Acknowledgment. We are indebted to Dr. R. W. Jeanloz for the authentic samples of 2-acetamido-2-deoxy-3-*O*-methyl-D-glucose, 2-acetamido-2-deoxy-3,6-di-*O*-methyl-D-glucose, and 2,4-di-*O*-methyl-*N*-phenyl-D-galactosylamine; to Prof. R. Kuhn for 2,4,6-tri-*O*-methyl-D-galactose; and to Prof. E. Chargaff for 2,3,4,6-tetra-*O*-methyl-D-galactose.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Synthesis of Amino Sugars by Reduction of Hydrazine Derivatives. 2-Amino-2-deoxy-L-lyxose (L-Lyxosamine) Hydrochloride[1-3]

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2-Amino-2-deoxy-L-lyxose (L-lyxosamine) has been synthesized as the crystalline hydrochloride by reduction and hydrolysis of the derivatives obtained by the action of hydrazine on methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-α,β-L-xylofuranoside. The mechanism of the displacement of the *p*-tolylsulfonyloxy group by hydrazine is discussed.

It is now well established[3-7] that the nucleophilic displacement of secondary *p*-tolylsulfonyloxy groups in sugar rings by hydrazine, amines, and probably ammonia takes place with Walden inversion when no suitably placed participating group is available. Hydrazinolysis of secondary *p*-toluenesulfonate esters proceeds under milder conditions than ammonolysis, and reduction of the resulting hydrazino sugars gives better yields of amino sugars. This synthetic route has been successfully used in this Laboratory for the preparation of the 2-amino-2-deoxy derivatives of the pentoses D-ribose,[3] L-ribose,[8] and D-lyxose.[3]

Although hydrazinolysis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranose[9] gives the 3-deoxy-3-hydrazino-D-allose derivative[5,6,8] as the major product, a side reaction leads to the formation of an unsaturated sugar, believed to be a 3,4-glycosene derivative.[9] This alternative reaction mechanism may be partly responsible for the relatively low yields of 2-amino-2-deoxy pentoses prepared by hydrazinolysis of *p*-toluenesulfonate esters.[3,8,10]

The present work is concerned with the synthesis of 2-amino-2-deoxy-L-lyxose, the enantiomorph of the previously described 2-amino-2-deoxy-D-lyxose.[3,10] Seven of the eight possible 2-amino-2-deoxypentoses have now been reported[3,6,8,10-12]; 2-amino-2-deoxy-L-xylose has not yet been described. The occurrence of rare amino sugars in a number of antibiotics is noteworthy,[13] and it is interesting that the sugar moiety of the antibiotic novobiocin, 3-*O*-carbamoylnoviose,[14] has the L-lyxose configuration. L-Lyxose has been reported[15] as a degradation product of an antibiotic.

The starting material for the synthesis, L-xylose, was prepared by the procedure described by Hamamura and co-workers,[16] and was converted, through methyl α,β-L-xylofuranoside, to methyl 3,5-*O*-isopropylidene-α,β-L-xylofuranoside, essentially by the procedure of Baker and co-workers[17] for the D-analogs. The two anomers were partially separated as distilled sirups and were converted into crystalline 2-*p*-nitrobenzenesulfonate esters. Sulfonylation of methyl 3,5-*O*-isopropylidene-α,β-L-xylofuranoside with *p*-toluenesulfonyl chloride gave crystalline methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-α-L-xylofuranoside (I) and the β-L anomer (II), the latter in two dimorphous forms. The physical constants of I and II were in good agreement with those reported by Anderson

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(2) Reported in part in *Abstracts Papers Am. Chem. Soc.*, 139, 2D (1961).

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(13) A. B. Foster and D. Horton, *Advances in Carbohydrate Chem.*, 14, 214 (1959).

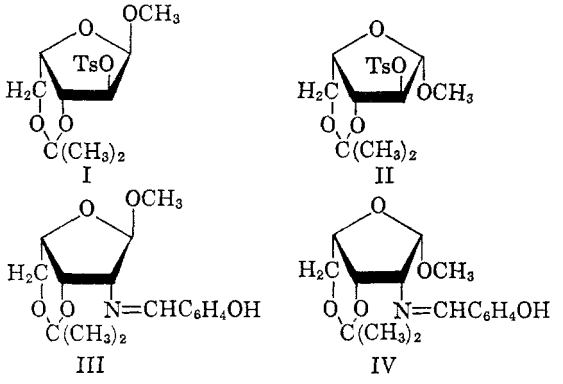
(14) E. Walton, J. O. Rodin, C. H. Stammer, F. W. Holly, and K. Folkers, *J. Am. Chem. Soc.*, 80, 5168 (1958).

(15) V. Deulofeu, personal communication.

(16) Y. Hamamura, M. Ôtsuka, and M. Suzumoto, *J. Agr. Chem. Soc. Japan*, 22, 24 (1948); *Chem. Abstracts*, 46, 10108 (1952). *Cf.* P. L. Stedehoder, *Rec. trav. chim.*, 71, 831 (1952).

