trated to a sirup. Paper chromatograms, irrigated and sprayed, with the reagents indicated previously, showed one major component having $R_{glucose}$ 1.3.

The sugar was purified by elution from a Celite column[19] using 1-butanol saturated with water as the mobile phase; $[\alpha]^{25}D$ −179° (*c* 0.9, water).

Anal. Calcd. for $C_6H_{12}O_5S$: S, 16.3. Found: S, 16.4.

A 26-mg. sample of this sugar was dissolved in 2% acetic acid solution and titrated with standard iodine solution. After 2 hr. at 25°, 2.0 ml. of 0.0530 *N* iodine solution was consumed.

A portion of the purified sugar was dissolved in water to an initial concentration of 3.8 mg./ml. and used in a series of measurements in a vapor pressure osmometer. Calcd.: mol. wt., 196. Found: mol. wt., 198.

Thioglycosides of 3-Amino-3-deoxy-D-mannose[1]

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The reaction of some D-mannose derivatives with ethanethiol and concentrated hydrochloric acid was investigated. Mercaptolysis of methyl 3-amino-3-deoxy-α-D-mannopyranoside hydrochloride (II) gives a mixture of the crystalline ethyl 3-amino-3-deoxy-1-thio-α- and β-D-mannopyranoside hydrochlorides (40% I and 60% III) in high yield, readily separable as the crystalline tetraacetates (IV and VII). The structures of I and III were established by periodate oxidation data on the corresponding *N*-acetyl derivatives (V and VIII). The behavior of a number of simple sugars in the mercaptalation reaction was examined.

The objective of this investigation was to study apparent anomalies in the reactions of D-mannose derivatives with ethanethiol in concentrated hydrochloric acid solution and to devise a suitable preparative route to 1-thioglycosides of 3-amino-3-deoxy-D-mannose.

The reaction between aldoses and alkanethiols in concentrated aqueous acid, at about 0°, leads to the formation of the acyclic dithioacetals in high yield when these products are removed from the reaction sphere by crystallization[2] or by rapid neutralization of the acid.[3] If this, apparently initial, product is not so removed or if the dithioacetal is put back into the system,[4] 1-thioglycosides are formed and hydrolysis to the aldose occurs. The 1-thioglycosides found, in the cases investigated, have been pyranosides. The reaction can be influenced by steric factors, such as sugar configuration, and by polar factors, such as those introduced by the presence of an amino group.

Prolonged treatment of D-mannose with ethanethiol and concentrated (12 *N*) hydrochloric acid at room temperature, under conditions wherein any dithioacetal formed would not separate, gave a 31% yield of the ethyl 1-thio-α- and β-D-mannopyranosides, isolated as the tetraacetates.[5] In our hands, a paper chromatographic study of this reaction (Table I) showed that after five minutes all of the D-mannose had reacted, and that the diethyl dithioacetal was the principal product, although small proportions of two thioglycosides were present. Levene and Meyer[6] reported isolation of D-mannose diethyl dithioacetal in 63% yield after five minutes under similar conditions. At longer reaction times, the intensities of the thioglycoside zones increased at the expense of the dithioacetal, and a weaker zone corresponding to D-mannose appeared. The distribution of the four products, by visual comparison, was essentially constant after four hours.

TABLE I

PAPER CHROMATOGRAPHIC DATA[a] ON MERCAPTOLYSIS OF ALDOSE DERIVATIVES AT 25°

Compound (*c* 10, 12 *N* HCl)	Time of reaction, min.	Observed products[b]			
		Aldose	Dithioacetal	Anomeric thiopyranosides[c]	
		R_{man} 1.00	R_{man} 2.66	R_{man} 2.11	R_{man} 2.39
D-Mannose[d]	5	...	++++	+	(+)
	60	+	++++	+++	++
	240	+	++++	+++	+++
	1440	++	+++	+++	+++
		R_g 1.00	R_g 2.75	R_g 2.23	R_g 2.52
D-Glucose[d]	5	(+)	++++	(+)	...
	60	(+)	++++	+	...
	240	++	++	++	+
	1440	+++	...	++	+
		R_{gal} 1.00	R_{gal} 2.85	R_{gal} 2.17	
D-Galactose[d]	5	+	++++	+	
	60	...	+++	+	
	240	...	+++	+	
	1440	++	(+)	++	

[a] Details given in Experimental. [b] Relative intensity, estimated visually. These values do not necessarily represent relative absolute intensities since the components vary in their reactivity with the spray reagent. [c] Probable identities, not compared with known samples. The zone R_{gal} 2.17 was elongated and possibly a mixture of two incompletely resolved zones. [d] The *R* values refer to the respective parent aldose; mannose, glucose, or galactose, denoted as a subscript, with a 4:1:5 1-butanol–ethanol–water system.

