hydroxide from a Beckman automatic titrator (Model K). After an additional 3 hr. at room temperature, the solution was adjusted to pH 7.5 and lyophilized. The residue was extracted with hot ethyl acetate and the extracts were concentrated and cooled. The crystalline product was collected on a sinter and dried: yield 3.2 g. (44%), m.p. 163–165° (after recrystallization from ethanol), $[\alpha]^{25}D$ −5.2° (*c* 2.0 in chloroform).

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.90; mol. wt., 146. Found: C, 49.33; H, 7.00; mol. wt., 154 (water), 300 (chloroform).

Reduction of 2,4-O-Ethylidene-D-threose.—To a solution of 11 (0.14 g.) in 90% ethanol (10 ml.) was added Raney nickel (1–2 g.), and the suspension was hydrogenated at room temperature and 100 p.s.i. for 7 hr. T.l.c. (acetone) indicated complete reduction, Raney nickel was removed by filtration, and the filtrate was concentrated to a syrup which crystallized spontaneously. Recrystallization from ether gave prisms of 1,3-O-ethylidene-D-threitol, m.p. 78–80°, $[\alpha]^{25}D$ −17.6° (c 2.5, chloroform).

Anal. Calcd. for $C_6H_{12}O_4$: C, 48.65; H, 8.15. Found: C, 48.82; H, 8.25.

Some Derivatives of 2,4-*O*-Ethylidene-D-erythrose and Erythritol[1]

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Alkaline conditions during the oxidation of 4,6-O-ethylidene-D-glucose have been found to facilitate aldol condensation of the 2,4-O-ethylidene-D-erythrose formed. Nitrogenous derivatives of 2,4-O-ethylidene-D-erythrose have been prepared and their structures have been studied. 1-Amino-1-deoxy-D-erythritol has been prepared as the crystalline *p*-toluenesulfonic acid salt.

For purposes of further synthesis, we were interested in preparing 1-aminobutane-2,3,4-triol. 1-Aminopolyols can be prepared by reduction of carbohydrate nitrogenous derivatives.[2] Reduction of a tetrose hydrazone can lead to the desired compound.

In an attempt to prepare the phenylhydrazone of a tetrose, 2,4-O-ethylidene-D-erythrose (II) was prepared from 4,6-O-ethylidene-D-glucopyranose (I) by oxidation with sodium metaperiodate according to Barker and MacDonald[3] or Rappoport and Hassid.[4] The crude tetrose derivative was extracted from the dried reaction mixture with ethyl acetate and treated with phenylhydrazine. Yields of the crystalline hydrazone ranged from 50% to zero. Later we observed that, when the above-mentioned procedures for the preparation of 2,4-O-ethylidene-D-erythrose (II) were followed, very frequently needle-shaped crystals formed in the ethyl acetate extract of the dried reaction mixture. The crystals melted at 210–215°, had a specific rotation of +50°, could be crystallized from ethyl acetate and petroleum ether (b.p. 40–60°), and reduced Fehling's solution when heated. In the infrared absorption spectrum, two bands for hydroxyl groups but none for a carbonyl group were revealed. The compound could be detected on the chromatogram with anilinium phthalate (but not with ammoniacal silver nitrate) or by t.l.c. (R_f 0.50). Elementary analysis of the crystals corresponded to $(C_6H_{10}O_4)_n$ and molecular weight determination showed that it could be a 2,4-O-ethylidene-D-erythrose dimer (mol. wt. 334, calcd. 292). The crystals were further characterized as a 2,4-O-ethylidene-D-erythrose derivative by the isolation, after acid hydrolysis, of the calculated amount of acetaldehyde 2,4-dinitrophenylhydrazone, and a 2,4-O-ethylidene-D-erythrose dimer structure was erroneously suggested for the compound by the authors.[5]

