hexenecarbonyl chloride, bp 53° (2.5 mm) (lit.[35] bp 203–204°), in 20 ml of dry pyridine was stirred at reflux for 6 hr. The resulting dark brown solution was concentrated *in vacuo* to a paste. A 30-ml portion of 95% ethanol was added, and the mixture was stirred for 30 min at reflux. The solvent was removed *in vacuo*, and the remaining semisolid was stirred for 1 hr at 25° with 50 ml of $CHCl_3$ and then filtered. The solid was washed with $CHCl_3$ and ether, dried, and recrystallized from ethanol with charcoal decolorization, giving 0.73 g (26%) of colorless microcrystals: mp 288–290° dec; uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 320 (sh, ϵ 10,300), 309 (ϵ 12,700), 295.5 (ϵ 12,900), 288 (sh, ϵ 12,000), and 222 nm (ϵ 19,600); (0.1 *N* HCl) 285.5 (ϵ 15,900) and 220 nm (ϵ 29,600); (0.1 *N* NaOH) 315.5 (ϵ 24,800) and 242 nm (ϵ 17,900); nmr (DMSO-d_6) τ 7.55–9.15 (m, 8, cyclohexyl H), 6.27 (d, 1, J = 5 Hz, CHC═O), 4.60 (m, 1, CHN$^+$), and 0.71 and 1.04 ppm (2 s, 2, purine H).

Anal. Calcd for $C_{12}H_{14}ClN_5O$: C, 51.52; H, 5.04; N, 25.04. Found: C, 51.51; H, 5.16; N, 24.80.

3,6a,7,8,9,10,10a,11-Octahydro-11-oxoquinazolino[2,1-*i*]purine (30).—To a stirred solution of 0.280 g (1.0 mmol) of **29** in 5 ml of H_2O was added 0.053 g (0.50 mmol) of solid Na_2CO_3, giving an evolution of CO_2 and a precipitate within 1 min. The mixture was cooled to 5° and filtered. The solid was washed with cold H_2O and acetone–ether and dried to yield 0.18 g (74%) of colorless microcrystals: mp 267–268° dec; uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 320 (sh, ϵ 15,700), 310 (ϵ 18,800), and 230 nm (ϵ 19,100); (0.1 *N* HCl) 286 (ϵ 15,900) and 220 nm (ϵ 29,400); (0.1 *N* NaOH) 316 (ϵ 25,100) and 243 nm (ϵ 18,100).

Anal. Calcd for $C_{12}H_{13}N_5O$: C, 59.25; H, 5.39; N, 28.79. Found: C, 59.24; H, 5.27; N, 28.91.

Registry No.—**4**, 21882-99-5; **5**, 5071-96-5; **6**, 21883-01-2; **7**, 21883-02-3; **8**, 21899-62-7; **9**, 6850-57-3; **10**, 21883-04-5; **11**, 21883-05-6; **12**, 21883-06-7; **13**, 21899-63-8; **14**, 21883-07-8; **15**, 21899-64-9; **16**, 21883-08-9; **17**, 21883-09-0; **18**, 21883-10-3; **19**, 21883-11-4; **20**, 21883-12-5; **22**, 21883-13-6; **23**, 21883-14-7; **24**, 21883-15-8; **25**, 21883-16-9; **26**, 21883-17-0; **27**, 21883-18-1; **29**, 21883-19-2; **30**, 21883-20-5.

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Nucleophilic Displacement in 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(*p*-tolylsulfonyl)-α-D-glucofuranose[1]

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Nucleophilic displacement of the *p*-tolylsulfonyloxy group in the 1,2:5,6-di-*O*-isopropylidene-3-*O*-(*p*-tolylsulfonyl)-α-D-glucofuranose (I) has been successfully accomplished, using sodium azide and potassium thioacetate, to give the corresponding α-D-allofuranose derivatives (II and IV). Selective hydrolysis of 3-*S*-acetyl-1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-allofuranose (IV) with 50% aqueous acetic acid affords 3-*S* acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose (VI), which is acetylated to give 5,6-di-*O*-acetyl-3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose (VII). Compound VII is desulfurized using Raney nickel in ethanol to give 5,6-di-*O*-acetyl-3-deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose, which is deacetylated to give 3-deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose (VIII) in an overall yield of 50% starting from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose.