Under similar conditions, D-glucose gives ethyl 1-thio-α-D-glucopyranoside in 15% yield, together with unchanged D-glucose and, probably, some β-D anomer; no diethyl dithioacetal was detected.[4] D-Glucose diethyl dithioacetal and ethyl 1-thio-α-D-glucofuranoside are converted into the acid-resistant[7] ethyl 1-thio-α-D-glucopyranoside by 22% hydrochloric acid under the same conditions, whether or not ethanethiol is present, and some D-glucose is formed.[4] Our paper chromatographic studies confirm these results and show that the behavior of D-galactose is closely similar (Table I); in each case the initial reaction of the sugar with ethanethiol and concentrated hydrochloric acid at room temperature is rapid, with almost complete

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(2) E. Fischer, *Ber.*, **27**, 673 (1894).

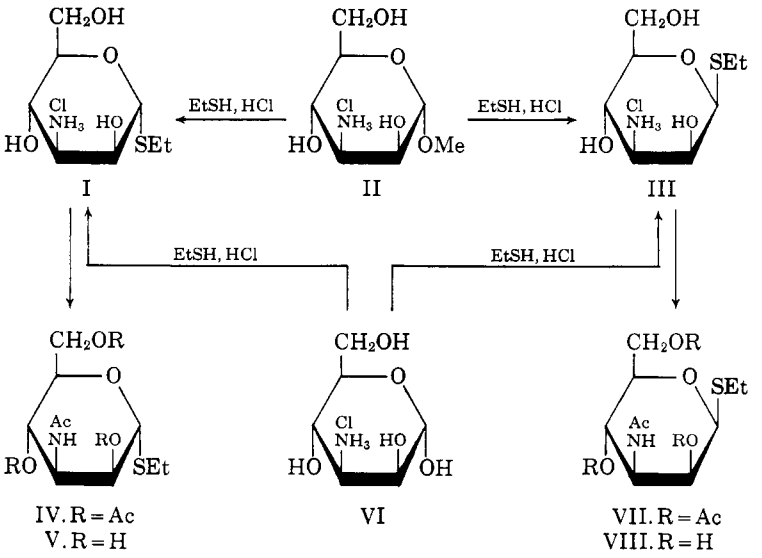
(3) M. L. Wolfrom, M. R. Newlin, and E. E. Stahly, *J. Am. Chem. Soc.*, **53**, 4379 (1931); M. L. Wolfrom and F. B. Moody, *ibid.*, **62**, 3465 (1940).

(4) E. Pacsu and E. J. Wilson, Jr., *ibid.*, **61**, 1930 (1939); P. Brigl, K. Gronemeier, and A. Schulz, *Ber.*, **72**, 1052 (1939).

(5) J. Fried and D. E. Walz, *J. Am. Chem. Soc.*, **71**, 140 (1949).

(6) P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **74**, 695 (1927).

(7) E. Pacsu and E. J. Wilson, Jr., *J. Am. Chem. Soc.*, **61**, 1450 (1939).



conversion to the dithioacetal in five minutes. Subsequently the dithioacetal undergoes conversion to other products and is present only in traces after twenty-four hours, while a small amount of the free sugar appears, and zones with the mobilities anticipated for thioglycosides form the principal detected products.

The results would suggest that the dialkyl dithioacetal is formed by a rapid, kinetically controlled reaction, which is followed by a slower acid-catalyzed reaction which gives at equilibrium the distribution of products according to their thermodynamic stabilities in the system.

Glycosidically linked sugars can also react with alkanethiol and hydrochloric acid to give dialkyl dithioacetals,[8] and this reaction is the basis of the mercaptolysis procedure[9] for fragmentation of oligo- and polysaccharides into dialkyl dithioacetals of component sugars or oligosaccharides. It has been noted[10] that D-mannose derivatives exhibit anomalous reactivity. Mercaptolysis of mannosidostreptomycin gave ethyl 1-thio-α- and β-D-mannopyranosides, rather than the expected dithioacetal, from the D-mannose moiety. Mercaptolysis of methyl α-D-mannopyranoside also gave the thioglycoside, ethyl 1-thio-β-D-mannopyranoside,[5] and, although the isolated yield (as the tetraacetate) was low (5%), the reaction offered for the present work the possibility of a one-step conversion of a mannopyranoside derivative into a 1-thiomannopyranoside derivative with avoidance of possible complications in proceeding through the free sugar.

