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Note

# Improved preparation and synthetic uses of 3-deoxy-D-*arabino*-hexonolactone: an efficient synthesis of *Leptosphaerin*

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## Abstract

Acetylation of D-glucono-1,5-lactone and subsequent treatment with triethylamine gave 2,4,6-tri-*O*-acetyl-D-*erythro*-hex-2-enono-1,5-lactone. Hydrogenation of the latter in the presence of palladium on carbon yielded 2,4,6-tri-*O*-acetyl-3-deoxy-D-*arabino*-hexono-1,5-lactone (**5**) in almost quantitative yield calculated from gluconolactone. Catalytic hydrogenation of **5** with platinum on carbon in the presence of triethylamine gave 2,4,6-tri-*O*-acetyl-3-deoxy-D-*arabino*-hexopyranose in quantitative yield. Deacetylation of **5** gave 3-deoxy-D-*arabino*-hexono-1,4-lactone, which was converted into 3-deoxy-5,6-*O*-isopropylidene-2-*O*-methanesulfonyl-D-*arabino*-hexono-1,4-lactone (**10**). The latter was converted into 2-acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone (*Leptosphaerin*). When **10** was boiled in water in the presence of acid, it gave a high yield of 2,5-anhydro-3-deoxy-D-*ribo*-hexonic acid.

*Keywords:* D-Glucono-1,5-lactone; 3-Deoxy-D-*arabino*-hexono-lactone; 3-Deoxy-D-*arabino*-hexose; Enamine; *Leptosphaerin*; 2,5-Anhydro-3-deoxy-D-*ribo*-hexonic acid

## 1. Introduction

In a previous paper, a procedure for the conversion of D-glucono-1,5-lactone (**1**) into 3-deoxy-D-*arabino*-hexono-1,4-lactone (**8**) was described [1]. It involved the partial rearrangement of **1** into D-glucono-1,4-lactone. Subsequent acetylation and catalytic hydrogenation in the presence of triethylamine gave a good yield of tri-*O*-acetyl-3-deoxy-D-*arabino*-hexono-1,4-lactone and a small amount of an isomeric product. Deacetylation gave **8** and ca. 5% of the corresponding *ribo*-isomer. This procedure has been used extensively and it has generally worked well. However, the amount of byproduct has been found to vary, and it was therefore of interest to find an improved procedure.

## 2. Results and discussion

It has now been found that **8** can be prepared readily and in high yield and purity directly from **1** via 2,4,6-tri-*O*-acetyl-D-*erythro*-hex-2-enono-1,5-lactone (**3**) avoiding the rearrangement to D-glucono-1,4-lactone. The unsaturated lactone **3** has previously been prepared by oxidation of 2,3,4,6-tetra-*O*-acetyl-D-glucose [2] or by acetylation of **1** in pyridine [3], or in *N*,*N*-dimethylformamide–triethylamine

