Anal. Calcd. for $C_{20}H_{25}N_3O_{11}S$: C, 46.60; H, 4.88; N, 8.15; S, 6.21. Found: C, 46.12; H, 5.19; N, 8.47; S, 6.45.

Conversion of IVa into 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranosyl Bromide (I).—A solution of ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-1-thio-β-D-glucopyranoside (IVb, 50 mg.) in methylene chloride (5 ml.) was treated at room temperature with a slight excess of bromine in methylene chloride. The solution was concentrated after 5 min. and the crystalline material which separated was filtered and washed with anhydrous ether, yield 40 mg. (80%), m.p. 162–164°, identical by mixture melting point and infrared spectrum with an authentic sample[9] of I.

Products from the Ortho Ester Form of Acetylated Maltose[1]

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Hot acetylation of β-maltose with sodium acetate and acetic anhydride leads to the formation of 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-β-maltose and its anomer in addition to the principal product, β-maltose octaacetate. The acid-catalyzed chloroform mutarotation of β-maltose heptaacetate is complex and involves its anomer as well as 3,6,2′,3′,4′,6′-hexa-*O*-acetyl-β-maltose. The latter compound is formed by the successive action on β-maltose octaacetate of acetic anhydride–hydrogen bromide and warm aqueous sodium acetate with the anomeric forms of 2,3,4,2′,3′,4′,6′-maltose heptaacetate being produced in addition. These findings are explained on the basis of the intermediate formation of a 1,2-orthoacetate structure.

In previous investigations in this laboratory, the readily crystallizable 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-β-D-maltose (hereinafter designated β-maltose heptaacetate) had been isolated, first from the acetolysis products of amylopectin[2] and then from acetylated acid-reverted mixtures from maltose and D-glucose.[3] This anomalous result warranted further investigation and in particular we wished to determine whether this partially acetylated maltose structure was a normal product, hitherto undetected, of the acetylation of maltose with hot acetic anhydride and sodium acetate. Such an acetylation mixture was accordingly investigated by column chromatographic methods as piloted by thin layer techniques. β-Maltose heptaacetate was indeed found among the acetylation products and in 0.3% yield. Furthermore, these sensitive techniques showed the presence of two other substances, in small amount, in addition to β-maltose octaacetate, the major product (85% yield). One of these substances was identified as the hitherto unknown anomer of 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-β-maltose or α-maltose heptaacetate. Its rotation in chloroform was found to be +128°, in excellent agreement with the value +131° calculated for it by Hudson and Sayre.[4] Confirmation of the anomeric nature of this substance was found by establishing it as a mutarotation product of the common β-D form. A partially acetylated aldose having its C-1 hydroxyl free would be expected to mutarotate and indeed Hudson and Sayre reported that a chloroform solution of β-maltose heptaacetate changed in rotation from $[\alpha]^{20}D$ +68 → +110° in 5 weeks. As sugar mutarotation is known to be subject to general acid–base catalysis, we found that this equilibrium could be attained in 5–10 hr. by acid catalysis[5]; Hudson and Sayre[4] had found the same on the addition of a trace of ammonia. An analysis of the equilibrated mixture by thin layer chromatographic methods showed two components besides the predominant starting material. Extrusive silicate column chromatography then served to isolate the products in crystalline form. One of these was the α-maltose heptaacetate and the other was a crystalline hexaacetate, m.p. 163–165°, $[\alpha]^{20}D$ +83 → +92° (chloroform). Both of these acetates produced β-maltose octaacetate on further acetylation under mild conditions (acetic anhydride and pyridine at room temperature).

The formation of maltose heptaacetate on acetylation of maltose can be rationalized by postulating an ortho ester intermediate. The ortho ester cation V, formed by attack (IV → V) of the neighboring *trans*-acetoxy group upon the glycosidic hydroxyl, can react with acetate ion to give the orthoacetate VI. On processing the reaction mixture with acidic water, as is customarily done in sodium acetate acetylations, the ortho ester VI would be hydrolyzed to maltose heptaacetate (IV, VIII). This anomerizable heptaacetate favors its β-D form (IV), as visually estimated by thin layer chromatography of the equilibrated mixture. Both anomers (IV and VIII) were, however, isolated.