The displacement of the *p*-tolylsulfonyloxy group in 1,2:5,6-di-*O*-isopropylidene-3-*O*-(*p*-tolylsulfonyl)-α-D-glucofuranose (I) with ammonia[2] and hydrazine[2–6] occurs with inversion of configuration at C-3 to give D-allofuranose derivatives. The *p*-tolylsulfonyloxy group at C-3 as in I is reported[2–5] to be very resistant to nucleophiles other than the ones cited above.

We wish to report that nucleophilic displacement is feasible with azide and thiolacetate anions to give the corresponding 3-azido and 3-thioacetyl derivatives having the D-*allo* configuration. The displacement with thioacetate anion followed by desulfurization with Raney nickel has enabled us to synthesize the 3-deoxy-D-*ribo*-hexofuranose derivative in high yields.

In connection with other work in progress which required large quantities of 3-deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose, the possibility of displacement of the *p*-tolylsulfonyloxy group in 1,2:5,6-di-*O*-isopropylidene-3-*O*-(*p*-tolylsulfonyl)-α-D-glucofuranose (I) was examined. Treatment of compound I at 115° in a current of nitrogen for 15 days in *N*,*N*-dimethylformamide (DMF) containing a slurry of sodium azide in water, so as to have DMF–water in the proportion of 19:1, affords a syrupy residue which exhibits strong absorptions at 2150 (azide) and at 1650 cm^{-1} suggestive of an olefin. Thin layer chromatographic examination of the syrupy product shows it to be composed of three main components, which are separated on a silica gel column to give a 53% yield of crystalline 3-azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (II), a 10% recovery of the starting material I, and a 12% yield of 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose. The infrared spectrum of compound II in Nujol shows a strong absorption at 2150 cm^{-1} (azide) and none for the tolylsulfonate group. The azide II, on reduction with Raney nickel, furnishes the known 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (III).

In a similar manner, compound I is heated at 115° in a current of nitrogen for 3 days in dry DMF containing potassium thioacetate to yield a syrupy residue which is acetylated in the usual manner. From this latter res-

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[1] This work was supported by the Agricultural Research Service, U. S. Department of Agriculture, Grant 12-14-100-7662, administered by the Northern Regional Laboratory, Peoria, Ill., Journal Paper No. 3670 of the Purdue Agricultural Experiment Station, Lafayette, Ind.

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[3] M. L. Wolfrom, J. Bernsmann, and D. Horton, *J. Org. Chem.*, **27**, 4505 (1962).

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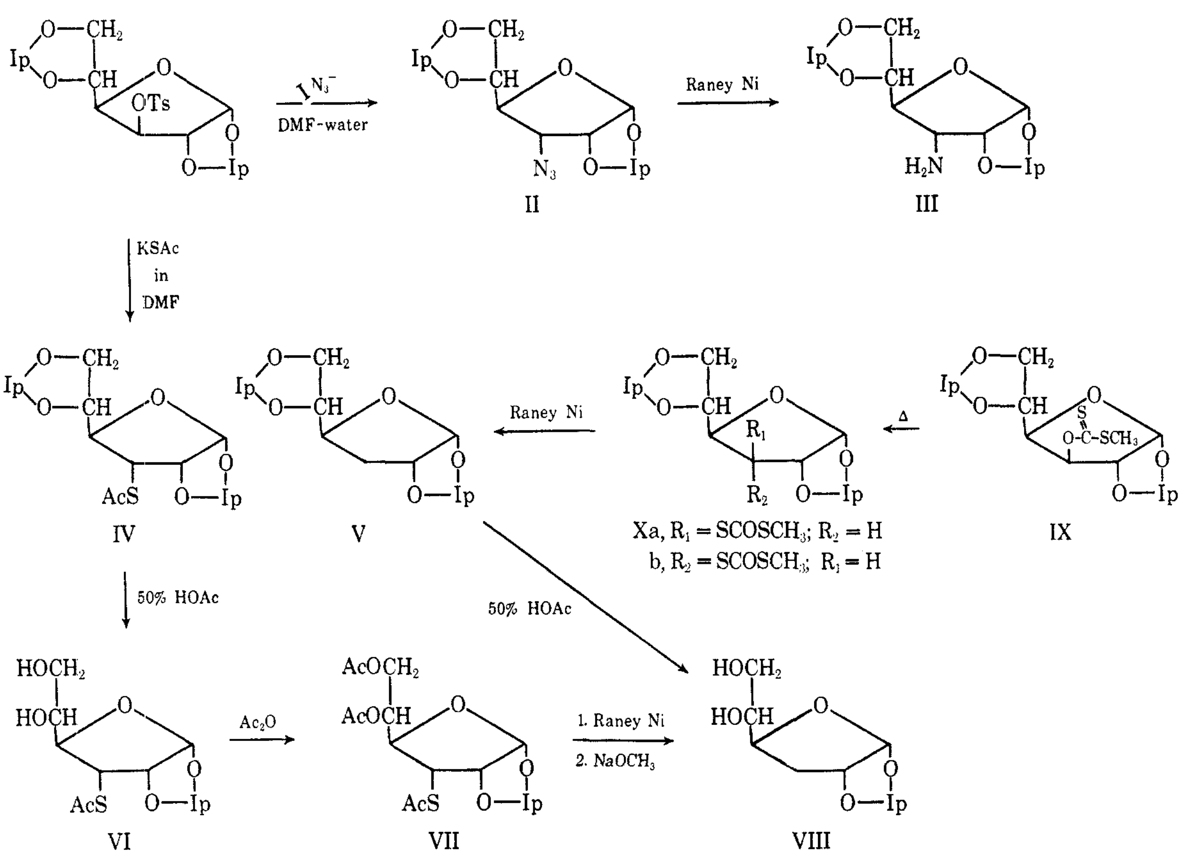

