yellow oil, $C_{16}H_{22}O_3$, levorotatory, insoluble in water, acid and alkaline solutions, and soluble in the common organic solvents.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXI. BETA-THIOPHENOL GLYCOSIDES OF GLUCOSE, XYLOSE, LACTOSE AND CELLOBIOSE[1,2]

BY CLIFFORD B. PURVES

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Although the glycosides of the hydroxy alcohols form a numerous group which has been submitted to detailed study and whose optical properties have been classified through the work of Hudson,[3] too few of the thioglycosides have been prepared to render possible a similar mathematical examination of their molecular rotations. Apart from the α- and β-glucosides of methyl, ethyl, propyl and benzyl mercaptan described by Schneider and his co-workers,[4] the only other simple members of the series found recorded in the literature are β-thiophenol glucoside and β-thiophenol lactoside, which together form the subject of a paper by Fischer and Delbrück.[5] The thioglycosides, nevertheless, are of interest from an optical point of view, for they differ from their oxygen analogs in containing a bivalent and therefore unsaturated sulfur atom directly united to the first asymmetric center of the carbohydrate residue. It is impossible to predict the nature and the extent of the changes which this difference may bring about in their behavior toward plane-polarized light and, in consequence, the present investigation is one of several designed to gain information on this subject by experimental methods. This article is mainly concerned with four glycosides of thiophenol and with their acetylated derivatives.

At an early stage in the research it became apparent that an acetobromo sugar in ethereal or benzene solution reacted very slowly and sometimes incompletely with sodium thiophenate dissolved in water. This was the

[1] Publication approved by the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] The author has arranged with Dr. C. S. Hudson, under whose direction the research was carried out, that it will be included as No. XXI in his series entitled "Relations between Rotatory Power and Structure in the Sugar Group." No. XX was published in THIS JOURNAL, **51**, 2788 (1929).

[3] Hudson, *ibid.*, **31**, 66 (1909).

[4] Schneider, Sepp and Stiehler, *Ber.*, **51**, 220 (1918).

[5] Fischer and Delbrück, *ibid.*, **42**, 1476 (1909).

method used by Fischer and Delbrück[5] for preparing the acetylated derivatives of thiophenol glucoside and lactoside, but its tedious nature and somewhat uncertain outcome led to its abandonment in the present work. The acetobromo sugars studied, however, swiftly condensed with potassium thiophenate when means were taken to render the system homogeneous, and the yield of the acetylated thioglycosides was satisfactory when the alkalinity of the solution was low. These conditions were readily obtained by adding the acetobromo sugar, dissolved in chloroform, to an equal bulk of 95% alcohol containing one equivalent of potassium hydroxide and a 10 to 15% excess of the mercaptan, an excess which was sufficient to render the alcoholic solution neutral to litmus and to phenolphthalein. After the reaction had been completed by heating, the clear liquor was washed free of potassium bromide, alcohol and thiophenol by very dilute aqueous sodium bicarbonate and the product was recovered in an almost pure condition from the chloroform residue. It will be seen that this procedure was very similar to that adopted by Schneider, Sepp and Stiehler[4] but differs from it in that a reacetylation of the glycoside was unnecessary. This was due to the strongly acidic nature of thiophenol and to the particular excess of the reagent which was used. Moreover, the acetobromo derivative was prepared from the fully acetylated sugar by the action of hydrogen bromide dissolved in a mixture of glacial acetic acid and chloroform. After the substitution of bromine for acetyl was complete, washing with water removed the free acids and the residual chloroform, containing almost the theoretical amount of the acetobromo sugar, was run into the solution of alcoholic potassium thiophenate without previous drying. This simplification rendered it possible to obtain a 70% yield of the β-thiophenol glycoside acetate from the crude, fully acetylated sugar in the course of six hours.

Five new compounds are described in the experimental portions: the β-thiophenol and the β-*p*-thiocresol glycosides of cellobiose together with the acetate of the former; β-thiophenol xyloside triacetate and β-thiophenol xyloside itself. In addition, it was necessary to repeat the work of Fischer and Delbrück on the thiophenol derivatives of glucose and lactose, partly to confirm and to extend the optical data which they record for these substances and partly to make sure that the new method gave products identical with those formerly described. All of the thioglycosides examined were crystalline and a summary of their physical properties will be found below.