The low yields of ortho ester reaction products from the sodium acetate acetylation of β-maltose is reasonable since the elevated reaction temperature does not favor ortho ester formation, as has been pointed out by Isbell and Frush[6] for the methyl orthoacetate form of acetylated D-mannose.

Ortho ester derivatives of maltose are known,[7] all of which have been obtained by further reaction of a hepta-*O*-acetylmaltosyl chloride of ortho ester structure discovered by Freudenberg and Ivers.[8] Freudenberg and co-workers[9] reported the isolation of a substance that may have been VI by reaction of the sensitive orthoacetyl chloride with silver acetate but the amorphous product was not characterized. If the orthoacetate VI is a product of the sodium acetate acetylation of maltose and leads to the formation of β-maltose heptaacetate on further processing with water, then maltose heptaacetate should not be formed if the acidic (acetic acid) water treatment be omitted. In

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(2) M. L. Wolfrom, J. T. Tyree, T. T. Galkowski, and A. N. O'Neill *J. Am. Chem. Soc.*, **73**, 4927 (1951).

(3) M. L. Wolfrom, A. Thompson, and R. H. Moore, *Cereal Chem.*, **40**, 182 (1963).

(4) C. S. Hudson and R. Sayre, *J. Am. Chem. Soc.*, **38**, 1867 (1916).

(5) *Cf.* C. E. Ballou, S. Roseman, and K. P. Link, *ibid.*, **73**, 1140 (1951).

(6) H. S. Isbell and H. L. Frush, *J. Res. Natl. Bur. Std.*, **43A**, 161 (1949)

(7) E. Pacsu, *Advan. Carbohydrate Chem.*, **1**, 80 (1945).

(8) K. Freudenberg and O. Ivers, *Ber.*, **55**, 929 (1922).

(9) K. Freudenberg, H. v. Hochstetter, and H. Engels, *ibid.*, **58**, 666 (1925).

one experiment the acetic anhydride was removed by distillation under reduced pressure and the resultant product contained no maltose heptaacetate. There was isolated, in small amount, a product of $[\alpha]^{20}D$ +99° (chloroform) which could not be purified in the amounts available to us. It may have been VI but, if so, it eluded purification and characterization as it did for Freudenberg and associates. The infrared absorption spectrum of the product showed no hydroxyl absorption.

The nature of the small amount of maltose hexaacetate, found in the acidic equilibrium mixture from β-maltose heptaacetate, intrigued us. Helferich and Zirner[10] obtained 1,3,6,2′,3′,4′,6′-hepta-*O*-acetylcellobiose as the sole isolated product (28% yield) on treatment of β-cellobiose octaacetate with hydrogen bromide in acetic acid followed by reaction with warm, aqueous sodium acetate. This procedure was repeated with β-maltose octaacetate and a low but significant yield of our hexaacetate was obtained. The principal product was again β-maltose heptaacetate (76%) along with some of its anomer. In this manner we obtained enough of the new maltose hexaacetate for further characterization. Periodate oxidation, in aqueous acetone solution, showed that the hexaacetate was slowly oxidizable and thus that a glycol group was present in the compound. The reaction was followed by thin layer chromatography with appropriate blanks being run. This finding would indicate that the hexaacetate probably is 3,6,2′,3′,4′,6′-hexa-*O*-acetylmaltose. The β-D anomeric configuration was assigned on the basis of its optical rotation (+83°) which is closer to that of the β-D-heptaacetate (+70°) than to that of the α-D-heptaacetate (+128°).

The formation of such a 3,6,2′,3′,4′,6′-hexa-*O*-acetyl-β-maltose by the action of acid chloroform upon β-maltose heptaacetate and also by the successive action on β-maltose octaacetate of acetic acid–hydrogen bromide and warm aqueous sodium acetate is in need of explanation. Its formation may be analogous to the production, noted by Perlin,[11] of 3,4,6-tri-*O*-acetyl-D-glucose on methanolysis of D-glucose 1,2-(ethyl orthoacetate) 3,4,-6-triacetate. The postulated ortho ester intermediate VI should be capable of opening in two ways, to give III or VIII. The acetate group on C-1 of III, being on the reducing carbon, would be inherently unstable toward acid and would be hydrolyzed to the hexaacetate II which could anomerize to I, the form actually crystallized. In the cellobiose structure, on the other hand, the balance of reaction rates leads to the isolation of the analogous 2-open III, not isolated in the maltose series, where formation of II (I) is favored.