Ip = $C(CH_3)_2$; Ts = $SO_2C_6H_4CH_3$; Ac = $COCH_3$

idue there is obtained a 69% yield of 3-*S*-acetyl-1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-allofuranose (IV), 10% of unreacted starting material (I), and 8% of the 3,4 olefin. The infrared spectrum of IV in Nujol shows a strong absorption at 1685 cm^{-1} (*S*-acetyl) but none for the tolylsulfonate group. The integrated nmr spectrum in $CDCl_3$ shows a total of 22 protons, 12 isopropylidene methyl protons as a multiplet (two doublets overlapping) between τ 8.5 and 8.7, three protons at τ 7.63 (*S*-acetyl group), and one anomeric proton as a doublet centered at τ 4.14 ($J_{1,2}$ = 3.5 Hz).

Desulfurization of IV with Raney nickel in refluxing ethanol affords a quantitative yield of 3-deoxy-1,2:5,6-di-*O*-isopropylidene-D-*ribo*-hexofuranose (V). The physical properties of V, however, do not agree with the reported values, especially the specific rotation, which is observed to be −0.475° compared with the reported[7,8] values of −5.78 and −8.6°. The selective hydrolysis of V with 0.01 *N* hydrochloric acid[8] for 6 hr or with 50% aqueous acetic acid gives not more than a 60% yield of 3-deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose (VIII). For this compound the specific rotation is observed to be −13.07°, compared with the reported[7] value of −37.8°. To verify these discrepancies, compounds V and VIII are prepared according to literature directions.[8]

The sodio derivative of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose is converted by successive treatment with carbon disulfide and methyl iodide to give a 95% yield of 1,2:5,6-di-*O*-isopropylidene-3-*O*-[(methylthio)thiocarbonyl]-D-glucofuranose (IX). The pyrolysis of IX in diphenyl ether at 300° for 5 hr in a current of nitrogen as suggested by Hedgley, *et al.*,[8] and removal of diphenyl ether by gentle fractional distillation gives an improved yield of 86% 1,2:5,6-di-*O*-isopropylidene-3-*S*-[(methylthio)carbonyl]-3-thio-D-hexofuranose (X), mp 137–141°. Compound X so obtained, on fractional crystallization, gives two isomeric products having mp 148–149°, $[\alpha]^{25}D$ −56.6° (Xa), and mp 117–120°, $[\alpha]^{25}D$ −13.9° (Xb), which is suggestive of a mixture of D-*gluco* and D-*allo* configurations. Furthermore, these isomers Xa and Xb, on desulfurization, each give 3-deoxy-1,2:5,6-di-*O*-isopropylidene-D-*ribo*-hexofuranose (V). The specific rotation of distilled V is observed to be −4.53°, but thin layer chromatographic examination in benzene–ethyl acetate (6:1) shows the presence of a minor component which in our hands failed to separate. However, the selective hydrolysis of V with 0.01 *N* hydrochloric acid gives 3-deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose (VIII) containing an unidentified minor component which can be separated on a silica gel column using chloroform–acetone (3:1) as eluent. Compound VIII obtained by this procedure has the same specific optical rotation as the compound obtained by the displacement reaction.

