

TABLE III

VALUES OF  $K$  IN 10 AND 20 PER CENT. METHYL AND ETHYL ALCOHOL SOLUTIONS

Methyl Alcohol Solutions							
°C.....	0	10	20	25	30	40	
10%	0.8812	0.8853	0.9173	0.9471	0.9093	0.8379	
20%	.6026	.6082	.5860	.5776	.5528	.5254	
Ethyl Alcohol Solutions							
10%	0.8625	0.8700	0.9000	0.9004	0.9061	0.9020	
20%	.6730	.7546	.7706	.7811	.7880	.7803	

The curvature of the lines in the plots relating ( $-\log K'$ ) to ionic strength was more pronounced in this investigation than in investigations using acids of smaller molecular size and media of higher dielectric strength. In solutions of lower dielectric

strength (as the 20% ethyl alcohol solutions) the curvature was sufficiently great to make accurate extrapolation difficult. This effect was greatest at higher temperatures.

### Summary

1. Electromotive force measurements have been made on cells of the type  $H_2(1 \text{ atm.}), (HPr(m_1), NaPr(m_2), NaCl(m_3))$  in  $x$  alcohol-water,  $AgCl(s) + Ag(s)$ , where  $x$  is the per cent., either 10 or 20, of methyl or ethyl alcohol.

2. Values of the ionization constants of the propionic acid in 10 and 20% alcohol-water solutions have been determined over the temperature range 0 through 40°.

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## NOTES

### Synthesis of 4,4'-Dicyanostilbene

BY SHOU-CHENG FU<sup>1</sup> AND PETER P. T. SAH<sup>2</sup>

4,4'-Dicyanostilbene, a valuable intermediate which has been used in the synthesis of the pharmacologically<sup>3</sup> interesting 4,4'-diamidinostilbene, has been prepared from *p*-cyanobenzaldehyde through the pyrolysis of the corresponding azine.

**4,4'-Dicyanobenzaldazine.**—*p*-Cyanobenzaldehyde<sup>4</sup> (4 g.) and hydrazine hydrate (40%, 1.5 g.) in 30 cc. of absolute ethanol were heated four hours under reflux. The reaction mixture was concentrated to ca. 5 cc.; the pale yellow needles which separated on cooling were collected and recrystallized twice from dilute ethanol, yellow needles (2.5 g.); m. p. 118–120° (uncor.).

*Anal.* Calcd. for  $C_{16}H_{10}N_4$ : N, 21.70. Found: N, 21.60.

**4,4'-Dicyanostilbene.**—4,4'-Dicyanobenzaldazine (2 g.), on heating first melted, then decomposed, then sublimed as beautiful long needles and narrow plates. Repeated sublimation gave 500 mg. of practically colorless 4,4'-dicyanostilbene, m. p. 278–280° (cor.), mixed with a sample prepared by the method of Lamb and White,<sup>5</sup> but purified by sublimation; m. p. 278–280° (cor.).

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(2) The authors wish to thank Dr. Hamilton H. Anderson, Professor of Pharmacology and Chairman of the Department, Peiping Union Medical College, for his kindness in suggesting this problem.

(3) Yorke, *Transactions of the Royal Society of Tropical Medicine and Hygiene*, **33**, 464 (1940).

(4) Moses, *Ber.*, **33**, 2624 (1900).

(5) Lamb and White, *J. Chem. Soc.*, 1253 (1939).

### Rotational Relationships of Alkyl Glucosides

BY LEONARD C. KREIDER AND ELMER FRIESEN<sup>1</sup>

The problem of finding simple relationships between the structures of glycosides and glycoside acetates and their optical rotations first attracted our attention when we noticed that the earlier theories proposed by Hudson<sup>2</sup> and Maltby,<sup>3</sup> stating that molecular rotations of glucosides increased in magnitude with increasing molecular weight, were inconsistent with the data more recently obtained on the higher homologs of the alkyl glucosides. In the effort to develop a consistent theory that suggested itself to us,<sup>4</sup> we have prepared a number of new glucoside acetates, following the method of Kreider and Evans,<sup>5</sup> and from these we have prepared the glucosides, following the method of Isbell,<sup>6</sup> and have measured the rotations and other properties of these substances. The resulting data are contained in Table I.

