# THE PREPARATION OF L-LYXURONIC ACID, L-LYXOSE, AND 5-DEOXY-L-LYXOSE[1]

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## ABSTRACT

D-Galactono-1,4-lactone (I) was oxidized by 1 mole of periodate to give L-lyxuronic acid isolated as methyl L-lyxuronate (II). The methyl L-lyxuronate was converted into methyl (methyl α-L-lyxofuranosid)uronate (III) which on reduction by borohydride afforded methyl α-L-lyxofuranoside (IV) from which L-lyxose (V) was obtained by mild acid hydrolysis.

5-Deoxy-L-lyxose was prepared from the methyl (methyl α-L-lyxofuranosid)uronate (III) by the following sequence of reactions: (III) → methyl (methyl 2,3-*O*-isopropylidene-α-L-lyxofuranosid)uronate (VI) → methyl 2,3-*O*-isopropylidene-α-L-lyxofuranoside (VII) → methyl 2,3-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-α-L-lyxofuranoside (VIII) → methyl 5-deoxy-5-iodo-2,3-*O*-isopropylidene-α-L-lyxofuranoside (IX) → methyl 5-deoxy-2,3-*O*-isopropylidene-α-L-lyxofuranoside (X) → 5-deoxy-L-lyxose (XI).

## DISCUSSION

Glycol-cleaving reagents have proved particulary useful in synthetic carbohydrate chemistry for the preparation of sugars from both substituted and unsubstituted sugar precursors. Perlin (1, 2) has shown that lead tetraacetate is especially suitable for differentiating between various kinds of glycol groups and has successfully used the reagent for the synthesis of a wide variety of sugars using this selective property. Periodate is less specific in its glycol-cleaving properties than lead tetraacetate and, in general, its use in synthetic work (3) has been limited to its action on suitably protected carbohydrates in which the cleavage of the glycol systems can be predicted. Some exceptions are found in the selective oxidation with one molar portion of periodate of the exocyclic glycol systems ($C_5$—$C_6$) in methyl D-gluco- and D-galacto-furanosides to give methyl D-xylo- and L-arabino-furanosides respectively after reduction of the products (4) and similarly the cleavage of the exocyclic glycol system ($C_6$—$C_7$) of methyl D-*glycero*-D-*gulo*-heptopyranoside in the synthesis of D-gulose (5). In the present work the selective cleavage of the exocyclic glycol system ($C_5$—$C_6$) in D-galactono-1,4-lactone by 1 mole of periodate to yield L-lyxuronic acid has been used as the first step in the synthesis of the acid which was subsequently used in the synthesis of the rare sugars L-lyxose and 5-deoxy-L-lyxose.[3]

Trial experiments showed that D-galactono-1,4-lactone was oxidized by 1 mole of periodate with the release of 0.98 moles of formaldehyde indicating that the glycol cleavage occurred almost exclusively at the $C_5$—$C_6$ bond. An aqueous solution of D-galactono-1,4-lactone (I) was oxidized by the addition of one molar portion of periodic acid, and after removal of the inorganic ions, the resulting solution of L-lyxuronic acid was converted into crystalline methyl L-lyxuronate (II) by repeated evaporation with dry methanol. The methyl L-lyxuronate had equivalent weight, molecular weight, and elemental analysis in agreement with the theoretically expected values, and on borohydride reduction (6) it was converted into L-arabinitol. Treatment of the methyl L-lyxuronate

