrystallization, the purity of the sugar should always be checked by observing its final specific rotation in water. This precaution, although necessary, is not sufficient for success in the preparation of the beta form in a state of optical purity. It has also been found essential to allow the crystallization to take place very slowly, preferably over a period of months.

Pure crystalline *l*-arabinose (50 g.) was left in an open dish at room temperature, protected from dust, in contact with distilled water (50 cc.) containing 10% of acetone to prevent bacterial action. More solvent was added from time to time so that all but 5 to 10% of the sugar remained in solution and after twelve weeks the crystals appeared to be all of one type and had ceased to change (increase) in initial specific rotation. The needles were filtered off, washed with 30% acetone followed by absolute alcohol and were dried to constant weight over calcium chloride under reduced pressure at room temperature. The yield was 3.8 g. Pure beta arabinose was also prepared by dis-

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Hudson, THIS JOURNAL, **47**, 268 (1925).

(3) Hudson and Yanovsky, *ibid.*, **39**, 1013 (1917); **52**, 1695 (1930).

(4) Riiber, *Forh. K. Norsk. Vidensk. Selsk*, Vol. III, 66 (1930).

(5) Austin and Walsh, THIS JOURNAL, **56**, 934 (1934).

(6) Dale, *ibid.*, **56**, 932 (1934).

(7) Both the *l*- and *d*-forms of pure arabinose were studied in the present research with agreeing numerical results except for the obvious differences in signs of the rotations.

solving the pure sugar (8 g.) in warm, redistilled pyridine (80 cc.) and keeping the solution for six months at 6°. The needles were washed with pyridine–ether mixtures and then with ether until they were free of pyridine. After drying the yield was 1.1 g.

The Initial Specific Rotation in Water of Beta *l*-Arabinose.—The unimolecular velocity coefficient of the mutarotation, $k_1 + k_2$, decreased progressively from 0.065 to 0.032.[8]

TABLE I

MUTAROTATION OF BETA *l*-ARABINOSE IN WATER

Concn. 4.000%; temp., 20.0 ± 0.5°

Time after soln., min.	$[\alpha]^{20°}_{D}$	$k_1 + k_2 = \frac{1}{t}\log\frac{r_0 - r_\infty}{r - r_\infty}$	(zero time = 8.5 min.)
0	[+201.5]		
1.0	+187.8		
1.5	181.8	0.065	
2.0	176.1	.066	
2.5	171.4	.064	
3.5	165.7	.054	
4.0	163.1	.051	
5.25	158.8	.044	
6.0	154.5	.047	
6.5	151.9	.044	
7.5	148.0	.043	
8.5	144.4	.044	
10.5	139.0	.040	0.032
12.5	134.2	.038	.032
14.5	129.8	.038	.033
19.5	121.8	.036	.032
22.5	119.9	.032	.028
28.5	116.0	.032	.031
24 hrs.	+105.1 (const.)		Av. 0.031

The measurements of the mutarotation are given in Table I. In calculating the initial rotation the velocity coefficient was taken to be the value observed during the first two minutes. This was reproducible with precision by independent observers and was 0.065. Employing this value for the extrapolation by the usual logarithmic formula, the specific rotation of beta *l*-arabinose was found to be +202 ± 1.5° in water.

A More Rapid Crystallization of *l*-Arabinose.—A 15% solution of the sugar in 80% methyl alcohol deposited crystals overnight as the familiar radiating clusters of square ended, well built prisms which had the correct final specific rotation of +105° in water. They differed, however, from pure beta arabinose in that their initial extrapolated specific rotation was near +186°. The mutarotation of this form of the sugar followed the unimolecular order as closely as could be observed, showing a velocity coefficient of 0.032, which is identical with the value found for the pure beta form in the later stages of its mutarotation (Table I, column 5). It is not possible to decide from present evidence whether such low rotating crystals represent a third form of arabinose or a mixture of two or more modifications which crystallize together.

