

the digestion with allyl iodide. As it is shown in Col. 7, Table V, that the total amount of ester recovered is smaller than that used, Col. 4, it follows that a considerable quantity of *O*-ester has been decomposed. As its normal decomposition product is 1-phenyl-4-methylurazole, with which ethyl bromide and ethyl iodide have been shown to react slowly, it would not be surprising that the much more highly reactive allyl iodide would yield some of the *N*-allyl ester. Furthermore, the allyl iodide and *O*-allyl ester may, to some extent, form an addition product which rearranges into the *N*-allyl ester. The increase in the actual amount of *N*-ester and the decrease in the amount of *O*-ester therefore raise the per cent. *N*-ester to 97.3% of the total ester isolated in Col. 8, of Table V.

TABLE V.—0.3 WEIGHT *N* SILVER SALT + 0.3 VOL. *N*-ALLYL IODIDE IN 40% ALCOHOL AT 60°; THE REACTION PRODUCT WAS THEN ISOLATED AND HEATED ONE HOUR WITH ALLYL IODIDE AT 100°.

Weight Ag salt.	Mols C ₃ H ₅ I.	Time in hours.	Total product.	Per cent. yield.	Mols C ₃ H ₅ I.	Wt. after re-heating.	<i>N</i> ester wt. after hydrolysis.	Per cent. <i>N</i> der. in reheated mixture.	Per cent. of total product found as <i>N</i> der. in reheated mixture.
0.447	1	0.25	0.1939	55.9	10	0.1755	0.1699	96.8	87.6
0.447	1	0.33	0.1547	44.6	1	0.1388	0.1356	97.7	87.7
Average, 97.3									87.7

Summary.

1. At 60° and below, the sodium, mercury, or silver salt of 1-phenyl-4-methylurazole gives with allyl iodide its own ratio of *N*-ester and *O*-ester which does not change with change in temperature or time.

2. It was observed that the silver salt of 1-phenyl-4-methylurazole and allyl iodide at 100° give a ratio of *N*-ester to *O*-ester, 98:2, which is considerably higher than that found at 60° and below, 79:21. It is here shown that this change is caused by an action of the allyl iodide at 100° on the *O*-allyl ester which results in its partial decomposition and the formation of some *N*-ester. This case is therefore somewhat like that of Wheeler who showed that imido esters are changed by alkyl halides into substituted amides.

MADISON, WIS.

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, U. S. DEPT. AGRICULTURE.]

THE PREPARATION OF BETA GLUCOSE.

BY A. W. MANGAM AND S. F. ACREE.¹

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Because of the difference between the rate of fermentation and the reactions of the alpha and beta derivatives of different sugars, and because

¹ Chief, Section of Derived Products, Forest Products Laboratory, Madison, Wisconsin.

both types occur in nature, any methods which will allow us to prepare the alpha and beta forms in a pure state are of importance.¹ The usual method for the preparation of beta glucose has been to allow it to crystallize from a hot aqueous solution of the alpha glucose. At the higher temperature the beta form is less soluble and the alpha compound is transformed by mutarotation into the beta as fast as the latter precipitates out. Experiments at the Forest Products Laboratory, however, have shown that this method does not always yield pure beta glucose. For example, when 100 g. of alpha glucose were melted in 10 cc. of water on a steam bath or open flame and the solution was seeded with a few crystals of beta glucose on a steam bath, crystals of sugar precipitated out. When this mass was freed from the gummy portion by rapid grinding with small portions of glacial acetic acid² in a mortar, filtered through a Büchner funnel and washed with alcohol, a yield of 76% was obtained. The substance melted at 142° rather sharply. The initial rotation was, however, 72.60°, and the final rotation, 52.69°. As the rotation of beta glucose is about 20° it is evident that this sample was chiefly alpha glucose instead of the beta form. In another similar experiment a yield of 66% of sugar was obtained with a melting point of 140°. The initial rotation was 74° and the final rotation was 52.84°.

We then attempted to develop the method described by Behrend,³ in which alpha glucose was dissolved in boiling pyridine. Behrend gave two experiments showing the rotation or purity of the beta glucose, and found that beta glucose crystallized out in a pure state in combination with 1 molecule of pyridine when the solution was cooled. His yields, however, were only about 35% and we have tried to improve them. We found, for example, that when five grams of pure alpha glucose were heated with 25 cc. of pure redistilled pyridine under a return condenser the sugar dissolved rather quickly. The solution was cooled, seeded with a few pieces of beta glucose and allowed to crystallize. It was then filtered through a Büchner funnel, washed with ether and spread out on paper to dry quickly. It was then placed over concentrated sulfuric acid in a desiccator and allowed to remain 2 hours. When dried in an oven at 105° a short time a yield of 60% was obtained. When dissolved in water the initial rotation was 35.41 and the final rotation was 50.63. The filtrate gave more crystals.

¹ See especially the fine work of Hudson and Dale on "The Preparation of Alpha and Beta Glucose and Their Mutarotation," *THIS JOURNAL*, 39, 320 (1917).

² Doctor I. K. Phelps has suggested and developed the use of glacial acetic acid as an excellent solvent for sugars. See also A. Wernicke, *Ber.*, 15, 3105 (1882); U. S. Patent No. 260,340, June 27, 1882. The writers are indebted to Doctor C. S. Hudson for much helpful coöperation in the development of methods for the preparation and purification of these sugars.