Prior to this, two 2,4-O-ethylidene-D-erythrose dimers have been described, one[6] of m.p. 149–150° ($[\alpha]^{22}D$ −40° initial; diacetate m.p. 171.5–172°; R_f of dimer by t.l.c. 0.59, see Experimental Section), and one[7] of m.p. 110–111° ($[\alpha]^{25}D$ −14° initial). Easy dimerization of erythrose and suitably substituted erythrose derivatives has been suggested by other authors.[8–10] The compound of m.p. 210–215°, reported above, yielded an acetate (m.p. 211–212°) and a benzoate (m.p. 182–183°). Elementary analysis of the esters corresponded, however, to a triester of $(C_6H_{10}O_4)_2$. A di-O-ethylidene branched octose, 1,3:5,7-di-O-ethylidene-3-C-formyl-D-*glycero*-D-*talo*-heptitol-3[1],6-pyranose (III), m.p. 228–229°, prepared[6] from dimeric 2,4-O-ethylidene-D-erythrose and whose structure has been proven by Schaffer,[6] has three esterifiable hydroxyl groups. The two compounds had the same optical rotation but differed in the reported melting point. The di-O-ethylideneoctose III, prepared according to the procedure of Schaffer, melted at 210–215° on a Fisher-Johns apparatus and showed no depression of melting point when mixed with the supposed dimer. Both compounds, however, separately and mixed, melted with prior softening at 227–228° in a liquid bath. This demonstrated that the alkaline conditions of the oxidation of 4,6-O-ethylidene-D-glucose, described by Rappoport and Hassid,[4] facilitated aldol condensation of the 2,4-O-ethylidene-D-erythrose (II) formed, and that the triacetate and tribenzoate obtained had structures IV and V, respectively (see Chart I).

To avoid dimerization or aldol condensation of 2,4-O-ethylidene-D-erythrose, the oxidation of the parent compound (I) was performed under acidic conditions. The reaction mixture was neutralized with barium carbonate and filtered. The filtrate was treated with benzylamine to form the crystalline 2,4-O-ethylidene-D-erythrose benzylamine Schiff base (VI) in 90% yield. The crystalline phenylhydrazone (VII) and 2,5-di-

(1) Part of this publication is taken from a thesis submitted by I. Z. to the Faculty of Science, The Hebrew University, in partial fulfillment of the requirements for the degree of M.Sc.

(2) M. L. Wolfrom, F. Shafizadeh, J. O. Wehrmuller, and R. K. Armstrong, *J. Org. Chem.*, **23**, 571 (1958).

(3) R. Barker and D. L. MacDonald, *J. Am. Chem. Soc.*, **82**, 2301 (1960).

(4) D. A. Rappoport and W. Z. Hassid, *ibid.*, **73**, 5524 (1951).

(5) I. Ziderman and E. Dimant, *Israel J. Chem.*, **2**, 297 (1964).

(6) R. Schaffer, *J. Am. Chem. Soc.*, **81**, 2838 (1959).

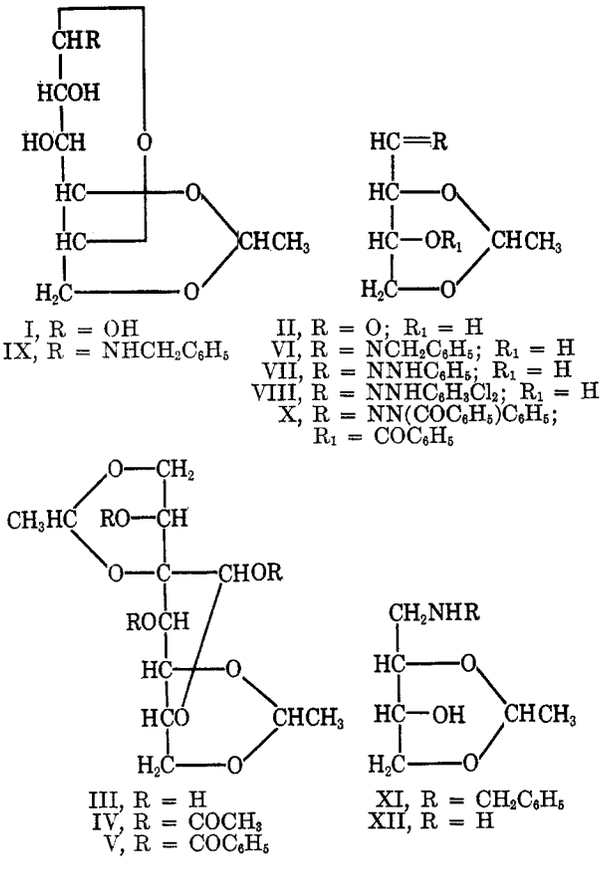
(7) A. S. Perlin, *Methods Carbohydrate Chem.*, **1**, 65 (1962).