(17) B. R. Baker, R. E. Schaub, and J. H. Williams, *J. Am. Chem. Soc.*, 77, 7 (1955).

and Percival[18] and by Kuhn and Baschang[10] for the D-enantiomorphs. Treatment of a mixture of I and II with anhydrous hydrazine for three days under reflux gave a 41% return of crystalline nitrogen-free material containing I and II, and a 54% yield of a nitrogen-containing sirup, which was treated with salicylaldehyde to produce a



mixture of two salicylidene Schiff base derivatives, separable by crystallization, in a total yield of 72%, based on the amount of I and II which had undergone hydrazinolysis. The two isomers had specific rotations of −99° and +28°, with closely similar infrared spectra, and were identified as methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-α-L-lyxofuranoside (III) and the corresponding β-L anomer (IV), respectively. Substance III had an infrared spectrum and x-ray powder diffraction pattern identical with that of the previously[3] isolated methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-D-lyxofuranoside, $[\alpha]_D$ + 99.5°, which identifies this derivative as the α-D anomer. The molecular rotation data in Table I for the anomeric methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-L-xylofuranosides I and II, and the anomeric methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-L-lyxofuranosides III and IV show good correlation of the 2A[19] values for the rotatory contribution of carbon 1. The 2B values, the contribution of the remainder of the molecule, showed a considerable shift, as would be expected with stereochemical inversion at carbon 2.

2-Amino-2-deoxy-L-lyxose hydrochloride could be isolated in high yield by acidic hydrolysis of III or IV, but losses involved in the isolation of III and IV lower the over-all yield of product. A more expedient procedure involved direct acidic hydrolysis of the product obtained after hydrazinolysis and reduction of a mixture of I and II. The amino sugar was readily separated without loss from the neutral products by adsorption on an acidic ion-exchange resin, from which it was subsequently eluted with acid,[10] and a 41% yield of

(18) J. M. Anderson and Elizabeth Percival, *J. Chem. Soc.*, 819 (1956).

(19) C. S. Hudson, *J. Am. Chem. Soc.*, **31**, 66 (1909).

TABLE I

MOLECULAR ROTATORY DATA

Compound	$[M]_D$ $CHCl_3$	2A	2B
Methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-α-L-xylofuranoside (I)	−25,000	−42,500	−7,500
Methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-β-L-xylofuranoside (II)	+17,500		
Methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-α-L-lyxofuranoside (III)	−30,500	−39,100	−21,900
Methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-β-L-lyxofuranoside (IV)	+8,600		

crystalline 2-amino-2-deoxy-α-L-lyxose hydrochloride was obtained. The product showed an x-ray powder diffraction pattern and infrared spectrum identical with those of the D-enantiomorph,[3] and co-crystallization of a mixture of the two enantiomorphs gave a racemic product with the same decomposition point and x-ray powder diffraction pattern. The initial and final specific rotations of the two enantiomorphs were of comparable magnitude, and differed in sign.

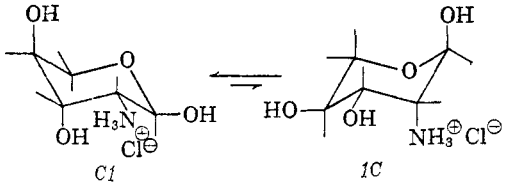
2-Amino-2-deoxy-α-L-lyxose hydrochloride (and the D-enantiomorph) exhibit infrared spectral absorption maxima at 12.00 μ and 11.34 μ, close to the wave lengths assigned by Whiffen and coworkers[20] to the deformation mode of equatorial and axial hydrogen atoms, respectively, at C-1 of a pyranose ring. This may be interpreted by consideration of the predictable conformational instability of 2-amino-2-deoxy-α-L-lyxopyranose hydrochloride, where each of the chair forms V and VI has two axial substituents and two equatorial. The significance of other pyranose conformations is, however, not excluded. There is no firm proof that 2 - amino - 2 - deoxy - α - L - lyxose hydrochloride exists in the pyranose ring form, but Kuhn and Baschang[10] have adduced evidence from optical rotatory data which suggests that the D-enantiomorph (and also the other three 2-amino-2-deoxy-D-pentose hydrochlorides) has a pyranose ring structure, in contrast to its *N*-acetyl derivative, which probably exists as the furanose form.

N-Acetylation of 2-amino-2-deoxy-α-L-lyxose hydrochloride by the method of Roseman and Ludowieg[21] gave 2-acetamido-2-deoxy-L-lyxose as a sirup.

(20) S. A. Barker, E. J. Bourne, M. Stacey, and D. H. Whiffen, *J. Chem. Soc.*, 171 (1954); S. A. Barker, E. J. Bourne, R. Stephens, and D. H. Whiffen, *J. Chem. Soc.*, 3468 (1954).