Selective hydrolysis of the 5,6-*O*-isopropylidene group in V is accompanied by extensive, undesired hydrolysis of the 1,2-*O*-isopropylidene group. To overcome this difficulty, compound IV is first hydrolyzed selectively with 50% aqueous acetic acid to obtain an 88% yield of 3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-D-allofuranose (VI), which on acetylation affords a quantitative yield of 5,6-di-*O*-acetyl-3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose (VII). Desulfur-

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ization of VII with Raney nickel in refluxing ethanol followed by deacetylation gives crystalline 3-deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose (VIII) in 93% yield.

The preparation of compound VIII in large quantities is best accomplished by the displacement reaction because of the high yields obtained, the low quantities of Raney nickel required, and the ease of crystallization without chromatographic purification.

Experimental Section

Analytical Methods.—Purity of products was determined by thin layer chromatography (tlc) on silica gel G[9] coated glass plates (5 × 13 cm) irrigated with (a) benzene–ethyl acetate (6:1); (b) benzene–ethyl acetate (20:1); (c) hexane–ethyl acetate (6:1); (d) chloroform–acetone (3:1); (e) benzene–ethyl acetate (4:1). Solvent ratios are based on volumes. Components were located by spraying with 5% sulfuric acid in ethanol and heating until permanent char spots were visible. Melting points were determined on a Fisher-Johns apparatus and are corrected. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian Associates A-60 instrument. Infrared (ir) spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer. Evaporations were done under reduced pressure with a bath temperature below 40°. Absorption chromatography was made on silica gel.[10] Comparison of materials with authentic compounds was made by mixture melting point determination, ir and nmr spectra, and thin layer chromatography. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(*p*-tolylsulfonyl)-α-D-glucofuranose (I).—Compound I was prepared in 90% yield by stirring a solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (130 g, 0.5 mol) in dry pyridine (500 ml) and *p*-tolylsulfonyl chloride (191 g, 1 mol) for 2 days. The crystalline compound I obtained after the usual work-up procedure was recrystallized from chloroform–hexane, mp 122–123°.

3-Azido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (II).—To a solution of compound I (12.42 g, 0.03 mol) in DMF (285 ml) was added a slurry of sodium azide (20 g) in water (15 ml). The mixture was heated at 115° under stirring in a current of nitrogen for 15 days. The reaction mixture was cooled and poured into xylene (1200 ml) under stirring and the mixture was filtered. The filtrate was then concentrated to dryness. The residue was taken into xylene (100 ml) and filtered again. The filtrate was then concentrated to a syrup, which was chromatographed over a silica gel column using solvent B as eluent. The proper azide fractions (having a slightly lower R_f than compound I) were collected and concentrated to a syrup (4.55 g, 53%) which was dissolved in hexane (25 ml) and left at 0° for 24 hr, whereupon the azido compound II crystallized in long needles: mp 38–39°; $[\alpha]^{25}\mathrm{D}$ +72° (*c* 1, $CHCl_3$). The ir spectrum in Nujol showed no "OH" absorption around 3500 cm^{-1} but showed a strong absorption at 2150 cm^{-1}.

Anal. Calcd for $C_{12}H_{19}N_3O_5$: C, 50.52; H, 6.71; N, 14.73. Found: C, 50.32; H, 6.68; N, 14.85.

The fractions containing the two faster moving components were combined and concentrated to a syrup (2 g) which was chromatographed over a silica gel column using solvent C as eluant. The fractions containing the faster moving component were combined and concentrated, whereupon the residue spontaneously crystallized (0.75 g, 10%). It was recrystallized from hexane, mp 51° (lit.[11] mp 51° for 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose). The ir spectrum in Nujol showed no "OH" absorption around 3500 cm^{-1} but showed a strong absorption at 1650 cm^{-1} (C=C). The fractions containing the slower moving component were combined and concentrated to give the starting material (1.25 g, 10%).

3-Amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (III).—Compound II (1 g) in absolute ethanol (25 ml) containing Raney nickel (5 g) was hydrogenated at 25° for 2 hr. The reaction mixture was filtered through a bed of charcoal and the filtrate was concentrated, whereupon the residue spontaneously crystallized. It was recrystallized from ether–hexane as long needles (880 mg, 96%): mp 92–93°; $[\alpha]^{25}\mathrm{D}$ +32° (*c* 1, $CHCl_3$) [(lit.[6] mp 92–93°); $[\alpha]^{25}\mathrm{D}$ +32.7° (*c* 2.37, $CHCl_3$)].