(8) A. S. Perlin and C. Brice, *Can. J. Chem.*, **33**, 1216 (1955).

(9) G. G. S. Dutton and K. N. Slessor, *ibid.*, **42**, 614 (1964).

(10) R. Barker and F. Wold, *J. Org. Chem.*, **28**, 1847 (1963).

CHART I



chlorophenylhydrazone (VIII) of 2,4-*O*-ethylidene-D-erythrose were similarly obtained in high yields.

The 2,4-*O*-ethylidene-D-erythrose benzylamine derivative was assigned the structure of a "true Schiff base" (VI). A cyclic structure with a four-membered ring is most improbable. This was confirmed by infrared spectral analysis which revealed an absorption band at 1670 cm.$^{-1}$. The reaction product of 4,6-*O*-ethylidene-D-glucopyranose (I) and benzylamine did not show any absorption in the 1610–1700-cm.$^{-1}$ region and thus is not a Schiff base but the *N*-benzyl-4,6-*O*-ethylidene-D-glucopyranosylamine (IX).

By analogy to the benzylamine Schiff base VI, the 2,4-*O*-ethylidene-D-erythrose phenylhydrazone was assigned the structure of an acyclic hydrazone (VII). Infrared spectral analysis of the hydrazone VII, however, did not show any absorption in the 1610–1700-cm.$^{-1}$ region, while its ultraviolet spectrum showed a peak at 280 mμ (ε 22,000), similar to the absorption of heptaldehyde methylphenylhydrazone [278 mμ (ε 21,100)].[11] Based on spectral analysis, an azo tautomeric structure for the 2,4-*O*-ethylidene-D-erythrose phenylhydrazone could not definitely be excluded. However, Bellamy and Guthrie[12] concluded on the basis of spectral absorption and n.m.r. analyses that phenylhydrazones do not tautomerize to a phenylazo structure in solution.

The monomeric, acyclic hydrazone structure of 2,4-*O*-ethylidene-D-erythrose phenylhydrazone (VII) was further shown by n.m.r. spectroscopy which revealed, in the 6.7–7.5-p.p.m. region, six hydrogen atoms linked to doubly bonded carbon atoms, five of the benzene ring and one of the CH=N grouping. Two "acidic" hydrogen atoms at 2.9 and 7.6 p.p.m. were assigned to the hydroxyl and the imino hydrogen atoms, respectively, of the hydrazone structure VII. The hydrazone VII yielded a diphenylformazan, thus confirming the assigned structure.

Benzoylation of the hydrazone VII produced a crystalline dibenzoate (X) the infrared absorption spectrum of which revealed bands at 1725, 1670, and 1625 cm.$^{-1}$, characteristic of the ester, amide, and C=N bonds, respectively, while n.m.r. analysis showed the 15 aromatic hydrogen atoms at 6.9–8.7 and a doublet at 6.7 p.p.m., assigned to the CH=N grouping hydrogen.

Catalytic reduction of 2,4-*O*-ethylidene-D-erythrose benzylamine Schiff base (VI) with Raney nickel yielded in our hands the crystalline *N*-benzyl-1-amino-1-deoxy-2,4-*O*-ethylidene-D-erythritol (XI), which could be hydrogenolyzed with palladium on carbon at room temperature and 3 atm. to the primary amine, 1-amino-1-deoxy-2,4-*O*-ethylidene-D-erythritol (XII). This compound has been prepared by Ikehara and Ohtsuka,[13] using a different route. The same amine (XII) was prepared by hydrogenolysis of the 2,4-*O*-ethylidene-D-erythrose benzylamine Schiff base (VI) or of the corresponding phenylhydrazone (VII) with palladium-on-carbon catalyst, or by hydrogenolysis of the phenylhydrazone VII with Raney nickel.