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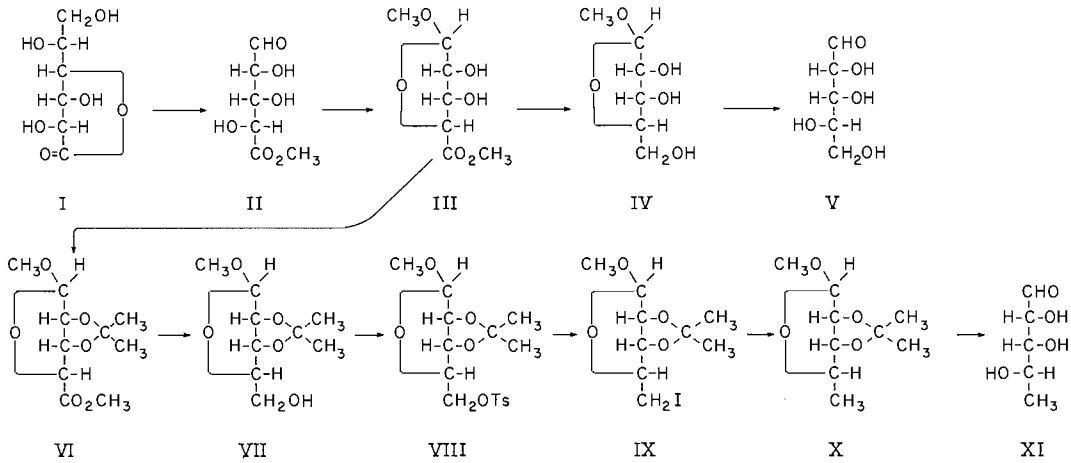
[3]*Dr. A. S. Perlin has independently studied the periodate oxidation of D-galactono-1,4-lactone and has prepared L-lyxuronic acid and related derivatives. The results of this work together with structural studies will be published by Dr. Perlin in due course.*



with 1 equiv of sodium hydroxide gave sodium L-lyxuronate. On borohydride reduction the sodium L-lyxuronate gave the expected L-arabonic acid which was identified by gas chromatography as its 2,3,5-tri-*O*-trimethylsilyl-aldono-1,4-lactone derivative (7). Removal of the sodium ions from the sodium L-lyxuronate by ion-exchange resin afforded L-lyxuronic acid as a syrup, which is probably a mixture of the free acid and its lactone.

Treatment of the methyl L-lyxuronate (II) with methanolic hydrogen chloride afforded crystalline methyl (methyl α-L-lyxofuranosid)uronate (III). Gas chromatographic analysis of the methanolysate indicated the presence of about 15% of the β-methyl glycoside; successive treatment with methanolic hydrogen chloride of the residues remaining after the removal of the crystalline α-anomer re-equilibrated the mixture and allowed increased yields of the methyl (methyl α-L-lyxofuranosid)uronate (total yield, 61%) to be obtained. Reduction of the methyl (methyl α-L-lyxofuranosid)uronate by sodium borohydride (6) in ethanol solution afforded crystalline methyl α-L-lyxofuranoside (IV). On mild acid hydrolysis compound IV gave crystalline α-L-lyxose (V), whose physical and chromatographic properties agreed with those recorded in the literature. The 2,4-dinitrophenylhydrazone and toluene-*p*-sulfonylhydrazone derivatives of the synthesized L-lyxose had melting points and infrared spectra identical with those of the corresponding derivatives prepared from authentic D-lyxose.

The above sequence of reactions, repeated without purification of the intermediates, showed that L-lyxose could be prepared from D-galactono-1,4-lactone in 87% overall yield.

5-Deoxy-L-lyxose was prepared in the following manner. On treatment with acetone in the presence of anhydrous copper sulfate catalyst, the methyl (methyl α-L-lyxofuranosid)uronate (III) afforded methyl (methyl 2,3-*O*-isopropylidene-α-L-lyxofuranosid)uronate (VI) which, on reduction with lithium aluminium hydride (8), was converted into methyl 2,3-*O*-isopropylidene-α-L-lyxofuranoside (VII). Treatment of this compound with *p*-toluenesulfonyl chloride in pyridine solution afforded crystalline methyl 2,3-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-α-L-lyxofuranoside (VIII) which, on heating with sodium iodide in acetone solution, gave methyl 5-deoxy-5-iodo-2,3-*O*-isopropylidene-α-L-lyxofuranoside (IX). Reduction of IX with hydrogen in the presence of Raney nickel afforded methyl 5-deoxy-2,3-*O*-isopropylidene-α-L-lyxofuranoside (X) which on mild acid hydrolysis gave 5-deoxy-L-lyxose (XI). At all stages in the above sequence of reactions the

purity of the products was established by gas chromatographic analysis of the compounds or their *O*-trimethylsilyl derivatives.