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

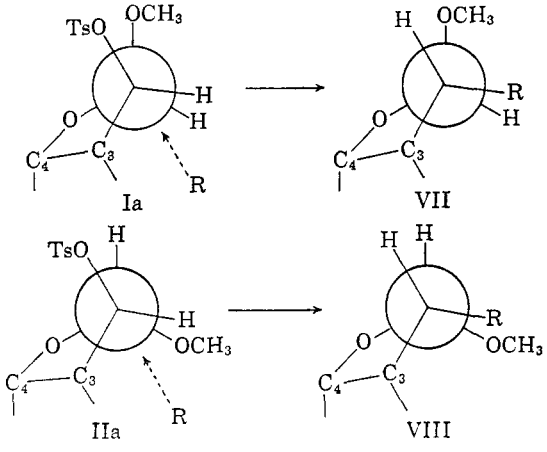
The hydrolytic conditions employed with the mixed methyl 2-amino-2-deoxy-3,5-*O*-isopropylidene-α- and β-L-lyxofuranosides, and with the corresponding Schiff base derivatives III and IV, give the free amino sugar hydrochloride and not a methyl glycoside as the principal product. Hydrolysis of methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-α-D-lyxofuranoside proceeds similarly.[8] Under similar hydrolytic conditions,



V VI

however, the methyl 2-deoxy-3,4-*O*-isopropylidene-2-salicylideneamino-β-D- and L-ribopyranosides yield the methyl 2-amino-2-deoxy-β-D- and L-ribopyranoside hydrochlorides as the principal products.[3,8] It is known that methyl pyranosides with a free amino group at C-2 are resistant to acidic hydrolysis,[22] but it would appear that the higher acid lability of furanosides is sufficient to counteract the electrostatic shielding effect of the $-NH_3^+$ group at C-2, which tends to stabilize the glycosidic linkage.

In order to study the steric factors involved in the displacement of the *p*-tolylsulfonyloxy group by hydrazine, the anomeric methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-α- and β-L-xylofuranosides (I and II) were treated, separately, with hydrazine, under milder conditions to those used in the preparative procedure. When the α-L anomer (I) was treated with anhydrous hydrazine under reflux for twenty hours, a product was obtained which, after reduction and hydrolysis, gave a 33% yield of crystalline 2-amino-2-deoxy-α-L-lyxose hydrochloride. Under similar conditions, however, the β-L-anomer (II) gave an 82% return of crystalline nitrogen-free product, apparently starting material, and, after reduction and hydrolysis, a very low yield of amino sugar. This difference in reactivity may be rationalized by consideration of the steric factors governing the approach of the nucleophile to the side of carbon 2 opposite to the *p*-tolylsulfonyloxy group. In the β-L anomer (II), the fused isopropylidene ring and the glycosidic methoxyl group are both on the same side of the furanose ring as the incoming group, and would be expected to offer more steric hindrance to the approach of the nucleophile than would these substituents in the α-L anomer (I) where the glycosidic methoxyl group is on the opposite side of the furanose ring. A related effect was observed by Cope and Shen[7] in systems of two fused five-membered rings, where it was shown that secondary *p*-tolylsulfonyloxy groups directed *into* the "V" formed by the two fused rings (*endo*) were more susceptible to nucleophilic displacement than similar groups directed *away* from the "V" (*exo*).[4] Comparison of the projections along the C-2 to C-1 axis in I and II in the corresponding projection formulas Ia and IIa shows that Ia has the unfavorable nearly eclipsed interaction of the OTs and OCH_3 groups absent in IIa. When the nucleophilic reagent R displaces the OTs group with inversion at C-2, the products VII and VIII are obtained from Ia and IIa, respectively. The greater



Ia VII

IIa VIII

reactivity of Ia as compared with IIa is understandable since Ia is likely to be thermodynamically less stable than IIa (owing to the near-eclipsed interaction between the OCH_3 and OTs groups in Ia) and should yield a transition state which is at least as stable as that for IIa, where the entering group must interact with the OCH_3 group. The significance of other factors in the displacement reaction is not excluded, since even at extended reaction times some starting material remained apparently unchanged.

EXPERIMENTAL[23]

Methyl 3,5,O-isopropylidene-α,β-L-xylofuranoside. L-Xylose, prepared[16] in 67% yield from 2,4-*O*-benzylidene-D-glucitol was converted into sirupy methyl α,β,-L-xylofuranoside by the procedure described by Levene and co-workers[24] for the D-enantiomorph. Conversion of this product into the 3,5-*O*-isopropylidene derivative according to the procedure of Percival and Zobrist[25] for the preparation of methyl 3,5-*O*-isopropylidene-α,β-D-xylofuranoside, gave, in two

(22) J. C. Irvine, D. McNicoll, and A. Hynd, *J. Chem. Soc.*, 99, 250 (1911); J. C. Irvine and A. Hynd, *J. Chem. Soc.*, 101, 1128 (1912); R. C. G. Moggridge and A. Neuberger, *J. Chem. Soc.*, 745 (1938); A. B. Foster, D. Horton, and M. Stacey, *J. Chem. Soc.*, 81 (1957).