The mutarotation of IV in chloroform must be complex and it could be predicted that the reactions would involve VII as well as IV, VIII, III, II, and I with both VI and VII being capable of existing in two diastereoisomeric forms in bond arrangements about each of the starred carbon atoms (see Scheme I).

Experimental

β-Maltose monohydrate (100 g.) was acetylated by heating with anhydrous sodium acetate (50 g.) and acetic anhydride (500 g.) according to the procedure described by Wolfrom and Thompson.[12] The acetylation mixture was poured into 2 l. of ice and water with stirring and the stirring was continued for 4 hr. The water was removed by decantation and fresh water was added to the solid which was nucleated with β-maltose octaacetate. After 2 days at 0°, β-maltose octaacetate had crystallized: yield 160 g. (85%), m.p. 159–161°, $[\alpha]^{20}D$ +63° (*c* 1.2, chloroform).

The mother liquors were extracted with chloroform and the extracts were processed in the usual manner; yield 6 g. of a clear sirup. Thin layer chromatography (solvent A, Table I) showed the presence of β-maltose octaacetate in the largest amount (R_f 0.60), β-maltose heptaacetate (R_f 0.30), and two faint spots with R_f 0.40 and 0.10, respectively. The sirup (3 g. in 20 ml. of benzene) was chromatographed on a column (40 × 340 mm.) of alumina (Wöelm, neutral, activity grade I). Elution was first effected with 2 l. of a mixture of ethyl acetate–benzene (3:7 v./v.); β-maltose octaacetate (1.55 g.) was crystallized from the eluate. Elution with 1.5 l. of ethyl acetate yielded β-maltose heptaacetate after evaporation and recrystallization from absolute ethanol: yield 0.485 g. (0.3%), m.p. 182–183°, $[\alpha]^{20}D$ +70.5° (*c* 0.92, chloroform), further confirmed by mixture melting point and X-ray powder diffraction data. Hudson and Sayre[4] reported m.p. 181° and $[\alpha]^{20}D$ +67.8° while Helferich and Steinpreis[13] gave m.p. 183–184° and $[\alpha]D$ +70° (chloroform).

Further elution with ethyl acetate–methanol (95:5 v./v.) yielded crystalline α-maltose heptaacetate: yield 20 mg., m.p.

SCHEME I

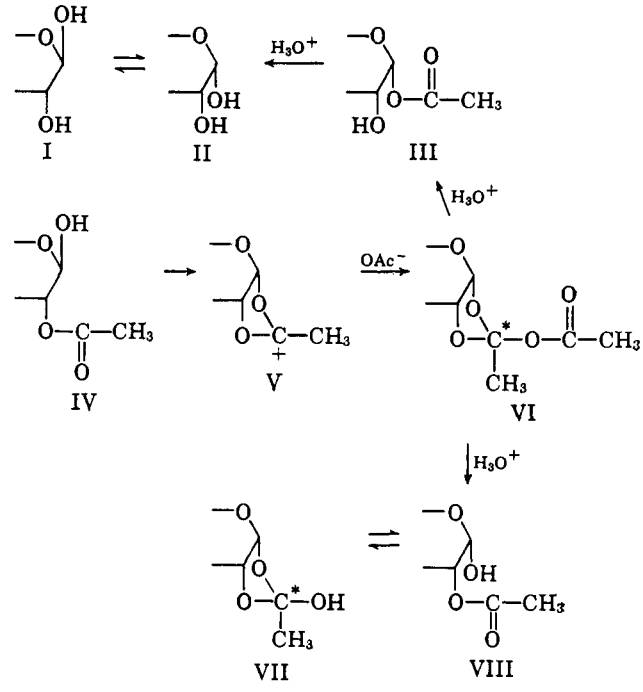

TABLE I

CHROMATOGRAPHIC PROPERTIES OF MALTOSE ACETATES[a]

