to 210°, but did not melt below 300°: $[\alpha]^{25}D$ −5.0° (*c* 0.747, water).

Anal. Calcd. for $C_{13}H_{17}NO_7$: C, 52.17; H, 5.73; N, 4.68. Found: C, 52.10; H, 6.02; N, 4.66.

(*o*-**Methoxycarbonylphenyl**) **2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside** (**Vd**).—To a mixture of 62.3 g. (450 mmoles) of anhydrous potassium carbonate, 34.7 ml. (41 g., 270 mmoles) of methyl salicylate, and 1380 ml. of acetone was added 57 g. (156 mmoles) of 2-acetamido-3,4,6-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride.[4,5] The mixture was stirred at room temperature for 21 hr., and the inorganic salts were removed by filtration. The filtrate was subjected to vacuum distillation to remove the acetone, and the residual oil was triturated with ether. The yield of crystalline Vd was 52 g. (69.5%), m.p. 202–203°.

An analytical sample was prepared by recrystallization from ethanol: m.p. 202–204°.

Anal. Calcd. for $C_{22}H_{27}NO_{11}$: C, 54.87; H, 5.65; N, 2.91. Found: C, 54.75; H, 5.76; N, 2.91.

(*o*-**Methoxycarbonylphenyl**) **2-Acetamido-2-deoxy-β-D-glucopyranoside** (**Ve**).—A solution of 52 g. (108 mmoles) of Vd in 780 ml. of methanol was warmed to 35°. A solution from 2.0 g. (87 mg.-atoms) of sodium metal and 85 ml. of methanol was added, and the mixture was stirred at 35–40° for 5 min. The product began to crystallize promptly. After cooling to 10° in an ice bath, the product was filtered, washed with cold methanol and with ether, and dried *in vacuo* to give 30.1 g. (78%), m.p. 205–207° dec.

Anal. Calcd. for $C_{16}H_{21}NO_8$: C, 54.08; H, 5.96; N, 3.94. Found: C, 53.93; H, 5.79; N, 3.68.

(*o*-**Carboxyphenyl**) **2-Acetamido-2-deoxy-β-D-glucopyranoside** (**Vf**).—To a suspension of 30.1 g. (84 mmoles) of Ve in 1 l. of water was added 87 ml. of 1 *N* sodium hydroxide solution. After stirring at room temperature for 3 hr., *ca.* 5 g. of Dry Ice was added to the clear solution. After the Dry Ice had dissolved, the solution was freeze dried to give 31 g. (quantitative yield) of an amorphous solid. The sodium salt may be crystallized from 98–99% ethanol, or from methanol–2-propanol mixtures to give a product which is still contaminated with sodium bicarbonate (4%) and with water (5–10%), on the basis of analytical results.

The sodium salt was converted to the acid by acidifying a cold concentrated aqueous solution of the salt, filtering quickly, and washing with a small amount of cold water. Recrystallization from methanol–acetone gave an analytical sample, m.p. 151–152° dec., $[\alpha]^{25}D$ −54° (*c* 0.84, water).

Anal. Calcd. for $C_{15}H_9NO_8$: C, 52.78; H, 5.61; N, 4.10. Found: C, 52.28; H, 5.78; N, 4.09.

(*o*-**Carboxyphenyl**) **2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside** (**Vg**).—A mixture of 3.5 g. of the sodium salt of (*o*-carboxyphenyl)-2-acetamido-2-deoxy-β-D-glucopyranoside (Vf), 15 ml. of acetic anhydride, and 15 ml. of pyridine was heated on the steam bath for 40 min. The cooled reaction mixture was poured into 300 ml. of ice–water containing 15 ml. of concentrated hydrochloric acid. The mixture was extracted five times with 40-ml. portions of methylene chloride. After drying with magnesium sulfate, the solvent was removed *in vacuo*, and the residue was crystallized from glacial acetic acid, affording needles, 3.7 g., m.p. 139–140°.

Anal. Calcd. for $C_{21}H_{25}NO_{11}\cdot C_2H_4O_2$: C, 52.37; H, 5.54; N, 2.72. Found: C, 52.88; H, 5.73; N, 2.82.

An unsolvated sample was prepared by recrystallization from ethyl acetate–ether: m.p. 139–140°.

Anal. Calcd. for $C_{21}H_{25}NO_{11}$: C, 53.96; H, 5.39. Found: C, 53.83; H, 5.79.

A sample of Vc, acetylated by the foregoing procedure, furnished Vg which was identical (melting point, mixture melting point, infrared absorption spectrum) with the specimen reported above.