3-*S*-Acetyl-1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-allofuranose (IV).—To a stirred solution of compound I (62.1 g, 0.15 mol) in DMF (700 ml), potassium thioacetate (68.4 g, 0.6 mol) was added and the mixture was heated at 115° for 3 days in a current of nitrogen with the exclusion of moisture. The reaction mixture was cooled in ice and poured under stirring into ice-cooled dry xylene (4.5 l.). The solution was stirred for 30 min and the precipitated salts were removed by filtration, using a little xylene to wash the precipitate. The xylene filtrate was then concentrated under reduced pressure, care being taken to keep a nitrogen atmosphere as far as possible. After all the xylene and DMF were removed, the residue was taken into xylene (500 ml), whereupon some more of the salts precipitated which were removed by filtration. The filtrate was concentrated to a deep orange syrup which was taken into dry pyridine (90 ml) and acetic anhydride (60 ml) and stirred at 25° for 16 hr. The reaction mixture was then poured into ice-cold water under stirring when the product started crystallizing. The crystals were removed by filtration and the filtrate was extracted once with toluene (500 ml). The toluene extract was used to dissolve the crystals and the resultant toluene solution was washed five to six times with water. The washed toluene solution was dried over anhydrous sodium sulfate and a little charcoal was added to decolorize the solution. The toluene solution was then filtered and the filtrate was concentrated under reduced pressure, whereupon the residue solidified. The solid was recrystallized from ethanol (300 ml) at 0° to give compound IV as needles, yield 23 g. Tlc examination of the filtrate in solvent A showed the presence of more of compound IV, compound I, the "3,4 olefin," and some other slower moving components. The filtrate was concentrated under reduced pressure to a syrup and was transferred to a silica gel column (100 × 5 cm) prepared in benzene. The column was eluted with benzene (3 l.) over a period of 3 hr and the eluent was concentrated, whereupon the residue crystallized. Tlc examination in solvent A showed it to be composed mainly of 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*erythro*-hex-3-enofuranose (absorption at 1650 cm^{-1} in the ir spectrum) and unreacted compound I, which was recovered by crystallization from hexane, yield 8 g (12%).

The silica gel column was eluted with solvent A (about 3 l. in 3 hr) until no more of compound IV was eluted (checked by tlc in solvent A). The eluent was concentrated under reduced pressure, whereupon the residue crystallized and was recrystallized from ethanol to furnish 10 g of compound IV. Total yield of compound IV was 33 g (69.9%). When recrystallized from ether–hexane, it had mp 88°; $[\alpha]^{25}\mathrm{D}$ +107.2° (*c* 1.014, $CHCl_3$). The ir spectrum in Nujol showed no "OH" or tosyl absorptions but showed a strong absorption at 1685 cm^{-1} (*S*-acetyl).

Anal. Calcd for $C_{14}H_{22}O_6S$: C, 52.81; H, 6.97; S, 10.07. Found: C, 52.82; H, 6.93; S, 10.03.

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-D-*ribo*-hexofuranose (V).—A solution of compound IV (5 g) in absolute ethanol (100 ml) was refluxed for 1 hr under mechanical stirring with Raney nickel of normal activity (10 g, W-2). Desulfurization was quantitative as indicated by tlc examination in solvent A. The reaction mixture was worked up in the usual manner and the deoxy compound V was distilled under reduced pressure: yield 3.6 g (90%); bp 79–80° (0.6 mm); $n^{20}\mathrm{D}$ 1.4495; $[\alpha]^{25}\mathrm{D}$ −0.475° (*c* 4.21, EtOH) [lit.[8] bp 74–78° (0.3 mm); $n^{18}\mathrm{D}$ 1.4523; $[\alpha]^{18}\mathrm{D}$ −5.78° (*c* 4.2, EtOH)] [lit.[7] $n^{21}\mathrm{D}$ 1.4513; $[\alpha]^{18}\mathrm{D}$ −8.6° (*c* 3.7, EtOH)].