Hydrolysis of the primary amine XII with *p*-toluenesulfonic acid yielded the required 1-amino-1-deoxy-D-erythritol as its crystalline *p*-toluenesulfonic acid salt.

Experimental Section[14]

Chromatography (descending) was carried out on Whatman No. 1 paper with 1-butanol–ethanol–water 45:5:49.[15] Reducing sugars were detected with alkaline silver nitrate,[16] nonreducing sugars with anilinium phthalate,[17] and primary amines with ninhydrin.[18] T.l.c. was performed on thin layers of silica gel[19] with the same developer used for paper chromatography. Compounds were detected with naphthoresorcinol–phosphoric acid.[20]

1,3:5,7-Di-*O*-ethylidene-3-*C*-formyl-D-*glycero*-D-*talo*-heptitol-3^1,6-pyranose[6] (III).—4,6-*O*-Ethylidene-D-glucose[3] was oxidized with sodium metaperiodate in the presence of sodium bicarbonate according to Rappoport and Hassid.[4] The concentrated reaction mixture was dried (phosphorus pentoxide, vacuum desiccator) and extracted with boiling ethyl acetate. Crystals appeared on cooling the extract to room temperature. The extract was concentrated and crystallized from absolute ethanol and petroleum ether (b.p. 30–40°). The crystals (7–10%) melted at 198–212° and t.l.c. revealed two spots the weaker of which had the mobility (R_f 0.59) of the dimeric 2,4-*O*-ethylidene-D-erythrose, m.p. 149–150°, reported by Schaffer.[6] Two additional crystallizations formed chromatographically pure (t.l.c. R_f 0.50) fiber-shaped crystals, m.p. 227.5° (liquid bath), $[\alpha]^{29}D$ +50° (*c* 1, water). The mixture melting point with an authentic sample[6]

(11) R. O'Connor, *J. Org. Chem.*, **26**, 4375 (1961).
(12) A. J. Bellamy and R. D. Guthrie, *Chem. Ind.* (London), 1575 (1964).
(13) M. Ikehara and E. Ohtsuka, *Chem. Pharm. Bull.* (Tokyo), **11**, 1095 (1963).
(14) All evaporations were carried out with a flash evaporator at 55° (bath temperature). Melting points were determined on a Fisher-Johns melting point apparatus, except where otherwise stated. Microanalyses were carried out by the Microanalysis Laboratory of the Weizmann Institute of Science, Rehovoth, Israel, except when otherwise specified.
(15) S. M. Partridge, *Biochem. J.*, **42**, 238 (1948).
(16) R. J. Block, E. L. Durrum, and G. Zweig, "Paper Chromatography and Paper Electrophoresis," 2nd Ed., Academic Press Inc., New York, N. Y., 1958, p. 178.
(17) Reference 16, p. 181.
(18) Reference 16, p. 124.
(19) Kieselgel D-5, silica gel for t.l.c., Camag, Muttenz, Switzerland.
(20) K. Randerath, "Thin-Layer Chromatography," D. D. Libman, transl., Verlag Chemie, Weinheim, 1963, p. 200.

was undepressed and the two samples were indistinguishable by t.l.c.: infrared spectrum[21] (Nujol), 3360 and 3425 cm.$^{-1}$ (two bonded hydroxyl groups), no absorption in the 1600–1850-cm.$^{-1}$ region (C=O).

Anal.[22] Calcd. for $C_{12}H_{20}O_8$: C, 49.31; H, 6.9; mol. wt., 292. Found: C, 49.46; H, 7.20; mol. wt., 334.

The di-*O*-ethylideneoctose III (0.2 g.) was hydrolyzed[6] in 0.25 *N* sulfuric acid (10 ml.), and the acetaldehyde was trapped by an ice-cooled, saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid (150 ml.).[23] The acetaldehyde 2,4-dinitrophenylhydrazone was collected on a sintered glass filter, washed, and dried over concentrated sulfuric acid under vacuum, m.p. 157–159° (yield 100%) and no depression with authentic acetaldehyde 2,4-dinitrophenylhydrazone (m.p. 164°). The neutralized hydrolysate, $[\alpha]^{28}D$ +8° (*c* 1.65, water, initial), was chromatographically free of 2,4-*O*-ethylidene-D-erythrose and in some preparations showed several spots, while in others only one (R_f: paper 0.056, t.l.c. 0.30).

