needles which have a melting point of 92°. It is insoluble in water, fairly soluble in alcohol, ether or ligroin, readily soluble in benzene or chloroform.

0.2084 g. subs. gave 0.0892 g. AgCl.   Calc. for $C_{19}H_{17}O_4Cl$: Cl, 10.33; found: 10.58.

Saponification of 9 g. of the ester by means of a solution of 3.2 g. of potassium hydroxide in a mixture of 75 cc. of water and 25 cc. of alcohol yielded 50% of the theoretical amount of a substance, identical in melting point, and undistinguishable in other physical properties from the 4-chlorodiphenacyl, described above.
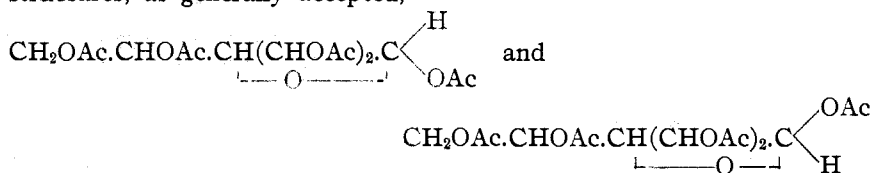
URBANA, ILL.

A COMPARISON OF THE OPTICAL ROTATORY POWERS OF THE ALPHA AND BETA FORMS OF CERTAIN ACETYLATED DERIVATIVES OF GLUCOSE.
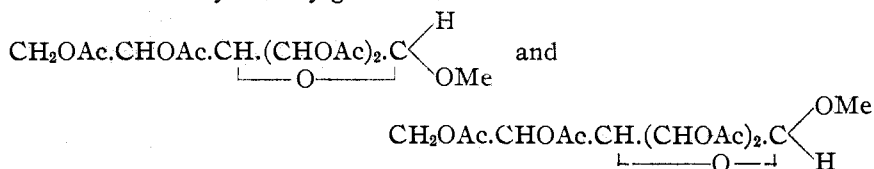
BY C. S. HUDSON AND J. K. DALE.[1]

If the alpha and beta forms of glucose pentacetate have the isomeric structures, as generally accepted,

$$CH_2OAc.CHOAc.CH(CHOAc)_2.C \underset{\underset{\text{O}}{\big|}}{\overset{\displaystyle H}{\big\diagup}} \quad \text{and}$$

$$CH_2OAc.CHOAc.CH(CHOAc)_2.C \overset{\displaystyle OAc}{\underset{\underset{\text{O}}{\big|}}{\diagdown H}}$$

the molecular rotations of the substances may be regarded as having the values $(A + B)$ for one form, and $(-A + B)$ for the other, according to the considerations which have been presented by one of us in a previous article.[2]   The quantity A represents the rotation which is due to the end asymmetric carbon atom, and B denotes the rotation of the remainder of the structure.   In similar manner, the rotations of the alpha and beta forms of tetracetyl methylglucoside,

$$CH_2OAc.CHOAc.CH.(CHOAc)_2.C \underset{\underset{\text{O}}{\big|}}{\overset{\displaystyle H}{\big\diagup}} \quad \text{and}$$

$$CH_2OAc.CHOAc.CH.(CHOAc)_2.C \overset{\displaystyle OMe}{\underset{\underset{\text{O}}{\big|}}{\diagdown H}}$$

may be written $(A' + B)$ and $(-A' + B)$, where A' is of different value from A, on account of the replacement of the acetyl by the methyl radical, but B remains of constant value.   The deduction may be drawn that the

[2] THIS JOURNAL, 31, 66 (1909).

sum of the molecular rotations of the two pentacetates (2B) is presumably equal to the sum of those of the two tetracetyl methylglucosides (2B), and this conclusion can be tested by experiment. Schliephacke[1] has calculated the data and finds that the sum is 39,700 for the pentacetates and 54,900 for the tetracetyl methylglucosides, the rotations of the four substances being measured in benzene solution. The disagreement is clear, and Schliephacke concludes that the foregoing theoretical views do not apply to the acetylated derivatives of glucose. In this connection, however, it is to be noticed that one of the four substances, namely, α-tetracetyl methyl glucoside, has been found by Moll van Charante[2] to form a crystalline compound with benzene and to have in benzene solution a specific rotation (173°) much larger than in alcoholic solution (137°). The corresponding beta form was found to have nearly identical rotations

TABLE I.—SPECIFIC ROTATIONS OF THE GLUCOSE PENTACETATES AND THE TETRACETYL METHYLGLUCOSIDES.

