chloric acid and water, and dried. If an oil resulted, it was extracted with ether and the ether solution washed with water and dried (sodium sulfate). Evaporation of the ether gave an oil which could be crystallized from petroleum ether. Crude product was obtained in yields of 40–95%. After recrystallization over-all yields were 35–85% (Table IV).

Conversion of Acylaminobenzenesulfonamides (I) to II and III.—I (10–20 g.) was heated at 240–250° for 1–2 hr. The crude reaction mass was extracted with boiling benzene[9] and filtered hot giving crude II as the insoluble portion. The benzene solution was concentrated and chromatographed on an alumina column (10 g. of alumina per gram of I). III was eluted with benzene and additional II was obtained by elution with chloroform. The products of the reaction were further purified by recrystallization where necessary (Tables I, IV and V).

Reaction of 2-Amino-4,5-dichlorobenzenesulfonamide (VI) with Substituted Acetic Acids VII.—An equimolar mixture of 2-amino-4,5-dichlorobenzenesulfonamide and the appropriate substituted acetic acid was heated at 240–250° for 1.5 hr. The crude reaction mixture was extracted with hot benzene (100 ml. per gram of VI) giving II as the insoluble portion. The benzene solution was concentrated and chromatographed on an alumina column (10 g. of alumina per gram of I). III was eluted with benzene and additional II was obtained by elution with chloroform. The products of the reaction were further purified by recrystallization where necessary (Tables II, IV and V).

3-(α-Cyclohexyl)benzyl-6,7-dichloro-2*H*-1,2,4-benzothiadiazine 1,1-Dioxide.—A solution of I [R = $CH(C_6H_{11})C_6H_5$] (6.1 g.) and sodium hydroxide (1.1 g.) in water (100 ml.) was refluxed for 16 hr., cooled, and acidified with concentrated hydrochloric acid to give crude product (5.7 g.). This was extracted with boiling benzene (300 ml.) giving II [R = $CH(C_6H_{11})C_6H_5$] (5.1 g., 88%), m.p. 268–270°, as the insoluble portion. The benzene solution was concentrated and chromatographed on an alumina column (60 g. of alumina). No III [R = $CH(C_6H_{11})C_6H_5$] was isolated.

(9) With R = $CH(n\text{-}C_5H_7)C_5H_9$, complete solution in benzene was effected.

Acknowledgment.—The authors are indebted to Drs. P. J. L. Daniels and C. H. Robinson for helpful discussions and to Mr. E. Conner of the Physical and Analytical Chemical Research Department, Schering Corporation, for the microanalyses.

The Configuration of Paromose[1]

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Received April 25, 1963

The diaminohexose (paromose) in the antibiotic paromomycin is shown to be 2,6-diamino-2,6-dideoxy-L-idose. The alkaline degradation of 1,1-bis(alkylsulfonyl)hexitol derivatives was extended to 2,6-diacetamido-2,6-dideoxyhexitol derivatives and afforded 5-acetamido-5-deoxy-L-xylofuranose and the isomeric 5-acetamido-5-deoxy-L-xylopyranose. Deamination of methyl tetra-*O*-acetylparomobiosaminide dihydrochloride followed by acid hydrolysis gave L-galactose and D-ribose. The hexose is shown to be derived from the diaminohexosyl moiety by acetate participation followed by inversion at C-2 and C-3.

Previous communications[2] from these laboratories have dealt with the structure of the antibiotic paromomycin.[3] The configuration at C-2 in the 2,6-diamino-2,6-dideoxyhexose (paromose) in paromomycin was established as being "D-glycero."[2] The total configuration of paromose has now been established; the sugar is shown to be 2,6-diamino-2,6-dideoxy-L-idose.

The 2,6-diamino-2,6-dideoxyhexose in Neomycin B has been suggested to possess the L-ido stereochemistry[4,5] on the basis of optical rotation data of periodate oxidation products and biogenetic considerations. The 2,6-diamino-2,6-dideoxy hexose in Neomycin C was assigned the D-gluco stereochemistry[6] and the assignment was confirmed by the synthesis of 2,6-diamino-2,6-dideoxy-D-glucose.[7,8]

The degradation of the hexoses,[9] 2-amino-2-deoxyhexoses[10] and 3-amino-3-deoxyhexoses,[11] to the lower pentose by reaction of the respective 1,1-bis(alkylsulfonyl) derivatives with aqueous ammonia has been shown. In the case of 2-amino-2-deoxy sugars, the reaction was studied in detail with 2-acetamido-2-deoxy-D-glucose diethyl dithioacetal and a mechanism was proposed for the degradation.[10] Thus, peroxypropionic acid oxidation of the dithioacetal derivative afforded 2-amino-1,1-bis(ethylsulfonyl)-2-deoxy-D-glucitol peroxypropionate which was degraded to D-arabinose in aqueous ammonia. With 3-acetamido-3-deoxy-D-allose[11] and 3-acetamido-3-deoxy-D-altrose[11] derivatives, degradation to the lower pentose occurred during the oxidation of the respective dithioacetals with peroxypropionic acid under nonalkaline conditions.

Alkaline degradation of N,N¹-diacetyl-1,1-bis-(alkylsulfonyl)paromitol derivatives afforded 5-acetamido-5-deoxy-L-xylofuranose[12] (I) and 5-acetamido-5-deoxy-L-xylopyranose (II) thus providing the configuration at the remaining asymmetric carbon atoms in paromose. The success of the reaction with 2,6-diamino-2,6-dideoxyhexose derivatives constitutes an important extension of the degradation. Furthermore, the degradation was possible with N-acetylated 1,1-bis-

(1) Preliminary communication; Abstracts of Papers of the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 19C.

(2) T. H. Haskell, J. C. French, and Q. R. Bartz, *J. Am. Chem. Soc.*, **81**, 3480, 3481, 3482 (1959). The previously reported $[\alpha]D$ for the *p*-nitrophenylhydrazone of N,N′-diacetylparomose is in error. The corrected value is $[\alpha]D^{23}$ +72.2° (*c* 0.5, in 50% methanol-water).

(3) Parke, Davis & Company, U. S. Patent 2,916,485 (December 8, 1959).

(4) (a) K. L. Rinehart, Jr., and A. D. Argoudelis, Abstracts of the 17th National Organic Symposium, Bloomington, Ind., June 25–29, 1961, p. 96; (b) Abstracts of the 1st Interscience Conference on Antimicrobial Agents and Chemotherapy, New York, N. Y., October 31–November 2, 1961.

(5) K. L. Rinehart, Jr., M. Hichens, A. D. Argoudelis, W. S. Chilton, H. E. Carter, M. Georgeadis, C. P. Schaffner, and R. T. Schillings, *J. Am. Chem. Soc.*, **84**, 3218 (1962).

(6) K. L. Rinehart, Jr., P. W. K. Woo, and A. D. Argoudelis, *ibid.*, **80**, 6461 (1958).

(7) H. Weidmann and H. K. Zimmermann, Jr., *Angew. Chem.*, **72**, 750 (1960).

(8) K. L. Rinehart, Jr., M. Hichens, K. Streigler, K. R. Rover, T. P. Culbertson, S. Tatsuoka, S. Horii, T. Yamaguchi, H. Hitomi, and A. Miyake, *J. Am. Chem. Soc.*, **83**, 2964 (1961).