Crystalline Calcium Chloride Double Compounds of Alpha and Beta Arabinose

(A) Beta Arabinose Calcium Chloride Monohydrate.[6]—Pure *l*-arabinose[9] (16 g.) and calcium chloride dihydrate (32 g.) were dissolved in 28 cc. of water by quick heating just to boiling.[10] This solution was filtered with active carbon, mixed with 56 cc. of absolute ethyl alcohol and kept at 6° for three days[10] before being concentrated in a vacuum at a temperature of not more than 15° to a weight of 66 g. Absolute alcohol (37 cc.) was shaken vigorously for three minutes with the mixture of sirup and crystals after which the latter were isolated on a 10-cm. Büchner funnel by a rapid filtration. The fine prismatic needles were washed three times with 20-cc. portions of absolute alcohol and dried over anhydrous calcium chloride in a desiccator to an approximately constant weight; yield 11.2 g. or 37.6%; m. p. 210° with decomposition. In the preparation of this calcium chloride double compound and the one described below, it was essential to filter off the product in the way indicated before it could become contaminated with lower rotating substances. This invariably occurred when there was delay before or during filtration.

Anal. Calcd. for $C_5H_{10}O_5 \cdot CaCl_2 \cdot H_2O$: pentose, 53.76; Ca, 14.35; Cl, 25.41. Found: pentose by Cajori's method, 53.67; Ca, 14.36; Cl, 25.65.

Beta *l*-arabinose calcium chloride monohydrate had an initial, extrapolated specific rotation in water of +201.7°, changing to a final constant value of +105.2°, calculated on its arabinose content. The unimolecular velocity coefficients diminished as the mutarotation proceeded and the optical rotation–time curve was superposable on one derived from the data given in Table I for pure beta *l*-arabinose itself.

(B) Alpha *l*-Arabinose Calcium Chloride Tetrahydrate.[5]—The preparation of this compound from pure *l*-arabinose[9] (24 g.) and calcium chloride dihydrate (24 g.) dissolved in water (42 cc.) by quick heating to not more than 60°[10] was from this stage on a duplicate of the preparation described in (A). After drying over anhydrous calcium chloride to nearly constant weight, alpha *l*-arabinose calcium chloride tetrahydrate was obtained (15 g.) in 28% of the theoretical yield as a mass of thin six sided plates melting at 204°, after discoloring at 185°.

Anal. Calcd. for $C_5H_{10}O_5 \cdot CaCl_2 \cdot 4H_2O$: pentose, 45.06; Ca, 12.03; Cl, 21.28. Found: pentose by Cajori's method, 45.08; Ca, 12.11; Cl, 21.37.

The measurements of the mutarotation of this substance are given in Table II. The optical change was not detectable with certainty during the first few minutes but proceeded with a nearly constant unimolecular velocity coefficient of $k_1 + k_2 = 0.030$ in the later stages of the mutarotation.[11] In this case it was therefore unnecessary

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(8) The mutarotation of alpha galactose, which is similar in configuration to beta arabinose, also proceeds with a diminishing unimolecular velocity coefficient [Smith and Lowry, *J. Chem. Soc.*, 666 (1928)].

(9) We have failed to prepare these calcium chloride double compounds in a state of optical purity from specimens of arabinose which were only slightly impure, of $[\alpha]^{20}_{D}$ about +102°.

(10) Prolonged heating or immediate concentration of this solution reduced the initial specific rotation of the arabinose in the calcium chloride double compound crystallized from it.

(11) The mutarotation of beta galactose, which is similar in configuration to alpha arabinose, is associated with similar optical behavior.[8]

to extrapolate the data in order to obtain the correct initial specific rotation of +89.4° in water for alpha *l*-arabinose. The observation of the final specific rotation, +105.1°, provided a check on the purity of the preparation.