Solvent.	Con-centra-tion.	Rotation.	Specific rotation $[\alpha]_D^{20}$	Molecular rotation.[3] (Average.)	Con-centra-tion.	Rotation.	Specific rotation $[\alpha]_D^{20}$	Molecular rotation. (Average.)
		α-Glucose pentacetate.				β-Glucose pentacetate.		
		Degrees.	Degrees.			Degrees.	Degrees.	
Benzene............	5.302	+20.51	+ 96.7	....	5.061	+0.45	+ 2.2	...
	6.313	+24.42	+ 96.7	+37,800	6.544	+0.71	+ 2.7	...
	10.132	+39.60	+ 97.7	....	10.243	+1.35	+ 3.3	+1,100
Chloroform........	5.252	+21.35	+101.6	....	6.303	+0.98	+ 3.9	...
	6.738	+27.38	+101.6	+39,600	6.801	+1.04	+ 3.8	+1,500
	10.906	+44.36	+101.7	....	10.386	+1.59	+ 3.8	...
Acetic ac. (99.5%)..	6.325	+27.48	+108.6	....	6.267	+0.93	+ 3.7	...
	10.399	+45.24	+108.8	+42,400	10.621	+1.87	+ 4.4	+1,600
Acetic ac. (50%)....	3.919	+16.95	+108.1	+42,200	3.641	+0.47	+ 3.2	+1,200
Absolute alc........	0.5204	+ 2.1	+100.9	+39,400	0.5411	+0.04	+ 1.9	+ 740
Methyl alc.........	1.4932	+ 6.25	+104.6	+40,800	1.2102	+0.24	+ 4.9	+1,900
		α-Tetracetyl methylglucoside.				β-Tetracetyl methylglucoside.		
Chloroform........	4.284	+22.36	+130.5	....	3.813	−2.78	−18.2	...
	8.178	+42.72	+130.6	+47,300	8.0396	−5.88	−18.3	−6,600
Acetic ac. (99.5%)..	1.690	+ 9.08	+134.3	....	4.359	−3.40	−19.5	...
	3.769	+20.16	+133.7	+48,500	8.544	−6.66	−19.5	−7,100
Acetic ac. (50%)....	2.107	+10.60	+125.8	....	3.757	−3.34	−22.2	...
	3.882	+19.76	+127.2	+45,800	8.002	−7.28	−22.7	−8,130
Methyl alc.........	2.138	+11.60	+135.6	+49,200	2.297	−2.00	−21.8	−7,890
Benzene[4]..........	4.8166	+33.84	+175.5	+63,530	4.6884	−4.28	−22.8	−8,290
Absolute alc[5].......	1.1736	+ 6.42	+136.8	+49,500	1.48	−1.46	−24.6	−8,910

[1] *Ann.*, **377,** 182 (1910).

[2] *Rec. trav. chim. Pays Bas*, **21,** 42 (1902).

[3] The molecular weights which are used are, 390 for glucose pentacetate and 362 for tetracetyl methylglucoside.

[4] Quoted from Koenigs and Knorr, *Ber.*, **34,** 970 (1901).

[5] Moll van Charante (*Loc. cit.*) found this value to be $[\alpha]_D^{20} = +137.3°$.

in the two solvents.[1] It has seemed to us desirable to compare the rotations of the four substances in several solvents other than benzene since the relations seem to be complicated in the case of that solvent by the formation of a compound with one of the substances. The pentacetates of glucose and the tetracetates of methylglucoside were prepared as described in detail further on and the specific rotations of the pure substances were found to have the following values (Table I). The measurements refer to a temperature of 20°, sodium light, circular degrees of rotation, and the concentrations which are recorded signify the grams of substance which were contained in 100 cc. of solution, the weighings having been made in air with brass weights. The tube length in all cases is 4 decimeters. The chloroform used was *chloroformum purificatum*, U. S. P.