(23) Melting points were taken on a Fisher-Johns apparatus. The infrared spectra were determined with a Model 21 Perkin-Elmer infrared spectrophotometer. The potassium bromide pellets were pressed from a finely ground mixture of the dried crystalline substance with dry analytical reagent grade potassium bromide.

(24) P. A. Levene, A. L. Raymond, and R. T. Dillon, *J. Biol. Chem.*, 95, 699 (1932).

(25) Elizabeth E. Percival and R. Zobrist, *J. Chem. Soc.*, 4306 (1952).

separate experiments, a sirup which charred with extensive decomposition on attempted high vacuum distillation. The conditions described by Baker and co-workers[17] for the D-enantiomorph proved satisfactory, and a 64% yield (based on L-xylose) of methyl 3,5-*O*-isopropylidene-α,β-L-xylofuranoside was obtained as a pale yellow distilled sirup, b.p. 85–120° (0.15 mm.), $[\alpha]_D^{23}$ −5.3° (*c*, 0.848, chloroform); $\lambda_{max(\mu)}^{film}$ 2.78 (OH), 7.23 (CCH_3).

In separate experiments the product was fractionated at 0.15-mm. pressure. A 33-g. batch of L-xylose gave 6.6 g. (15%) of a colorless mobile sirup, b.p. 86–88° (0.15 mm.), $[\alpha]_D^{24}$ −34° (*c*, 1.073, chloroform), probably predominantly the α-L anomer.

Anal. Calcd. for $C_9H_{16}O_5$: C, 52.94; H, 7.91. Found: C, 53.05; H, 8.11.

For methyl 3,5-*O*-isopropylidene-α-D-xylofuranoside Anderson and Percival[18] quote b.p. 60–70° (0.05 mm.), $[\alpha]_D$ +75° (chloroform). Baker and co-workers[17] quote b.p. 85–88° (0.10 mm.), $[\alpha]_D^{24}$ +17.6° (water).

A second fraction (6.1 g., 14%) distilled as a viscous pale yellow sirup, b.p. 120–125° (0.15 mm.), $[\alpha]_D^{25}$ +25° (*c*, 2.05, chloroform).

Anal. Calcd. for $C_9H_{16}O_5$: C, 52.94; H, 7.91. Found: C, 53.33; H, 7.83.

For methyl 3,5-*O*-isopropylidene-β-D-xylofuranoside Anderson and Percival[18] quote b.p. 90–100° (0.05 mm.), $[\alpha]_D$ −80° (chloroform), and Baker and co-workers[17] quote b.p. 108–110° (0.1 mm.), $[\alpha]_D^{24}$ −64.2° (water). The product with $[\alpha]_D^{25}$ +25° isolated in the present work was probably a mixture of the α-L and β-L anomers, with the latter predominating. The infrared spectra of the two fractions were indistinguishable from that of the α,β mixture.

A third fraction (3.3 g.) distilled as a highly viscous yellow sirup, b.p. 210–220° (0.1 mm.), $[\alpha]_D^{25}$ +3° (*c*, 0.655, chloroform), $\lambda_{max(\mu)}^{film}$ 2.80–2.90 (OH).

Anal. Calcd. for $C_9H_{16}O_5$: C, 52.94; H, 7.91. Found: C, 53.96; H, 7.61.

Its infrared spectrum differed from that of methyl 3,5-*O*-isopropylidene-α,β-L-xylofuranoside.

Methyl 3,5-O-isopropylidene-2-O-p-tolylsulfonyl-α- and β-L-xylofuranoside (I and II). A solution of 2.1 g. of methyl 3,5-*O*-isopropylidene-α,β-L-xylofuranoside {$[\alpha]_D$ +25° (*c*, 2.05, chloroform)} in 10 ml. of dry pyridine was treated with 2.9 g. (1.5 mol.) of *p*-toluenesulfonyl chloride. Pyridinium chloride began to separate after 1 hr. at 24°, and after 24 hr. the solution was treated with ice and the product was extracted with 1,2-dichloroethane. The organic layer was washed successively with water, ice cold *N* sulfuric acid, and sodium bicarbonate solution, then dried (magnesium sulfate) and concentrated to a sirup. The sirup was dissolved in a small quantity of methanol and stored at −10° for 3 weeks, when *methyl 3,5-O-isopropylidene-2-O-p-tolylsulfonyl-β-L-xylofuranoside* (II) crystallized in large prisms, yield 1.25 g. (34%), m.p. 80–82°, $[\alpha]_D^{25}$ +49° (*c*, 0.45, chloroform). A sample recrystallized from hexane had m.p. 81.5–83°, $\lambda_{max(\mu)}^{KBr}$ 6.22, 6.67 (aryl C=C), 7.20, 7.29 (CCH_3), 8.49 (sulfonate), 12.00 (*p*-disubstituted benzene), OH absent; x-ray powder diffraction data[26]: 13.12 vw, 8.22 vs (1,1), 7.31 m, 6.79 w, 6.27w, 5.92 m, 5.50 vw, 5.27 vs (2), 5.00 s (3), 4.48 vs (1,1), 4.25 vw, 4.18 s.