In addition, we have measured the rotations in chloroform of the following substances kindly supplied to us by Noller and Rockwell<sup>7</sup> for this

(1) Present address: Redman Scientific Company, Los Angeles, California.

(2) C. S. Hudson, *THIS JOURNAL*, **31**, 66 (1909).

(3) J. C. Maltby, *J. Chem. Soc.*, **123**, 1404 (1923).

(4) Preliminary report, Meeting of the Kansas Academy of Science, April 4, 1941.

(5) L. C. Kreider and W. L. Evans, *THIS JOURNAL*, **58**, 797, 1661 (1936).

(6) H. S. Isbell, *Bur. Standards J. Research*, **5**, 1179 (1930).

(7) C. R. Noller and C. W. Rockwell, *THIS JOURNAL*, **60**, 2076 (1938).

TABLE I  
 PROPERTIES OF  $\beta$ -ALKYL GLUCOSIDES AND THEIR TETRAACETATES

Name	M. p., °C. (cor.)	- <i>d</i> -Glucoside -		Analyses, %				- <i>d</i> -Glucoside tetraacetate -				
		$[\alpha]_D$ in H <sub>2</sub> O	$[M]_D$ in H <sub>2</sub> O	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	M. p., °C. (cor.)	Acetyl no. <sup>a</sup> Calcd.	Acetyl no. <sup>a</sup> Found	$[\alpha]_D$ in CHCl <sub>3</sub>	$[M]_D$ in CHCl <sub>3</sub>
<i>n</i> -Propyl <sup>b,c</sup>	102.5-3.5	-39.5	-8,780	48.64	48.4	8.16	8.3	103	10.26	10.21	-21.3	-8,300
<i>n</i> -Butyl <sup>b,d</sup>	66-67	-37.4	-8,830	50.83	50.7	8.53	8.6	65-66	9.90	9.83	-21.2	-8,560
<i>n</i> -Amyl	89.5-90.0	-35.7	-8,930	52.78	52.5	8.86	9.1	46-47	9.57	9.62	-21.5	-8,990
<i>n</i> -Heptyl	76-78	-33.1	-9,200	56.09	55.9	9.42	9.5	68.0-8.5	8.97	9.03	-19.7	-8,800
<i>i</i> -Propyl <sup>b,c,e</sup>	128.5-9.5	-37.6	-8,350	48.64	48.5	8.16	8.3	136-137	10.26	10.15	-22.9	-8,930
<i>i</i> -Butyl <sup>b,d</sup>	113-114	-38.2	-9,010	50.83	50.7	8.53	8.5	122.5-3.0	9.90	9.91	-20.2	-8,160
<i>t</i> -Butyl <sup>d,f</sup>								148	9.90	9.90	-12.8	-5,130

<sup>a</sup> A. Kunz and C. S. Hudson, *THIS JOURNAL*, **48**, 1978 (1926). <sup>b</sup> E. Bourquelot and M. Bridel, *Ann. chim. phys.*, [8] **29**, 145 (1913). <sup>c</sup> S. Veibel and F. Eriksen, *Bull. soc. chim.*, [5] **3**, 277 (1936). <sup>d</sup> S. Veibel and H. Lillelund, *Bull. soc. chim.*, [5] **5**, 494 (1938). <sup>e</sup> W. J. Hickenbottom, *J. Chem. Soc.*, 3140 (1928). <sup>f</sup> S. Veibel and E. Nielsen, *Compt. rend.*, **203**, 126 (1936).

purpose, they having originally reported the rotations of these compounds in methanol.

TABLE II

MOLECULAR ROTATION IN CHLOROFORM OF ALKYL-*d*-GLUCOSIDE TETRAACETATES

	$\beta$ - <i>n</i> -Hexyl <sup>a</sup>	$\beta$ - <i>n</i> -Nonyl-	$\beta$ - <i>n</i> -Decyl-	$\beta$ - <i>n</i> -Dodecyl-
$[\alpha]_D$	-20.0	-19.3	-18.6	-16.6
$[M]_D$	-8,640	-9,150	-9,070	-8,110

<sup>a</sup> E. Pacsu, *THIS JOURNAL*, **52**, 2563 (1930).