Tanret[2] has found for the specific rotation of α-glucose pentacetate the value +99° in benzene solution, 8 g. per 100 cc., and +101.7° in chloroform, 9 g. per 100 cc., and for the beta form of glucose pentacetate, he has found +2.8 in benzene, 8 g. per 100 cc., and +3.7 in chloroform, 14 g. per 100 cc. Our measurements confirm these values except in the case of the alpha form in benzene solution. Since we obtain for this substance in chloroform the same value as Tanret, it appears to us that his value in benzene must be high.

The data are now at hand for a comparison of the sums of the molecular rotations of the alpha and beta forms of glucose pentacetate and tetracetyl methylglucoside.

TABLE II.

Sum of the molecular rotations of the alpha and beta forms.

Substance.	Chloroform.	Benzene.	Acetic acid. 99.5%.	50%.	Absolute alcohol.	Absolute methyl alcohol.
Glucose pentacetate....	41,100	38,900	44,000	43,400	40,100	42,700
Tetracetyl methylglucoside.............	40,700	55,240	41,400	37,700	40,600	41,300

The divergence of the sums for benzene solution has already been discussed. The difference in the values in 99.5% acetic acid is 2,600 in molecular rotation or approximately 7° in specific rotation, which seems larger than the uncertainty of the four measurements, and the divergence between the sums becomes greater when the proportion of water in the solvent is increased (50% acetic acid). In methyl alcoholic solution the sums differ only slightly beyond the limits of experimental error. The

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[1] There is evidently a numerical error in Moll van Charante's calculation of the specific rotation of the β-form in alcohol from the measurements which he records, and, likewise, the value in benzene is incorrectly quoted from Koenigs and Knorr, but, nevertheless, the conclusion that the β-form has nearly identical rotations in benzene and alcohol is correct, according to our measurements in Table I.

[2] *Bull. soc. chim.*, **13**, III, 261 (1895).

difference in chloroform solution is only 400 in molecular rotation or about 1° in specific rotation, which constitutes good agreement with the theory. The agreement between the sums in absolute alcoholic solution is also good.

Concerning the Rotatory Powers of the Two Octacetates of Cellose.— The difference between the molecular rotations of the alpha and beta forms of glucose pentacetate is +38,100 in chloroform solution. According to the theory, the difference is the quantity 2A, which should presumably have the same value for all the acetylated aldoses, in which the end asymmetric carbon atom is acetylated. The octacetate of cellose has been prepared in two crystalline forms, of specific rotation in chloroform solution +41° and —8°.[1] Assuming that these are the alpha and beta forms, respectively, their molecular difference (2A) becomes 33,200 which is smaller than the difference for the two pentacetates of glucose by 4,900 or approximately 7° in specific rotation, since the molecular weight of cellose octacetate is 678. The considerable divergence suggests that the α- and β-cellose octacetates may not yet have been obtained in a pure or fully separated condition.

Experimental.

Preparation of the α- and β-Pentacetates of Glucose and their Correlation with the Alpha and Beta Forms of Glucose.—The alpha and beta forms of glucose pentacetate have been correlated with the alpha and beta forms of glucose by the experiments of Behrend and Roth[2] in 1904 and of Behrend[3] in 1907, which show that the acetylation of α-glucose in pyridine solution at zero degrees by the action of acetic anhydride yields α-pentacetate, while β-glucose, under the same conditions, gives rise to β-pentacetate. Recently, we have observed that a similar correlation may be obtained when glucose is acetylated with acetic anhydride and zinc chloride, provided the temperature is kept near zero. Before our experiments on this subject are described, it may be well to record the results which we obtained in repeating the work of Behrend and Roth, since our confirmatory data furnish a more nearly quantitative proof of the correlation in question.

Fifty grams of acetic anhydride were mixed with sixty-seven grams of commercial pyridine bases, the mixture cooled to 0°, 10 g. of pure crystalline α-glucose added and the mixture kept at 0° with occasional shaking during seven hours. The sugar had then dissolved completely. After standing seventeen hours longer at room temperature, the solution was poured into ice water and upon vigorous stirring the pentacetate crystallized in a few minutes. In three experiments, there were obtained from 10 g.