Anal. Calcd. for $C_{16}H_{22}O_7S$: C, 53.62; H, 6.19; S, 8.95. Found: C, 53.74; H, 6.30; S, 9.12.

The product deteriorated on storage; the first crop of crystals liquefied after 6 weeks, while recrystallized material liquefied after 8 months. The liquefied material showed the same principal infrared absorption peaks as the crystalline material. In subsequent preparations a second form of II was encountered with m.p. 122–123.5°, $[\alpha]_D^{26}$ +53° (*c*, 2.38, chloroform); x-ray powder diffraction data[26]: 8.93 s (2,2), 7.11 s (2,2), 6.72 vw, 5.88 m, 5.35 m, 5.18 vw, 4.87 vs (1), 4.40 s (3), 4.20 w, 4.08 s (2,2). Subsequent to the isolation of the second form it was found that stored samples of the first form had spontaneously changed to the second one.

For methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-β-D-xylofuranoside the following constants have been reported: m.p. 120°, $[\alpha]_D^{15}$ −45° (in methanol)[25]; m.p. 119–120°, $[\alpha]_D^{17}$ −53° (in chloroform)[18]; and m.p. 75–77°, $[\alpha]_D^{24}$ −55.4° (in methanol).[10]

From the mother liquors of the crystallization of II a crystalline mixture (1.72 g., 47%), m.p. 65–68°, $[\alpha]_D^{20}$ −33° (*c*, 0.915, chloroform) was obtained, which on recrystallization from 1-propanol, then from petroleum ether (b.p. 30–60°) gave pure methyl *3,5-O-isopropylidene-2-O-p-tolylsulfonyl-α-L-xylofuranoside* (I), m.p. 73–74°, $[\alpha]_D^{23}$ −70° ± 0.2°, (*c*, 1.414, chloroform); $\lambda_{max(\mu)}^{KBr}$ 6.24, 6.67 (aryl C=C), 7.30 (CCH_3), 8.48 (sulfonate), 12.05 (*p*-disubstituted benzene), OH absent; x-ray powder diffraction data[26]: 7.76 s (3,3), 7.25 s (3,3), 5.62 vw, 5.36 vs (1), 4.74 vw, 4.62 w, 4.40 vw, 3.99 s (2).

Anal. Calcd. for $C_{16}H_{22}O_7S$: C, 53.62; H, 6.19; S, 8.95. Found: C, 53.58; H, 6.43; S, 9.19.

For methyl 3,5-*O*-isopropylidene-2-*O*-tolylsulfonyl-α-D-xylofuranoside the following constants have been reported: m.p. 79–80°, $[\alpha]_D^{18}$ +68° (in chloroform[18]); and 75–78°, $[\alpha]_D$ +71.2° (in chloroform).[10]

The crystallization of I from petroleum ether was accompanied by a decrepitation-like sound.

Methyl 3,5-O-isopropylidene-2-O-(p-nitrophenylsulfonyl)-α-L-xylofuranoside. A solution of 5.20 g. of methyl 3,5-*O*-isopropylidene-α,β-L-xylofuranoside {$[\alpha]_D^{24}$ −34° (*c*, 1, chloroform)} in 15 ml. of anhydrous pyridine was treated at 0° with 7.60 g. (1.5 mol.) of *p*-nitrobenzenesulfonyl chloride. After 2 days at 0° and 2 days at room temperature the solution was poured on ice and the product (4.7 g., 48%) was filtered and recrystallized from methanol; yield 3.15 g., m.p. 124–126°, $[\alpha]_D^{28}$ −65° (*c*, 1.9, chloroform); $\lambda_{max(\mu)}^{KBr}$ 6.19, 6.30, 6.77 (aryl C=C), 6.44, 6.56, 7.41 (aromatic NO_2), 8.60 (sulfonate), 11.74 (*p*-disubstituted benzene), OH absent. Further recrystallization from hexane raised the m.p. to 125–126.5°. The product darkened on storage.

Anal. Calcd. for $C_{15}H_{19}NO_9S$: C, 46.27; H, 4.92; N, 3.61; S, 8.23. Found: C, 46.45; H, 4.96; N, 3.55; S, 8.35.

Methyl 3,5-O-isopropylidene-2-O-(p-nitrophenylsulfonyl)-β-L-xylofuranoside. This compound was prepared from methyl 3,5-*O*-isopropylidene-α,β-L-xylofuranoside {$[\alpha]_D^{25}$ +25° (*c*, 2, chloroform)} in 42% yield essentially by the procedure used for the α-L anomer; recrystallized from methanol it had m.p. 81.5–84°. The product decomposed on storage.