The 5-deoxy-L-lyxose, obtained as a syrup, had the physical and chromatographic properties expected from those recorded in the literature for 5-deoxy-D-lyxose (9). The *p*-bromophenylosazone and 2,5-dichlorophenylhydrazone derivatives of the 5-deoxy-L-lyxose were obtained in a crystalline form.

L-Lyxose is reported to occur in the hydrolysis products of yeast nucleic acid (10) and of curamycin, an antibiotic produced by *Streptomyces curacoi* (11). L-Lyxose has been prepared from calcium L-galactonate using the Ruff degradation procedure (40% yield) (9, 12), and by the periodate oxidation of 2,3,4-tri-*O*-benzyl-D-galactitol prepared from allyl 6-*O*-allyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (13).

L-Lyxuronic acid has not been found in nature but D-lyxuronic acid is reported to be produced from D-glucose by *Acetobacter melanogenum* (14). 5-Deoxy-L-lyxose has not been found in nature but the related compounds 5-deoxy-3-*C*-formyl-L-lyxose (streptose) and 4-*O*-methyl-5,5-dimethyl-L-lyxose (noviose) are of considerable interest.

## EXPERIMENTAL

Paper chromatography was performed by the descending method (15) on Whatman No. 1 filter paper using the following solvent systems: (A) butan-1-ol – acetic acid – water (4:1:5 v/v, top layer), and (B) pyridine – ethyl acetate – water (2:5:5 v/v, top layer). Detection of the sugars was made using the spray reagents: (*a*) 1% silver nitrate in acetone followed by 2% sodium hydroxide in ethanol (16), and (*b*) 2% *p*-anisidine hydrochloride in butan-1-ol (17). The rates of movement of the sugars on the chromatograms are quoted relative to D-galactose ($R_{gal}$ = 1.0).

Gas–liquid chromatography was carried out using a Pye argon chromatograph fitted with an ionization detector ($^{90}Sr$ 20 μcuries) and employing a straight glass column (120 × 0.5 cm. i.d.) packed with 10% (w/w) neopentylglycol sebacate polyester on 100–120 mesh acid washed Chromosorb W. The column was maintained at 170° and development was made with dry argon at a flow rate of 120 ml/min. Chloroform solutions of the sugars were analyzed directly or were converted to their *O*-trimethylsilyl derivatives by treatment with hexamethyldisilazane and trimethylchlorosilane in pyridine solution (18). The retention times of the compounds are quoted relative to methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucoside ($T_g$ = 1.00).

Melting points were determined on a hot stage and are corrected. Optical rotations were measured at 22°. Solutions were concentrated in a rotary evaporator under reduced pressure below 50°.

### 1. *Preparation of* L-*Lyxuronic Acid*

#### (*a*) *Methyl* L-*Lyxuronate*

A solution of D-galactono-1,4-lactone (89 g) in water (600 ml) was cooled to 5° and a solution of periodic acid ($H_5IO_6$, 114 g) in water (600 ml) was added dropwise with stirring over 1 h. After keeping the reaction mixture for a further 4 h at room temperature, barium acetate (64 g) in water (200 ml) was added and the insoluble precipitate of barium iodate was removed by filtration. The filtrate was passed down columns of Amberlite IR-120($H^+$) and IR-45($OAc^-$) ion-exchange resins and the eluate and washings were concentrated to a syrup (68 g, 96%). The product was evaporated to dryness with dry methanol (5 × 500 ml), and the resulting syrup was dissolved in methanol (50 ml) and kept overnight at 5°. The crude crystalline methyl L-lyxuronate (61 g) having m.p. 136–138° was collected and was found after two recrystallizations from methanol to have m.p. 140° and $[\alpha]_D$ −37.7° → −23° (*c*, 1.8 in water) and $[\alpha]_D$ −68° → −45° (*c*, 1.6 in methanol).