1,3:5,7-Di-*O*-ethylidene-3-*C*-formyl-D-*glycero*-D-*talo*-heptitol-3^1,6-pyranose Triacetate (IV).—Di-*O*-ethylideneoctose (III) (0.3 g., 1.03 mmoles) dissolved in pyridine (24 ml.) was acetylated with acetic anhydride (6 ml., 61 mmoles) at ice-bath temperature. The reaction mixture was left at room temperature for 5 hr., treated with ice, and lyophilized. The residue was crystallized from boiling ethanol to form white needles, m.p. 209° (0.30 g., 78%). One crystallization from ethanol raised the melting point to 211–212°, $[\alpha]^{29}D$ +42° (*c* 1.2, chloroform).

Anal. Calcd. for $C_{18}H_{26}O_{11}$ (418): C, 51.67; H, 6.21. Found: C, 51.80; H, 6.50.

Acid hydrolysis of the acetate IV (258 mg.), performed as described above, yielded 266.5 mg. of acetaldehyde 2,4-dinitrophenylhydrazone (12.91% C_2H_4, calcd. 13.39%).

1,3:5,7-Di-*O*-ethylidene-3-*C*-formyl-D-*glycero*-D-*talo*-heptitol-3^1,6-pyranose Tribenzoate (V).—Di-*O*-ethylideneoctose (III) (0.73 g., 2.5 mmoles) dissolved in pyridine (15 ml.) was treated with benzoyl chloride (2.9 ml., 25 mmoles) at ice-bath temperature. After 5 hr. at this temperature, the reaction mixture was poured into ice–water and left overnight. The oily product, dissolved in benzene, was washed with acid and alkali, dried (calcium chloride), treated with Norit, concentrated, and crystallized from benzene and petroleum ether (b.p. 60–80°) to a constant melting point of 182–183°, $[\alpha]^{30}D$ −2.2° (*c* 4.38, chloroform).

Anal. Calcd. for $C_{33}H_{32}O_{11}$ (604): C, 65.56; H, 5.29. Found: C, 65.60; H, 5.20.

2,4-*O*-Ethylidene-D-erythrose Benzylamine Schiff Base (VI).—A solution of 20.6 g. of 4,6-*O*-ethylidene-D-glucose (0.1 mole) in 50 ml. of water was added in portions to a magnetically stirred solution of 42.8 g. of sodium metaperiodate (0.2 mole) in 250 ml. of water, the temperature of the reaction mixture being kept at 20–25° to avoid crystal formation. One hour after all the sugar derivative had been added, the solution was neutralized by careful addition of 29 g. of barium carbonate (0.15 mole) with magnetic stirring. The neutral solution (litmus) was filtered by suction and the cake of inorganic salts was washed with a little cold water. T.l.c. of the clear filtrate showed the presence of 2,4-*O*-ethylidene-D-erythrose (R_f 0.59) only. Benzylamine (16 ml., 0.15 mole) was added dropwise to the filtrate with magnetic stirring and ice-bath cooling. After a short time, the emulsion formed started to crystallize. Stirring and cooling were continued for 1 hr. The crystalline mass was collected by suction, washed with a little cold water, and dried under vacuum with phosphorus pentoxide: m.p. 80–83° (yield 92%). The product was contaminated with some inorganic salts. The Schiff base was soluble in ethanol or ethyl acetate and moderately soluble in warm petroleum ether. The crude dried product was recrystallized from ether to a constant melting point of 88–89°: $[\alpha]^{28}D$ +54.6° → +29.8° (42 hr., *c* 1.98, chloroform); infrared (chloroform), 1670 (C=N strong), 3360 cm.$^{-1}$ (bonded OH strong); n.m.r.[24] 7.1–7.5 (five aromatic hydrogens), 7.9 p.p.m. (one aldehydic hydrogen). The compound is not very stable and turns yellow on storage at room temperature.

Anal. Calcd. for $C_{13}H_{17}NO_3$ (235): C, 66.38; H, 7.23; N, 5.95. Found: C, 66.12; H, 7.15; N, 5.72.