Anal. Calcd. for $C_{15}H_{19}NO_9S$: N, 3.61. Found: N, 3.87.

2-Amino-2-deoxy-α-L-lyxose hydrochloride. Methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-α,β-L-xylofuranoside (19.3 g.) was boiled under reflux with 100 ml. of anhydrous hydrazine for 72 hr. in an all-glass apparatus under a stream of nitrogen.[27] The cooled solution was extracted with four 150-ml. portions of peroxide-free ether, the ether extract was evaporated to dryness, and the residue, dissolved in aqueous methanol, was treated with Raney nickel at room temperature for 2 hr. to decompose excess hydrazine. The solution was then hydrogenated at 45 p.s.i. pressure for 18 hr. in the Parr apparatus. Attempts to prepare a salicylidene derivative of the product led to only partially crystalline sirups, and the product was hydrolyzed by boiling the sirup with 100 ml. of *N* hydrochloric acid for 2 hr.; volatile products were then removed by repeated codistillation with toluene. An aqueous solution of the resultant sirup was passed through a column, 25 cm. × 3.5 cm., of Amberlite IR-120 resin (H^+), the column was eluted with water until the eluate no longer reduced Fehling solution, and the

(26) Interplanar spacing, Å, CuK_α radiation. Relative intensity, estimated visually: s, strong; m, medium; w, weak; v, very. First few strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities.

(27) This procedure is potentially hazardous and was conducted behind explosion screens.

eluate (1500 ml.) was discarded. Elution was continued with *N* hydrochloric acid until 2 l. had been collected and the eluate was again nonreducing. The acid eluate was concentrated to a sirup which was co-distilled with toluene to remove acid. The sirup crystallized from aqueous methanol; yield 4.10 g. (41%), m.p. 150–160° (dec.), $[\alpha]_D^{25}$ −16° (2 min.) → −8° (5 min.) → +5° (1 hr., final, *c*, 1.21, water), $\lambda_{max(\mu)}^{KBr}$ 2.95–3.00 (associated OH), 4.95, 6.16, 7.67, 12.49 (—NH_3^+), 11.34 (axial H at C-1), 12.00 (equatorial H at C-1). Recrystallized from methanol it had a m.p. of 161–163° dec. Its infrared spectrum and x-ray powder pattern were identical with those of 2-amino-2-deoxy-D-lyxose hydrochloride.[3] The compound was chromatographically homogeneous, gave positive ninhydrin and reducing sugar tests, and had an R_f value identical to that of 2-amino-2-deoxy-D-lyxose hydrochloride by descending chromatography on Whatman No. 1 paper with a pyridine, ethyl acetate, water, acetic acid (5:5:3:1)[28] solvent system.

Anal. Calcd. for $C_5H_{12}ClNO_4$: C, 32.36; H, 6.52; Cl, 19.11; N, 7.55. Found: C, 32.57; H, 6.39; Cl, 18.91; N, 7.72.

A sample of 2-amino-2-deoxy-α-D-lyxose hydrochloride[3] showed $[\alpha]_D^{22}$ +23° (2 min.) → +7° (5 min.) → −5° (1 hr., final, *c*, 0.17, water).

2-Amino-2-deoxy-α-DL-lyxose hydrochloride. Equal weights of 2-amino-2-deoxy-D- and L-lyxose hydrochlorides were dissolved in warm ethanol and allowed to crystallize. An 86% yield of product, m.p. 147–165° dec. was obtained, which had an x-ray powder diffraction pattern and infrared spectrum identical with those of the separate enantiomorphs, indicating that the crystals are not a racemic compound.

Methyl 2-deoxy-3,5-O-isopropylidene-2-salicylideneamino-α- and β-L-lyxofuranoside (III and IV). A mixture of the sirupy methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-α-and β-L-xylofuranosides (39 g.) was refluxed with 100 g. of anhydrous hydrazine for 74 hr. under a slow stream of nitrogen.[27] The cooled solution was extracted with ether (4 × 100 ml.), the extract was concentrated, and the resultant sirup was treated with 100 ml. of water and sufficient methanol to effect solution. Excess hydrazine was destroyed and the solution hydrogenated as in the foregoing preparation. The solution was filtered and concentrated to a sirup which crystallized slowly from aqueous methanol to give a total of 16 g. (41% calculated as starting material) of nitrogen-free product. The first crop of this product had a m.p. of 116–121° with an x-ray powder diffraction pattern identical with that of the high melting dimorph of methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-β-L-xylofuranoside (II). The second crop had a m.p. of 73–75°, $[\alpha]_D^{26}$ −68° (*c*, 1.8, chloroform) and had an x-ray powder diffraction pattern identical with that of methyl 3,5-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-α-L-xylofuranoside (I). Concentration of the mother liquors gave 11.8 g. of sirup (54% calculated as methyl 2-amino-2-deoxy-3,5-*O*-isopropylidene-L-lyxofuranoside) which contained nitrogen and gave a strong ninhydrin test. A solution of the sirup in 100 ml. of ether was treated with 4.6 ml. of salicylaldehyde, warmed for 10 min., treated with petroleum ether, and left at room temperature to crystallize. A total yield of 12.93 g. (72% from the sirupy methyl 2-amino-2-deoxy-3,5-*O*-isopropylidene-L-lyxofuranoside) of crystalline methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-α- and β-L-lyxofuranosides (III and IV) was obtained. The two anomers tended to co-crystallize, but a dextrorotatory product which crystallized first, as dense prismatic aggregates, was separated mechanically from a levorotatory product which appeared as fine needles later in the crystallization. Both forms were recrystallized from ether–petroleum ether (b.p. 30–60°) until their specific rotations were constant. The levorotatory anomer was assigned the structure of *methyl 2-deoxy-3,5-O-isopropylidene-2-salicylideneamino-α-L-lyxofuranoside* (III); m.p. 113–114°, $[\alpha]_D^{22}$ −99° ± 1° (*c*, 0.41, chloroform), $\lambda_{max(\mu)}^{KBr}$ 2.83 (OH), 6.07 (C=N), 6.27, 6.62 (aryl C=C), 7.22 (CCH_3), 13.14 (*o*-disubstituted benzene).