Compd.	R_f Solvent A[b]	R_f Solvent B[c]
Octa-*O*-acetyl-β-maltose	0.61	0.81
2,3,6,2′,3′,4′,6′-Hepta-*O*-acetyl-β-maltose	0.30	0.55
2,3,6,2′,3′,4′,6′-Hepta-*O*-acetyl-α-maltose	0.08	0.22
3,6,2′,3′,4′,6′-Hexa-*O*-acetyl-β-maltose	0.10	0.27
Unidentified	0.38	0.71

[a] Thin layer (0.25 mm.) chromatography on silica gel G (E. Merck, Darmstadt, Germany); indications by spraying with concentrated sulfuric acid or alkaline silver nitrate followed by heating for 15 min. at 160° for the former and at 110° for the latter spray. [b] Ethyl acetate–benzene, 1:1 (v./v.). [c] Ethyl acetate–benzene, 7:3 (v./v.).

(10) B. Helferich and J. Zirner, *Ber.*, **96**, 385 (1963).
(11) A. S. Perlin, *Can. J. Chem.*, **41**, 555 (1963).
(12) M. L. Wolfrom and A. Thompson, *Methods Carbohydrate Chem.*, **1**, 334 (1962).
(13) B. Helferich and R. Steinpreis, *Ber.*, **91**, 1794 (1958).

149–151° (after recrystallization from acetone), $[\alpha]^{20}D$ +127° (*c* 0.5, chloroform).

Anal. Calcd. for $C_{26}H_{36}O_{18}$: C, 49.05; H, 5.70. Found: C, 49.63; H, 5.77.

Another acetylation was performed in the same manner but the excess of acetic anhydride was eliminated from the mixture by vacuum distillation with the aid of benzene codistillation. The dark sirup obtained was extracted with chloroform and the extracts were evaporated under reduced pressure. β-Maltose octaacetate (85 g.) crystallized from ether. The ether mother liquors were concentrated to a sirup in which thin layer chromatography (solvent A, Table I) showed the presence of β-maltose octaacetate in largest amount, R_f 0.61, and another compound of R_f 0.38; no β-maltose heptaacetate was detected. Separation of the compound of R_f 0.38 was attempted by flowing chromatography on a silica gel column and by extrusive chromatography on Magnesol–Celite,[14] but the pure compound could not be obtained. An enriched fraction from the silica gel column was further purified by preparative thin layer chromatography to yield an amorphous product that failed to crystallize: yield 15 mg., $[\alpha]^{20}D$ +99° (*c* 0.56, chloroform), no hydroxyl absorption in the infrared (potassium bromide pellet). The substance was partially decomposed when purification from hot ethanol was attempted. By thin layer chromatography (solvent B, Table I), a substance, R_f 0.51, was detected in the mixture together with the starting material.

Acid-Catalyzed Mutarotation of β-Maltose Heptaacetate in Chloroform.—β-Maltose heptaacetate (2.990 g.) was dissolved in chloroform (200 ml.) containing 2 drops of ether nearly saturated with hydrogen chloride at 0°. The following specific rotations were observed at the indicated times (min.): 8, +98.5°; 11, +101°; 14, +102°; 19, +104°; 37, +106°; 289, +108°; and 386, +108.5°. Hudson and Sayre[4] reported mutarotation in chloroform to an equilibrium value of +110° after 5 weeks. Thin layer chromatography (solvent B, Table I) of the equilibrated mixture showed the presence of β-maltose heptaacetate, R_f 0.55, still present in the largest amount, and two other spots with R_f values of 0.27 and 0.22. If a higher concentration of acid was used, deacetylation was observed since thin layer chromatography detected products of lower R_f values. The chloroform solution was evaporated to dryness under reduced pressure at 40°. The residue was chromatographed on a Magnesol–Celite[14] (5:1 w./w.) column (240 × 52 mm.). The mixture (2 g.) was dissolved in 20 ml. of a chloroform–benzene (1:1, v./v.) mixture and added at the top of the column previously wet with benzene. The chromatogram was developed with 3 l. of benzene–*t*-butyl alcohol (94:6, v./v.). β-Maltose heptaacetate was obtained from the effluent, yield 1.20 g. An alkaline permanganate streak[14] on the extruded column indicated two zones located at 0–70 mm. and 90–130 mm. from the column top. The column was sectioned and each section was eluted with acetone. Crystalline material was obtained from the eluate of the top zone, yield 150 mg. Repeated recrystallization from a small amount of acetone provided chromatographically pure α-maltose heptaacetate: m.p. and m.m.p. 149–151°; $[\alpha]^{20}D$ +127° (*c* 0.55, chloroform); X-ray powder diffraction data[15] 12.81 (s), 11.19 (s, 3), 9.56 (m), 7.96 (m), 6.83 (w), 6.21 (w), 5.70 (s, 1), 5.25 (s), 4.94 (m), 4.65 (m), and 4.28 (s, 2).