The results of this investigation show that methyl 3-amino-3-deoxy-D-mannopyranoside hydrochloride (II),[11] which can be readily prepared[12] from methyl α-D-glucopyranoside, can be converted by mercaptolysis into the ethyl 3-amino-3-deoxy-1-thio-α- and β-D-mannopyranoside hydrochlorides (40% I and 60% III) in high (71%) yield. The two products are formed in the indicated ratios, based on the rotation of the mixture, and are best separated through their acetylated derivatives (IV and VII). *O*-Deacetylation of IV and VII with methanolic ammonia gave the corresponding ethyl 3-acetamido-3-deoxy-1-thio-α- and β-D-mannopyranosides (V and VIII). The pyranoside ring structure in all six thioglycoside derivatives was established by periodate oxidation (Table II) of V and VIII, since in each case formaldehyde was not released in the oxidation. Both derivatives consumed one mole of oxidant per mole during a three-hour period and no further uptake was observed. The consumption of one mole of oxidant per mole by thioglycosides, in excess of that required for a Malaprade type of oxidation, has been generally observed,[13,14] and appears to involve, at the sulfur function, a reaction whose nature has not been fully established. The lack of further oxidation in the case of V and VIII is fully consistent with the pyranoside structure, deduced from the absence of formaldehyde in the oxidation product and establishes that V and VIII are anomers, assigned the α-D and β-D configurations, respectively, on the basis of Hudson's rules of rotation.[15] The structures assigned to the derivatives I, III, IV, and VII follow from the identification of configuration and ring size in V and VIII.

Table III lists the molecular rotations of the six derivatives of ethyl 3-amino-3-deoxy-1-thio-D-mannopyranoside, together with corresponding data on the ethyl 1-thio-D-mannopyranosides.[5] The A value (rotatory contribution of C-1) shows good correlation between the three pairs of derivatives, and with the reported[5] value for the anomeric ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-mannopyranosides.

The two thioglycosides I and III have paper chromatographic mobilities R_m (R_m = mobility of II) of 1.43 and 1.22, respectively. The reaction product

TABLE II

PERIODATE OXIDATION OF ETHYL 3-ACETAMIDO-3-DEOXY-1-THIO-α- AND β-D-MANNOPYRANOSIDES (V AND VIII)[a]

Compound	Time, min.	Oxidant uptake[b]	Formaldehyde release[b]	Formic acid release[b]
V	10	0.67	..	..
	20	.94	..	..
	60	.98	..	..
	120	..	0.00	0.00
	180	.98	..	..
	360	.98	..	..
	1440	1.04	..	0.00
VIII	10	0.61	..	..
	20	.93	..	..
	60	.95	..	..
	120	.95	0.00	0.00
	180	1.03	..	..
	480	1.03	..	..
	1440	1.03	..	0.00

[a] Details given in Experimental. [b] Moles per mole of sample.

(8) F. J. McEvoy, B. R. Baker, and M. J. Weiss, *J. Am. Chem. Soc.*, **82**, 209 (1960).

(9) M. L. Wolfrom and J. C. Sowden, *ibid.*, **60**, 3009 (1938); C. Araki and S. Hirase, *Bull. Chem. Soc. Japan*, **26**, 463 (1953); A. N. O'Neill and D. K. R. Stewart, *Can. J. Chem.*, **34**, 1700 (1956); M. L. Wolfrom and A. Thompson, "Methods in Carbohydrate Chemistry," R. L. Whistler and M. L. Wolfrom, Ed., Vol. III, Academic Press, New York, N. Y., 1963, p. 150.

(10) J. Fried and H. E. Stavely, *J. Am. Chem. Soc.*, **69**, 1549 (1947); H. E. Stavely and J. Fried, *ibid.*, **71**, 135 (1949).

(11) H. H. Baer and H. O. L. Fischer, *ibid.*, **83**, 1132 (1961).