A simple way of analyzing the molecular rotations of the fully acetylated thioglycosides is to adopt the method used by Hudson[6] to calculate the rotation, A_{Cl}, of the potentially reducing asymmetric carbon atom of the acetochloro sugars. Assuming, as a first approximation, that substitution

[6] Hudson, THIS JOURNAL, **46**, 462 (1924).

in this position does not affect the optical rotatory power of the other asymmetric centers in the molecule, the combined molecular rotation in chloroform of the latter may be denoted by B. The values of B for the various acetylated sugar residues were obtained by the above author from his study of the α- and β-acetates themselves and are listed in the table below. Then if A_{SPh} be the molecular rotation due to the asymmetric carbon atom to which the thiophenyl radical is attached, $B-A_{SPh}$ is the observed molecular rotation of the β-thiophenol glycoside acetate and the magnitude of A_{SPh} may be calculated in each case. These values, together with those quoted from the work of Hudson for A_{Cl}, the sum A_{SPh} plus A_{Cl} and the difference, A_{SPh} minus A_{Cl}, are also given.

TABLE I

COMPARISON OF THE QUANTITIES A_{SPh} AND A_{Cl}, THE MOLECULAR ROTATIONS, RESPECTIVELY DUE TO THE TERMINAL ASYMMETRIC ATOM IN THE β-THIOPHENOL GLYCOSIDE ACETATES AND IN THE ACETOCHLORO DERIVATIVES OF THE SUGARS

Sugar	$B-A_{SPh}$	B	A_{SPh}	A_{Cl}	$A_{Cl}-A_{SPh}$	$A_{Cl}+A_{SPh}$
Xylose	−21,670	10,200	−31,870	38,500	70,370	6,630
Cellobiose	−20,740	8,800	−29,540	39,000	68,540	9,460
Lactose	−14,270	16,900	−31,170	38,100[7]	69,270	6,930
Glucose	− 7,700	20,700	−28,400	40,200	68,600	11,800
		Mean value M_D	−30,500	38,950	69,200 in $CHCl_3$	

Inspection of the data shows that A_{SPh}, like A_{Cl}, is an almost constant quantity and that the greatest deviation from the mean value occurs with tetra-acetyl thiophenol glucoside. This error corresponds to less than 5° in specific rotation and the agreement may be considered fair. Thiophenol glycoside acetates, therefore, obey the regularities discovered by Hudson for other similar series of sugar derivatives and the possession of an unsaturated sulfur atom does not necessarily render invalid the principle of optical superposition on which such regularities are founded. It is worthy of note that the molecular rotation of the *p*-thiocresyl group, M_D 29,580 as obtained from that of hepta-acetyl β-*p*-thiocresol cellobioside, M_D −20,780 in chloroform, is practically the same as that of A_{SPh}, as might have been expected from the close structural similarity between these two radicals.

While it is true that A_{SPh} is approximately constant, the deviations from the average value would individually be zero if the law of optical superposition were obeyed with rigor. This is obviously not the case and different substituents occasion varying small but definite changes in the rotation of the rest of the molecule. The remarkable constancy of the sum $A_{Cl} + A_{SPh}$, as compared with the gross variations in their difference, $A_{Cl} - A_{SPh}$, indicates that in the former case the secondary

[7] Hudson and Kunz, THIS JOURNAL, **47**, 2052 (1925).

deviations were largely compensated and were, therefore, very similar in magnitude and opposite in sign. As the thiophenyl glycoside acetates, from their method of preparation, possessed the β-configuration and were therefore contrary in this respect to the acetochloro sugars, it may be concluded that the thiophenyl group very closely resembles a chlorine atom in its effect upon the rotation of an acetylated sugar molecule as a whole. Indeed, an exhaustive series of similar calculations showed that this parallelism between thiophenyl, *p*-thiocresyl and chlorine substituents in the reducing position of the four sugar acetates studied was as close as that between chlorine and iodine in the acetohalogen derivatives, much better than that between chlorine and bromine, chlorine and α-methoxy or β-thiophenyl and β-methoxyl. In a word, the molecular rotations of the thiophenol glycoside acetates in chloroform are appropriately compared with those of the acetochloro derivatives and not with the acetylated glycosides of the hydroxy alcohols.