(9) D. L. MacDonald and H. O. L. Fischer, *ibid.*, **74**, 2087 (1952); D. L. MacDonald and H. O. L. Fischer, *Biochim. Biophys. Acta*, **12**, 203 (1953); R. Barker and D. L. MacDonald, *J. Am. Chem. Soc.*, **82**, 2297 (1960).

(10) L. Hough and M. I. Taha, *J. Chem. Soc.*, 3564 (1957).

(11) B. Coxon and L. Hough, *ibid.*, 1463, 1643 (1961).

(12) S. Hanessian and T. H. Haskell, *J. Org. Chem.*, **28**, 2604 (1963).

(alkylsulfonyl) derivatives which unveils a novel aspect of the general reaction.

Methyl paromobiosaminide dihydrochloride[2] (III) reacted with α-toluenethiol and ethanethiol in the presence of fuming hydrochloric acid to yield, respectively, paromose dibenzyl dithioacetal dihydrochloride (IV) and paromose diethyl dithioacetal dihydrochloride (V). Conventional acetylation followed by de-*O*-acetylation of IV and V afforded crystalline N,N′-diacetylparomose dibenzyl dithioacetal (VII) and N,N′-diacetylparomose diethyl dithioacetal (VIII), respectively. Oxidation of VII and VIII with peroxypropionic acid in aqueous methanol at −10° afforded N,N′-diacetyl-1,1-bis(benzylsulfonyl)-1-deoxyparomitol (IX) and N,N′-diacetyl-1,1-bis(ethylsulfonyl)-1-deoxyparomitol (X), respectively. It is noteworthy to mention that no amide cleavage was observed as in the oxidation[10] of 2-acetamido-2-deoxy-D-glucose diethyl dithioacetal under the same conditions. Oxidation of VII with peroxypropionic acid at 0° or at room temperature, however, gave products that contained at least two ninhydrin-positive components on paper chromatograms indicating amide cleavage. The products IX and X were chromatographically homogenous, slightly hygroscopic powders which gave no reaction with acidified potassium iodide solution, barium chloride solution, ninhydrin reagent, and pyridine. The reaction of IX in aqueous ammonia was studied in greater detail. Solutions of IX at pH 10–12 deposited crystalline bis(benzylsulfonyl)methane in two to three hours. Carrying out the reaction at 35–40° or for periods longer than five to six days at room temperature did not offer any advantages. The progress of the reaction was followed by paper chromatography and revealed the formation of the pentose derivatives I and II within as little as ten minutes. This is unusually rapid, since in the case of 2-amino-1,1-bis(ethylsulfonyl)-2-deoxy-D-glucitol peroxypropionate[10] no arabinose was detected after five hours. In the latter case it was shown that a transformation of the intermediate 2,6 - anhydro - 1,1 - bis(ethylsulfonyl) - D - glucotrihydroxyhexane into the corresponding D-manno derivative preceded the degradation to arabinose. Due to the rapid reaction of IX it was not possible to detect similar intermediates on paper chromatograms. The low yields of I and II is ascribed to a competing side reaction and to the instability of I and II in aqueous ammonia.[12] Another factor may be the required elimination of acetamide in place of ammonium chloride as postulated by Hough and Taha.[10] The reaction products were separated by cellulose column chromatography or preparative paper chromatography depending on the amounts available. The pentose derivatives I and II were thus isolated as a colorless sirup and crystalline solid, respectively, and compared with synthetic samples in the D-series.[12] They were converted to the same crystalline 5-acetamido-5-deoxy-L-xylose benzylphenylhydrazone (XI) and 5-acetamido-5-deoxy-L-xylitol (XII). Since the optical rotations of I, II, and XI were of small magnitudes, the rotation of XII in ammonium molybdate solution was studied. In accord with the behavior of other alditols in the same solution,[13] the rotation was increased to a reliable and reproducible magnitude, thus allowing the assignment of an L configuration to I and II and, hence, to paromose. The X-ray diffraction patterns of II and XI were identical with those of the synthetic enantiomorphs.[12] However, a cocrystallized mixture of enantiomorphic II and XI samples showed different X-ray patterns than the individual components. Similarly, the melting points of such cocrystallized mixtures were depressed. Such a behavior is common with enantiomorphic mixtures. Solutions of I or II in distilled water were stable at room temperature but were preferably stored at 5°.[14] Traces of acidic and basic impurities, or heating solutions of pure I or II revealed the presence of the other isomer when examined on paper chromatograms immediately after the elution process. This could be due to effect of impurities on the paper or due to the slight acidity of the solvent mixture (1-butanol–ethanol–water, 4:1:5 by volume). It was shown by Coxon and Hough[15] that 2-acetamido-2-deoxy-D-arabinose and 2-acetamido-2-deoxy-D-ribose were equilibrated in aqueous ammonia in contrast to the corresponding unsubstituted pentoses in which equilibration was insignificant. The equilibration was ascribed to the effect of the 2-acetamido group which would facilitate the enolization of the 2-hydrogen atom. The behavior of I and II in aqueous ammonia was similar to that of ordinary pentoses in that no epimerization was detected.[16] The presence of a 5-acetamido group in I and II, however, induces an equilibration involving a change in *ring size*. It is, therefore, difficult to conclude whether I or II is stereoselectively produced during the degradation process, and rapidly equilibrated, or that I and II are produced simultaneously. Preliminary experiments tentatively favor the first possibility, since paper chromatograms after five to ten minutes of reaction showed a larger proportion of II by comparing the intensities of spots produced by the silver nitrate reagent.[17] After longer periods, the intensities became more or less equal. In general, about 0.5 g. of 2,6-diacetamido-1,1-bis-(alkylsulfonyl)-1,2,6-trideoxyhexitol would give enough 5-acetamido-5-deoxypentose (10–20 mg.) for identification purposes. The 5-acetamido-5-deoxypentose benzylphenylhydrazones in the L-arabino and D-ribo series also have been prepared,[12] so that the configuration of 2,6-diamino-2,6-dideoxyhexoses possessing the gluco or manno, allo or altro, and gulo or ido stereochemistry could be established conveniently by this method.

The alkaline degradation of IX was accompanied by the liberation of benzaldehyde[18] and the formation of a crystalline side-product in high yield. The novel structure of 2,6-diacetamido-2,6-dideoxy-L-idosyl (?) benzylsulfone (XIII) is assigned to this compound. Acetylation of XIII afforded a crystalline diacetate (XIV) indicating the presence of two acetylatable hy-

(13) N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **73**, 2249 (1951).