Anal. Found: C, 40.32; H, 5.54. $C_6H_{10}O_6$ requires C, 40.45; H, 5.66.

The trimethylsilyl derivative of the methyl L-lyxuronate on gas chromatographic analysis gave a single peak, $T_g$ 1.440.

Methyl L-lyxuronate had a neutralization equivalent, determined by titration with 0.02 *N* sodium hydroxide, of 178 (calcd. equiv. wt. 178) and a molecular weight, determined by hypoiodite oxidation (19), of 176 (calcd. mol. wt. 178). Methyl L-lyxuronate (0.1 g) in water (5 ml) was reduced by the addition of sodium borohydride (58 mg) to give crystalline L-arabinitol (70 mg) having m.p. and mixed m.p. 103° and giving an acetate derivative which had the same gas chromatographic retention time as penta-*O*-acetyl-L-arabinitol (20).

#### (*b*) *Sodium* L-*Lyxuronate*

Methyl L-lyxuronate (1.78 g) in water (10 ml) was neutralized by the slow addition of *N* sodium hydroxide solution (10 ml); after 1 h ethanol (120 ml) was added to the stirred solution and the precipitated sodium L-lyxuronate (1.8 g) was collected. The product had $[\alpha]_D$ +8.1° (*c*, 3.5 in water).

Anal. Found: C, 32.8; H, 4.0. $C_5H_7O_6Na$ requires C, 32.3; H, 3.78.

Paper chromatographic examination of the sodium L-lyxuronate showed a single spot $R_{gal}$ 0.93 (solvent A) which gave a yellow color with the *p*-anisidine hydrochloride spray. Sodium L-lyxuronate (10 mg) was reduced with sodium borohydride (6 mg) to give L-arabonic acid, which gave an *O*-trimethylsilyl derivative having the same gas chromatographic retention time as authentic 2,3,5-tri-*O*-trimethylsilyl-L-arabono-1,4-lactone (7).

*(c) L-Lyxuronic Acid (and Lactone)*

Sodium L-lyxuronate (0.93 g) in water (10 ml) was passed down a column of Amberlite IR-120($H^+$) ion-exchange resin, and the eluate and washings were concentrated to a syrup (0.78 g) which was dried over phosphorus pentoxide under high vacuum for 3 d. Paper chromatographic examination of the product (solvent A) showed two spots having $R_{gal}$ 0.92 (acid) and $R_{gal}$ 1.61 (lactone) with considerable tailing between them. The preparation had $[\alpha]_D$ −10° (*c*, 2 in water).

Anal. Found: C, 34.8; H, 4.99. $C_5H_8O_6.\frac{1}{2}H_2O$ requires C, 34.7; H, 5.17.

*2. Preparation of L-Lyxose*

*(a) Methyl (Methyl α-L-Lyxofuranosid)uronate*

Methyl L-lyxuronate (53 g) was boiled under reflux for 1 h with 1% methanolic hydrogen chloride (1.5 l), and the cooled solution was neutralized with silver carbonate and filtered. After treatment with hydrogen sulfide and refiltration, the filtrate was concentrated to a syrup (58 g). The syrup was dissolved in chloroform and ether was added to incipient turbidity; on keeping at 5°, crystals of methyl (methyl α-L-lyxofuranosid)-uronate (16 g) were collected. The mother liquors were concentrated and again treated with methanolic hydrogen chloride and worked up as described above. The procedure was repeated twice to give a total yield of product of 35 g (61%), m.p. 85°, $[\alpha]_D$ −94° (*c*, 2 in methanol).

Anal. Found: C, 43.72; H, 6.30. $C_7H_{12}O_6$ requires C, 43.75; H, 6.29.

The trimethylsilyl derivative of methyl (methyl α-L-lyxofuranosid)uronate on gas chromatographic analysis gave a single peak, $T_g$ 1.250. The trimethylsilylated product of the original methanolyzate gave two peaks having $T_g$ 1.250 (85%) and $T_g$ 1.781 (15%); the minor peak is probably the β-anomer.