While the acetylated thiophenol glycosides display the normal relationship to each other in their optical behavior, no such claim can be made for the β-glycosides themselves. The following data are based throughout upon measurements made in water, while a_{SPh} and b have their old significance but with respect to the new solvent. An article by Hudson[8] furnished the data from which the value of b was calculated from the molecular rotations of the β-sugars in the usual way. It will be seen that the variation in the magnitude of a_{SPh} is very great.

TABLE II

VALUE OF THE QUANTITY, a_{SPh}, THE ROTATION OF THE END ASYMMETRIC CARBON ATOM FOR β-THIOPHENOL GLYCOSIDES

Sugar	M_D in water $b - a_{SPh}$	M_D b	M_D a_{SPh}
Xylose	−17,130	7,250	24,380
Cellobiose	−25,690	13,970	39,660
Lactose	−17,060	20,470	37,530
Glucose	−19,180	11,870	31,050

If the very probable assumption be made that the deacetylation of the acetylated thioglycosides by means of alcoholic ammonia was accompanied by no other structural change in the molecule, only two explanations seem to be able to account for the inconstancy of a_{SPh}. The first of these would postulate that the unsaturated sulfur atom in the thioglycoside formed an unstable addition compound with an hydroxy group in the carbohydrate residue or with the elements of the water used as a solvent in the optical determinations. In this case the experimental observations could be attributed to the constitutional dissimilarity of the compounds studied. On the other hand, the anomalies may be due to the failure of

[8] Hudson, THIS JOURNAL, **47**, 268 (1925).

the principle of optical superposition to apply even approximately to the glycosides of thiophenol, but it then becomes difficult to understand why the same irregularities are not more marked among the rotations of the fully acetylated derivatives. The exploration of this possibility would involve the study of reducing sugars substituted in the first position by other highly acidic radicals such as chlorine in the unknown chloro sugars. In the meantime, however, it is unsafe to make use of an optical property as a guide to the stereochemical arrangement of the unsubstituted thioglycosides.

Experimental

The Preparation of Triacetyl β-Thiophenol Xyloside.—A solution of 10 g. of pure β-xylose tetra-acetate in 25 cc. of dry chloroform was made up to 50 cc. with glacial acetic acid saturated with hydrogen bromide. The optical rotation of the mixture increased to a constant value within thirty minutes, when the substitution of bromine for the acetyl group on the first carbon atom of the molecule was taken to be complete. After three successive washings with ice water had removed acetic acid and hydrogen bromide, the residual chloroform solution of acetobromoxylose, together with small chloroform extracts of the aqueous liquors, was added at room temperature and without drying to the equivalent amount (51 cc.) of 0.612 *N* alcoholic caustic potash in which 3.5 cc. or a 10% excess of thiophenol had previously been dissolved. Warming on the water-bath for thirty minutes rendered the condensation complete, after which the clear liquor, with its deposit of crystalline potassium bromide, was repeatedly washed in a separatory funnel with a dilute aqueous solution of sodium bicarbonate until the odor of the thio-alcohol became faint. The chloroform layer, after being finally extracted with water and dried over anhydrous calcium chloride, was evaporated under diminished pressure to a thin sirup, from which an 80% yield of triacetyl-β-thiophenol xyloside was precipitated by the cautious use of light petroleum. The product, which occurred as small, well-formed prisms, was readily recrystallized by adding petroleum ether to its ethereal solution and after two such purifications possessed a specific rotation in chloroform of $[\alpha]_D$ −58.71° (0.2566 g. in 25 cc. rotated plane-polarized light 1.205° to the left when a 2-dm. tube was used). Another recrystallization failing to change this value appreciably (found, $[\alpha]_D^{20}$ −59.0°; 0.3758 g. in 25 cc. of chloroform gave an observed reading of 1.774° to the left when in a 2-dm. tube), the specific rotation of pure triacetyl-β-thiophenol xyloside in chloroform was accepted as $[\alpha]_D^{20}$ −58.9°. The compound was readily soluble in all of the usual organic solvents save petroleum ether and melted sharply at 78°.