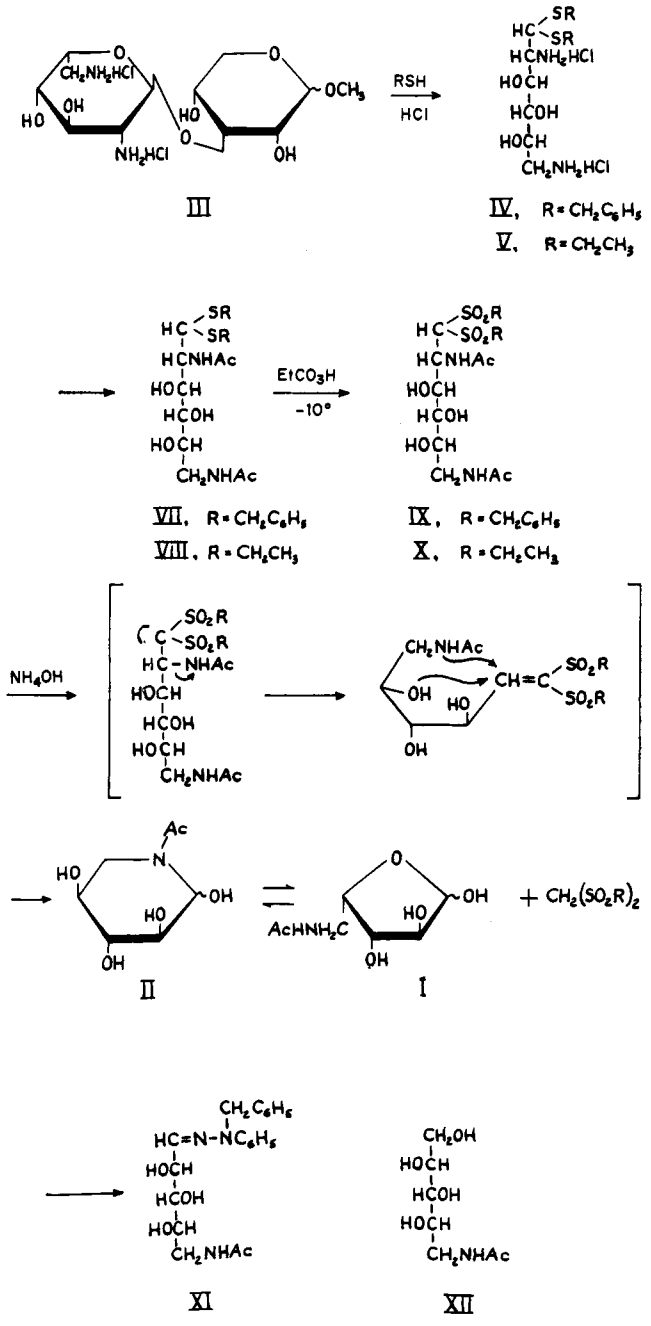
(14) The stability of I and II in the D-series has been studied (see ref. 12).

(15) B. Coxon and L. Hough, *J. Chem. Soc.*, 1577 (1961).

(16) Since the expected 2-epimer, 5-acetamido-5-deoxy-L-lyxose, is unknown, its presence in a minor amount cannot be totally eliminated.

(17) W. E. Trevelyan, D. P. Proctor, and J. S. Harrison, *Nature*, **166**, 444 (1950).

(18) The unexpected formation of benzaldehyde presents an interesting problem. A possible explanation is that the anionic intermediate resulting from the abstraction of the 1-hydrogen in IX could deviate from the expected path of degradation and expel $C_6H_5CH_2SO_2^-NH_4^+$ which could eventually give benzaldehyde.



droxyl groups in a ring structure.[19] Compounds XIII and XIV were investigated by n.m.r. spectroscopy at 60 Mc. The spectrum of XIII in deuterium oxide, using tetramethylsilane as external standard, showed a strong signal at δ 2.45 due to the six hydrogens of the two N-acetyl groups. The signals at δ 5.0 and 7.95 were assigned to the benzylic and aromatic hydrogens, respectively. A series of weak signals in the region δ 3.7–4.4 were attributed to the ring hydrogens. A very weak signal presumably due to the C-1 hydrogen was detected at δ 5.8. This hydrogen, being highly activated by the benzylsulfone grouping, could undergo rapid exchange with deuterium from the solvent causing the observed negligible absorption.

The spectrum of XIV in deuteriochloroform, using tetramethylsilane as internal standard, showed a signal at δ 1.94 due to the six hydrogens of the N-acetyl groups. Sharp signals at δ 2.02, 2.05, 2.08, and 2.12 were assigned to the six hydrogens of the two acetoxy groups. The benzylic and aromatic hydrogens showed signals at δ 4.35 and 7.42, respectively. The C-1 hydrogen appeared as a doublet at δ 5.30. The small spin coupling observed (4 c.p.s.) and the position of the doublet at low field indicates that the C-1 hydrogen is equatorial[20-22] in agreement with the β configuration assigned to XIII and XIV.

Hydrolysis of XIII with 6 *N* hydrochloric acid afforded a nonreducing sirup, which gave a positive test with the ninhydrin reagent and formed a crystalline disalicylidene derivative XV. Thus, acid treatment of XIII caused cleavage of the amide bonds rather than the benzylsulfone grouping. In this respect, the stability of 2-acetamido-2-deoxy-β-D-glucopyranosyl ethylsulfone to dilute acid was previously observed.[10] That XIII was not an intermediate in the degradation of IX, but rather a side-product was ascertained by its stability in aqueous ammonia (pH 10–12) in which it remained unchanged as evidenced by paper chromatography. Paper chromatography experiments also showed that XIII was formed in the degradation after about ten minutes, hence, as rapidly as the formation of I and II from IX. Conditions whereby this competing side-reaction would be suppressed were not investigated. It would seem advantageous to stop the reaction after two to three days in order to minimize the destruction of the formed pentose derivatives in the basic medium. The degradation of X in aqueous ammonia also resulted in poor yields of I and II. Even though a side product equivalent to XIII was not isolated, its possible formation was indicated by paper chromatography.

The mercaptolysis of III produced a crystalline side product in low yield. Chemical analysis and solubility properties suggested that this product was benzylthio paromoside dihydrochloride (XVI). Acetylation gave benzylthio N,N′-diacetylparomoside diacetate (XVII). Selective N-acetylation[23] of XVI or de-*O*-acetylation of XVII gave benzylthio N,N′-diacetylparomoside (XVIII). Oxidation of XVIII with peroxypropionic acid in aqueous methanol at $-10°$ gave N,N′-diacetylparomose benzylsulfone (XIX) which was different from XIII with respect to optical rotation and X-ray diffraction pattern data. They had similar melting points (minor depression when mixed), infrared spectra, and chromatographic properties. These data suggests that XIII and XIX are anomeric compounds. Since XIII had a less negative rotation $[\alpha]^{23}D$ $-13.2°$, than XIX $[\alpha]^{23}D$ $-92°$, the β and α configurations, respectively, are tentatively assigned to XIII and XIX. The benzylthio paromoside derivatives XVII and XVIII had large negative rotations also.[24]

The L-ido stereochemistry assigned to paromose was confirmed by a different approach. When III was deaminated in aqueous acetic acid at 5°, in the pres-

(19) A pyranose ring structure is assigned to XIII, although a furanose form is also possible. Periodate oxidation studies to determine ring size were not done.

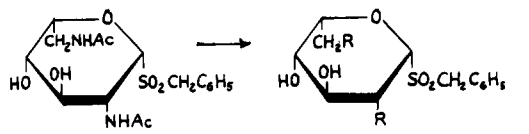
(20) J. N. Shoolery and M. T. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958).

(21) P. W. K. Woo, H. W. Dion, and L. F. Johnson, *ibid.*, **84**, 1066 (1962).