(12) A. C. Richardson, *J. Chem. Soc.*, 373 (1962).

(13) L. Hough and M. I. Taha, *ibid.*, 2042 (1956).

(14) S. Okui, *Yakugaku Zasshi*, **75**, 1262 (1955); M. L. Wolfrom and Z. Yosizawa, *J. Am. Chem. Soc.*, **81**, 3477 (1959); M. L. Wolfrom, Z. Yosizawa, and B. O. Juliano, *J. Org. Chem.*, **24**, 1529 (1959).

(15) C. S. Hudson, *J. Am. Chem. Soc.*, **31**, 66 (1909).

TABLE III
MOLECULAR ROTATORY DATA

Compound	α-D-Anomer [α]D	α-D-Anomer [M]D	β-D-Anomer [α]D	β-D-Anomer [M]D	Solvent	Partial molecular rotation[a] A
	degrees		degrees			
Ethyl 3-amino-3-deoxy-1-thio-D-mannopyranoside hydrochloride (I and III)	+137	35500	−95	−24650	H_2O	30,100
Ethyl 3-acetamido-2,4,6-tri-*O*-acetyl-3-deoxy-1-thio-D-mannopyranoside (IV and VII)	+57	22300	−95	−37150	$CHCl_3$	29,700
Ethyl 3-acetamido-3-deoxy-1-thio-D-mannopyranoside (V and VIII)	+93	24650	−146	−38700	MeOH	31,650
Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-mannopyranoside[b]	+104	40800	−67	−26300	$CHCl_3$	33,500

[a] See ref. 15. [b] See ref. 5.

contained a third, minor component, R_m 1.85. Its mobility was that expected of the dithioacetal, but it could not be isolated in the crystalline state. In addition a trace of a zone R_m 0.70, with chromatographic behavior identical to that of 3-amino-3-deoxy-D-mannose hydrochloride (VI), was present. Chromatographic analysis of the product at shorter reaction times (Table IV) revealed the presence of starting material (II), but at no intermediate time could a greater amount of the zone R_m 1.85 be detected. When the reaction was conducted for five days at 10° the isolated yield of crystalline I + III was only 34%, although chromatography showed that the remaining sirup still contained these products. The zone R_m 1.85 was still only a minor component, although significantly more of the zone R_m 0.70, apparently 3-amino-3-deoxy-D-mannose hydrochloride (VI), was present in the sirup.

The results indicate that mercaptolysis of II is an excellent preparative route for I and III, but it was considered of interest to study the course of the mercaptalation reaction on free 3-amino-3-deoxy-D-mannose hydrochloride (VI).

Dithioacetal formation from 2-amino-2-deoxy-D-glucose hydrochloride is known to be sluggish,[16] unless forcing conditions, with fuming hydrochloric acid, are used,[17] or the charged amino group is eliminated by use of the acetamido analog.[16] In contrast it was found that 3-amino-3-deoxy-D-mannose hydrochloride (VI) reacts rapidly with 12 *N* hydrochloric acid and ethanethiol at room temperature, and only a trace of VI was present after four hours (Table IV). Considerable conversion to the thioglycosides R_m 1.43 (I) and 1.22 (III) had occurred after five minutes, and a relatively larger proportion of product of R_m 1.85 (probably the dithioacetal) was also present. At longer reaction times, the thioglycosides became the preponderant products, although, even after one day, the proportion of the product of R_m 1.85 present was greater than that formed in the mercaptolysis of II. It is evident that the reactivity of VI is very different from that of 2-amino-2-deoxy-D-glucose and is qualitatively closely similar to the behavior of D-mannose on mercaptalation. The lower over-all reaction rate of VI is presumably due to inhibition, by the positively charged $-NH_3^+$ group in the molecule, of protonation at the glycosidic center, this protonation being the first stage in the mercaptalation reaction.

TABLE IV
PAPER CHROMATOGRAPHIC DATA[a] ON MERCAPTOLYSIS OF 3-AMINO-3-DEOXY-D-MANNOSE DERIVATIVES AT 25°

Compound (*c* 10, 12 *N* HCl)	Time of reaction, min.	Observed products[b,c]: VI, R_m 0.70	II, R_m 1.00	III, R_m 1.22	I, R_m 1.43	Dithioacetal, R_m 1.85
VI	5	++		++	+	++
	60	+		++	++	+++
	240	(+)		++	+++	++
	1440	(+)		++	++++	++
II	5	+	+++	(+)	...	...
	60	+	++	+	+	+
	240	+(+)	+	++	++	+
	1440	++	(+)	++	+++	++

[a] See footnote *a* of Table I. [b] See footnote *b* of Table I. [c] R_m values denote mobility relative to II.