Acknowledgment.—The authors are indebted to Mr. R. Boos and his colleagues for the elemental analyses reported herein. R. H. is pleased to acknowledge stimulating discussions with Dr. D. Taub of these laboratories and with Dr. D. Horton of The Ohio State University.

Photochemistry of Carbohydrate Derivatives. Photolysis of D-Galactose Diethyl Dithioacetal[1]

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Irradiation of a methanolic solution of D-galactose diethyl dithioacetal (I) with ultraviolet light gives 1-*S*-ethyl-1-thio-D-galactitol (II), isolable in 60% yield. Further irradiation converts this substance into L-fucitol (III), together with two minor products. One of the later is shown to be 1-deoxy-1-ethylsulfinyl-D-galactitol (IV), and the other, formed in lesser proportion, was identified as galactitol (V). Irradiation of IV gives V. Nmr data for the products are presented and discussed. Ultraviolet absorption data for a range of aldose dithioacetal derivatives are tabulated.

Simple dithioacetals exhibit ultraviolet absorption in the 230–250-mμ region, with absorptivities generally in the range[2-4] ε 300–850. Similar absorption is observed with dithioacetals of sugars (Table I), whereas the unsubstituted sugars possess no chromophores in this spectral region. It was of interest to study the photolytic cleavage of carbon–sulfur bonds in carbohydrate dithioacetals, as part of a general study of photochemical transformations in carbohydrate systems. This paper describes the transformations observed when a methanolic solution of D-galactose diethyl dithioacetal (I) was irradiated with ultraviolet light.

A high-pressure mercury lamp mounted in a quartz immersion well was used to irradiate a methanolic solution of the dithioacetal I, and no special precautions were taken to exclude air. The progress of the reaction was monitored by cellulose thin layer chromatography on aliquot samples. It was observed that the starting dithioacetal (I), R_f 0.76, was transformed into a product having R_f 0.63, together with small proportions of slower moving components, R_f 0.35 and 0.28. The major product, R_f 0.63, could be isolated crystalline in 55–60% yield, and it was shown to be 1-*S*-ethyl-1-thio-D-galactitol

(1) (a) Supported in part by the Agricultural Research Service, U. S. Department of Agriculture, Grant No. 12-14-100-7208 (71) (The Ohio State University Research Foundation Project 1827), administered by the Northern Utilization Research and Development Division, Peoria, Ill. Funds for purchase of the nmr spectrometer were provided by the National Science Foundation. (b) Preliminary report: Abstracts, 151st National Meeting of the American Chemical Society, Phoenix, Ariz., Jan 1966, p 4c.

(2) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).

(3) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., New York, N. Y., 1962, pp 51–55.

(4) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 437 (1964).

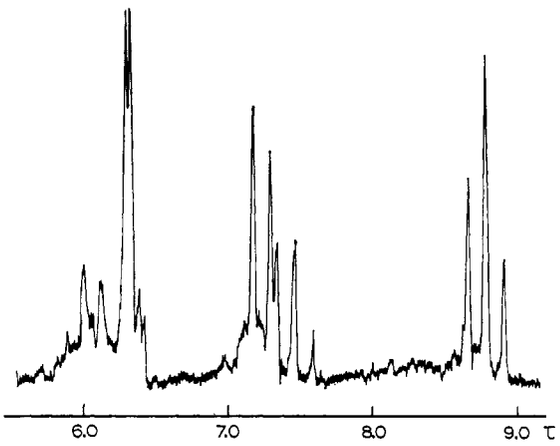


Figure 1.—The nmr spectrum of 1-*S*-ethyl-1-thio-D-galactitol (II) at 60 Mcps in deuterium oxide.