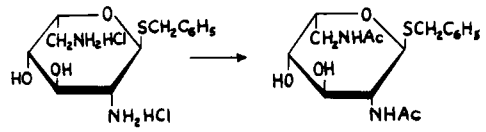
(22) P. W. K. Woo, H. W. Dion, L. Durham, and H. S. Mosher, *Tetrahedron Letters*, 735 (1962).

(23) S. Roseman and J. Ludowieg, *J. Am. Chem. Soc.*, **76**, 301 (1954).

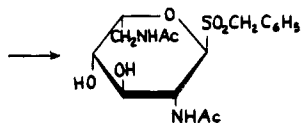
(24) It is assumed that compounds such as XIII and XIX exhibit similar rotational properties as *O*- and *S*-glycosides. In compliance with Hudson's rules [C. S. Hudson, *ibid.*, **31**, 66 (1909); *cf.* W. Pigman, in "The Carbohydrates," Academic Press, Inc., New York, N. Y., 1957, p. 70], the form with the larger negative rotation is designated α.



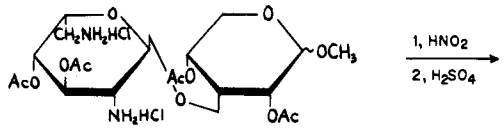
XIII XV, R = N=CH-



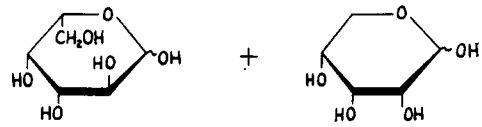
XVI XVIII



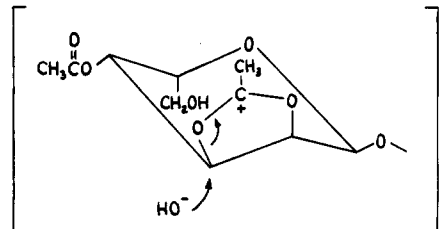
XIX



XXI



XXII D-Ribose



XXIV

ence of sodium nitrite, a complex mixture of products was obtained of which ribose in major part and galactose in trace amounts were identified by paper chromatography after acid hydrolysis of the deamination product. Paromobiosamine dihydrochloride (XX) also gave a mixture of products under the same conditions. It was observed in the case of III and XX that ribose was formed during the deamination reaction and prior to the final acid hydrolysis step. This would imply cleavage of the glycosidic bond during the deamination process, possibly by ring contraction and formation of anhydro derivatives. In order to avoid the formation of such side-products, attention was turned to the deamination of a suitably blocked derivative of III. Deamination of methyl tetra-*O*-acetylparomobiosaminide dihydrochloride (XXI) in aqueous acetic acid at 5° in the presence of sodium nitrite afforded a neutral product, which on acid hydrolysis gave L-galactose (XXII), identified as its crystalline methylphenylhydrazone pentaacetate (XXIII), and D-ribose. Due to the pyranoid ring structure of the diamino sugar moiety in XXI, inversion at C-5 is unlikely to occur during deamination, thus preserving the original configuration at that carbon. The galactose structure could be readily explained if acetate participation at C-2 is considered as in the intermediate XXIV, followed by attack of OH^- at C-3. The net result would be the inversion of configuration at C-2 and C-3. A third component with intermediate mobility between galactose and ribose was detected on paper chromatograms but not investigated further. This component could be L-idose (or L-sorbose)[25] arising from the attack of OH^- at C-2 and resulting in a net retention of configuration at C-2 and C-3. Amino sugars have been deaminated to give a variety of products.[26] To our knowledge, the present case is the first example of the deamination of a diamino sugar derivative.

(25) The facile transformation of L-idose into L-sorbose has been shown; L. Vargha, *Chem. Ber.*, **87**, 1351 (1954).

(26) V. G. Bashford and L. F. Wiggins, *Chem. Ind.* (London), 995 (1955); B. C. Bera, A. B. Foster, and M. Stacey, *J. Chem. Soc.*, 4351 (1956); S. Akiya and T. Osawa, *J Pharm. Soc.* (Japan), **76**, 1276 (1956); *Chem. Abstr.*, **51**, 4284 (1957); S. Inoue and H. Ogawa, *Chem. Pharm. Bull.* (Tokyo), **8**, 79 (1960); *Chem. Abstr.*, **55**, 6385 (1961).

Experimental

Paromose Dibenzyl Dithioacetal Dihydrochloride (IV). A. From III.—A solution containing 12.4 g. of III in 40 ml. of fuming hydrochloric acid was treated at 0° with 35 ml. of α-toluenethiol, and the solution was stirred for 7 days at room temperature. The dark solution was diluted with 10 ml. of water and extracted successively with three 50-ml. portions of benzene and heptane. The aqueous phase was diluted with cold water (20 ml.) and 20 ml. of heptane and stirred for 2 hr. The crystalline product was filtered, and washed with a mixture of isopropyl alcohol–water (1:1), followed by ether, to give 11.2 g. of crude IV. Recrystallization from 130 ml. of isopropyl alcohol containing 5 ml. of water gave pure material (10.6 g.), m.p. 225–230° dec.; $[\alpha]^{23}D$ −126° (*c* 2.5, in methanol).

Anal. Calcd. for $C_{20}H_{28}N_2O_3S_2 \cdot 2HCl \cdot H_2O$: C, 48.09; H, 6.46; N, 5.61; S, 12.84; Cl, 14.20. Found: C, 47.91; H, 6.69; N, 5.73; S, 13.01; Cl, 14.51.

B. From Paromose.[2]—A solution containing 1.5 g. of paromose[2] in 25 ml. of fuming hydrochloric acid was treated at 0° with 10 ml. of α-toluenethiol; the solution was stirred at room temperature for 24 hr., cooled, poured into 20 ml. of water, and processed as before to give 0.56 g. of IV.

Treatment of IV in sodium bicarbonate solution with salicylaldehyde in ethanol in the usual way gave N,N′-disalicylideneparomose dibenzyl dithioacetal (VI) as yellow needles, m.p. 77–78°.

Anal. Calcd. for $C_{34}H_{36}N_2O_5S_2$: C, 66.20; H, 5.88; N, 4.54; S, 10.39. Found: C, 66.49; H, 5.82; N, 4.40; S, 10.32.

N,N′-Diacetylparomose Dibenzyl Dithioacetal (VII).—A solution of IV (10.5 g.) in 50 ml. of pyridine was acetylated with 23 ml. of acetic anhydride and processed in the usual manner to give 13.2 g. of crude peracetylated product. Recrystallization from ethyl acetate–*n*-heptane (1:1) gave 11.85 g. of crystals, m.p. 91–93°. A solution containing 10 g. of this product in 150 ml. of methanol was treated with a small amount of sodium methylate and processed as usual to give 7.5 g. of crude VII. Recrystallization from ethanol–water gave 6.87 g. of pure product, m.p. 82–84°; $[\alpha]^{23}D$ −12.5° (*c* 1.0, in methanol).

Anal. Calcd. for $C_{24}H_{32}N_2O_5S_2 \cdot H_2O$: C, 56.44; H, 6.71; N, 5.48; S, 12.55. Found: C, 56.23; H, 6.81; N, 5.41; S, 12.55.