(16) M. L. Wolfrom and K. Anno, *J. Am. Chem. Soc.*, **74**, 6150 (1952).

(17) M. W. Whitehouse, P. W. Kent, and C. A. Pasternak, *J. Chem. Soc.*, 2315 (1954).

Experimental[18]

Reaction of Methyl 3-Amino-3-deoxy-α-D-mannopyranoside Hydrochloride (II) with Ethanethiol and Hydrochloric Acid.—Methyl 3-amino-3-deoxy-α-D-mannopyranoside hydrochloride (II) was prepared in 23% yield from methyl α-D-glucopyranoside by the sequence of Baer and Fischer[11] with the modifications described by Richardson.[12] A chilled solution of II (5 g.) in concentrated hydrochloric acid (20 ml.) was treated with ethanethiol (10 ml.), and shaken for 24 hr. at room temperature. After dilution with ethanol (100 ml.) the solution was neutralized with lead carbonate, filtered, and the combined filtrate and ethanol washings concentrated to give a crystalline solid; yield 4.0 g. (71%), $[\alpha]^{18}D$ +32 ± 1.5° (*c* 0.4, water). Paper chromatograms of this material showed zones of R_m 1.22 and 1.43. Repeated fractional recrystallization gave fine needles of pure ethyl 3-amino-3-deoxy-1-thio-β-D-mannopyranoside hydrochloride (III); R_m 1.22 as the less soluble component, m.p. 240–245° dec. (browning at 224°), $[\alpha]^{21}D$ −95 ± 0.6° (*c* 1.7, water); $\lambda_{max\ (\mu)}^{KBr}$ 3.0 (OH), 7.90 (SEt), 11.26 (axial H at C-1); X-ray powder diffraction data[19]: 12.72 s (2), 7.79 vs (1), 6.61 vw, 5.37 vw, 4.61 w, 4.37 m, 4.15 s (2,2), 3.99 m, 3.59 w, 3.29 m (3), 3.05 vw, 2.86 vw.

Anal. Calcd. for $C_8H_{18}ClNO_4S$: C, 36.99; H, 6.93; N, 5.39; S, 12.33. Found: C, 37.11; H, 7.48; N, 5.32; S, 12.02.

The second component, ethyl 3-amino-3-deoxy-1-thio-α-D-mannopyranoside hydrochloride (I), R_m 1.43, was isolated as needles from the mother liquors from crystallization of III; m.p. 218–220° dec. (browning at 195°), $[\alpha]^{21}D$ +137 ± 1.8° (*c* 0.55, water); $\lambda_{max\ (\mu)}^{KBr}$ 3.0 (OH), 7.91 (SEt), 11.86 (equatorial H at C-1); X-ray powder diffraction data[19]: 11.63 s (2), 9.36 vw, 7.86 vs (1), 6.71 vw, 6.21 m, 5.42 m, 4.78 vw, 4.52 s (2,2), 3.91 w, 3.57 m (3), 3.43 m, 2.95 vw.

(18) Melting points were taken with a Hershberg apparatus. Specific rotations were determined in a 2-dm. polarimeter tube. Infrared spectra were determined on a Perkin-Elmer Infracord infrared spectrophotometer with pellets pressed from a finely ground mixture of the sample with dried analytical reagent grade potassium bromide. Paper chromatography was carried out by the descending technique with the upper layer of a 4:1:5 1-butanol–ethanol–water system, and R_m refers to mobility relative to that of methyl 3-amino-3-deoxy-α-D-mannose hydrochloride. Zones were detected by the silver nitrate/sodium hydroxide procedure [W. E. Trevelyan, D. P. Proctor, and J. S. Harrison, *Nature*, **166**, 444 (1950)].

(19) Interplanar spacing, Å., CuKα radiation. Relative intensity, estimated visually: s, strong; m, medium; w, weak; v, very. First few lines are numbered (1, strongest); double numbers indicate approximately equal intensities.

Anal. Calcd. for $C_8H_{18}ClNO_4S$: C, 36.99; H, 6.93; N, 5.39; S, 12.33. Found: C, 37.24; H, 7.40; N, 5.58; S, 12.18.