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.52; H, 6.89; N, 4.56. Found: C, 62.61; H, 6.89; N, 4.30.

The x-ray powder diffraction pattern and infrared spectrum were identical with those of the methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-D-lyxofuranoside of $[\alpha]_D^{23}$ +99.5° (*c*, 1.67, chloroform) reported by Wolfrom and coworkers,[3] thus characterizing their derivative as the α-D-anomer.

The dextrorotatory product was designated *methyl 2-deoxy-3,5-O-isopropylidene-2-salicylideneamino-β-L-lyxofuranoside* (IV); m.p. 110°, $[\alpha]_D^{19}$ +28° (*c*, 0.45, chloroform); $\lambda_{max(\mu)}^{KBr}$ 2.83 (OH), 6.07 (C=N), 6.27, 6.62 (aryl C=C), 7.23 (CCH_3), 13.09 (*o*-disubstituted benzene). The infrared spectrum was closely similar to that of III. X-ray powder diffraction data[26]: 14.46 w, 8.65 m, 7.41 vs (2), 6.20 w, 5.75 w, 5.46 s (3), 5.14 w, 4.89 vs (1), 4.60 m, 4.37 vw, 4.20 w, 3.89 w, 3.72 w, 3.57 m.

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.52; H, 6.89; N, 4.56. Found: C, 62.77; H, 6.95; N, 4.47.

In subsequent repetitions of the above experiment on one occasion a low (6.5%) yield of a salicylidene Schiff base derivative differing from III and IV was isolated; m.p. 136–138.5°, $[\alpha]_D^{25}$ +19° (*c*, 0.16, chloroform); $\lambda_{max(\mu)}^{KBr}$ 2.88 (OH), 6.11 (C=N), 6.30, 6.65 (aryl C=C), 7.24 (CCH_3), 13.06 (*o*-disubstituted benzene). The infrared spectrum differed from those of III and IV in the region of 8.50–12.50 μ. X-ray powder diffraction data[26]: 12.51 m, 7.34 m, 6.37 m, 6.01 m, 5.49 w, 5.03 vs (1), 4.77 s (3), 4.37 w, 4.20 w, 3.92 s (2), 3.58 w, 3.44 m.

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.52; H, 6.89; N, 4.56. Found: C, 61.98; H, 6.44; N, 4.96.

The identity of this product is unknown.

2-Amino-2-deoxy-α-L-lyxose hydrochloride by hydrolysis of methyl 2-deoxy-3,5-O-isopropylidene-2-salicylideneamino-α,β-L-lyxofuranoside. A solution of 215.7 mg. of methyl 2-deoxy-3,5-*O*-isopropylidene-2-salicylideneamino-α,β-L-lyxofuranoside {$[\alpha]_D^{21}$ −29° (*c*, 0.8, chloroform)} in 25 ml. of *N* hydrochloric acid was left at room temperature for 1 hr., salicylaldehyde was removed by extraction with petroleum ether, and the aqueous solution was boiled for 2 hr. under reflux, concentrated at 40° to 5 ml. and the acid was removed by repeated codistillation with toluene and ethanol. The residual 2-amino-2-deoxy-L-lyxose hydrochloride sirup crystallized from ethanol-ether, yield 101 mg. (78%), m.p. 154–165° dec. with an x-ray powder diffraction pattern identical to that of the material described above.

2-Acetamido-2-deoxy-L-lyxose. 2-Amino-2-deoxy-α-L-lyxose hydrochloride (1.00 g.) was *N*-acetylated according to the procedure used by Roseman and Ludowieg[21] for 2-amino-2-deoxy-D-glucose hydrochloride. A colorless sirup was obtained which gave a negative ninhydrin test, and was dried over phosphoric anhydride at 0.01-mm. pressure; yield 1.03 g. (100%), $[\alpha]_D^{18}$ −31° (*c*, 4, water, 12 hr.); $\lambda_{max(\mu)}^{KBr}$ 3.11 (associated OH), 6.20, 6.60 (NHAc), no absorption at 5.7–5.8 (OAc). Attempts to crystallize the product were unsuccessful.