N,N′-Diacetylparomose Diethyl Dithioacetal (VIII).—A solution containing 4 g. of III in 50 ml. of fuming hydrochloric acid and 40 ml. of ethanethiol was stirred at room temperature for 7 days. The brown mixture was poured in ice–water and neutralized

with lead carbonate; the resulting precipitate was filtered and washed with water. The filtrate was extracted with three 20-ml. portions of chloroform, the aqueous phase was stirred briefly with Amberlite IR 45 (OH^-),[27] the pH was adjusted to 6 with dilute hydrochloric acid, and the resulting solution was evaporated below 40° to a sirup. Repeated evaporation from methanol afforded 3.8 g. of V as a glass which was not further purified. The sirup was dissolved in 20 ml. of pyridine and was treated dropwise with stirring with 15 ml. of acetic anhydride over a period of 30 min. After 24 hr. at room temperature, the mixture was processed in the usual manner to give 5.6 g. of a dark sirup containing crude N,N′-diacetylparomose diethyl dithioacetal triacetate. The latter was dissolved in 20 ml. of a mixture of isopropyl alcohol and ethyl acetate (1:1 by volume) and was added to a column (1.5 × 20 cm.) containing alumina (neutral grade).[28] The column was developed with 150 ml. of the same solvent mixture, and the pale yellow effluent was combined with 30 ml. of washings and evaporated to a pale yellow sirup. Evaporation of the sirup from ether gave a hygroscopic glass (3.8 g.); the infrared spectrum showed both ester and amide absorption bands and no hydroxyl bands.

The product was de-*O*-acetylated in the usual manner to give a glass. The latter was dissolved in isopropyl alcohol and filtered from some insoluble matter. The filtrate was evaporated to a colorless sirup which solidified under ether (24 hr.) to give VIII (1 g.), m.p. 137–139°; recrystallized from isopropyl alcohol–ether, m.p. 138–139°; $[\alpha]^{23}D$ −21.6° (*c* 1.11, in methanol).

Anal. Calcd. for $C_{14}H_{28}N_2O_5S_2$: C, 45.62; H, 7.65; N, 7.60; S, 17.40. Found: C, 45.85; H, 7.42; N, 7.72; S, 17.22.

Benzylthio Paromoside Dihydrochloride (XVI).—The aqueous filtrates from the preparation of IV were evaporated to dryness to give a tan gum. This was extracted with aqueous isopropyl alcohol. The extracts were then allowed to evaporate to dryness slowly to give a semicrystalline sirup. Recrystallization from ethanol–ether gave XVI (121 mg.), m.p. 230–232° dec.; $[\alpha]^{23}D$ −32.6° (*c* 0.43, in water).

Anal. Calcd. for $C_{13}H_{20}N_2O_3S\cdot 2HCl\cdot 0.5H_2O$: C, 42.62; H, 6.32; N, 7.64; S, 8.75. Found: C, 42.45; H, 6.23; N, 7.61; S, 8.74.

Acetylation of XVI in the usual manner gave XVII, m.p. 245–246°; $[\alpha]^{23}D$ −157° (*c* 0.78, chloroform).

Anal. Calcd. for $C_{21}H_{28}N_2O_7S$: C, 55.73; H 6.23; N, 6.19; S, 7.08. Found: C, 55.35; H, 6.28; N, 6.20; S, 7.08.

Benzylthio N,N′-Diacetylparomoside (XVIII). A. From XVI.—To a solution containing 0.372 g. of XVI in 10 ml. of methanol was added a small amount of sodium methylate. The solution was left 3.5 hr. at room temperature and evaporated to dryness, the residue was taken up in methanol and neutralized, and the solution was evaporated again. The solid residue (0.284 g.) was recrystallized from isopropyl alcohol to give XVIII, m.p. 225–227°; $[\alpha]^{23}D$ −206° (*c* 1.32, in methanol). The mother liquors afforded a further 38 mg. of product, m.p. 224–226°.

Anal. Calcd. for $C_{17}H_{24}N_2O_5S$: C, 55.41; H, 6.56; N, 7.60; S, 8.70. Found: C, 55.44; H, 6.38; N, 7.33; S, 8.65.

B. From XVII.—A solution of 24 mg. of XVII in 1 ml. of water and 0.1 ml. of methanol containing 0.8 ml. of Dowex-2 (CO_3^{-2})[29] was cooled to 5° and treated with 0.06 ml. of acetic anhydride. After stirring at 5° for 90 min., the mixture was filtered and processed as usual to give a crystalline product; recrystallization from isopropyl alcohol gave 10 mg. of XVIII.

N,N′-Diacetyl-1,1-bis(benzylsulfonyl)-1-deoxyparomitol (IX).—A solution containing 1.02 g. of VII in 10 ml. of methanol was cooled to −10° and treated dropwise with 4.3 ml. of 3.7 *M* peroxypropionic acid with stirring. After 1 hr. at −10° the solution was allowed to warm to room temperature, stirred 2 hr., and concentrated below 37° under vacuum to a sirup which was repeatedly evaporated from methanol to give a brittle gum. Trituration with ether afforded a white solid (1.19 g.) that liberated iodine from an acidified potassium iodide solution due to the presence of residual peroxypropionic acid, but did not give a precipitate with barium chloride solution.[10] The product was purified by repeated evaporation from methanol and precipitated by adding ether; yield 0.82 g., m.p. 125° (softens 108°); $[\alpha]^{23}D$ −31.4° (*c* 1.05, in methanol). The infrared spectrum showed strong amide bands at 1680 and 1540 $cm.^{-1}$. The ultraviolet spectrum in ethanol showed peaks at 217 (E^1_1 404), 253, 259, 264, and 270 mμ (E^1_1 6–10). The product migrated as a homogenous spot R_f 0.78 on paper chromatograms in the system 1-butanol–ethanol–water (4:1:5 by volume) (solvent A) and R_f 0.86 in pyridine–1-butanol–water (6:4:3 by volume) (solvent B); detected with the periodate–silver nitrate reagent or silver nitrate[17] alone (slow); no color with ninhydrin.

Anal. Calcd. for $C_{24}H_{32}N_2O_9S_2$: C, 51.78; H, 5.79; N, 5.03; S, 11.51. Found: C, 51.8; H, 5.76; N, 5.04; S, 11.5.

When the addition of peroxypropionic acid solution was done at 0° or at room temperature, the product consisted of several ninhydrin-positive components on paper chromatograms.

N,N′-Diacetyl-1,1-bis(ethylsulfonyl)-1-deoxyparomitol (X).—To a solution containing 0.7 g. of VIII in 70 ml. of methanol was added 25 ml. of 3.5 *M* peroxypropionic acid at −10° over a period of 30 min. The clear solution was stirred 1 hr. at −10°, stored at 5° overnight, and evaporated to a sirup which was repeatedly evaporated from methanol until only traces of peroxypropionic acid remained. The final sirup was taken up in methanol, and ether was added to the point of incipient turbidity to give 0.745 g. of X as a hygroscopic powder. This product was transformed to a glass on storing at room temperature; $[\alpha]^{23}D$ 12.8 (*c* 0.78, in methanol). X migrated as a homogenous spot, R_f 0.74 in solvent B.