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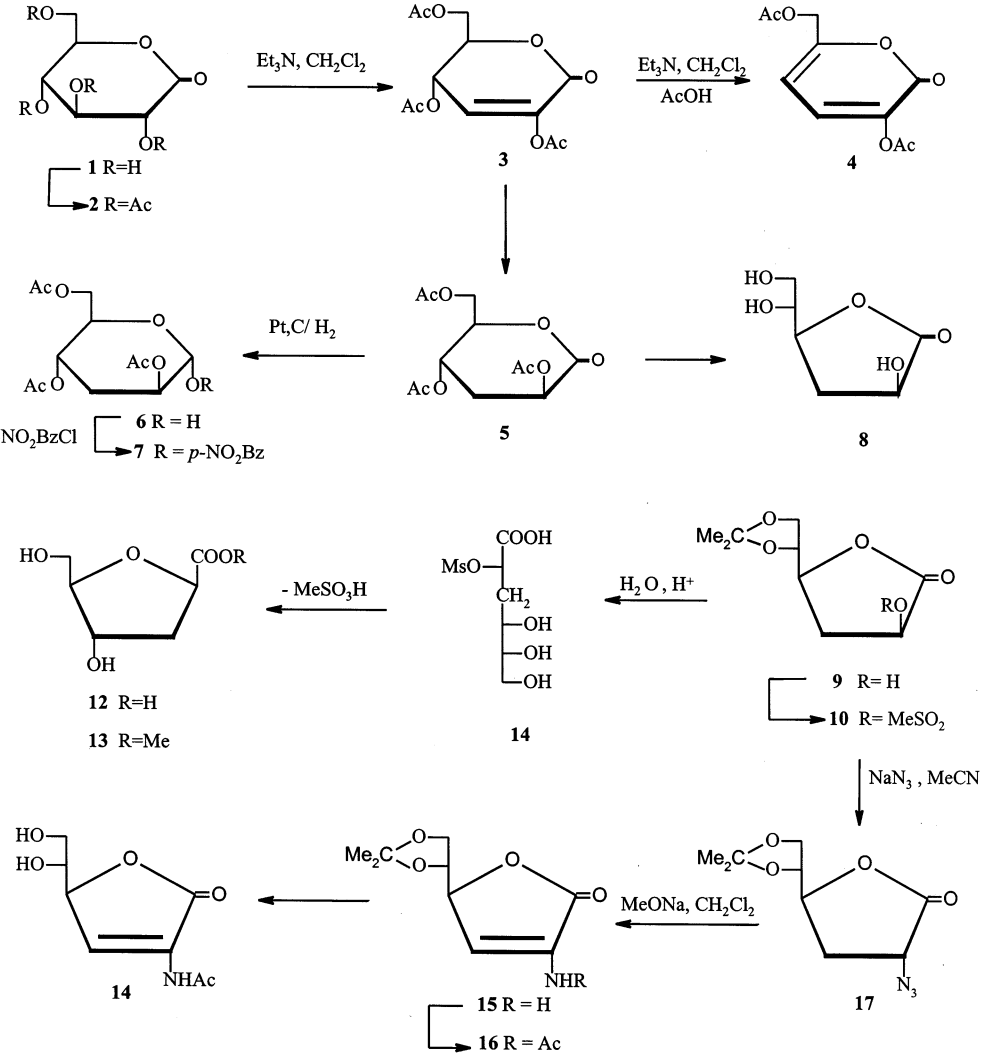
[4]. The latter two procedures gave, however, mixtures of **3** and products of di-elimination and pure **3** could only be obtained after distillation [2] or chromatographic purification [3,4]. The benzoylated analogue of **3** has been prepared in high yield by benzoylation of **1** in pyridine [5] (Scheme 1).

Acid catalyzed acetylation of **1** gave the corresponding tetraacetate (**2**) as the only product [6]. Treatment of the latter with triethylamine in dichloromethane solution for a few minutes resulted in exclusive formation of the 2,3-unsaturated lactone **3**. Further elimination of acetic acid was not observed when the mixture was kept for 24 h. The selective elimination of 1 mol of acetic acid from **2** with triethylamine in dimethyl sulfoxide has been reported previously [7], and it was first observed during the preparation of **3** as mentioned above [2]. Formation of the di-eliminated product **4** during acetylation of **1** in pyridine has been explained by a combination of acid and base catalysis [3]. In order to test this, **2** was treated with 1.2 equiv of triethylamine in chloroform solution and the reaction was monitored by NMR spectroscopy. This gave **3** as the only product in spite of the fact that one equivalent of acetic acid was liberated. When, however, an additional equiv of acetic acid was added further elimination to **4** took place rapidly. Similar results were obtained when the unsaturated lactone **3** was dissolved in pyridine. No formation of **4** was observed until acetic acid was added, thus confirming the catalytic action of acetic acid in the second elimination step [3].



Scheme 1.

Catalytic hydrogenation of **3** gave 2,4,6-tri-*O*-acetyl-3-deoxy-D-*arabino*-hexono-1,5-lactone (**5**) as virtually the only product [8]. Subsequent deacetylation yielded 3-deoxy-D-*arabino*-hexono-1,4-lactone (**8**) in 97% yield, calculated from D-gluconolactone. The isolation of impure **8** after the reduction of the tetraacetate **2** in the presence of triethylamine, reported in Ref. [1], was probably due to contamination of **2** with acetic acid.

Having ready access to **5** and **8**, both were utilized for further synthesis. Thus reduction of **5** with bis(3-methyl-2-butyl)borane gave, as expected [9], the triacetyl 3-deoxy-hexose **6**. Surprisingly it was found that this conversion could be performed more readily and in quantitative yield by catalytic hydrogenation in ethyl acetate and triethylamine using 5% platinum on carbon as the catalyst. The syrupy **6** was converted into the crystalline α-1-*O*-*p*-nitrobenzoate **7**. Acetylated 3-deoxy-1,4-lactones, such as 3-deoxy-D-*arabino*- and D-*xylo*-hexono-1,4-lactone, were not reduced under these conditions. Acetylated 2,3-dideoxy-1,4- and 1,5-lactones do not appear to be reduced [10]. The catalytic reduction of other 3-deoxy-1,5-lactones is being studied.