Anal. Calcd. for $C_{26}H_{36}O_{18}$: CH_3CO, 47.4. Found: CH_3CO, 47.2.

Material from the eluate of the second zone (0.120 g.) crystallized from ether but was shown by thin layer chromatography (solvent B, Table I) to be a mixture of about equal amounts of the α-heptaacetate, R_f 0.22, and the other compound, R_f 0.27. This mixture could not be separated by fractional crystallization. The mixture, dissolved in 5 ml. of chloroform–benzene (1:1), was rechromatographed on a Magnesol–Celite (5:1) column (135 × 32 mm.) previously wet with benzene. The chromatogram was developed with 1 l. of benzene–*t*-butyl alcohol (94:6, v./v.). The column was extruded and an alkaline permanganate streak[14] located two zones, the first, 50 mm. in length, located 20 mm. from the top of the column and the second of 30-mm. length located 80 mm. from the top. These zones were sectioned and eluted with acetone. From the eluate of the top zone 40 mg. of α-maltose heptaacetate was obtained. From the second zone, after evaporation of the acetone eluate and crystallization from absolute ethanol, 30 mg. of β-maltose hexaacetate was obtained as white needles: m.p. 163–165°; $[\alpha]^{20}D$ +82.7 (12 min.) → +92.1° (24 hr.) (*c* 0.95, chloroform); X-ray powder diffraction data[15] 13.29 (s, 1), 11.26 (vw), 9.36 (vw), 7.80 (m), 7.14 (vw), 6.61 (w), 6.19 (vw), 5.63 (s, 2), 5.11 (m, 3), 4.89 (m), 4.62 (w), 4.33 (m), 4.19 (m), and 4.02 (w).

Anal. Calcd. for $C_{24}H_{34}O_{17}$: C, 48.48; H, 5.76; CH_3CO, 43.5. Found: C, 48.27; H, 5.74; CH_3CO, 44.3.

Acetylation of α-Maltose Heptaacetate.—α-Maltose heptaacetate (0.030 g.) was dissolved in 1 ml. of acetic anhydride–pyridine (1:1, v./v.), previously cooled to 0°. The solution was maintained overnight at room temperature. Thin layer chromatography showed complete acetylation. The solution was then evaporated in a vacuum desiccator (over potassium hydroxide) with the aid of methanol coevaporation. The resultant crystalline product showed $[\alpha]^{20}D$ +84° (*c* 0.5, chloroform). Recrystallization from absolute ethanol afforded β-maltose octaacetate with m.p. and m.m.p. 159–160°.

Acetylation of β-Maltose Hexaacetate.—β-Maltose hexaacetate (0.025 g.) was acetylated as described above. The crystalline residue obtained on evaporation from absolute ethanol showed $[\alpha]^{20}D$ +61° (*c* 1, chloroform). Recrystallization from absolute ethanol yielded β-maltose octaacetate with m.p. and m.m.p. 159–160°.