*(b) Methyl α-L-Lyxofuranoside*

Methyl (methyl α-L-lyxofuranosid)uronate (30 g) in ethanol (400 ml) kept at 0° was reduced by the addition of sodium borohydride (12 g) in ethanol (150 ml). The mixture was kept at 0° for 5 h and then at room temperature for 60 h. The reaction mixture was treated with Amberlite IR-120($H^+$) ion-exchange resin to destroy the excess of borohydride and remove sodium ions, and the filtered solution was then evaporated with dry methanol (6 × 250 ml) to remove boric acid. When the product was kept in the presence of a small quantity of methanol it gave crystals (22.8 g, 89%) which were collected after trituration with a chloroform–ether mixture. After recrystallization from ethyl acetate, the methyl α-L-lyxofuranoside had m.p. 93°, $[\alpha]_D$ −125° (*c*, 3 in water) and $[\alpha]_D$ −160° (*c*, 2 in methanol) (lit. $[\alpha]_D$ − 160° (methanol) and m.p. 93° (21)) and had an infrared spectrum identical with authentic methyl α-D-lyxofuranoside.

Anal. Calcd. $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 43.70; H, 7.34.

Gas chromatographic analysis of the *O*-trimethylsilyl derivative of the methyl α-L-lyxofuranoside gave a single peak $T_g$ 0.582 having the same retention time as the trimethysilyl derivative prepared from authentic methyl α-D-lyxofuranoside. When the methyl α-L-lyxofuranoside (0.1 g) was heated with 0.5 *N* sulfuric acid (10 ml) on a boiling water bath for 20 min, the optical rotation changed from $[\alpha]_D$ −123° to +12.4°.

Paper chromatographic examination of the methyl α-L-lyxofuranoside showed a single red spot with the *p*-anisidine hydrochloride spray having $R_{gal}$ 3.18 (solvent A) and $R_{gal}$ 4.40 (solvent B).

*(c) L-Lyxose*

Methyl α-L-lyxofuranoside (10 g) in 0.5 *N* sulfuric acid (100 ml) was heated on a boiling water bath for 25 min, and the cooled solution was neutralized ($BaCO_3$) and filtered. The filtrate was passed through small columns of Amberlite IR–120($H^+$) and Duolite A4($OH^-$) ion-exchange resins, and the eluate was concentrated to a syrup (9 g). The syrup was dissolved in hot ethanol (10 ml); on standing, crystals of α-L-lyxose (7.8 g) were obtained, m.p. 104° and $[\alpha]_D$ +13.9° (*c*, 3 in water, equilibrium value) (lit. m.p. 105° and $[\alpha]_D$ +13.5° (9, 12)).

Anal. Calcd. $C_5H_{10}O_5$: C, 40.00; H, 6.71. Found: C, 40.11; H, 6.64.

On paper chromatograms the L-lyxose gave a red spot with the *p*-anisidine hydrochloride spray having $R_{gal}$ 1.57 (solvent A) and $R_{gal}$ 2.06 (solvent B) corresponding in mobility with authentic D-lyxose. The trimethylsilyl derivative prepared from the crystalline α-L-lyxose on gas chromatographic analysis gave a single peak with $T_g$ 0.41, whereas the product prepared from a sample of the α-L-lyxose equilibrated in aqueous solution showed two peaks, $T_g$ 0.41 and 0.58, which corresponded to the trimethylsilyl derivatives prepared from authentic samples of crystalline α-D-lyxopyranose and β-D-lyxopyranose respectively.

The α-L-lyxose gave a crystalline 2,4-dinitrophenylhydrazone derivative having m.p. 171–172° (lit. m.p. 171–172° for D-lyxose 2,4-dinitrophenylhydrazone (12)) and a toluene-*p*-sulfonylhydrazone derivative having m.p. 142° (lit. m.p. 141° for D-lyxose toluene-*p*-sulfonylhydrazone (22)). The infrared spectra of the two derivatives were identical with the corresponding derivatives of D-lyxose.