An acetyl determination was carried out by the method of Kunz;[9] 0.3174 g. required 26.13 cc. of decinormal alkali in place of the theoretical amount, 25.88 cc., for triacetyl thiophenol xyloside. In the estimation of sulfur the accurate and expeditious method due to Waters[10] was adopted: 0.3566 g. gave 0.2346 g. of Ba_2SO_4. Calcd.: S, 8.70. Found: S, 9.02.

Hepta-acetyl-β-thiophenol Cellobioside.—Pure β-cellobiose octa-acetate. 30 g., was allowed to stand for three hours at room temperature in chloroform (90 cc.) and glacial acetic acid containing 20% by weight of hydrogen bromide (75 cc.). Occasional shaking had enabled the acetate to dissolve completely and a solution of the acetobromo sugar in chloroform was isolated from the mixture as described in the preceding para-

[9] Kunz and Hudson, THIS JOURNAL, **48**, 1982 (1926).

[10] Waters, *J. Ind. Eng. Chem.*, **12**, 482 (1920).

graph. The condensation of the acetobromocellobiose with the theoretical amount (96 cc.) of 0.455 *N* alcoholic caustic potash and with 4.8 cc. (10% excess) of thiophenol was also carried out exactly as in the case of triacetyl thiophenol xyloside and, on isolation, a 78% yield of crude crystalline acetylated thioglycoside was obtained. A single recrystallization from 16 times its weight of hot alcohol lowered the specific rotation of the preparation to $[\alpha]_D^{20}$ −26.57° in chloroform but this method did not succeed in eliminating all of the impurities. The crude material, which contained no halogen and displayed little reducing power on hot Fehling's solution, was eventually dissolved in 100 cc. of warm chloroform and was fractionally recrystallized as minute needles by the cautious addition of hot absolute alcohol. This procedure gave a small first fraction with a specific rotation of $[\alpha]_D^{16}$ −27.2° in chloroform (0.2485 g. in 25 cc. had α −0.541° in a 2-dm. observation tube) and a large second fraction with $[\alpha]_D^{16}$ −28.5° (0.4633 g. in 25 cc. of chloroform gave an observed reading of 1.056° to the left in a 2-dm. tube). The specific rotation of the latter fraction did not change appreciably on repeated purification in the same manner; after the first recrystallization, $[\alpha]_D^{17}$ −28.33° (0.5428 g. in 25 cc. of chloroform had α −1.230° in a 2-dm. tube); after the fourth, $[\alpha]_D^{18}$ −28.58° (0.5421 g. gave an observed reading of 1.230° to the left); and after the fifth, $[\alpha]_D^{20}$ −28.20° (0.5343 g. had α −1.205° observed in 25 cc. of chloroform with a 2-dm. tube). Accordingly, $[\alpha]_D^{20}$ −28.5° was accepted as the true specific rotation of hepta-acetyl-β-thiophenol cellobioside in chloroform. The compound decomposed in the neighborhood of 295° and dissolved freely in chloroform and acetone, was sparingly soluble in hot alcohol and was almost insoluble in ether or petroleum ether.

In an acetyl estimation, 0.2287 g. required 21.8 cc. of decinormal alkali, the amount calculated for the same weight of thiophenol cellobioside acetate being 22.0 cc. The preparation contained 4.57% of sulfur in place of the theoretical amount, 4.40% (0.5349 g. gave 0.1785 g. of $BaSO_4$).

Hepta-acetyl-β-*p*-thiocresol Cellobioside.—The method used to obtain hepta-acetyl-β-thiophenol cellobioside was also adopted in the preparation of the analogous *p*-thiocresol derivative and gave rise to the product as long, silky needles in a yield which was 80% of the theoretical. The specific rotation of the crude product was $[\alpha]_D^{21}$ −22.8° in chloroform (0.3323 g. in 25 cc. had α −0.606° in a 2-dm. tube) but two recrystallizations from alcohol reduced this figure to $[\alpha]_D^{20}$ −28.2° (0.3438 g. gave an observed reading of 0.776° to the left). No change occurred after the next purification (found, $[\alpha]_D^{20}$ −27.75°; 0.3385 g. in 25 cc. of chloroform gave an observed reading of 0.751° to the left) and $[\alpha]_D^{20}$ −28.0° was taken to be the correct rotation of hepta-acetyl-β-*p*-thiocresol cellobioside in this solvent. The substance melted sharply at 217°.