[1] Schliemann, *Ann.*, **378**, 372 and 374 (1911).
[2] *Ann.*, **231**, 369 (1904).
[3] *Ibid.*, **353**, 109 (1907).

of α-glucose 19.0, 19.5 and 18.5 g. of pentacetate with specific rotations in chloroform solution of 91.3°, 90.9° and 92.1°. The weight of pentacetate which is the equivalent of 10 g. of glucose is 21.7 g.

In another experiment, the same quantities of α-glucose, acetic anhydride and pyridine were kept at 0° for 24 hrs. There were obtained 19.8 g. of pentacetate with a specific rotation of 94° in chloroform. Since the specific rotation of pure α-glucose pentacetate in chloroform is about 101.6°, while that of the beta is only 3.9°, it is evident that the crystalline product consisted largely of the alpha isomer.

β-Glucose acetylates more readily than the alpha isomer. The β-glucose used had a specific rotation of 20–21°. With the same amounts of sugar, acetic anhydride and pyridine as were used in acetylating α-glucose, there were crystallized after acetylation at 0° during 3, 5, 6 and 24 hours, respectively, 14, 18, 19.5 and 20.5 g. of pentacetate of specific rotations varying between +5.5 and +5.8 in chloroform. It is evident that the product was almost wholly β-pentacetate.

It was found that powdered glucose can be acetylated readily at 0° by a solution of zinc chloride in acetic anhydride. Four grams of fused zinc chloride were dissolved in 40 g. acetic anhydride, the solution was cooled to 0°, 10 g. of pure α-glucose were added, a little at a time, and the mixture was kept at zero with an occasional shaking for five hours. During this time most of the sugar dissolved but there remained some which had not been attacked; the weight of this portion, after filtering it off, was found to be 2.85 g. The filtrate crystallized in a few minutes after falling into water and yielded 7.15 g. of dry pentacetate, of specific rotation 92° in benzene. The water from which these crystals were obtained was then shaken out with chloroform, and by evaporating the chloroform solution nearly to dryness and pouring it again into water, a second lot of crystalline pentacetate was obtained, showing a specific rotation of 86° and weighing 3.64 g. when dry. An extraction of the second water with chloroform yielded 2.26 g. of a very viscous sirup which did not crystallize. Summing up these weights, there were obtained 13.05 g. of acetylated material from 7.15 g. of sugar, the latter being equivalent by theory to 15.44 g. pentacetate. Since the specific rotation of α-glucose pentacetate in benzene is about 96.7°, while that of the β-pentacetate in benzene is only 2.7°, it is evident that the crystalline product consisted largely of the alpha isomer.

In a second similar experiment, the time of reaction was increased to 45 hours with the result that only 0.33 g. glucose remained undissolved. There were obtained 15.20 g. of pentacetate of specific rotation 78°, 3.03 g. of 59°, and 1.30 g. of sirupy residue, making 19.53 g. of acetylated product against 19.89 g. of pentacetate by theory. There is evidence from the rotatory powers of the crystals that a partial change of the α-

pentacetate to the β form took place during the prolonged time of the reaction; this change is just detectable in the first experiment. It has been found during numerous preparations of this substance that 10 g. of pure α-glucose will yield under constant stirring of the acetylation mixture for 8 hours about 13 g. of pentacetate of specific rotation 83°, from which the pure α form may be readily obtained by the usual recrystallization from alcohol.

With the same proportions of sugar, zinc chloride and acetic anhydride that are recorded in the experiments just mentioned, 10 g. of crystalline β-glucose, of specific rotation 21°, after 5 hours' reaction at 0°, yielded 2.73 g. undissolved sugar, 10.75 g. pentacetate of rotation 8.7°, 2.22 g. of 18°, and 1.06 g. of viscous sirup, making a total of 14.03 g. of acetylated product against 15.75 g. of pentacetate by theory. The crystals from this experiment yielded pure β-pentacetate on recrystallization. In a second similar experiment the time of reaction was extended to 24 hours and there were found 0.43 g. sugar remaining undissolved, 15.10 grams pentacetate of rotation 14°, 3.43 g. of rotation 43°, and 1.20 g. of sirup, making 19.73 g. of acetylated product against 20.73 g. pentacetate by theory. It is again noticeable from the rotations of the product that the longer duration of the reaction causes isomeric change, in this instance transforming some of the β-pentacetate into the alpha form. It has been found that 10 g. of crystalline β-glucose will yield, with eight hours' stirring in the acetylation mixture, about 17 g. of pentacetate of specific rotation 17°, from which the pure β-pentacetate may be readily obtained by recrystallization from alcohol.