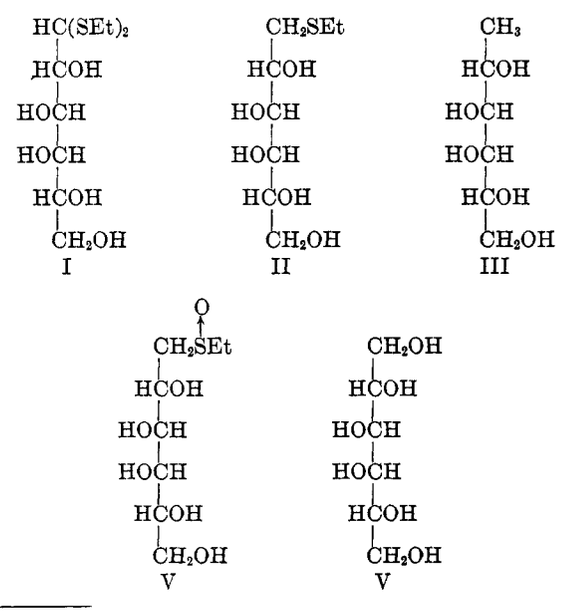
TABLE I
ULTRAVIOLET ABSORPTION DATA FOR ALDOSE DITHIOACETALS

Dithioacetal	λ_{max}^{EtOH}, mμ (ε)
2-Acetamido-2-deoxy-D-glucose, diethyl	213 (1900), 242 sh[a] (680)
2-Amino-2-deoxy-D-glucose, diethyl	211 (1910), 242 sh[a] (680)
D-Arabinose, diethyl	213 (1350), 241 (680)
D-Arabinose, diphenyl[b]	216 (11,100), 260 (6500)
D-Galactose, diethyl	212 (1310), 243 (590)
D-Glucose, diethyl	213 (1630), 242 (670)
D-Lyxose, diethyl	212 (1380), 232 (600)
D-Mannose, diethyl	212 (1100), 232 (870)
L-Rhamnose, diethyl	212 (1870), 233 (700)
D-Ribose, diphenyl[b]	217 (11,840), 257 (8900)

[a] Shoulder. [b] See ref 14.

(II) (Chart I) by microanalysis and by direct comparison with an authentic sample of II prepared by a different method.[5] Acetylation of II gave a crystalline pentaacetate identical with authentic 2,3,4,5,6-penta-*O*-acetyl-1-*S*-ethyl-1-thio-D-galactitol.[5]

CHART I



(5) J. K. N. Jones and D. L. Mitchell, *Can. J. Chem.*, **36**, 206 (1958).

The minor component, R_f 0.35, from the photolysis reaction was identified as 1-deoxy-D-galactitol (L-fucitol) (III). The component having R_f 0.28 was isolated crystalline, in low yield, and was shown to be 1-deoxy-1-ethylsulfinyl-D-galactitol (IV) (see below). Irradiation of the dithioacetal I for an extended period gave a mixture containing larger proportions of L-fucitol (III) and the sulfoxide IV, together with a component, R_f 0.14, identified as galactitol (V). The initial conversion of I into II proceeded much more rapidly than the subsequent conversion into III, IV, and V. Longer times of irradiation were required when the scale of the experiment was increased.

Photolytic decomposition of pure 1-*S*-ethyl-1-thio-D-galactitol (II) in methanolic solution proceeded slowly compared with the conversion of I into II under the same conditions. The photolysis product from II contained L-fucitol (III), R_f 0.35, isolated crystalline in 44% yield, together with the sulfoxide IV, R_f 0.28, isolated crystalline in 3% yield, and galactitol (V), R_f 0.14, isolated crystalline in 2% yield. Photolysis of the pure sulfoxide IV in methanol solution gave galactitol, isolated in 58% yield.

Formulation of the product, R_f 0.28, as 1-deoxy-1-ethylsulfinyl-D-galactitol (IV) was based on the evidence of microanalytical data for IV and its pentaacetate, together with infrared and nmr spectroscopic data. Confirmatory proof was provided by the identity of the product with a sample of 1-deoxy-1-ethylsulfinyl-D-galactitol which had been prepared[6] by oxidation of 1-*S*-ethyl-1-thio-D-galactitol (II) with bromine water or hydrogen peroxide.

The elemental analyses of IV and its pentaacetate were in accord with the given structures and exclude a sulfone-type structure. The infrared spectrum of IV revealed absorption at 9.68 μ, characteristic of the hydrogen-bonded sulfoxide group,[7] and no sulfone absorption in the 7.3–7.6- and 8.6–9.0-μ spectral regions. The pentaacetate of IV showed sulfoxide absorption at 9.45 μ. Comparison of the nmr spectra of IV and 1-*S*-ethyl-1-thio-D-galactitol (II), and those of the respective pentaacetates, provided further structural confirmation. The nmr spectrum of II in deuterium oxide (Figure 1) shows the anticipated three-proton triplet and two-proton quartet for the ethyl group, the methylene portion of which gives a signal at τ 7.41. A two-proton doublet at τ 7.22 was assigned to the C-1 methylene group, and the signals at lower field (τ 5.81–6.40) were assigned to the protons on the remainder of the chain. The spectrum of IV was very similar in general appearance to that of II, indicative of the general structural similarity of the two compounds, but the signals for the methylene of the ethyl group, and the C-1 methylene group signals, appear 0.2–0.3 ppm downfield in IV, relative to their positions in II. This small shift accords with the weakly electron-withdrawing character of the sulfoxide group;[8] a considerably larger downfield shift might be expected for the sulfone analog of II.

(6) D. Horton and J. S. Jewell, to be published.