Reaction of IX with Aqueous Ammonia.—To 50 ml. of a 2 *N* ammonium hydroxide solution was added IX (2.2 g.) with stirring. The pH was adjusted to 12 with 2 *N* ammonium hydroxide and the final volume of the solution adjusted to 65 ml. The solids dissolved within a few minutes and the solution was transferred to a stoppered flask from which aliquots were withdrawn and chromatographed on paper in solvent A. After 10 min. a sample showed essentially four spots consisting of unchanged IX, a slower spot R_f 0.68, and two pentose spots R_f 0.39 and 0.25. Only the pentose spots reacted with aniline hydrogen phthalate reagent.[30] A fine precipitate usually appeared within 2–3 hr., and a strong odor of benzaldehyde could be detected in the reaction mixture. Chromatography after 5 days showed the same spots except that the IX spot was virtually absent. The intensity of the spot with R_f 0.68 was increased substantially while the spots having R_f 0.39 and 0.25 were only moderately increased compared to a chromatogram run after a 24-hr. reaction period. When reaction was judged complete (about 3–5 days), the precipitate was filtered and washed with a little water followed by petroleum ether (b.p. 30–60°) to give 300 mg. of bis(benzylsulfonyl)methane, m.p. 217° (lit.[31] m.p. 207.5°).

Anal. Calcd. for $C_{15}H_{16}O_4S_2$: C, 55.53; H, 4.97; S, 19.76. Found: C, 55.61; H, 4.95; S, 19.68.

The filtrate was extracted with three 50-ml. portions of chloroform, and the aqueous phase was evaporated *in vacuo* below 40° to a small volume. The solution was stored at 5° overnight and filtered from a small amount of insoluble residue. The filtrate was evaporated to dryness and the residue, in turn, evaporated several times from ethanol and finally from ether to give a brittle pale yellow solid (1.9 g.). Chromatography in solvent A showed the same three spots R_f 0.68, 0.39, and 0.25.

Isolation of 5-Acetamido-5-deoxy-L-xylofuranose (I) and 5-Acetamido-5-deoxy-L-xylopyranose (II).—The preceding solid (1.9 g.) was dissolved in 10 ml. of the solvent mixture ethyl acetate–pyridine–water (12:5:4 by volume) (solvent C), the solution was added to a column containing 100 g. of cellulose powder,[32] the column was developed with solvent C, and fractions (6 ml.) were collected with an automatic collector. Examination of the fractions by thin layer chromatography on silica gel[33] plates (dried at room temperature) using the solvent system ethyl acetate–isopropyl alcohol–water (195:75:35 by volume) and by paper chromatography using solvent A, revealed that fractions 40–80 contained the component with R_f 0.68 together with some X, fractions 80–108 contained the component with R_f 0.39, and fractions 110–128 contained the R_f 0.25 component. The intermediate fractions were combined and evaporated to dryness *in vacuo* below 40°, the residue was dissolved in a little water and filtered through a pad containing Celite and Darco G-60, and the filtrate was evaporated to give I as a colorless sirup (50 mg.). When chromatographed in solvent A, I showed one spot, R_f 0.39, and a

(27) A product of Rohm and Haas Co., Philadelphia, Pa.

(28) A product of M. Woelm, Germany.

(29) A product of the Dow Chemical Co., Midland, Mich.

(30) S. M. Partridge, *Nature*, **164**, 443 (1949).

(31) E. Lanes, *Ber.*, **25**, 347 (1925).

(32) Genuine Whatman, standard grade, W. and R. Balston, Ltd., England.

(33) Silica gel G for thin layer chromatography, E. Merck, Darmstadt, Germany.

trace of the component with R_f 0.25; it gave an orange color with the aniline hydrogen phthalate[30] spray. A portion (20 mg.) was purified by preparative paper chromatography using solvent A. The zone with R_f 0.39 was located, cut, and eluted with water. Examination of the eluate on paper chromatograms still showed the presence of the R_f 0.25 component in addition to I, indicating a transformation of I into the component with R_f 0.25 during the elution or chromatography processes.

Fractions containing the R_f 0.25 component were similarly combined and processed as before to give a semicrystalline sirup (70 mg.). Examination on paper chromatograms revealed the presence of I in trace amounts in addition to the expected II. Trituration of the sirup with moist ethanol and acetone gave 10 mg. of II as colorless crystals, m.p. 160–162° (lit.[12] m.p. 163–164° for the synthetic D-enantiomorph). X-Ray powder diffraction data[34] were 8.22 wm, 7.34 m, 6.17 s, 5.80 m, 5.16 m, 4.23 m, 4.08 s, 3.75 m, 3.64 w, 3.48 w, 3.39 w, and 3.23 w. II gave a pink color with the aniline hydrogen phthalate[30] spray.

A sample of II (2 mg.) was cocrystallized with 2 mg. of the crystalline synthetic enantiomorph[12] from moist ethanol–acetone to give a product (m.p. 150–155°) having a different X-ray diffraction pattern than either enantiomorph. Crystalline II was stable and remained homogenous in neutral aqueous solution for a period of 2 weeks. Dilute acids or bases caused equilibration between I and II as evidenced by paper chromatography experiments. Prolonged exposure of either I or II to dilute acids or bases produced slow moving ninhydrin-positive spots on paper chromatograms.

5-Acetamido-5-deoxy-L-xylose Benzylphenylhydrazone (XI).—A solution containing 14 mg. of I in 1 ml. of water and 3 ml. of ethanol was treated with 18 mg. of benzylphenylhydrazine hydrochloride and 41 mg. of sodium acetate, and the mixture was gently refluxed for 2.5 hr. The solution was cooled, treated with decolorizing carbon, filtered through a thin bed of Celite, and the filtrate was evaporated to dryness. The residue was suspended in 3 ml. of water, and extracted with three 15-ml. portions of chloroform; the extracts were dried over anhydrous sodium sulfate and evaporated to a sirup. This was dissolved in ethanol and filtered from a trace of insoluble matter. The filtrate was evaporated, and the residue crystallized from a mixture of ether–petroleum ether. The product (12 mg.) was recrystallized from a mixture of methanol, ether, and petroleum ether to give XI (8 mg.), m.p. 128° (lit.[12] m.p. 132–133°), m.m.p. 127–129°; $[\alpha]^{23}D$ 0 + 2° (*c* 0.26, in methanol).[35]

The same product was obtained when II was used instead of I in essentially the same yield and purity.

Anal. Calcd. for $C_{20}H_{25}N_3O_4$: C, 64.67; H, 6.78; N, 11.31. Found: C, 64.31; H, 6.58; N, 11.10.

A sample of XI (2 mg.) was cocrystallized with 2 mg. of the synthetic D-enantiomorphic benzylphenylhydrazone[12] from a mixture of methanol, ether, and petroleum ether. The product had an X-ray diffraction pattern different from either enantiomorphic derivative and the melting point was depressed, m.p. 122–123°.

5-Acetamido-5-deoxy-L-xylitol (XII).—A solution containing 15 mg. of I in 2 ml. of water was cooled to 5° and treated with 20 mg. of sodium borohydride. After 3 hr. at 5°, the solution was acidified with 2 *N* acetic acid (pH 5.5), and passed over a column containing 2 ml. of Dowex 50 X 2 (H^+). The effluent evaporated to yield a nonreducing sirup (10 mg.); $[\alpha]^{23}D$ −41.4° (*c* 0.7, in 5% ammonium molybdate).[36] The product showed a single spot, R_f 0.26, when chromatographed on paper in solvent A.