These acetylations of α- and β-glucose, with acetic anhydride and zinc chloride, correlate these substances with the α- and β-pentacetates of glucose, respectively, and confirm the similar correlation by Behrend, who used pyridine as the catalyst.

The purification of the samples of the pentacetates which were used in making the measurements recorded in Table I was accomplished by recrystallizing from 95% alcohol until the rotation became constant. The crystals were dried by raising the temperature gradually to 100°. The pure alpha pentacetate melted at 112–113°, corrected.

Two acetyl estimations made by boiling in a quartz flask with reflux condenser 0.5 g. of pentacetate with 90 cc. of 0.3 N sulfuric acid during three hours gave 76.73% and 76.97% acetic acid; calc. 76.93%.

The pure beta pentacetate melted at 132°, corrected, and yielded 77.16% acetic acid after hydrolysis. Both pentacetates were found to yield the theoretical amount of glucose after the hydrolysis of 5 g. of pentacetate with 50 cc. of 5% sulfuric acid during two hours on the steam bath, the estimation of the glucose being taken from a measurement of the rotation of the hydrolyzed solution.

Preparation of α-Tetracetyl Methyl Glucoside.—This substance was prepared by acetylating α-methylglucoside with acetic anhydride and sodium acetate, according to the directions of Koenigs and Knorr.[1] It was recrystallized from 95% alcohol until a constant specific rotation was obtained. It melted at 100–101° corrected.

Preparation of β-Tetracetyl Methylglucoside.—This compound has been prepared by Koenigs and Knorr[2] from β-bromoacetyl glucose and from β-acetonitroglucose, and Moll van Charante[3] has prepared it from β-methylglucoside. We followed Koenigs and Knorr's procedure slightly modified, using β-bromoacetyl glucose. Twenty-five g. of β-bromoacetyl glucose were dissolved in 200 cc. methyl alcohol. To this were added 12.5 g. silver nitrate dissolved in 200 cc. methyl alcohol and 50 cc. water. The filtrate from the silver bromide precipitate was treated with hydrogen sulfide and then shaken with barium carbonate. The filtrate from this was evaporated to a thick syrup on the steam bath under diminished pressure. On cooling, it crystallized to an almost solid mass. It was recrystallized from absolute methyl alcohol until the specific rotation was constant. The yield was 13.5 g., having a melting point of 104–105° (corr.).

THE ISOMERIC OCTACETATES OF LACTOSE.

By C. S. HUDSON AND J. M. JOHNSON.[4]

Schutzenberger and Naudin[5] acetylated lactose by boiling it with acetic anhydride but did not obtain a crystalline product. Herzfeld[6] crystallized lactose octacetate by acetylating the sugar with acetic anhydride and anhydrous sodium acetate (the Liebermann[7] method), and found the substance to melt at 86°, but did not learn its rotatory power. Schmöger[8] prepared the octacetate by this method, reported a higher melting point, 95–100°, and observed a specific rotation of —3.5° in chloroform. Fischer and Armstrong[9] found this octacetate to melt at 106°,

[1] *Ber.*, **34,** 970 (1901).

[2] *Loc. cit.,* 969 and 977.

[3] *Loc. cit.*

[4] Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture. A preliminary notice was read at the Cincinnati meeting of the American Chemical Society, April, 1914. The authors desire to express their appreciation of the valuable services of Mr. A. S. Eastman, who has repeated during the summer of 1914 the preparation of the new octacetyl lactose. The data of the present article are partly taken from his work.

[5] *Bull. soc. chim.,* II, **12,** 208 (1869).

[6] *Ber.*, **13,** 265 (1880).

[7] *Ibid.,* **11,** 1619 (1878).

[8] *Ibid.,* **25,** 1452 (1892).

[9] *Ibid.,* **35,** 841 (1902).