The Schiff base VI could be converted to 2,4-*O*-ethylidene-D-erythrose phenylhydrazone (VII) by adding 10% excess of phenylhydrazine to its ethyl acetate or ethanolic solution, and concentrating after 24 hr. The residual syrup or crystalline mass was crystallized from ethyl acetate and petroleum ether.

2,4-*O*-Ethylidene-D-erythrose Phenylhydrazone (VII).—4,6-*O*-Ethylidene-D-glucose (20.6 g., 0.1 mole) was oxidized with 42.8 g. of sodium metaperiodate (0.2 mole) as described above. A solution of 10.8 ml. of phenylhydrazine (11.9 g., 0.11 mole) in 6.6 ml. of acetic acid and 6.6 ml. of water was added dropwise, with magnetic stirring, to the neutral, aqueous filtrate containing 2,4-*O*-ethylidene-D-erythrose. The crystalline hydrazone formed immediately. The hydrazine solution was added during 0.5 hr., and the stirring was continued for 1 hr. more with cooling in an ice bath. The white crystals were collected by suction and washed with cold dilute acetic acid and with cold water. The dried hydrazone (21 g., 90%) melted at 124–126° and was recrystallized from ethyl acetate and petroleum ether to form white needles: m.p. 127°; $[\alpha]^{25}D$ +54.7° → +37.6° (20 hr., *c* 0.60, chloroform); infrared, no absorption at 1610–1700 cm.$^{-1}$; λ_{max} 280 mμ (ϵ 22,000)[21]; n.m.r. 2.9 and 7.6 (a hydroxylic and an iminic hydrogen), 6.7–7.5 p.p.m. (one aldehydic and five aromatic hydrogens).

Anal. Calcd. for $C_{12}H_{16}N_2O_3$ (236): C, 61.01; H, 6.78; N, 11.86. Found: C, 61.07; H, 6.82; N, 11.89.

2,4-*O*-Ethylidene-D-erythrose 2,5-Dichlorophenylhydrazone (VIII).—2,5-Dichlorophenylhydrazine (9.7 g., 0.055 mole) was dissolved in 100 ml. of water containing 5.0 ml. of concentrated hydrochloric acid with warming. The solution was filtered, cooled, and added dropwise with magnetic stirring to a neutral, filtered solution containing 2,4-*O*-ethylidene-D-erythrose prepared from 0.05 mole 4,6-*O*-ethylidene-D-glucose as described above. The gum formed solidified on vigorous shaking. The reaction mixture was stirred for 1 hr. more and a quantitative yield of the hydrazone, m.p. 140–141°, was collected by suction. Crystallization from ethyl acetate and petroleum ether yielded needles of m.p. 142–143°, $[\alpha]^{23}D$ +26.1° (*c* 2.41, chloroform).

Anal. Calcd. for $C_{12}H_{14}Cl_2N_2O_3$ (304.9): C, 47.22; H, 4.59; N, 9.18. Found: C, 46.96; H, 4.29; N, 9.02.

***N*-Benzyl-4,6-*O*-ethylidene-D-glucopyranosylamine (IX).**—To a solution of 10.3 g. of 4,6-*O*-ethylidene-D-glucose (0.05 mole) in 50 ml. of ethanol was added 5.5 ml. of benzylamine (0.05 mole). The solution was placed on a boiling-water bath for 10 min., a pale yellow coloration appeared, the solution was filtered, and to the filtrate was added 250 ml. of ether. Very long needles or threads started to appear after a short time. Two crystallizations from ethanol and ether did not change the melting point of 125–126°, $[\alpha]^{28}D$ −36.2° → −18.0° (51 hr., *c* 0.52, chloroform). The *N*-glucoside was soluble in methanol, ethanol, ethyl acetate, or dioxane, insoluble in benzene: infrared (Nujol), no absorption at 1610–1700 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{21}NO_5$ (295): C, 61.01; H, 7.11; N, 4.74. Found: C, 60.90; H, 6.92; N, 4.86.