Reaction of β-Maltose Hexaacetate with Periodate.—β-Maltose hexaacetate (2 mg., 0.003 mmole) was dissolved in 0.1 ml. of acetone and to the solution 0.2 ml. of sodium metaperiodate aqueous solution (0.2 *M*) was added. The mixture was kept in the dark for 4 days. Thin layer chromatography (solvent B, Table I) showed complete oxidation after this time. A spot of R_f 0.39 was present. A blank of β-maltose hexaacetate in acetone–water alone, kept during the same time, showed by thin layer chromatography a small spot, R_f 0.12, besides the β-maltose hexaacetate spot. This spot, R_f 0.12, did not appear in the thin layer chromatogram in the course of the periodate oxidation of the β-hexaacetate.

When β-maltose heptaacetate was incubated with sodium metaperiodate solution under the same conditions as with the β-hexaacetate, no reaction was detected by thin layer chromatography.

Formation of β-Maltose Hexaacetate from β-Maltose Octaacetate.—The general procedure of Helferich and Zirner[10] for the preparation of 1,3,6,2′,3′,4′,6′-hepta-*O*-acetylcellobiose was adapted to the maltose structure. β-Maltose octaacetate (10 g.) was dissolved in a mixture of 40 ml. of acetic acid and 50 ml. of acetic acid nearly saturated with hydrogen bromide at 0°. The solution was stirred magnetically at room temperature for 20 min. and was then kept at room temperature for 2 hr. At the end of this time a solution of 40 g. of sodium acetate in 40 ml. of water was added followed by an additional 40 g. of sodium acetate (stirring). The solution was kept at 45–50° for 1 hr. and then overnight at room temperature. At the end of this period a crystalline precipitate had formed. The entire mixture was poured into 500 ml. of iced water and filtered. Recrystallization from absolute ethanol afforded β-maltose heptaacetate, yield 6 g., m.p. and m.m.p. 180–181°. The aqueous mother liquors were extracted with chloroform and the combined extracts were washed successively with water, saturated aqueous sodium bicarbonate solution, and again with water. The residual sirup obtained on solvent removal from the dried (sodium sulfate) extract was dissolved in ether and β-maltose heptaacetate crystallized on standing overnight at 0°, yield 360 mg. The ethereal mother liquors were evaporated to dryness and the residue (3.100 g.) was shown by thin layer chromatography (Table I, 3:2 developer ratio) to contain traces of β-maltose octaacetate, R_f 0.62; β-maltose heptaacetate, R_f 0.43 (main compound); β-maltose hexaacetate, R_f 0.19; α-maltose heptaacetate, R_f 0.13; and two other faint spots of R_f 0.55 and 0.22. This material was dissolved in 30 ml. of benzene and added to the top of a 240 × 52 mm. column of Magnesol–Celite (5:1) previously wet with benzene. The chromatogram was developed with 3 l. of *t*-butyl alcohol–benzene (6:94, v./v.). From the effluent β-maltose heptaacetate was crystallized, yield 800 mg. (76% total). The mother liquors were shown by thin layer chromatography (Table I, solvent B) to contain the compound of R_f 0.55 as the main product. This could not be crystal-

(14) M. L. Wolfrom, R. de Lederkremer, and L. E. Anderson, *Anal. Chem.*, **35**, 357 (1963).

(15) Interplanar spacing, Å., Cu Kα radiation; relative intensity by visual measurement: s, strong; m, medium; w, weak; three strongest lines are numbered, 1 = strongest.

lized even by rechromatography. An alkaline permanganate streak on the extruded column indicated two zones at 40 and 50 mm. from the column top. The eluate from the top zone provided α-maltose heptaacetate after solvent removal and recrystallization from acetone: yield 50 mg., m.p. 149–151° unchanged on admixture with the product obtained from β-maltose heptaacetate, $[\alpha]^{20}D$ +128° (*c* 0.77, chloroform).

β-Maltose hexaacetate was obtained from the eluate of the second zone: yield 40 mg., m.p. 163–165° (after recrystallization from absolute ethanol). This product was identical with the above-mentioned β-maltose hexaacetate by mixture melting point and X-ray powder diffraction pattern.