Reduction of II at 5° overnight afforded a product identical with the one obtained before.

Reaction of X with Aqueous Ammonia. Isolation of I and II.—A solution of 0.61 g. of X in 60 ml. of aqueous ammonia was adjusted to pH 11. The pale yellow solution deposited a crystalline precipitate within 24 hr. An aliquot showed spots corresponding to I and II on paper chromatograms in addition to starting material and an intermediate spot, R_f 0.54. After 3 days the precipitate was filtered and washed with ether to give 15 mg. of bis-(ethylsulfonyl)methane, m.p. 100° (lit.[10] m.p. 102°). The filtrate was extracted with three 15-ml. portions of chloroform. The aqueous layer was evaporated under 40° to give a dark yellow sirup (0.58 g.). The latter was separated on three Whatman no. 3 sheets (17 × 40 cm.) in solvent A. Zones corresponding to I and II were cut, eluted with water, and processed as described before to give I (15 mg.) and II (12 mg.) as homogenous sirups. The same XI was obtained from either I or II.

Isolation of N,N′-Diacetylparomose β(?)-Benzylsulfone (2,6-Diacetamido-2,6-dideoxy-L-idosyl-β(?)-benzylsulfone) (XIII).—Fractions containing the R_f 0.68 component from the cellulose column chromatography experiment described in the reaction of IX with aqueous ammonia were allowed to evaporate slowly to dryness. The crystalline residue was triturated with a mixture of ethanol and acetone (1:1); the crystals were filtered and washed with cold ethanol and then ether to give 0.72 g. of product in two crops, m.p. 175–176°. Recrystallization from a mixture of methanol, ether, and pentane gave 0.6 g. of XIII, m.p. 177–178°; $[\alpha]^{23}D$ −13.2 (*c* 0.53, in water). The product did not reduce warm Fehling solution and exhibited characteristic amide bands in the infrared spectrum and aromatic absorption in the ultraviolet spectrum. It was homogenous on paper chromatograms in solvent A and had R_f 0.69. X-Ray powder diffraction data[34] were 12.9 vs, 11.63 vw, 6.83 m, 6.55 wb, 5.45 vw, 4.56 vs, 4.37 m, 4.07 s, 3.98 wb, 3.80 w, 3.62 w, 3.33 wm, and 3.20 w.

Anal. Calcd. for $C_{17}H_{24}N_2O_7S \cdot 0.5H_2O$: C, 49.87; H, 6.15; N, 6.84; S, 7.83. Found: C, 50.06; H, 6.62; N, 6.57; S, 7.42.

Hydration was confirmed by v.p.c.

An amount (10 mg.) of XIII was dissolved in 4 ml. of aqueous ammonia (pH 11). Aliquots were withdrawn at intervals and chromatographed on paper in solvent A. After 27 hr. only XIII could be detected.

N,N′-Diacetylparomose β(?)-Benzylsulfone Diacetate (XIV).—To a solution containing 40 mg. of XIII in 1 ml. of pyridine was added 1 ml. of acetic anhydride with cooling. The solution was left standing at room temperature overnight, poured into ice–water, stirred for 2 hr., and extracted with chloroform. Drying and evaporation of the extract gave a residue which was recrystallized twice from a mixture of methanol, ether, and heptane to give 48 mg. of the diacetate XIV, m.p. 135–137°; $[\alpha]^{23}D$ −22.6° (*c* 1.42, in chloroform).

Anal. Calcd. for $C_{21}H_{28}N_2O_9S$: C, 52.19; H, 5.84; N, 5.79; S, 6.63. Found: C, 51.96; H, 6.16; N, 5.35; S, 6.10.

N,N′-Disalicylideneparomose β(?)-Benzylsulfone (XV).—A solution containing 50 mg. of XIII in 2 ml. of 6 *N* hydrochloric acid was heated on a steam bath for 3 hr. The solution was neutralized with Amberlite IR 45 (OH^-), and filtered and evaporated to a nonreducing colorless sirup which gave a positive test with ninhydrin. The product was dissolved in 5 ml. of water and treated with solid sodium bicarbonate until the solution was slightly alkaline, then treated with 1 ml. of ethanol containing 0.2 ml. of salicylaldehyde. The turbid solution was stirred for a few minutes, treated with a few drops of ethanol followed by water, and stored in the icebox. The product was recovered by filtration and washed with cold water to give yellow needles (50 mg.). Recrystallization was effected by dissolving in a minimum amount of hot ethanol, centrifugation to remove a trace of insoluble material, and addition of water to the clear yellow supernatant to the point of incipient turbidity, m.p. 98–99°.

Anal. Calcd. for $C_{27}H_{28}N_2O_7S$: N, 5.33; S, 6.11. Found: N, 5.23; S, 6.29.

N,N′-Diacetylparomose α(?)-Benzylsulfone (2,6-Diacetamido-2,6-dideoxy-L-idosyl-α(?)-benzylsulfone (XIX).—To a solution containing 0.18 g. of XVIII in 50 ml. of methanol was added 1.5 ml. of 3 *M* peroxypropionic acid at −10° with stirring. After 1 hr. at −10° the solution was kept at 5° overnight and stirred with Amberlite IR 45 (OH^-). The resin was filtered; the filtrate was evaporated to a sirup and the latter evaporated from methanol several times. The final sirupy residue was taken in a small volume of methanol and ether was added to precipitate the product (62 mg.). Two recrystallizations from a mixture of methanol, ether, and pentane gave pure material, m.p. 172–174°; mixed with XIII, m.p. 176–178°; $[\alpha]^{23}D$ −92° (*c* 0.5, in water). The infrared spectrum was identical with that of XIII. On paper chromatograms in solvent A, XIX moved slightly faster (R_f 0.71) than XIII. X-Ray powder diffraction data gave 15.23 w, 13.19 s, 11.85 m, 9.82 ms, 8.46 vw, 7.08 wb, 6.39 m, 5.62 vw, 4.65 ms, 4.40 m, 4.03 wm, 3.83 wb, and 3.45 wb.

Anal. Calcd. for $C_{17}H_{24}N_2O_7S \cdot H_2O$: N, 6.69; S, 7.66. Found: N, 6.27; S, 8.07.

Methyl Tetra-*O*-acetylparomobiosaminide Dihydrochloride (XXI).—A solution containing 2 g. of III in 2 ml. of methanol was

(34) Interplanar spacing, Å., Cu Kα radiation. Relative intensities estimated visually: s, strong; m, medium; w, weak; v, very; b, broad.