*3. Preparation of 5-Deoxy-L-lyxose*

*(a) Methyl (Methyl 2,3-O-Isopropylidene-α-L-lyxofuranosid)uronate*

Methyl (methyl α-L-lyxofuranosid)uronate (43 g) and anydrous copper sulfate (95 g) in acetone (800 ml) were boiled under reflux for 16 h. The filtered reaction mixture was concentrated to a syrup which was then extracted with hot light petroleum (b.p. 60–100°), and after concentration of the extract, the methyl (methyl 2,3-*O*-isopropylidene-α-L-lyxofuranosid)uronate (45 g, 87%) was obtained as a syrup. This syrup had $[\alpha]_D$ −47.6° (*c*, 5 in methanol) and $[\alpha]_D$ −2.6 (*c*, 2.6 in chloroform), and on gas chromatography it gave a single peak $T_g$ 0.932.

Anal. Found: C, 51.78; H, 6.88. $C_{10}H_{16}O_6$ requires C, 51.72; H, 6.94.

A distilled sample of the product (bath temperature 130° at 0.4 mm) had the same physical properties as those given above.

*(b) Methyl 2,3-O-Isopropylidene-α-L-lyxofuranoside*

Methyl (methyl 2,3-*O*-isopropylidene-α-L-lyxofuranosid)uronate (30 g) in dry ether (375 ml) was added dropwise with stirring to a cooled mixture of lithium aluminium hydride (15 g) in ether (600 ml). On completion of the addition, the stirred reaction mixture was heated under reflux for 6 h, and the reduction was then allowed to proceed at room temperature for 16 h. Moist ethyl acetate (220 ml) was added dropwise to the stirred, cooled reaction mixture followed by water (200 ml). The ether layer was separated and combined with the ether washings of the precipitated material, dried (anhyd. $Na_2SO_4$), and filtered. The filtrate was then concentrated to a syrup (25.5 g, 96%); $[\alpha]_D$ −51° (*c*, 3 in chloroform); $\eta_D^{22}$ 1.4506; g.l.c. single peak with $T_g$ 0.832.

Anal. Found: C, 53.2; H, 8.1. $C_9H_{16}O_5$ requires C, 52.9; H, 7.9.

*(c) Methyl 2,3-O-Isopropylidene-5-O-(p-tolylsulfonyl)-α-L-lyxofuranoside*

Methyl 2,3-*O*-isopropylidene-α-L-lyxofuranoside (21.4 g) in dry pyridine (80 ml) was cooled to 0° and treated with *p*-toluenesulfonyl chloride (27.8 g), and after 2 h at ice-bath temperature the mixture was kept at room temperature for 15 h. The reaction mixture was poured onto crushed ice and after 30 min the crude crystalline methyl 2,3-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-α-L-lyxofuranoside (34.8 g, 92%) m.p. 62–68°, was collected. After recrystallization from aqueous ethanol, the pure product (29 g) was found to have m.p. 76–77° and $[\alpha]_D$ −41.7° (*c*, 3.2 in methanol).

Anal. Found: C, 53.64; H, 6.15. $C_{16}H_{22}O_7S$ requires C, 53.63; H, 6.19.

*(d) Methyl 5-Deoxy-5-iodo-2,3-O-isopropylidene-α-L-lyxofuranoside*

Methyl 2,3-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-α-L-lyxofuranoside (26.1 g) and sodium iodide (15 g) dissolved in dry acetone (180 ml) was heated in sealed glass tubes at 115° for 60 h. After cooling, the insoluble sodium *p*-toluenesulfonate was removed by filtration and the filtrate was concentrated to a syrup. The syrup was dissolved in chloroform (250 ml) and the solution was washed with water (2 × 100 ml), dried (anhydrous $Na_2SO_4$), and concentrated to a syrup (22.9 g, 100%). The product was distilled (80–85° at 0.05 mm) and the methyl 5-deoxy-5-iodo-2,3-*O*-isopropylidene-α-L-lyxofuranoside (21 g) was obtained as a colorless oil, $[\alpha]_D$ −70.4° (*c*, 2 in methanol), $\eta_D^{22}$ 1.4975.