(7) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949); K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 54.

(8) H. H. Szmant in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press Ltd., Oxford, 1961, p 165.

The nmr spectrum of the pentaacetate of II, in deuteriochloroform (Figure 2 and Experimental Section), shows the three-proton triplet anticipated for the methyl moiety of the ethyl group, together with an apparent doublet at τ 7.45, assigned to the C-1 methylene group, superimposed upon the signal for the methylene moiety of the ethyl group. The group of signals at τ 4.55–5.00 may be assigned to the methine protons, and the eight-peak multiplet at τ 5.5–6.35 may be assigned to the methylene protons of C-6. A very similar spectrum was observed for the pentaacetate of the sulfoxide IV, but the signals of the methylene groups attached to the sulfoxide function are observed about 0.2 ppm to lower field.

The signals assigned to the C-6 methylene protons in the pentaacetates of II and IV fall in the spectral region anticipated[9,10] for a CH_2OAc group at the end of an acetylated sugar chain. In each case the methylene protons are nonequivalent, and their signals are observed as the AB portion of ABX system.[11] The signals for the C-1 methylene protons in II, IV, and their pentaacetates are observed at high field, presumably because sulfur exerts a deshielding effect less than that of oxygen; similar effects have been observed in related $-CH_2S-$ systems.[12] It is noteworthy that the C-1 methylene signal appears in each case as an apparent doublet, indicating near equivalence of the methylene protons in the $-CH_2SR$ group.

The sulfoxide IV and its pentaacetate can both be formulated in two stereoisomeric forms, differing in configuration at the sulfur atom. The substances isolated in this work behaved as single compounds; the stereochemical configuration at the sulfur atom was not determined.

The nmr spectrum of L-fucitol (III) in deuterium oxide showed a three-proton doublet, τ 8.77, for the C-1 methyl group. The appearance of this signal could be used to monitor the progress of the photolysis reactions.

The transformations undergone by D-galactose diethyl dithioacetal (I) on photolysis resemble the behavior of I upon treatment with aged Raney nickel, when desulfurization to L-fucitol (III) can be interrupted at the stage when only one ethylthio group has been removed.[5] A potentially useful feature of the photolytic reaction is the fact that transformation of I into II is much more rapid than the subsequent conversion of II into other products. It can be seen (Figure 3) that the dithioacetal I has a much greater absorptivity in the ultraviolet absorption band near 240 mμ than the 1-thioalditol derivative II.

The aldose diethyl dithioacetals exhibit an ultraviolet absorption maximum near 213 mμ, and a second maximum in the 232–243-mμ region (Table I), thus resembling the dialkyl dithioacetals of simple aldehydes.[2,4] The shorter wavelength absorption corresponds to photoexcitation of the carbon–sulfur bond,[13]

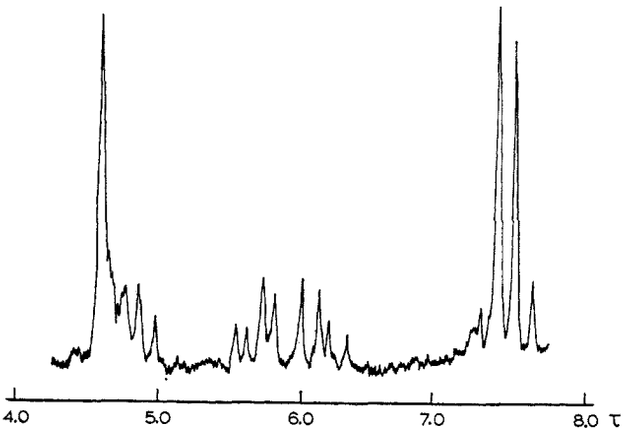


Figure 2.—The low-field portion of the nmr spectrum of 2,3,4,5,6-penta-*O*-acetyl-1-*S*-ethyl-1-thio-D-galactitol at 60 Mcps in deuteriochloroform.

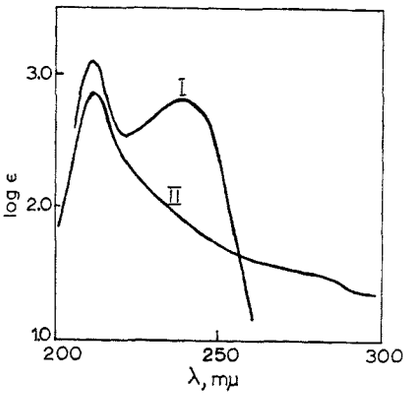
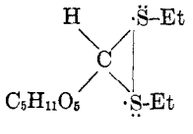