In an acetyl estimation 0.2726 g. required 25.04 cc. of decinormal alkali, the theoretical amount being 25.15 cc.; 0.4923 g. also gave 0.1529 g. of $BaSO_4$. Found: S, 4.26; hepta-acetyl thiocresol cellobioside requires S, 4.31.

Hepta-acetyl-β-thiophenol Lactoside.—The acetylated thioglycoside was prepared from 40 g. of crude lactose octa-acetate, free from inorganic salts but not recrystallized, exactly as in the case of the same derivative of cellobiose, and the yield of the crude crystalline product averaged 70% of the theoretical. Recrystallization from 130 cc. of hot 95% alcohol reduced the specific rotation to $[\alpha]_D^{20}$ −19.25° (0.3552 g. had a reading of 0.547° to the left in 25 cc. of chloroform and a 2-dm. tube), while after the next purification a value of $[\alpha]_D^{20}$ −19.6° was observed (0.2916 g. in 25 cc. with a 2-dm. tube gave 0.457° to the left). The product from the third recrystallization had $[\alpha]_D^{20}$ −19.72° (0.3270 g. gave a reading of −0.516°) and $[\alpha]_D^{20}$ −19.6° was the specific rotation of pure hepta-acetyl-β-thiophenol lactoside in chloroform solution at a concentration of about 1.5%.

Fischer and Delbrück[5] quote $[\alpha]_D^{20}$ −17.7° as the specific rotation of the substance

in a 7.165% chloroform solution; the present preparation gave an observed reading of 2.599° to the left in a 2-dm. tube under the same conditions and therefore possessed a specific rotation of $[\alpha]_D^{20}$ −18.14° at this concentration. The compound melted at 155–156°.

In an acetyl estimation, 0.1652 g. required 15.88 cc. of decinormal alkali while the value demanded by the same weight of acetylated thiophenol lactoside is 15.85 cc. The sulfur estimation on 0.4831 g. gave 0.1567 g. of $BaSO_4$. Found: S, 4.46; calcd., S, 4.40.

Tetra-acetyl-β-thiophenol Glucoside.—The substance was prepared by the above method in 70% yield from crude crystalline glucose penta-acetate and was recrystallized from 95% alcohol as long needles with a specific rotation of $[\alpha]_D^{20}$ −22.25° in chloroform (0.1653 g. in 25 cc. had an observed reading of 0.294° to the left in a 2-dm. tube). Two fractions were obtained in the third recrystallization with rotations of $[\alpha]_D^{19}$ −17.5° and $[\alpha]_D^{20}$ −17.38°, respectively (0.6482 g. had α −0.907°; 0.6786 g. had α −0.943° under the usual conditions) and the next recrystallization did not change the determination (found, $[\alpha]_D^{20}$ −17.63°; 0.6745 g. had α −0.951°). Pure tetra-acetyl-β-thiophenol glucoside, therefore, had a specific rotation in chloroform of $[\alpha]_D^{20}$ −17.5° for a concentration of about 2.5%.

Fischer and Delbrück[5] made an observation in toluene of $[\alpha]_D^{20}$ −40.1° for a concentration of 4.6784%; two determinations in this solvent, carried out under comparable conditions, gave values of $[\alpha]_D^{21}$ −40.85° and $[\alpha]_D^{21}$ −40.7° for the specific rotation, or a mean value of $[\alpha]_D^{21}$ −40.8°, in good agreement with the earlier observations (0.1696 g. in 25 cc. of toluene had α −3.823°; 1.1410 g. in 25 cc. had α −3.699°).