3-Deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose (VIII).—Compound V (48 g) was selectively hydrolyzed according to published directions.[8] The syrupy residue obtained after the usual work-up was chromatographed over silica gel using solvent D as eluent. The fractions containing the deoxy compound VIII were combined and concentrated. The residue spontaneously crystallized and was recrystallized from ether or chloroform–hexane as needles: yield 27 g (60%); mp 82–83°; $[\alpha]^{25}\mathrm{D}$ −13.07° (*c* 0.635, EtOH) [lit.[7,8] mp 84°; $[\alpha]^{18}\mathrm{D}$ −37.8° (*c* 0.635, EtOH)].

3-*S*-Acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose (VI).—Compound IV (31.8 g, 0.1 mol) was taken into 50% aqueous acetic acid (500 ml) and stirred at 25° for 10 hr in a current of nitrogen. The reaction mixture was then concentrated under reduced pressure to a syrup, which was taken into chloroform (500 ml) and washed successively with water, dilute aqueous

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[9] L. Merck Ag, Darmstadt, Germany. Distributors: Brinkmann Instruments Inc., Westbury, N. Y. 11590.

[10] J. T. Baker Chemical Co., Phillipsburg, N. J.

[11] K. Freudenberg and F. Brauns, *Ber.*, 3233 (1922).

sodium bicarbonate, and water until neutral. The washed chloroform solution was dried over anhydrous sodium sulfate and filtered. The chloroform filtrate was concentrated under reduced pressure, whereupon the residue solidified. This was recrystallized as flocculent needles from chloroform–hexane: yield 24.5 g (88%); mp 105°; $[\alpha]^{25}\mathrm{D}$ +117.4° (*c* 1.02, $CHCl_3$). The infrared spectrum in Nujol showed absorptions at 3450 (OH) and 1685 cm^{-1} (*S*-acetyl).

Anal. Calcd for $C_{11}H_{18}O_6S$: C, 47.47; H, 6.52. Found: C, 47.39; H, 6.41.

5,6-Di-*O*-acetyl-3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose (VII).—A solution of compound VI (25 g, 0.09 mol) in dry pyridine (90 ml) and acetic anhydride (60 ml) was stirred at 25° for 3 hr. Acetylation was complete as examined by tlc in solvent E. The reaction mixture was worked up in the usual manner and compound VII was recrystallized from chloroform–hexane as long needles (29 g) and was removed by filtration. Concentration of the chloroform–hexane filtrate under reduced pressure and recrystallization of the residue gave another 3 g of compound VII. Total yield of compound VII was 32 g (98.5%); mp 99°; $[\alpha]^{25}\mathrm{D}$ +102.16° (*c* 1.02, $CHCl_3$). The ir spectrum in Nujol showed no "OH" absorption (3500-cm^{-1} region) but showed strong absorptions at 1730 (*O*-acetyl) and 1685 cm^{-1} (*S*-acetyl).

Anal. Calcd for $C_{15}H_{22}O_8S$: C, 49.71; H, 6.12; S, 8.85. Found: C, 49.68; H, 6.11; S, 8.65.

3-Deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose (VIII).—A solution of compound VII (54 g, 0.15 mol) in absolute ethanol (800 ml) was refluxed under mechanical stirring with Raney nickel (100 g) for 1 hr, after which the reaction mixture was cooled and another batch of Raney nickel (50 g) was added and refluxed for 1 hr. Desulfurization was complete as indicated by tlc in solvent E. The reaction mixture was worked up in the usual manner and the syrupy 5,6-di-*O*-acetyl-3-deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose was taken into methanol (200 ml) and deacetylated using a catalytic amount of sodium methoxide. Deacetylation was complete in 30 min and the reaction mixture was deionized with methanol-washed IR-120 [H^+] and filtered. The methanolic filtrate was concentrated under reduced pressure, whereupon the residue solidified. It was recrystallized from chloroform–hexane as long needles: yield 28.5 g (93%); mp 82–83°; $[\alpha]^{25}\mathrm{D}$ −13.07° (*c* 0.635, EtOH).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-[(methylthio)thiocarbonyl]-D-glucofuranose (IX).—Compound IX was prepared in 95% yield by following essentially the literature directions.[12] To an ice-cooled solution of the sodio derivative of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose [prepared from diacetone glucose (78 g, 0.3 mol) and powdered sodium (7.6 g, 0.33 g-atom)] in dry ether (1 l.), carbon disulfide (91.2 g, 1.2 mol) was added under stirring and the solution was stirred for 2 hr. Methyl iodide (50.76 g, 0.36 mol) was added dropwise under stirring over a period of 30 min and the solution was stirred for an additional 1 hr. The reaction was complete as examined by tlc in solvent E. The reaction mixture was filtered and the ether filtrate was concentrated under reduced pressure to a yellow syrup which was taken into hexane (700 ml) and washed twice with water. The washed petroleum ether solution was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated to a syrup which was distilled under reduced pressure: bp 150–152° (0.3 mm); yield 100 g (95%). The distillate was taken into hexane (500 ml) and cooled at 0° for 24 hr, whereupon compound IX crystallized out as needles, mp 61° (lit.[12] mp 61°).