Figure 3.—Ultraviolet absorption curves for D-galactose diethyl dithioacetal (I) and 1-*S*-ethyl-1-thio-D-galactitol (II).

while the longer wavelength absorption is indicative of a photoexcited state involving direct geminal interaction of the sulfur atoms.[2–4,13] The latter state is probably stabilized by extra delocalization of the electrons, made possible by expansion of the sulfur valence shell beyond eight electrons through use of the 3d orbitals, in a structure[3,4] of the type



The two aldose diphenyl dithioacetals[14] noted in Table I exhibit strong absorption near 260 mμ, similar to that observed for thioanisole.[13]

Photolytic conversion of I into II, and II into III, presumably involves radicals of the type $R\dot{C}HSEt$ and $R\dot{C}H_2$, formed by homolytic cleavage of carbon–sulfur bonds. The energy required for carbon–sulfur bond cleavage is known[15] to be normally less than that required for carbon–carbon on carbon–oxygen bond cleavage. The $R\dot{C}HSEt$ radical is very probably stabilized by electron delocalization involving the 3d orbitals of sulfur, a factor which would facilitate the photolytic conversion of the dithioacetal I into the

(9) M. L. Wolfrom, G. Fraenkel, D. R. Lineback, and F. Komitsky, Jr., *J. Org. Chem.*, **29**, 457 (1964).

(10) D. Horton and Martha J. Miller, *ibid.*, **30**, 2457 (1965).

(11) For details of the ABX notation, see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959; J. D. Roberts, "An Introduction to Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1962.

(12) D. Horton and W. N. Turner, *Carbohydrate Res.*, in press.

(13) R. C. Passerini, ref 8, pp 57–74; H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 474–481.

(14) D. Horton and J. D. Wander, unpublished data.

(15) J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023 (1952); L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 85.

sulfide II. Subsequent conversion of II into III, through a nonstabilized radical $R\dot{C}H_2$, would predictably be more difficult to effect.

Experimental Section

General Methods.—Solutions were concentrated below 50°. Melting points were determined with a Hershberg-type apparatus[16] and are uncorrected. Specific rotations were determined in a 2-dm polarimeter tube. Infrared spectra were measured with a Perkin-Elmer Infracord Model 137 infrared spectrometer. Ultraviolet spectra were measured with a Bausch and Lomb Spectronic 505 spectrometer. Nmr spectra were measured at 60 Mcps with a Varian A-60 nmr spectrometer; chemical shifts are given on the τ scale with tetramethylsilane (τ 10.00) or sodium 4,4-dimethyl-4-silapentane-1-sulfonate (τ 10.00) as internal standards for deuteriochloroform and deuterium oxide solutions, respectively. Microanalyses were determined by W. N. Rond. X-Ray powder diffraction data are interplanar spacings, in angstroms, for CuKα radiation. Relative intensities were estimated visually: s, strong; m, moderate; w, weak; v, very. The strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities. Thin layer chromatography was performed with microcrystalline cellulose[17] as the support,[18] with 4.2:2.1:1.9 1-butanol–ethanol–water as the developer; detection was by the silver nitrate–sodium hydroxide procedure.[19] The crystalline compounds described in this work were homogeneous in this system.

Irradiation Procedure.—The ultraviolet source used was a 450-w Hanovia Type L mercury-arc lamp,[20] Model 679A, with a 4.5-in. arc. The lamp was placed, without a filter, in a water-cooled quartz immersion well (Hanovia Model 19431), and the whole assembly was mounted in a Pyrex reaction vessel, with the lamp below the level of the solution to be irradiated. The reaction vessel was equipped with a magnetic stirrer bar, and provision was made for sampling the solution during irradiation. Periodic sampling and examination by thin layer chromatography permitted determination of the most suitable irradiation times for the preparative runs.