Treatment of **8** with acetone and sulfuric acid yielded the 5,6-*O*-isopropylidene derivative **9**, which was converted into the 2-methanesulfonyloxy derivative **10** in 70% yield. The latter product was previously prepared from D-isoascorbic acid via D-mannonolactone [11], and also from D-glyceraldehyde through a lengthy series of reactions [12]. Treatment of **10** with sodium azide in acetonitrile produced the azide **17** in high yield [11,13]. When the latter was treated with methanolic sodium methoxide in dichloromethane, it rapidly cleaved off nitrogen to give the enamine **15** in 90% yield [14,15]. Acetylation gave the acetate **16** [12,16], and subsequent partial hydrolysis produced the natural product *Leptosphaerin* (**14**), identical with the product previously described [12,16]. Through the present procedure, this product can be prepared readily.

Finally, when the methanesulfonate **10** was heated in water in the presence of acid, it was converted into the 2,5-anhydride **12**. The reaction probably proceeds through the hydrolyzed intermediate **11**, which undergoes ring closure with inversion of the configuration at C-2 [17,18]. The yield was quantitative as seen from $^{13}$C NMR spectra of the reaction mixture which showed only the signals of **12** and that of methanesulfonic acid. To obtain pure **12**, it was converted into its methyl ester **13**. The sulfonic acid was then removed with an ion exchange resin and subsequent hydrolysis gave **12**. On concentration of an aqueous solution of **12** byproducts were formed as seen from $^{13}$C NMR spectra, which showed extra signals close to those of **12**. This is probably due to formation of intermolecular esters. When the mixture was heated in water, it was hydrolyzed to pure **12**.

## 3. Experimental

Melting and boiling points are uncorrected. Optical rotations were measured on a Perkin–Elmer 141 polarimeter. $^{13}$C NMR spectra were recorded on Bruker AC-250 or AM-500 instruments; all $^{1}$H NMR spectra were measured at 500 MHz. Chemical shifts are given in $\delta$ values. Microanalyses were performed by Dr J. Theiner, Mikroanalytisches Laboratorium der Universität Wien.

*2,4,6-Tri-*O*-acetyl-3-deoxy-*D-erythro-*hex-2-enono-1,5-lactone* (**3**).—D-Glucono-1,5-lactone (**1**) (40 g, 225 mmol) was added in portions during 10–15 min to $Ac_2O$ (100 mL, 1 mol) containing a few drops of 60% aq $HClO_4$. The mixture was kept for 1 h at room temperature (rt) and the clear solution was then concd in vacuum at 70 °C. The syrupy residue consisted of virtually pure 2,3,4,6-tetra-*O*-acetyl-D-glucono-1,5-lactone (**2**) containing small amounts of acetic anhydride and acetic acid. The $^{1}$H NMR spectrum was identical with that previously reported [1]. $^{13}$C NMR ($CDCl_3$): $\delta$ 170.0, 169.7, 169.3 169.0 (Me*CO*), 164.4 (C-1), 75.6 (C-5), 70.2, 70.0, 66.4 (C-2,3,4), 61.2 (C-6), 20.1–20.4 (4 *Me*CO).

The product was dissolved in $CH_2Cl_2$ (300 mL) and cooled to 0 °C, and $Et_3N$ (48 mL, 1.5 mol) was added in one portion. The yellow solution was kept for 15 min at 0 °C. It was then washed with 2 M aq HCl and with water, dried (MgSO$_4$), filtered through carbon and concd leaving 65 g (~100%) of **3** as a yellow syrup. The $^1$H NMR spectrum was identical with that previously reported [2,3,19]. A sample was distilled in vacuum, bp ~170 °C (0.2 mm), $[\alpha]_D^{20}$ +129° (*c* 2, CHCl$_3$), lit +108° [3,4,19]. The $^1$H NMR spectrum was identical with that described [19]. $^{13}$C NMR (CDCl$_3$): δ 170.1, 169.4, 167.9 (Me*CO*), 156.9 (C-1), 139.3 (C-2), 125.9 (C-3), 77.6 (C-6), 63.9, 61.7 (C-4, C-6), 20.4–20.0 (*Me*CO).