1,2:5,6-Di-*O*-isopropylidene-3-*S*-[(methylthio)carbonyl]-3-thio-D-hexofuranose (X).—Compound IX (50 g) in diphenyl ether (200 g) was heated at 300–310° for 5 hr in a current of nitrogen. The bath temperature was lowered to 150–160° and diphenyl ether was removed by fractional distillation using a 20 × 1.5 cm Vigreux column, bp 89–90° (2 mm). The distillate was examined by tlc in solvent E and there was no starting material or reaction product present (R_f values for compound IX and X are the same in all pairs of solvents and the compounds are chromatographically indistinguishable). The bath temperature was raised to 200° to remove the last traces of diphenyl ether and the boiling point started rising to 140°, at which time the distillation was discontinued. The residue in the distillation flask solidified on cooling and was extracted with ether. The ether extract was decolorized with a little charcoal and filtered. The ether filtrate was concentrated, whereupon the residue solidified and was recrystallized from ethanol. Needle-shaped crystals separated to yield 37 g (74%) of compound X, mp 137–142°. The ethanol filtrate was set aside. These crystals, having mp 137–142°, were recrystallized from ethyl acetate as gritty needles of Xa: yield 17 g; mp 148–149°; $[\alpha]^{25}\mathrm{D}$ −56.6° (*c* 3.6, $CHCl_3$) [lit.[8] mp 143–144°; $[\alpha]^{18}\mathrm{D}$ −61.2° (*c* 3.6, $CHCl_3$)].

The ethyl acetate filtrate and the ethanol filtrate were combined and concentrated to a syrup which solidified on standing. The solid was recrystallized from ethanol in the cold to give 26 g of fluffy small needles of Xb: mp 117–120°; $[\alpha]^{25}\mathrm{D}$ −13.9° (*c* 3.6, $CHCl_3$). Total yield of X was 43 g (86%).

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-D-*ribo*-hexofuranose (V).—Compound Xa (mp 148–149°, 13 g) was desulfurized with Raney nickel in refluxing ethanol. The reaction product, worked up in the usual manner, was chromatographed over silica gel column using solvent A as eluent. The fractions containing the deoxy sugar V and contaminated with another slightly faster moving component were combined and concentrated to a syrup which was distilled under reduced pressure: yield 6 g (50%); bp 78–80° (0.6 mm); $[\alpha]^{25}\mathrm{D}$ −4.53° (*c* 4.24, EtOH). The distilled V was still not pure as examined by tlc in solvent A.

In a similar manner, compound Xb (26 g, mp 117–120°) was desulfurized and worked up as for V above from Xa. Compound V so distilled (13.5 g, 75%) had bp 78–80° (0.6 mm) and was chromatographically impure.

3-Deoxy-1,2-*O*-isopropylidene-D-*ribo*-hexofuranose (VIII).—Compounds V (19.5 g), obtained as above from compounds Xa and Xb, were combined and selectively hydrolyzed using 50% aqueous acetic acid (500 ml) at 25° for 6 hr, after which time the reaction mixture was concentrated to a syrup under reduced pressure. The last traces of water and acetic acid were removed by coevaporation under reduced pressure with several portions of absolute ethanol. The syrupy residue was chromatographed over silica gel using solvent D as eluent. The pure fractions containing compound VIII were combined and concentrated, whereupon the residue spontaneously crystallized. It was recrystallized from chloroform–hexane to obtain needles: yield 9.78 g (60%); mp 82–83°; $[\alpha]^{25}\mathrm{D}$ −13.07° (*c* 0.635, EtOH).

Registry No.—I, 3253-75-6; II, 21870-78-0; IV, 21870-79-1; VI, 21870-80-4; VII, 21870-81-5; VIII, 4494-96-6.

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[12] K. Freudenberg and A. Wolf, *Ber.*, **60**, 232 (1927).