³ *Ann.*, 353, 106; 377, 220.

In another similar experiment beta glucose was placed over sulfuric acid and allowed to remain overnight. A yield of 45% was obtained. The initial rotation was 41.46 and the final rotation 50.90.

As the initial rotation in these two cases was considerably higher than that generally given for pure beta glucose, *viz.*, about 20, it is probable that in beta glucose prepared in this way there is still some pyridine which causes a partial mutarotation of the beta glucose into the equilibrium mixture before the first readings can be made. It was, therefore, found advisable to dry the beta glucose better in an oven at 105°, or in a desiccator, in order to drive off the pyridine. When this is done the initial rotation of the beta glucose is very much lower, *viz.*, about 20 to 25, the final rotation remaining about the same, *viz.*, about 50 to 52. For example, 23.5 g. of alpha glucose were dissolved in 25 cc. of boiling pyridine and set aside overnight to crystallize. When filtered through a Büchner funnel, washed with ether, dried as much as possible and then spread out on paper a few minutes it weighed 24.37 g. When dried in an oven at 105° for 30 minutes it weighed 17.57 g. When dried 2 hours over sulfuric acid in a desiccator it weighed 17.05 g., and when allowed to stand 8 hours longer in the desiccator the weight was 16 g., which was practically constant. The loss in weight corresponds approximately to one molecule of pyridine. The yield of beta glucose was 68%, the initial rotation was 23.84 and the final rotation was 51.39. This method was used a number of times by different workers and found to be very satisfactory. In only one case, (*d*), was alpha glucose apparently in excess in the final product and in that case some crystals of alpha glucose had remained undissolved. The initial rotation was 83.65° and the final 51.83°.

The following table gives a résumé of the rate of loss of pyridine and the yields of beta glucose obtained. In general, if 25 cc. of boiling pyri-

DRYING OF BETA GLUCOSE FROM PYRIDINE.

Material.	Weight alpha glucose. G.	Pyridine. Cc.	Weight after suction. G.	In air.	G.	In oven at 105 degrees. Hr.	G.	Over sul- furic acid. Hrs.	G.	Per cent. yield.
(a) Alpha glucose	5	25	...	Overnight	3	1	2.96		59.2
			(approx.)							
(b) Alpha glucose	10	25	...	Overnight	4.5	1	4.44		44.4
			(approx.)							
(c) Alpha glucose	23.5	25	24.37		...	1/2	17.57	2	17.05	68
			(approx.)					8	16.00	
(d) Beta (?)	25	25	...	Overnight	17.76		2	17.76	71
(e) Beta (?)	15.76	25	...	Short time	15.1		1 1/2	14.75	70
								18	12.25	
								24	11.6	
								42	11.00	
(f) Alpha glucose	10	25	1	7.3		73
(g) Alpha glucose	10	25	1	8.4		84
(h) Alpha glucose	10	25	1	6.9		69

dine dissolve 10 g. of alpha glucose and the solution is not seeded crystallization will begin in an hour and a half and in 5 hours probably 2.5 g. of material have precipitated. The solution should be allowed to stand at least 24 hours in an ice box, and much better yields are obtained if 25 g. of glucose are used to 25 cc. of pyridine.

The following table gives a résumé of the specific rotations of the alpha glucose used and of the beta glucose obtained from it. It will be noted that the change of rotation of the beta glucose takes place rather slowly in pure water and is complete after 24 hours; extrapolations of the readings to the initial rotations are not given.

Material.	SPECIFIC ROTATIONS OF GLUCOSE.					
	Immediately.	30 min.	1 hr.	2 hrs.	3 hrs.	4 hrs. 24 hrs.
Alpha.....	82.49	65.21	47.94	const. ...
Alpha-2nd.....	Crys., 85.72	74.49	59.94	50.53	49.23	const. ...
Beta-(a).....	35.41	50.63	const.
Beta-(b).....	41.46	48.37	...	50.90	const.
Beta-(c).....	23.84	39.30	...	47.51 51.39
Beta-(d).....	83.65 51.83
Beta-(f).....	23.80 50.70
Beta-(g).....	25.40 50.20
Beta-(h).....	26.90 51.90
Beta-(i).....	25.50	50.60 52.00
Beta-(j).....	25.90	49.30 52.10

Conclusions.

It has been found that alpha glucose dissolves readily in hot pyridine and precipitates out readily as the beta form in combination with one molecule of pyridine, as previously described by Behrend. This molecule of pyridine of crystallization is readily lost in the air, or in a vacuum desiccator containing concentrated sulfuric acid, or in an oven at 105°. When dried thoroughly and dissolved in water the beta glucose has an initial rotation of 20-25 and a final rotation of 50-52 when equilibrium is established. As yields of 70-85% can be obtained easily, Behrend's method is very satisfactory.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE INFLUENCE OF VARYING CONCENTRATION OF HYDROGEN ION ON THE OPTICAL ROTATION OF THE ISOMERIC ALKALOIDS, CINCHONINE, CINCHONIDINE AND CINCHOTOXINE.

By H. C. BIDDLE AND THOMAS WATSON.

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Introduction.

The effect of dilution upon the specific rotation of the salt of an optically active base or acid in solution has been studied by several investiga-