β-Thiophenol Xyloside.—Pure triacetyl-β-thiophenol xyloside was dissolved in six times its weight of methyl alcohol which had previously been saturated at room temperature with dry ammonia gas. After standing overnight the evaporation of the solvent left a sirup which was repeatedly extracted with warm dry ether to remove acetamide. The product then crystallized in almost quantitative yield as stout prisms with a specific rotation in water of $[\alpha]_D^{20}$ −69.7° after a single purification from alcohol (0.2905 g. in 25 cc. gave a reading of 1.621° to the left in a 2-dm. tube). A second recrystallization gave a product with $[\alpha]_D$ −71.0° (0.2748 g. had α −1.562°) which was not changed by the third or by the fourth (found, $[\alpha]_D^{20}$ −70.5° and $[\alpha]_D^{20}$ −71.0°; 0.2933 g. gave a reading of 1.654°, 0.3420 g. one of 1.943° to the left in a 2-dm. tube when dissolved in 25 cc. of water). β-Thiophenol xyloside thus possessed a specific rotation of $[\alpha]_D^{20}$ −70.8° in a 1.4% aqueous solution. In acetone the optical property was very different (0.1581 g. in 25 cc. of the pure solvent gave an observed reading of 1.101° to the left in a 2-dm. tube and $[\alpha]_D^{20}$ was −87.05°). The compound melted sharply at 144° and in addition to a ready solubility in water and alcohol it dissolved freely in acetone and ethyl acetate.

In an estimation of sulfur, 0.1951 g. gave 0.1894 g. of $BaSO_4$. Found: S, 13.33; calcd. for thiophenol xyloside, S, 13.23.

β-Thiophenol Cellobioside.—After the deacetylation of the pure hepta-acetate with methyl alcoholic ammonia and the removal of acetamide with ether, the addition of a little alcohol caused the glycoside to crystallize in a yield of 67% of the theoretical. The minute crystals separated over the course of days from methyl alcohol containing a little ether and possessed a rotation of $[\alpha]_D^{16}$ −54.7 in water (0.2584 g. in 25 cc. had α −1.131°). Two similar recrystallizations raised this value to $[\alpha]_D^{16}$ −59.0° (0.3836 g. gave a reading of α −1.811°), which was not changed by further purification (found $[\alpha]_D^{17}$ −59.3°; 0.4020 had α −1.907°). β-Thiophenol cellobioside, therefore, had a specific rotation of $[\alpha]_D^{17}$ −59.2° in water for a 1.5% solution. The melting point was sharp at 230°.

The sulfur estimation, carried out on 0.3696 g., gave 0.2029 g. of $BaSO_4$. Found: S, 7.54; calcd., S, 7.37.

β-Thiophenol Lactoside.—By the deacetylation of the pure acetate, crystalline thiophenol lactoside was obtained in 80% of the theoretical yield. Two recrystallizations from 95% alcohol rendered the compound nearly pure (found, $[\alpha]_D^{19}$ −38.45°; 0.2477 g. in 25 cc. of water had α −0.762°). After the third, the specific rotation was $[\alpha]_D^{19}$ −39.45° (0.2436 g. rotated plane-polarized light 0.786° to the left under the usual conditions), while no significant change was observed after the fourth purification (found, $[\alpha]_D^{19}$ −39.13°; 0.2345 g. in 25 cc. of water had α −0.734° when observed in a 2-dm. tube). The specific rotation of pure β-thiophenol lactoside in about 1% aqueous solution was thus $[\alpha]_D^{19}$ −39.3°. At a higher concentration, 6.5632%, the rotation of this glycoside was $[\alpha]_D^{19}$ −40.36° (1.6408 g. in 25 cc. of water gave a reading of 5.296° to the left in a 2-dm. tube), in good agreement with the value, $[\alpha]_D^{20}$ −40.1°, obtained by Fischer and Delbrück[5] under the same conditions. β-Thiophenol lactoside melted sharply at 220°.

In a sulfur estimation, 0.5004 g. gave 0.2651 g. of $BaSO_4$. Found: S, 7.28; calcd. for thiophenol lactoside, S, 7.37.