1-*S*-Ethyl-1-thio-D-galactitol (II) by Irradiation of D-Galactose Diethyl Dithioacetal (I). A. Analytical.—A solution of D-galactose diethyl dithioacetal (I, 1.0 g) in methanol (150 ml) was irradiated as described for 35 min. Evaporation of the solution gave a crude crystalline product, yield 0.65 g, which was resolved by chromatography on 16 chromatoplates (20 × 20 cm, with 1.25-mm support coating); zones were located by spraying guide strips at the edges of each plate with the detecting reagent. Extraction of a zone, R_f 0.76, corresponding in mobility to unchanged starting material, with hot 1-propanol gave a product, which on recrystallization from 1-propanol gave pure D-galactose diethyl dithioacetal (I), yield 220 mg, mp 132–133°, indistinguishable from authentic starting material by mixture melting point and by infrared and ultraviolet spectrum. Extraction of a zone, R_f 0.32, gave a syrup, yield 25 mg, shown to be L-fucitol (III). The major reaction product, R_f 0.63, was extracted and crystallized from ethanol: yield 380 mg (60% based on unrecovered starting material). Recrystallization from ethanol gave pure 1-*S*-ethyl-1-thio-D-galactitol (II): mp 149–150°; $[\alpha]^{22}D$ −10 ± 2° (*c* 1.5, water); λ_{max}^{KBr} 3.08 (OH), 6.95 μ (SEt); λ_{max}^{EtOH} 211 mμ (ϵ 740), 264 mμ (ϵ 40) (see Figure 3); nmr data in deuterium oxide (see Figure 1), τ 8.80 (three-proton triplet, J = 7.1 cps, CH_3 of ethyl group), 7.41 (two-proton quartet, J = 7.1 cps, CH_2 of ethyl group), 7.22 (two-proton doublet, $J_{1,2}$ = 7.6 cps, H-1,1′), 5.81–6.40 (six-proton multiplet, H-2,3,4,5,6,6′); X-ray powder diffraction data, 11.30 vs (2), 8.23 vw, 5.41 w, 5.03 s (3,3), 4.75 s (3,3), 4.22 vs (1), 3.81 w, 3.48 s, 3.38 m, 3.03 w, 2.93 vw, 2.75 w, 2.62 vw, 2.53 m A.

Anal. Calcd for $C_8H_{18}O_5S$: C, 42.48; H, 7.96; S, 14.16. Found: C, 42.35; H, 7.85; S, 14.33.

For this compound prepared by a different route, Jones and Mitchell[5] reported mp 149–151°, $[\alpha]^{25}D$ −9 ± 2° (water). A sample of II prepared by the procedure of Jones and Mitchell was identical with that isolated in the present work by mixture melting point and by infrared spectral comparison.

When the procedure was repeated, but with irradiation for 20 hr, no starting material, R_f 0.76, was detected in the reaction mixture. Four products were present, R_f 0.63 (II), 0.35 (III), 0.28, and 0.14, in the approximate proportion 1:4:2:1. The product, R_f 0.14, was indistinguishable from galactitol (V) by chromatography.

B. Preparative.—D-Galactose diethyl dithioacetal (I, 15.0 g) in methanol (2.25 l) was irradiated as described for 36 hr. The reaction mixture was evaporated to give a crude yellow crystalline product which was washed with 1-propanol and recrystallized from ethanol: yield 6.49 g (55%), mp 148–150°. The product was identical with 1-*S*-ethyl-1-thio-D-galactitol (II) isolated from the analytical experiment by mixture melting point, thin layer chromatography, and infrared spectrum. The mother liquors from this preparation were shown by thin layer chromatography to contain no residual starting material. There were present, in addition to substance II (R_f 0.63), two minor components, R_f 0.35 and 0.28, in about 4:1 proportion. The product, R_f 0.35, was identical by thin layer chromatography with fucitol (III). Concentration of the solution gave a crystalline product, 200 mg (1.2%), mp 177–178°, R_f 0.28, indistinguishable by thin layer chromatography from the product, R_f 0.28, in the mixture. This product was shown to be 1-deoxy-1-ethylsulfinyl-D-galactitol (IV) (see below).

2,3,4,5,6-Penta-*O*-acetyl-1-*S*-ethyl-1-thio-D-galactose.—1-*S*-Ethyl-1-thio-D-galactose (II, 2.0 g) was acetylated with acetic anhydride in pyridine essentially as described by Jones and Mitchell:[5] yield 2.9 g (75%); mp 151–152°; $[\alpha]^{22}D$ +9 ± 1° (*c* 2.1, chloroform); λ_{max}^{KBr} 5.78 (OAc), 6.98 μ (SEt); nmr data in deuteriochloroform (see Figure 2), τ 8.78 (three-proton triplet, J = 8 cps, CH_3 of ethyl group), 7.89, 7.91, 7.98 (singlets, nine protons, three protons, and three protons, OAc), 7.45 (four-proton multiplet, H-1, H-1′, and CH_2 of ethyl group), 6.15 (1-proton quartet, $J_{6,6'}$ = 11.7 cps, $J_{5,6}$ = 7.3 cps, H-6), 5.70 (one-proton quartet, $J_{6,6'}$ = 11.7 cps, $J_{5,6'}$ = 5.0 cps, H-6′), 4.55–5.00 (four-proton multiplet, H-2, H-3, H-4, H-5); X-ray powder diffraction data, 11.00 s (3), 8.04 w, 7.03 s (2), 6.39 w, 5.36 vw, 4.93 vs (1), 4.28 vw, 4.00 w, 3.72 m, 3.49 m, 3.42 vw, 3.06 w, 2.76 m A.