The reaction was repeated with the same quantities of reactants, but with shaking 5 days at 10° before isolation of products. Crystalline I + III were isolated; combined yield 34%. The residual sirup showed on chromatography zones R_m 1.22 and 1.43 corresponding to III and I, plus additional zones R_m 0.70 and 1.85. The product R_m 0.70 showed chromatographic behavior identical to that of 3-amino-3-deoxy-D-mannose hydrochloride.

At reaction times shorter than 24 hr., at room temperature, the product contained some unchanged starting material, a weak zone R_m 1.85, and a product R_m 0.70, apparently 3-amino-3-deoxy-D-mannose hydrochloride.

Ethyl 3-Acetamido-2,4,6-tri-*O*-acetyl-3-deoxy-1-thio-β-D-mannopyranoside (VII).—The crystalline mixture of I and III from the preceding preparation (1.0 g.) was treated with pyridine (16 ml.) and acetic anhydride (16 ml.) for 24 hr. at room temperature; the mixture was poured into iced water (50 ml.) and after 1 hr. the solution was extracted with two 50-ml. portions of chloroform. The extracts were washed with water, dried (magnesium sulfate), evaporated, and the sirup was crystallized from ether (50 ml.); yield 0.68 g. (45%). The product was recrystallized from ethanol with little loss to give pure VII as needles; m.p. 162–164°, $[\alpha]^{22}D$ −95 ± 1.3° (*c* 0.76, chloroform); $\lambda^{KBr}_{max\,(\mu)}$ 5.77 (OAc), 5.95, 6.60 (NHAc), 11.14 (axial H at C-1); X-ray powder diffraction data[19]: 10.40 s (1), 7.69 vw, 6.76 s (3), 5.52 vw, 4.63 m, 4.45 vw, 4.13 s (2), 3.81 m, 3.32 w, 2.77 w, 2.70 vw, 2.31 vw.

Anal. Calcd. for $C_{16}H_{25}NO_8S$: C, 49.10; H, 6.39; N, 3.58. Found: C, 48.69; H, 6.47; N, 3.61.

The melting point of the product was undepressed on admixture with a sample of VII prepared from pure ethyl 3-amino-3-deoxy-1-thio-β-D-mannopyranoside hydrochloride (III) by a similar acetylation procedure.

Ethyl 3-Acetamido-2,4,6-tri-*O*-acetyl-3-deoxy-1-thio-α-D-mannopyranoside (IV).—Concentration of the ether mother liquors from the preceding preparation gave a sirup which crystallized on trituration with petroleum ether; yield 0.52 g. (35%). Recrystallization from ether gave pure IV as fine needles; m.p. 122–124°, $[\alpha]^{22}D$ +57 ± 0.9° (*c* 0.52, chloroform); $\lambda^{KBr}_{max\,(\mu)}$ 5.75 (OAc), 6.05, 6.65 (NHAc), 11.86 (equatorial H at C-1); X-ray powder diffraction data[19]: 15.11 vw, 10.17 w, 9.03 m, 7.94 vs (1), 6.78 m, 5.81 s (2), 5.32 vw, 5.05 vw, 4.62 s (3), 4.43 s (3,3), 4.18 vw, 3.95 s (2,2), 3.70 w, 3.64 w.

Anal. Calcd. for $C_{16}H_{25}NO_8S$: C, 49.10; H, 6.39; N, 3.58. Found: C, 49.36; H, 6.28; N, 3.66.

The melting point of the product was undepressed on admixture with a sample of IV prepared from pure ethyl 3-amino-3-deoxy-1-thio-α-D-mannopyranoside hydrochloride (I) by a similar acetylation procedure.

Ethyl 3-Acetamido-3-deoxy-1-thio-α-D-mannopyranoside (V).—Dry ammonia gas was passed for 30 min. through a solution of ethyl 3-acetamido-2,4,6-tri-*O*-acetyl-3-deoxy-1-thio-α-D-mannopyranoside (IV, 0.20 g.) in methanol (10 ml.) at 0°. After 1 hr. at room temperature the solution was evaporated and the crystalline product was recrystallized from ethanol; yield 0.10 g. (74%); m.p. 224–226°, $[\alpha]^{22}D$ +93 ± 1.5° (*c* 0.34, methanol); $\lambda^{KBr}_{max\,(\mu)}$ 3.0 (OH), 6.05, 6.45 (NHAc), 7.88 (SEt), 11.86 (equatorial H at C-1); X-ray powder diffraction data[19]: 8.42 m, 7.23 w, 6.39 s (2), 5.81 vs (1), 4.90 vw, 4.80 w, 4.20 m (3), 3.88 vw, 3.67 vw, 3.51 vw, 3.20 vw, 2.99 vw.