*2,4,6-Tri*-O-*acetyl-3-deoxy*-D-arabino-*hexono-1,5-lactone* (**5**).—The unsaturated lactone **3** (65 g) was dissolved in EtOAc (300 mL) and hydrogenated overnight at $5 \times 10^6$ Pa in the presence of 5% Pd/C. Filtration and concentration gave **5** (65 g, ~100%) as a colorless syrup, $[\alpha]_D^{20}$ +67.5° (*c* 6, CHCl$_3$), lit $[\alpha]_D$ +16° [8]. A sample was distilled, bp 165 °C (0.2 mm), $[\alpha]_D^{20}$ +68.7° (*c* 1.6, CHCl$_3$). $^1$H NMR (CDCl$_3$, previously reported at 60 MHz [8]): δ 5.55 (dd, 1H, $J_{2,3}$ 12.2, $J_{2,3'}$ 7.0 Hz, H-2), 5.17 (dt, 1H, $J_{4,5}$ 6.0 Hz, H-4), 4.61 (m, 1H, $J_{5,6}$ 3.5, $J_{5,6'}$ 5.0 Hz, H-5), 4.33 (dd, 1H, $J_{6,6'}$ 12.3 Hz, H-6), 4.24, (dd, 1H, H-6′), 2.41 (ddd, 1H, $J_{3,3'}$ 14.0, $J_{3,4}$ 6.0 Hz, H-3), 2.29 (ddd, 1H, $J_{3',4}$ 3.0 Hz, H-3′), 2.14, 2.12, 2.06 (MeCO). $^{13}$C NMR: δ 169.9, 169.4, 169,3 167.2 (C=O), 76.9 (C-5), 65.3, 63.7, 62.3 (C-2, C-4, C-6), 30.1 (C-3), 20.5, 20.3 (*Me*CO). Anal. Calcd for C$_{12}$H$_{16}$O$_8$: C, 50.00; H, 5.60. Found: C, 49.95; H, 5.46.

*3-Deoxy*-D-arabino-*hexono-1,4-lactone* (**8**).—The acetate **5** (65 g) was deacetylated with MeONa in MeOH and then treated with Amberlite IR-120 (H$^+$) to remove the sodium ions. Evaporation and trituration with EtOAc gave 35.5 g (97%) of **8**, mp 80–85 °C. The product was pure as seen from a $^{13}$C NMR spectrum [1] and was used for subsequent reactions. A sample was recrystallized from dioxane to give a product with mp 91.5–93 °C, lit 92–93 °C [20]; $[\alpha]_D^{20}$ +6.1° (*c* 1.7, H$_2$O), lit +6.4° [20].

*2,4,6-Tri*-O-*acetyl-3-deoxy*-D-arabino-*hexopyranose* (**6**).—A soln of **5** (24 g, 83 mmol) in EtOAc (150 mL) and Et$_3$N (23 mL, 166 mmol) was hydrogenated overnight at $5 \times 10^6$ Pa in the presence of 10% Pt/C (100 mg). The mixture was then filtered and concd leaving 24 g of **6** as a colorless syrup. $^{13}$C NMR, α anomer: δ 170.7, 170.1, 169.7 (CO), 90.4 (C-1), 69.8, 67.9, 64.2 (C-2,4,5), 62.8 (C-6), 28.1 (C-3), 20.7, 20.6, 20.3 (OAc). β anomer (7%): 93.3 (C-1), 77.1, 74.7, 68.7 (C-2,4,5), 64.5 (C-6), 31.0 (C-3).