2,4-*O*-Ethylidene-D-erythrose Diphenylformazan.—A benzenediazonium chloride solution (22 mmoles) was kept on ice and added[25] dropwise to a magnetically stirred solution of 2,4-*O*-ethylidene-D-erythrose phenylhydrazone (4.74 g., 20 mmoles, in 20 ml. of pyridine), cooled to −5°. The solution turned dark red and was kept at 3–8° during the addition of the diazonium salt. The solution was stirred for 30 min. more and poured into 200 ml. of ice–water. The dark red precipitate was filtered, washed with cold water, suspended in water, refiltered, and dried over phosphorus pentoxide under vacuum. The crude crop (m.p. 172–175°, 6.8 g., 100%) was recrystallized from ethanol three times, from glacial acetic acid and water, and finally from ethanol and water, m.p. 178°.

Anal. Calcd. for $C_{18}H_{20}N_4O_3$ (340): C, 63.52; H, 5.88; N, 16.47. Found: C, 63.41; H, 6.17; N, 16.31.

3-*O*-Benzoyl-2,4-*O*-ethylidene-D-erythrose *N*-Benzoylphenylhydrazone (X).—Benzoyl chloride (25 ml., 0.22 mole) was added portionwise to an ice-cooled and magnetically stirred solution of 21.5 g. of crude 2,4-*O*-ethylidene-D-erythrose phenylhydrazone (0.1 mole) dissolved in 100 ml. of pyridine. The re-

(21) Infrared spectra were taken with a Perkin-Elmer Model 12C spectrophotometer equipped with a sodium chloride prism. Ultraviolet spectra were taken with a Beckman DU spectrophotometer.

(22) Elementary analysis done by Drs. G. Weiler and F. B. Strauss, Oxford, England.

(23) H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

(24) N.m.r. spectra were determined in deuteriochloroform solution (*ca.* 10%) on a Model A-60 spectrometer, Varian Associates, Inc. The chemical shifts are relative to tetramethylsilane, used as an internal standard.

(25) L. Mester and A. Major, *J. Am. Chem. Soc.*, **77**, 4297 (1955).

action mixture was left at room temperature overnight, most of the pyridine was removed under vacuum, and the residue was poured into ice–water. The oil which separated solidified after a short time. The crystals were dissolved in ethyl acetate and the solution was washed. The residue left after removal of the solvent was crystallized from ethanol to give pointed prisms, m.p. 130–133°. Two additional crystallizations raised the melting point to 134°: $[\alpha]^{21}D$ −40.0° (*c* 3.0, chloroform); infrared, 1725 (ester), 1670 (benzamide), 1625 cm.$^{-1}$ (C=N); n.m.r. 5.7 (one aldehydic hydrogen), 6.9–8.7 p.p.m. (15 aromatic hydrogens).

Anal. Calcd. for $C_{26}H_{24}N_2O_5$ (444): C, 70.27; H, 5.40; N, 6.30. Found: C, 70.23; H, 5.34; N, 6.17.

***N*-Benzyl-1-amino-1-deoxy-2,4-*O*-ethylidene-D-erythritol (XI).**—Crude 2,4-*O*-ethylidene-D-erythrose benzylamine Schiff base (20 g., 0.085 mole) was dissolved in 100 ml. of ethanol. The filtered solution was reduced in a Parr hydrogenation apparatus at room temperature with Raney nickel catalyst[26] at 55 p.s.i. When no more hydrogen was absorbed (*ca.* 24 hr.), the catalyst was filtered off, the filtrate was concentrated to dryness, and the solid residue was crystallized from ethanol (10 g., 43%). Alternate crystallizations from ether and from ethanol to constant melting point formed orthorhombic prisms, m.p. 111°, $[\alpha]^{25}D$ +23.0° (*c* 1.01, chloroform).

Anal. Calcd. for $C_{13}H_{19}NO_3$ (237): C, 65.82; H, 8.01; N, 5.90. Found: C, 65.93; H, 7.91; N, 5.83.