Anal. Calcd for $C_{18}H_{28}O_{10}S$: C, 49.53; H, 6.47; S, 7.35. Found: C, 49.46; H, 6.36; S, 7.54.

For this compound Jones and Mitchell reported[5] mp 150.5–151.0°, $[\alpha]^{22}D$ +8 ± 1° (chloroform).

Irradiation of 1-*S*-Ethyl-1-thio-D-galactitol (II).—A solution of 1-*S*-ethyl-1-thio-D-galactitol (II, 1.0 g) in methanol (150 ml) was irradiated as described for 24 hr. Thin layer chromatographic examination indicated that, in addition to starting material (R_f 0.63), there were products present having R_f 0.35, 0.28, and 0.14. The product, R_f 0.35, was identical with L-fucitol (III) by chromatography and was present in higher proportion than the other two products. Resolution of the reaction product on 12 chromatoplates (20 × 20 cm, with 1.0-mm support coating) gave from the zone R_f 0.63 unchanged starting material, 95 mg, mp 148–150°. Extraction of the zone, R_f 0.35, with hot ethanol and crystallization of the product from ethanol gave L-fucitol (III): yield 340 mg (44% based on unrecovered starting material); mp 155–156°; $[\alpha]^{19}D$ +20 ± 1° (*c* 1.5, ethanol); n.m.r. data (D_2O), τ 8.77 (three-proton doublet, $J_{1,2}$ = 6.3 cps, CH_3), ethyl group signals absent. The product was identical by mixture melting point and X-ray powder diffraction pattern with an authentic sample of L-fucitol.

The zones, R_f 0.28 and 0.14, from three experiments performed under the above conditions were extracted with water, and the products were crystallized from 95% ethanol. From the zone, R_f 0.28, was obtained 1-deoxy-1-ethylsulfinyl-D-galactitol (IV): yield 75 mg (3% based on unrecovered starting material); mp 178.0–178.5°; $[\alpha]^{20}D$ −89 ± 1° (*c* 0.9, water); λ_{max}^{KBr} 3.01 (OH), 9.68 μ (sulfoxide); λ_{max}^{EtOH} 226 mμ (ϵ 380); nmr data (D_2O), τ 8.73 (three-proton triplet, J = 7.1 cps, CH_3 of ethyl group), 7.12 (two-proton quartet, J = 7.1 c.p.s., CH_2 of ethyl group), 6.99 (two protons, H-1,1′), 5.93–6.53 (six-proton multiplet, H-2,3,4,5,6,6′); X-ray powder diffraction data, 13.29 s (4), 5.92 m, 5.54 w, 5.01 w, 4.51 vs (1), 4.40 s (3), 4.11 vs (2), 4.19 m, 3.69 w, 3.28 s, 3.00 m, 2.77 w, 3.69 m, 2.47 w, 2.33 m, 2.28 m A.

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Anal. Calcd for $C_8H_{16}O_6S$: C, 39.66; H, 7.49; O, 39.63; S, 13.23. Found: C, 39.62; H, 7.28; O,[21] 39.26; S, 12.99.

This product was identical by mixture melting point and X-ray powder diffraction pattern with the product, mp 177–178°, from the preceding preparation, and with an authentic sample of IV which had been prepared[6] from 1-*S*-ethyl-1-thio-D-galactitol (II) by treatment with aqueous bromine or hydrogen peroxide.

From the zone, R_f 0.14, was obtained D-galactitol (V), 30 mg (2% based on unrecovered starting material), mp 181–183°, identical by mixture melting point and X-ray powder diffraction pattern[22] with an authentic sample of V.