β-Thiophenol Glucoside.—The sirupy mixture of acetamide and thioglucoside which remained from the deacetylation of pure tetra-acetyl-β-thiophenol glucoside was dissolved in 7 times its weight of warm ethyl acetate and 86% of the theoretical amount of thiophenol glucoside crystallized as the solution cooled. After two further recrystallizations from ethyl acetate containing a little methyl alcohol, the product had a rotation of $[\alpha]_D^{20}$ −70.34° in water (0.5352 g. in 25 cc. had an observed rotation of 3.012° to the left in a 2-dm. tube) and melted sharply at 133°. These values were not changed on further purification (found, $[\alpha]_D^{19}$ −70.75°; 0.5323 g. had α −3.012°) and the specific rotation of β-thiophenol glucoside in a 2% aqueous solution was regarded as $[\alpha]_D^{19}$ −70.5°. When the concentration was 9.774%, the rotation fell to $[\alpha]_D^{19}$ −72.15° (observed in a 2-dm. tube, 14.76° to the left) in good agreement with the values of $[\alpha]_D$ −72.3° and $[\alpha]_D$ −72.5° found by Fischer and Delbrück for the same solution.

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Summary

1. The specific rotations of the following thioglycoside acetates have been measured in chloroform solution: triacetyl-β-thiophenol xyloside, m. p. 78°, $[\alpha]_D^{20}$ −58.9°; hepta-acetyl-β-thiophenol cellobioside, decomposition point about 295°, $[\alpha]_D^{20}$ −28.5°; hepta-acetyl-β-*p*-thiocresol cellobioside, m. p. 217°, $[\alpha]_D^{20}$ −28.0°; hepta-acetyl-β-thiophenol lactoside, m. p. 155–156°, $[\alpha]_D^{20}$ −19.6°; tetra-acetyl-β-thiophenol glucoside, m. p. 117°, $[\alpha]_D^{20}$ −17.5°.

2. It has been shown that the molecular rotation of the potentially reducing carbon atom in the above acetylated thioglycosides, A_{SPh}, is approximately constant at M_D 30,500. The deviations from this value in the case of individual sugars are similar in magnitude but opposite in sign to those of A_{Cl}, the molecular rotation of the terminal asymmetric atom of the acetochloro derivatives.

3. The following specific rotations were measured with precision in aqueous solution; β-thiophenol xyloside, m. p. 144°, $[\alpha]_D^{20}$ −70.8°; β-thiophenol cellobioside, m. p. 230°, $[\alpha]_D^{17}$ −59.2°; β-thiophenol lactoside, m. p. 220°, $[\alpha]_D^{19}$ −39.3° and β-thiophenol glucoside, m. p. 133°, $[\alpha]_D^{19}$ −70.5°.

4. The molecular rotations in water of the above four β-thiophenol glycosides displayed irregularities which could not be explained. In consequence, optical data cannot at present be safely used as an aid in determining the stereochemical configuration of the thioglycosides.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXII. EVIDENCE CONCERNING THE RINGED STRUCTURE OF BETA-THIOPHENOL CELLOBIOSIDE AND OF BETA-THIOPHENOL LACTOSIDE[1,2]

BY CLIFFORD B. PURVES

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A noteworthy property of the β-thioglycosides which serves to distinguish them from the isomeric α-forms, and also from the glycosides of the hydroxy alcohols, may be seen in their great stability toward acid hydrolysis.[3] The glycosidic unions in β-thiophenol lactoside and cellobioside are no exceptions to the general rule and the comparative indifference of the thio linking in such derivatives of the disaccharides makes possible a simple way of examining their constitution. For example, if thiophenol lactoside be submitted to the action of aqueous acid under conditions just sufficiently drastic for the complete hydrolysis of the disaccharide itself, the union of thiophenol with the potentially reducing carbon atom of the sugar residue is largely preserved and galactose and a thiophenol glucoside may be expected to form the main products of the reaction. The former component may readily be modified before its examination, either as regards the position of the oxygen ring or otherwise, and the isolation of galactose of the ordinary type therefore provides no evidence concerning its original state in the disaccharide molecule. It is otherwise

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[2] The author has arranged with Dr. C. S. Hudson, under whose direction the research was carried out, that it will be included as No. XXII in his series entitled "Relations between Rotatory Power and Structure in the Sugar Group." No. XXI was published in THIS JOURNAL, **51**, 3619 (1929).

[3] Schneider, Sepp and Stiehler, *Ber.*, **51**, 220 (1918).