1-Amino-1-deoxy-2,4-*O*-ethylidene-D-erythritol (XII).—The crude 2,4-*O*-ethylidene-D-erythrose benzylamine Schiff base (VI) (23.5 g., 0.1 mole) was dissolved in 100 ml. of ethanol, filtered, and reduced with 1.5 g. of palladium-on-carbon catalyst[27] for 24 hr. as described above. The catalyst was removed by filtration and the filtrate was concentrated to dryness. The crystalline residue was recrystallized from 30 ml. of boiling dioxane to form orthorhombic prisms and pyramids. The crystals were collected by suction and washed with benzene, m.p. 140–142° (10.6 g., 72%, R_f paper 0.28), $[\alpha]^{26}D$ −62.6° (*c* 2.95, water).

Anal. Calcd. for $C_6H_{13}NO_3$ (147): C, 48.97; H, 8.84; N, 9.52. Found: C, 48.68; H, 8.85; N, 9.69.

Reduction of crude 2,4-*O*-ethylidene-D-erythrose phenylhydrazone (VII) (47.2 g., 0.2 mole, in 150 ml. of ethanol) with palladium on carbon (4.0 g.) as described above yielded the amine XII (13.5 g., 46%), m.p. 140°. Reduction of the hydrazone (23.6 g., 0.1 mole) with Raney nickel yielded the amine XII in 74% yield. Some reductions of 0.5 mole of the phenylhydrazone VII or of the Schiff base VI were performed in an autoclave at 80–85° with initial pressure of 1800 p.s.i., with 78% yield.

A solution of the secondary amine XI (12 g.) in ethanol (100 ml.) was catalytically hydrogenated with palladium on carbon. After working up as above, 6.4 g. (75%) of the primary amine XII was obtained.

1-Amino-1-deoxy-D-erythritol *p*-Toluenesulfonic Acid Salt.—A solution of 1-amino-1-deoxy-2,4-*O*-ethylidene-D-erythritol (2.94 g., 0.02 mole) and *p*-toluenesulfonic acid (5.7 g., 0.03 mole) in 100 ml. of water was refluxed for 1 hr. with a stream of air being sucked through the boiling solution. The cooled solution was concentrated under vacuum to a syrup, which was dissolved in boiling methanol, treated with Norit, and crystallized by the addition of ether to turbidity to give elongated prisms, m.p. 112° (5.1 g., 87%). Two recrystallizations from the same solvents yielded the salt of m.p. 112–113°, $[\alpha]^{23}D$ −63.2° (*c* 2.94, water), R_f (paper) 0.06.

Anal. Calcd. for $C_{11}H_{19}NO_6S$ (293): C, 45.05; H, 6.48; N, 4.77; S, 10.92. Found: C, 44.89; H, 6.40; N, 4.79; S, 10.61.

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Neighboring-Group Participation. The Preparation of Derivatives of D-Ribose and L-Lyxose from L-Arabinose[1]

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The selective tosylation of the 3-hydroxyl of methyl 2-O-benzoyl-β-L-arabinopyranoside (I) to give methyl 2-O-benzoyl-3-O-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (II) illustrates the preferential sulfonation of an equatorial hydroxyl over an axial hydroxyl. Treatment of the resulting *trans*-benzoyloxysulfonate II with sodium fluoride in N,N-dimethylformamide caused the displacement of the tosylate and gave methyl 2(3)-O-benzoyl-β-L-lyxopyranoside after hydrolysis of the intermediate ortho ester ion (XI). Similar treatment of methyl 2-O-benzoyl-3,4-di-O-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (III) gave methyl α-D-ribopyranoside derivatives (VII)—an inversion of both carbon atoms originally bearing tosyl groups by means of two successive ortho ester ion intermediates. An analogous series of reactions starting from D-arabinose gave derivatives of L-ribose.

The use of the N-acylate as a participating group in carbohydrates to effect the elimination of a secondary *trans* sulfonate ester and generate a *cis* amino alcohol system is well established.[3] In recent years it has been demonstrated that the O-acyl group can undergo similar reactions,[4,5] albeit not so readily as the N-acyl. There are examples of the failure of the O-acyl group to undergo participation,[6] so it is apparent that the mere occurrence of a sulfonate grouping in the *trans* relationship to an O-acyl group is not in itself sufficient to ensure a participation reaction. Two different reagents have been used successfully in this transformation—sodium benzoate in N,N-dimethylformamide (DMF)[4,5] and sodium fluoride in DMF.[4,7]

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