(35) The failure to observe optical rotation was not due to the low concentrations used, since concentrations of 2–3% showed negligible rotations when 5-acetamido-5-deoxy-D-xylose benzylphenylhydrazone was studied.[12]

(36) The enantiomorphic 5-acetamido-5-deoxy-D-xylitol[12] showed $[\alpha]^{23}D$ 73.2° (*c* 0.43, in 5% ammonium molybdate).

treated with 30 ml. of 0.5 *N* perchloric acid in anhydrous acetic acid[37] followed by 16 ml. of acetic anhydride. The solution was left at room temperature for 5 hr., diluted with 30 ml. of water, and stored at 5° overnight. The pale yellow solution was passed over a column containing 50 ml. of Amberlite IRA-410 (acetate form) and the column was washed with water. The effluent and washings were combined, treated with 4 ml. of 2 *N* hydrochloric acid, and lyophilyzed to give 2.74 g. of XXI as a very hygroscopic solid. The infrared spectrum showed no amide bands but exhibited large bands at 1750 and 1605 cm.$^{-1}$ due to acetate and amine hydrochloride groups. The product became discolored and decomposed after 48 hr. at room temperature. For microanalysis a sample was dried at room temperature overnight in a vacuum desiccator. In subsequent preparations the product was used in the next step within 24 hr.

Anal. Calcd. for $C_{20}H_{34}N_2O_{12}\cdot 2HCl\cdot 4H_2O$: N, 4.41; Cl, 11.17. Found: N, 4.42; Cl, 11.17.

Deamination of XXI. Isolation and Characterization of L-Galactose (XXII).—To a cooled (0°) solution containing 1.72 g. of XXI in 10 ml. of water and 5 ml. of 2 *N* acetic acid was added a cold solution of 0.46 g. of sodium nitrite in 5 ml. of water with stirring in an atmosphere of nitrogen. The solution was allowed to stand at 5° overnight, and then extracted with three 30-ml. portions of ethyl acetate. The extracts were dried over sodium sulfate and evaporated to a sirup (0.96 g.). The sirup showed an elongated spot (5 cm.) $R_{galactose}$ 2.42 in isopropyl alcohol–water (4:1 by volume, solvent D). The sirup (0.9 g.) was dissolved in 50 ml. of 1 *N* sulfuric acid and heated on a steam bath for 1.5 hr. The cooled solution was extracted with two 15-ml. portions of ethyl acetate and the extracts were discarded. The aqueous phase was evaporated to a small volume and neutralized with barium hydroxide. The precipitate was filtered through a thin bed of Celite and the filtrate was passed over a column containing 15 ml. of Dowex 50X4 (H^+). The effluent was stirred with Amberlite IR45 (OH^-) until neutral, and evaporated to a colorless sirup (0.32 g.). Examination on paper chromatograms in solvent D showed essentially three distinct spots with R_f 0.3, 0.38, and 0.45 in increasing order of intensity. The medium and fast spots were subsequently identified as galactose and ribose, respectively. The sirup was separated on two Whatman no. 3 sheets (19 × 40 cm) in solvent D. The respective zones were cut and eluted to give three fractions: (1) R_f 0.45, 0.2 g. (ribose); (2) R_f 0.38, 37 mg. (galactose) and (3) R_f 0.30, 21.9 mg. (not further investigated).

A solution containing 22 mg. of material from fraction 2 was dissolved in 0.5 ml. of water and treated with 0.16 ml. of a solution containing 12 ml. of methylphenylhydrazine in 50 ml. of ethanol and 1.5 ml. of acetic acid. The solution was warmed briefly, then cooled, and the crystalline product was filtered to give 12 mg. of L-galactose methylphenylhydrazone. Recrystallization from aqueous ethanol gave pure material, m.p. 191–192°. An authentic sample of D-galactose methylphenylhydrazone prepared in the same way had m.p. 191–192°, m.m.p. 190–191°.

A portion (8 mg.) was acetylated in pyridine and acetic anhydride to give L-galactose methylphenylhydrazone pentaacetate (XXIII), m.p. 141–142°; $[\alpha]^{23}D$ −28° ± 0.7° (*c* 0.142, in 95% ethanol).[38] An authentic sample of D-galactose methylphenylhydrazone pentaacetate had m.p. 142–143°; mixed with XXIII, m.p. 129–131°; $[\alpha]^{23}D$ 38.9° ± 0.7° (*c* 0.142, in 95% ethanol).[38]

In another experiment the deamination product was hydrolyzed with 1 *N* sulfuric acid and processed as before. A portion of the neutralized hydrolyzate (0.15 g.) was dissolved in solvent C and added to a column containing 20 g. of cellulose powder[32]; the column was developed with the same solvent mixture and 3-ml. fractions were collected. The fractions consisting mainly of galactose were combined and evaporated to give 8 mg. of a sirup. Purification by preparative paper chromatography gave 6 mg. of a sirup having a strong negative rotation. On paper chromatograms the sirup gave one spot corresponding to galactose.

Deamination of III and XXIII.—To a solution containing 65 mg. of III in 3 ml. of water was added 0.12 g. of sodium nitrite followed by 4 ml. of 10% acetic acid at 0°. After standing at 5° overnight, the solution was passed over a cold column containing 3 ml. of Dowex 50X 4 (H^+), and the effluent and washings were evaporated to a small volume. Paper chromatography at this stage showed the presence of ribose and a faster elongated zone. The product was hydrolyzed with dilute hydrochloric acid and processed as before to give a dark sirup (20 mg.). Chromatography on paper showed the presence of ribose (strong), galactose (weak), and considerable tailing.

Deamination of XX in the same way showed the presence of ribose and galactose as before. When deamination was arrested after 2 hr. at 0° and processed as before, paper chromatography showed the presence of ribose (strong), galactose (weak), and at least two faster moving spots which gave a pink color with aniline hydrogen phthalate.[30]

NOTE ADDED IN PROOF.—2,6-Diamino-2,6-dideoxy-L-idose has been synthesized recently and found to be identical with paromose.[39]

Acknowledgment.—The authors wish to thank Dr. J. M. Vandenbelt and his associates of Parke, Davis & Company for spectral, X-ray diffraction, and optical rotation data, and C. E. Childs and associates for microanalyses.

(37) Prepared by mixing 1.43 g. of 70% perchloric acid with 2.3 ml. of acetic anhydride and diluting to 100 ml. with acetic acid.

(38) Measured with the Bendix-Ericsson polarimeter. We wish to thank Miss E. M. Tanner of Parke, Davis & Co., Hounslow, England, for this measurement.

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Synthesis of 5-Acetamido-5-deoxypentoses. Sugar Derivatives Containing Nitrogen in the Ring[1]

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Received April 25, 1963

The synthesis of 5-acetamido-5-deoxypentopyranoses and the isomeric 5-acetamido-5-deoxypentofuranoses having the D-xylo, D-ribo, and L-arabino configurations is described. In the D-ribo series, 5-acetamido-5-deoxy-D-ribofuranose was the predominant product of two independent syntheses. The stability, chromatographic properties, and n.m.r. spectra of these compounds are reported. The pentopyranose derivatives represent a new class of carbohydrate derivatives in which the ring oxygen is replaced by nitrogen.

In a preceding publication[2] the successful adaptation of the alkaline degradation of 1,1-bis(alkylsulfonyl)aminohexitol derivatives[3] to a 1,1-bis(alkylsulfonyl)-2,6-diacetamido-2,6-dideoxyhexitol was demonstrated. The expected degradation product was a 5-acetamido-5-deoxypentose. Since the 5-acetamido-5-deoxypentoses were not known at that time, their synthesis for use as model compounds was undertaken in this laboratory. Such derivatives are shown to be formed as an equilibrium mixture of 5-acetamido-5-

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