TABLE II

MUTAROTATION OF ALPHA *l*-ARABINOSE CALCIUM CHLORIDE TETRAHYDRATE IN WATER

Concn. 4.000%; temp., 20.0 ± 0.5°

Time after soln., min.	$[\alpha]^{20°}_D$	$k_1 + k_2 = \frac{1}{t}\log\frac{r_0 - r_\infty}{r - r_\infty}$
0		
1.0	+ 89.4	
2.0	88.9	
3.0	88.5	
4.0	88.9	
5.0	88.9	
7.0	90.8	0.028
8.5	92.0	.027
11.5	94.6	.030
14.0	96.6	.031
21.0	100.4	.034
25.0	100.9	.029
30.0	101.8	.028
37.0	103.8	.030
24 hrs.	+105.1 (const.)	
	Av.	.030

Behavior of the Arabinose–Calcium Chloride Double Compounds when Heated.—Beta *l*-arabinose calcium chloride monohydrate with an initial specific rotation of +202°, and alpha *l*-arabinose calcium chloride tetrahydrate, with an initial rotation of +89° in water, both calculated on the arabinose content, were heated at 95° for four days in an oven. The product in each case was a white powder which gave a clear colorless aqueous solution with an initial specific rotation of +186°, calculated for the arabinose. Evidently the drying of these compounds at elevated temperature changes the arabinose forms contained in them.

Summary

The values of the initial rotation of beta *l*-arabinose recorded in the literature (175–192°) are low; by crystallizing the pure pentose very slowly we find the value $[\alpha]^{20}_D$ +202° in water. This value agrees with that which we find for the arabinose component of Dale's beta *l*-arabinose calcium chloride monohydrate. The alpha form of arabinose has never been crystallized, but its crystalline calcium chloride compound recently discovered by Austin and Walsh exhibits the initial rotation of +89° for its alpha *l*-arabinose component. These observed rotations agree closely with the values that may be calculated for the alpha and beta forms of arabinose from the known rotations of the alpha and beta methyl arabinosides by the isorotation rules.

WASHINGTON, D. C. RECEIVED JUNE 7, 1934

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

The Diamylenes Produced from Methylisopropylcarbinol by Sulfuric Acid[1]

BY NATHAN L. DRAKE, G. M. KLINE AND W. G. ROSE

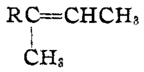
Many investigators have studied the polymerization of amylenes, but to date no *conclusive* proof of the structure of any of the polymers has been offered.[2,3,4,5,6,7]

Previous work on the structures of the decenes produced by sulfuric acid from methylisopropylcarbinol has likewise been inconclusive.[8,9]

The present paper advances evidence that 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2 result from the action of warm sulfuric acid on methylisopropylcarbinol. These substances are produced in approximately equal quantities, and no evidence of the presence of other decenes has been found.

The formation of 3,5,5-trimethylheptene-2 would be predicted according to the theory advanced by Whitmore[10] to explain the mechanism of the polymerization of olefins by acid catalysts. However, only a radical intramolecular rearrangement of one of the hypothetical intermediates which would be expected according to Whitmore's theory could result in the formation of 3,4,5,5-tetramethylhexene-2.

The proof of the structures of the two decenes was obtained as follows. Ozonolysis yielded acetaldehyde and two ketones, $C_8H_{16}O$, which were demonstrated to be methyl ketones by the haloform reaction. The two decenes must, therefore, possess the structure



$$R\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3$$

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[1] From the Ph.D. dissertations of G. M. Kline and W. G. Rose.

[2] Wischnegradsky, *Ber.*, **8**, 434 (1875).

[3] Schneider, *Ann.*, **157**, 207 (1871).

[4] Michael and Brunel, *Am. Chem. J.*, **41**, 118 (1909).

[5] Michael and Zeidler, *Ann.*, **385**, 252 (1911).

[6] Schindelmeiser, *Chem.-Ztg.*, **45**, 566 (1921).

[7] Norris and Joubert, THIS JOURNAL, **49**, 873 (1927).

[8] Cooke, Dissertation, U. of Md., 1929.

[9] Wheeler, Dissertation, U. of Md., 1931.

[10] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).