2,3,4,5,6-Penta-*O*-acetyl-1-deoxy-1-ethylsulfinyl-D-galactitol.—Acetic anhydride (1.0 ml) was added to a solution of 1-deoxy-1-ethylsulfinyl-D-galactitol (IV, 125 mg) in pyridine (2 ml), the mixture was kept for 18 hr at room temperature, and ice–water (70 ml) was added. The mixture was extracted with chloroform (two 25-ml portions); the extract was washed with water (two 15-ml portions), dried (magnesium sulfate), and evaporated. The residue was freed from traces of pyridine by codistillation with benzene, and the product was crystallized from benzene (5 ml) and petroleum ether (bp 98–110°, 5 ml): yield 128 mg (55%); mp 146–148°; $[\alpha]^{20}D$ −51 ± 2° (*c* 1.0, chloroform); λ_{max}^{KBr} 5.75 (OAc), 9.45 μ (sulfoxide); λ_{max}^{EtOH} 214 mμ (ε 3800); nmr data (deuteriochloroform), τ 8.68 (three-proton triplet, J = 7.5 cps, CH_3 of ethyl group), 7.86, 7.89, 7.91, 7.98 (singlets, six protons, three protons, three protons, three protons, OAc), 7.28 (two-proton quartet, CH_2 of ethyl group), 7.23 (two-proton doublet, $J_{1,2}$ = 7.0 cps, H-1,1′), 6.15 (one-proton quartet, $J_{5,6}$ = 7.8 cps, $J_{6,6'}$ = 11.6 cps, H-6), 5.69 (one-proton quartet, $J_{5,6'}$ = 4.7 cps, $J_{6,6'}$ = 11.6 cps, H-6′), 4.17–4.42, 4.52–5.80 (one- and three-proton multiplets, H-2,3,4,5); X-ray powder diffraction data, 11.00 m, 8.19 w, 7.01 s (2), 6.46 m, 4.92 vs (1), 4.33 vw, 4.00 w, 3.79 w, 3.67 m, 3.50 m A.

Anal. Calcd for $C_{18}H_{28}O_{11}S$: C, 47.78; H, 6.24; O, 38.90; S, 7.09. Found: C, 47.86; H, 6.51; O,[21] 38.99; S, 6.79.

Irradiation of 1-Deoxy-1-ethylsulfinyl-D-galactitol (IV).—A solution of IV (10 mg) in ethanol (10 ml) was irradiated as described for 8 hr. Crystallization of the resultant dark syrup from ethanol gave galactitol (4 mg, 58%), R_f 0.14, mp 180–183°, undepressed on admixture with authentic galactitol.

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Preparation of Glycosyl Phosphates. β-D-Fructopyranose 2-Phosphate

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A D-fructopyranose 2-phosphate has been prepared by the reaction of the acetylated sugar with anhydrous phosphoric acid. Modifications of the fusion technique using a solvent and using polyphosphoric acid have been investigated, as have been some aspects of the effect of anomeric configuration on the reaction.

The sugar nucleotide "guanosine diphosphate fructose" has been detected in the mold *Eremothecium ashbyii*,[2] and "uridine diphosphate D-fructose" has been isolated from dahlia tubers.[3] The properties of the latter sugar nucleotide were such as to suggest that the D-fructose was present as a glycosyl phosphate, thus making the nucleotide a derivative of D-fructose 2-phosphate. In an effort to gain more insight into this question, a chemical synthesis of such a phosphate was undertaken.

At the time that parts of this work were first reported,[4] chemical syntheses of both D-fructopyranose 2-phosphate and D-fructofuranose 2-phosphate had just been reported by Pontis and Fischer.[5] These workers used a novel synthesis in which the 2-phosphates were prepared from D-fructose 1-phosphate utilizing a carbodiimide-induced cyclization followed by ring opening using alkaline hydrolysis. This procedure, which has also been used to prepare certain aldose 2-phosphates from the corresponding 1-phosphates,[6] gave in low yield either a D-fructopyranose 2-phosphate or a D-fructofuranose 2-phosphate, depending on the conditions used for the cyclization. The products, which were isolated as an amorphous barium salt and as a solution of the sodium salt, respectively, were both assigned the β configuration on the basis of their optical rotations.

In the present paper, the results of some efforts to modify the procedure for glycosyl phosphate formation by fusion are reported, and a simple synthesis of a D-fructopyranose 2-phosphate, using one such modification, is recorded. In its original form,[7] the formation of glycosyl phosphates by the fusion method involved treatment of a fully acetylated reducing sugar (1 mole) with 100% phosphoric acid (4 moles) *in vacuo* at a temperature of 50°, which is just above the melting point of crystalline phosphoric acid. Under these conditions the esters used, namely the penta-*O*-acetates of β-D-glucopyranose and β-D-galactopyranose, dissolved quite readily, and after 2 hr, the reactions were worked up, giving in each instance the α-1-phosphates in purified yields of 30–35%. The procedure was used by Kim and Davidson[8] for the preparation of the α-1-phosphates of 2-acetamido-2-deoxy-α-D-glucopyranose and 2-acetamido-2-deoxy-α-D-galactopyranose from the β-pentaacetates of the corresponding amino sugars. Subsequently, O'Brien[9] carried out a fusion on 2-amino-2-deoxy-α-D-glucopyranose pentaacetate and, by ion-exchange chromatography, was able to isolate both the α and β anomer of the 1-phosphate formed in the reaction. The conditions

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