Anal. Found: C, 34.33; H, 4.69. $C_9H_{15}O_4I$ requires C, 34.4; H, 4.8.

On gas chromatography the product gave a single peak with $T_g$ 1.07.

*(e) Methyl 5-Deoxy-2,3-O-isopropylidene-α-L-lyxofuranoside*

Methyl 5-deoxy-5-iodo-2,3-*O*-isopropylidene-α-L-lyxofuranoside (14 g) in methanol (200 ml) containing 2.2 *N* methanolic potassium hydroxide (23 ml) and Raney nickel (10 g) was shaken for 5 h at room temperature in a Parr low-pressure shaker-type catalytic apparatus under 50 lb pressure of hydrogen. The nickel catalyst was removed by centrifugation and the supernatant and methanol washings of the catalyst were concentrated to a syrup (6.88 g, 82%) which was distilled (50–55° at 0.05 mm) to yield methyl 5-deoxy-2,3-*O*-isopropylidene-α-L-lyxofuranoside (6.2 g) as a colorless oil. The product on gas chromatographic analysis gave a single peak with $T_g$ 0.128 and had $[\alpha]_D$ −92.7° (*c*, 4.7 in methanol) and $\eta_D^{22}$ 1.4280.

Anal. Found: C, 57.31; H, 8.50. $C_9H_{16}O_4$ requires C, 57.43; H, 8.57.

*(f) 5-Deoxy-L-lyxose*

Methyl 5-deoxy-2,3-*O*-isopropylidene-α-L-lyxofuranoside (6 g) was heated for 2 h on a boiling water bath with 0.5 *N* sulfuric acid (50 ml). After cooling, the mixture was neutralized ($BaCO_3$) and filtered. The filtrate was passed through a small column of mixed Amberlite IR-120($H^+$) and IR-45($OH^-$) ion exchange resins and was concentrated to a syrup (4.05 g, 95%). The 5-deoxy-L-lyxose had $[\alpha]_D$ −30.0° (*c*, 2.5 in water) (lit. $[\alpha]_D$ +32.4° for 5-deoxy-D-lyxose (23)).

Anal. Found: C, 44.54; H, 7.26. $C_5H_{10}O_4$ requires C, 44.77; H, 7.51.

Paper chromatographic examination of the 5-deoxy-L-lyxose showed a single spot $R_{gal}$ 2.74 (solvent A) and $R_{gal}$ 3.33 (solvent B). The trimethylsilyl derivative on gas chromatographic analysis showed two peaks $T_g$ 0.226 (major) and $T_g$ 0.286 (minor).

A portion of the 5-deoxy-L-lyxose (0.1 g) was converted into 5-deoxy-L-lyxose *p*-bromophenylosazone (0.11 g) which had m.p. 153–154° (lit. m.p. 143–144° for 5-deoxy-D-lyxose *p*-bromophenylosazone (23)).

Anal. Found: C, 43.35; H, 3.81; N, 11.7. $C_{17}H_{18}O_2N_4Br_2$ requires C, 43.43; H, 3.86; N, 11.92.

5-Deoxy-L-lyxose (0.22 g) in methanol (15 ml) containing 2,5-dichlorophenylhydrazine (0.28 g) was boiled under reflux for 2 h; the mixture was then concentrated to dryness and the residue was extracted with ethyl acetate. The extract was concentrated and the residue was taken up in hot ether–petroleum mixture (b.p. 40–60°). When this solution cooled, 5-deoxy-L-lyxose 2,5-dichlorophenylhydrazone crystallized, (0.15 g), m.p. 113–114°.

Anal. Found: C, 44.7; H, 4.6. $C_{11}H_{14}O_3N_2Cl_2$ requires C, 45.0; H, 4.8.

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