Kuhn and Baschang[10] quote $[\alpha]_D^{22}$ +19° (*c*, 2.3, water) for sirupy 2-acetamido-2-deoxy-D-lyxose.

Hydrazinolysis of methyl 3,5-O-isopropylidene-2-O-p-tolylsulfonyl-α- and β-L-xylofuranosides under comparative conditions. Each anomer was boiled for 20 hr. under reflux with ten parts by weight of anhydrous hydrazine, and the product was extracted and reduced as before. On treatment with aqueous methanol, the reaction product from the β-L anomer gave crystalline starting material; yield 82%. Hydrolysis of the mother liquors with *N* hydrochloric acid at 100° for 3 hr. followed by evaporation gave a product from which crystalline 2-amino-2-deoxy-L-lyxose hydrochloride was isolated,

(28) F. G. Fischer and H. J. Nebel, *Z. physiol. Chem.*, **302**, 10 (1955).

yield 2%. The product from hydrazinolysis of the α-L anomer failed to crystallize directly, but after acidic hydrolysis crystalline 2-amino-2-deoxy-L-lyxose hydrochloride was obtained; yield 30%, m.p. 155–164° dec.

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[CONTRIBUTION FROM RAYONIER INC., OLYMPIC RESEARCH DIVISION]

The Ultraviolet Irradiation of Model Compounds Related to Cellulose[1]

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Cellobiose and cellopentaose, models for unmodified cellulose chains with terminal carbonyl groups, methyl β-cellobioside, model for an unmodified cellulose chain with a protected terminal carbonyl group, and cellobiitol and cellopentaitol, models for cellulose chains devoid of carbonyl groups, were irradiated with light of 2200–4000 Å, in the presence of air.

All five model compounds were fragmented, yielding comparable amounts of acidic compounds, of substances absorbing near 2600 Å, of monosaccharides, and of most of the predicted oligosaccharides of a lower degree of polymerization. These results were interpreted to show that ultraviolet light will, in the presence of air, initiate the fragmentation of oligosaccharide molecules and presumably also that of cellulose, whether carbonyl groups are present in the molecules or not.

The ultraviolet irradiation of cellulose is known to cause yellowing, reduction of the degree of polymerization, formation of carbonyl and carboxyl groups, and fragmentation of the molecules to a diversity of neutral and acidic non-volatile, volatile and gaseous products.[2–11] The following fragments have been identified: hydrogen,[9] carbon monoxide,[2,9] carbon dioxide,[2,3,9] D-glucose, and D-arabinose.[11] Also identified were di- and trisaccharides composed of D-glucose units and the corresponding compounds in which the terminal reducing glucose unit was replaced by D-arabinose.[11] Also observed but not identified were water-soluble acidic substances[11] and a water-soluble compound showing considerable ultraviolet absorption with a weak maximum near 2600 Å.[8,11]

Far ultraviolet radiation was shown to be considerably more effective in bringing about this degradation than light of the near ultraviolet.[5–7,11] Quantum yields of approximately 10^{-3} were calculated from the amount of carbon dioxide formed during degradation caused by radiation of 2537 Å.[5,9] Light of this wave length is commonly assumed to cause photolysis; the lesser degradation caused by light of the near ultraviolet is frequently referred to as photooxidation.[4,5,12]

The requirement for photolytic cleavage of a bond in a molecule is the absorption of light energy equal to, or greater than, the bond energy. For C—O and C—C bonds this would have to be light of a wave length less than 3400 Å. No absorption of light by the molecule is required for photooxidative degradation; the energy transfer occurs by collision of the molecule with some excited species created by action of light of the near ultraviolet upon such compounds of the environment as metallic impurities, peroxides, and dyes. Both kinds of degradation proceed, no doubt, by free radical mechanisms.

One of the unclarified aspects of the photodegradation of cellulose is the initiation of photolysis. A basic requirement would seem to be a chromophore absorbing below 3400 Å. Of these, only hydroxyl, carboxyl, and carbonyl groups occur commonly in cotton cellulose or wood celluloses. Hydroxyl and carboxyl groups would have to be ruled out, because they absorb below, or near 2000 Å—*i.e.* below the wave lengths which have been most frequently employed for the ultraviolet irradiation of cellulose. Potential carbonyl groups are present at C_1 in each terminal reducing D-glucose unit; carbonyl groups or potential carbonyl groups also occur as a result of oxidative damage at C_2, C_3, or C_6 of D-glucose units.[13] As carbonyl groups absorb near 2800 Å, they should theoretically be capable of initiating photolysis of the cellulose molecules, and are thus frequently held re-

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