These data and similar data in the literature agree with the findings of Pigman and Isbell<sup>8</sup> that the molecular rotations of the *N*-alkyl- $\beta$ -*d*-glucosides having more than three carbon atoms in the aglucone lie between 8700 and 9200 in water, while those of the corresponding tetraacetates lie between 8300 and 9200 in chloroform. It can also be seen that while the molecular rotations of the secondary and/or iso series of alkyl  $\beta$ -*d*-glucosides, both free and acetylated, are about the same, those of the corresponding tertiary series are considerably lower, measured under the same conditions.

(8) W. W. Pigman and H. S. Isbell, *Bur. Standards J. Research*, **27**, 9 (1941).

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### D-Mannosan <1,5> $\beta$ <1,6> from $\beta$ -Phenyl-D-mannoside

BY EDNA M. MONTGOMERY, NELSON K. RICHTMYER  
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The syntheses of epi-cellobiose and cellobiose which have been described recently by Haskins, Hann and Hudson<sup>1</sup> involve the use of *D*-mannosan-<1,5> $\beta$ <1,6>; the total synthesis of this anhydride of *D*-mannose is thus a necessary step for attaining totality in the syntheses of the disac-

(1) Haskins, Hann and Hudson, *THIS JOURNAL*, **63**, 1724 (1941); **64**, 1289 (1942).

charides. The total synthesis of *D*-mannose was accomplished by Emil Fischer<sup>2</sup>; the problem therefore reduces to the conversion of *D*-mannose to *D*-mannosan <1,5> $\beta$ <1,6>. This transformation has been effected during the course of our study of the action of alkali upon certain glycosides,<sup>3</sup> and it may well be described separately at this time.

**The Alkaline Degradation of  $\beta$ -Phenyl-D-mannoside to *D*-Mannosan <1,5> $\beta$ <1,6>.**—Tetraacetyl- $\beta$ -phenyl-*D*-mannoside, of m. p. 169° and rotation<sup>4</sup> -62.9° in chloroform (*c*, 2), was obtained in small yield as a by-product in the preparation of tetraacetyl- $\alpha$ -phenyl-*D*-mannoside from  $\alpha$ -pentaacetylmannose, phenol and zinc chloride by a modification<sup>5</sup> of the method used by Helferich and Winkler.<sup>6</sup> Deacetylation produced  $\beta$ -phenyl-*D*-mannoside of m. p. 175° and rotation -71.7° in water (*c*, 1). All these data are in agreement with those of Helferich and Winkler.

A solution of 5.000 g. of pure  $\beta$ -phenylmannoside in 250 cc. of 2.6 *N* aqueous potassium hydroxide in a metallic vessel (a clean beer can) was boiled gently under a reflux condenser; the rotation changed in the course of five days from -70.6°, calculated as mannoside, to a constant value of -114°, calculated as mannosan. The yellow solution was cooled, neutralized to methyl orange with 3 *N* sulfuric acid, and concentrated *in vacuo* to dryness. The product was extracted from the potassium sulfate with hot absolute alcohol, and the extract concentrated *in vacuo* to a sirup. Acetylation of this sirup with acetic anhydride and pyridine produced 4.4 g. of pure 2,3,4-triacetyl-*D*-mannosan <1,5> $\beta$ <1,6>, of m. p. 89-90° and rotation -123.8° in chloroform (*c*, 2) in agreement with the published data.<sup>7</sup>

By deacetylation of the triacetate catalytically with

(2) Fischer, *Ber.*, **23**, 370 (1890).

(3) Montgomery, Richtmyer and Hudson, unpublished results from this Laboratory; see *Science*, **93**, 438 (1941).

(4) Throughout the article the rotations are specific rotations at 20° for sodium light; *c* designates concentration in grams per 100 cc. of solution.

(5) Montgomery, Richtmyer and Hudson, *THIS JOURNAL*, **64**, 690 (1942).

(6) Helferich and Winkler, *Ber.*, **66**, 1556 (1933).

(7) Zemplén, Gerecs and Valatin, *ibid.*, **73**, 575 (1940); Knauf, Hann and Hudson, *THIS JOURNAL*, **63**, 1447 (1941).