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Mass Spectrometry in Carbohydrate Chemistry. Dithioacetals of Common Monosaccharides

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The mass spectra of the dialkyl and ethylene dithioacetals of D-glucose, D-arabinose, 2-deoxy-D-glucose, 6-deoxy-L-galactose, 6-deoxy-L-mannose, 2-*O*-methyl-D-glucose, and 3-*O*-methyl-D-glucose are interpreted in terms of structural differences among the compounds. The dialkyl dithioacetals exhibit molecular-ion peaks ranging from 5–20% of the base peak; the ethylene dithioacetals exhibit no discernible molecular-ion peak or one of very low intensity relative to the base peak. It is possible to relate peaks in the mass spectra to the position of deoxy and methoxyl groups in these molecules.

A frequently employed procedure for the isolation of carbohydrate residues which are present in complex molecules is hydrolysis of glycosidic bonds with a thiol and a strong acid. This mercaptolysis technique has been useful in determining the structure of streptomycin,[1] lincomycin,[2] and other compounds containing sugar moieties.

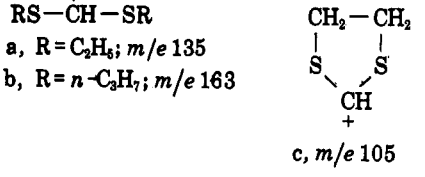
Recently mass spectral studies of monosaccharide diethyl dithioacetal[3] and ethylene dithioacetal[4] peracetates have been reported. The mass spectra of these peracetyl derivatives of mercaptolysis products can be readily interpreted in terms of structural differences such as molecular weight and substitution. Only a fraction of a milligram of material is required for obtaining this wealth of information. These considerations lead one to anticipate that mass spectrometry combined with mercaptolysis may soon be a powerful tool in the structure elucidation of the carbohydrate portion of complex molecules.

With the advent of commercially available mass spectrometers equipped with inlet systems which allow insertion of samples of relatively low vapor pressure directly into the ion source, the dithioacetal derivatives of carbohydrates can be studied without having to acetylate to increase volatility. The mass spectra of a number of common dithioacetal monosaccharide derivatives have been obtained using this direct-insertion technique and are discussed here. Their mass spectra are much less complex than those of the acetylated analogs, yet they are very sensitive to structural differences.

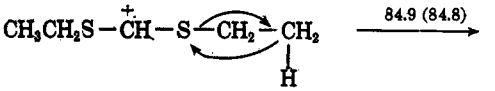
Results

Molecular-Ion Peaks.—The mass spectra of D-arabinose diethyl dithioacetal (Figure 1) and di-*n*-propyl dithioacetal (Figure 2), of D-glucose diethyl dithioacetal (Figure 3) and di-*n*-propyl dithioacetal (spectrum not shown), of 2-deoxy-D-glucose diethyl dithioacetal (Figure 4), of 6-deoxy-L-mannose diethyl dithioacetal (Figure 5), of 3-*O*-methyl-D-glucose diethyl dithioacetal (Figure 6) and di-*n*-propyl dithioacetal (Figure 7), and of 2-*O*-methyl-D-glucose diethyl dithioacetal (Figure 8) exhibit molecular-ion peaks ranging from 5–20% of the base peak in the spectra; from their mass spectra, their molecular weight can be directly determined. In contrast, the mass spectra of D-arabinose ethylene dithioacetal (Figure 9), D-glucose ethylene dithioacetal (Figure 10), 2-deoxy-D-glucose ethylene dithioacetal (Figure 11), and 6-deoxy-L-galactose ethylene dithioacetal (Figure 12) either exhibit no discernible molecular-ion peak or one of intensity 0.03–1.5% of the base peak.

The Dithioacetal Fragments.—In all of the mass spectra studied, except that of 2-deoxy-D-glucose diethyl dithioacetal (Figure 4), the base peak results from C-1–C-2 cleavage with charge retention on the dithioacetal carbon atom, C-1, where it is stabilized by two adjacent sulfur atoms. This fragment is characteristic of C-1 and its substituents.



Metastable-ion peaks and peak shifts from changes in the R groups show that the dialkyl dithioacetal



$$CH_3CH_2S-\overset{+}{C}H-S-H + CH_2=CH_2 \quad (1)$$

m/e 107

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