Anal. Calcd. for $C_{10}H_{19}NO_5S$: C, 45.28; H, 7.17; N, 5.28. Found: C, 45.06; H, 7.13; N, 5.17.

Ethyl 3-Acetamido-3-deoxy-1-thio-β-D-mannopyranoside (VIII).—This compound was prepared from ethyl 3-acetamido-2,4,6-tri-*O*-acetyl-3-deoxy-1-thio-β-D-mannopyranoside (VII) by the same procedure as that used for the α-D anomer, and was obtained as needles from ethanol; yield 74%; m.p. 234–235°, $[\alpha]^{22}D$ −146 ± 2° (*c* 0.25, methanol); $\lambda^{KBr}_{max\,(\mu)}$ 3.0 (OH), 6.05, 6.50 (NHAc), 7.90 (SEt), 11.26 (axial H at C-1); X-ray powder diffraction data[19]: 11.87 m, 10.78 s (3), 4.73 vw, 4.47 s (2), 4.24 s (2,2), 3.74 s (1), 3.01 vw, 2.70 vw, 2.52 vw, 2.41 w, 2.20 vw.

Anal. Calcd. for $C_{10}H_{19}NO_5S$: C, 45.28; H, 7.17; N, 5.28. Found: C, 44.90; H, 7.02; N, 5.15.

Periodate Oxidation of Ethyl 3-Acetamido-3-deoxy-1-thio-α- and β-D-mannopyranosides (V and VIII).—Solutions of the sample (20 mg., 0.75 mmoles) in water were treated with 0.25 *M* sodium metaperiodate solution (10 ml., 2.5 mmoles) and at once made up to 100 ml. and stored at room temperature in the dark. Blanks were prepared similarly, omitting the sample. Periodate uptake was determined on 5-ml. aliquots by the arsenite–iodine method,[20] and formic acid was determined after addition of 2 drops of ethylene glycol by titration with 0.02 *N* sodium hydroxide to the end point with methyl red. Formaldehyde was determined by the chromotropic acid method.[21] The results are summarized in Table II.

Reaction of D-Mannose and 3-Amino-3-deoxy-D-mannose Hydrochloride (VI) with Ethanethiol and Hydrochloric Acid at 25°.—A mixture of the sugar (100 mg.), concentrated hydrochloric acid (1.0 ml.), and ethanethiol (1.0 ml.) was shaken at room temperature (*ca.* 25°). Aliquots of the reaction were withdrawn at selected time intervals, neutralized by stirring with lead carbonate in ethanol, filtered, and evaporated. Paper chromatography of the products revealed, in the case of D-mannose, the presence of a product R_{man} 2.66 corresponding to D-mannose diethyl dithioacetal, and two products, R_{man} 2.11 and 2.39, believed to be thioglycosides. In the case of 3-amino-3-deoxy-D-mannose hydrochloride, products with R_m 1.43 and 1.22, corresponding to I and III, respectively, together with a product R_m 1.85, believed to be the dithioacetal, and a product R_m 0.70, apparently starting material, were obtained. The approximate intensities of the zones on the chromatograms, estimated visually, at various reaction times, are listed in Table IV. Comparable data for the mercaptolysis of methyl 3-amino-3-deoxy-α-D-mannopyranoside hydrochloride (II) also are listed.

Reaction of D-Glucose and of D-Galactose with Ethanethiol and Hydrochloric Acid at 25°.—The procedure used in the preceding experiment was followed, and the results are recorded in Table I. The zones R_g 1.00 and R_{gal} 1.00 corresponded to the respective parent sugars, and the zones R_g 2.75 and R_{gal} 2.85 corresponded in mobility and behavior to those given by the diethyl dithioacetals of D-glucose and D-galactose, respectively. In both cases rapid conversion of the free sugar to the dithioacetal appeared to take place, followed by a slower reaction wherein the dithioacetal disappeared, the free sugar was formed, and products with mobilities corresponding to thioglycosides appeared.

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