When the syrup was kept for ca. 1 month, small amounts of crystals were formed. Addition of Et$_2$O (20 mL) and cooling gave 3 g of crude crystals which were recrystallized twice from ether to give 0.7 g of 2,4,6-tri-*O*-acetyl-3-deoxy-α-D-*arabino*-hexopyranose, mp 65–67 °C, $[\alpha]_D^{20}$ +45.5→45.9° (48 h) (*c* 1.2, CHCl$_3$). The $^{13}$C NMR spectrum was identical with that described above. $^1$H NMR (C$_6$D$_6$): δ 5.28 (dt, 1H, $J_{4,5}$ 10.5 Hz, H-4), 5.01 (bd, 1H, $J_{1,2}$ 0.5 Hz, H-1), 4.94 (dt, 1H, $J_{2,3eq}$ 3.1, $J_{2,3ax}$ 3.3 Hz, H-2), 4.35 (dd, 1H, $J_{6,6'}$ 11.7 Hz, H-6), 4.26 (dd, 1H, H-6′), 4.17 (ddd, 1H, $J_{5,6}$ 5.0, $J_{5,6'}$ 2.6 Hz, H-5), 2.20 (ddd, 1H, $J_{3eq,4}$ 4.2, $J_{3eq,3ax}$ 14.4 Hz, H-3eq), 2.02 (m, 1H, $J_{3ax,4}$ 11.0 Hz, H-3ax), The α configuration was confirmed from a $^{13}$C–$^1$H coupled $^{13}$C NMR spectrum which showed that $J_{C1,H1}$ was 171 Hz [21]. Anal. Calcd for C$_{12}$H$_{18}$O$_2$: C, 49.65; H, 6.75. Found: C, 49.86; H, 6.02.

p-*Nitrobenzoyl-2,4,6-tri*-O-*acetyl-3-deoxy-α*-D-arabino-*hexopyranose* (**7**).—To a stirred and ice-cold soln of **6** (4.5 g, 15.5 mmol) in pyridine (15 mL), *p*-nitrobenzoyl chloride (3.7 g, 20 mmol) was added in portions in the course of 20 min. The mixture was kept overnight at rt and then diluted with water and extracted with CH$_2$Cl$_2$. The extract was washed with aq NaHCO$_3$, aq HCl and water. The soln was dried (MgSO$_4$), filtered and concd leaving 5.8 g (94%) of a syrup which crystallized from EtOAc–hexane to give 3.8 g (61%) of **7**, mp 111–113 °C. A sample was recrystallized from EtOH, mp 112–113 °C, $[\alpha]_D^{20}$ +45.5° (*c* 1.7, CHCl$_3$). $^1$H NMR (C$_6$D$_6$): δ 7.68 and 7.64 (dd, 4H, C$_6$H$_4$), 6.45 (br s, 1H, $J_{1,2}$ 1 Hz, H-1), 5.35 (dt, 1H, $J_{4,5}$ 10.5 Hz, H-4), 5.02 (dt, 1H, $J_{2,3eq}$ 1, $J_{2,3ax}$ 3.2 Hz, H-2), 4.35 (dd, 1H, $J_{6,6'}$ 12.5 Hz, H-6), 4.17 (dd, 1H, H-6′), 4.09 (ddd, 1H, $J_{5,6}$ 5.3, $J_{5,6'}$ 2.6 Hz, H-5), 2.37 (m, 1H, $J_{3,3}$ 14.0, $J_{3eq,4}$ 4.9 Hz, H-3eq), 1.90 (ddd, 1H, $J_{3ax,4}$ 11.2 Hz, H-3ax), 1.68, 1.67, 1.56 (3s, 9H, OAc). $^{13}$C NMR (CDCl$_3$): 169.8, 169,6, 169.5 (Me*CO*), 162.0 (PhC = O), 151, 134.3, 130.8, 123.6 (Ph), 91.1 (C-1), 71.1, 67.7, 63.6 (C-2, C-4,5), 62.3 (C-6), 29.3 (C-3), 20.8, 20.6 (*Me*CO). Anal. Calcd for $C_{19}H_{21}NO_{11}$: Calcd: C, 51.94; H, 4.82; N, 3.19. Found: C, 51.92; H, 4.83; N, 3.22.

*3-Deoxy-5,6-*O*-isopropylidene-2-*O*-methanesulfonyl-*D-arabino*-hexono-1,4-lactone* (**10**).—Crude **8** (31 g), acetone (300 mL), sulfuric acid (1 mL) and anhyd $MgSO_4$ (20 g) were stirred overnight at rt. The mixture was then neutralized by stirring with $NaHCO_3$, filtered through carbon and concd leaving 35.8 g (93%) of 3-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hexono-1,4-lactone (**9**) which crystallized. A sample was recrystallized from $CH_2Cl_2$–pentane, mp 84–85 °C, lit 89–90 °C [12]. $^1H$ and $^{13}C$ NMR spectra were identical to those reported [12].

The crude **9** (35.8 g, 180 mmol) was dissolved in pyridine (80 mL) and $MeSO_2Cl$ (27.7 mL, 360 mmol) was added with stirring and ice-cooling in the course of 30 min. The mixture was kept for 1 h at 0 °C. Ice and water (400 mL) were added, keeping the temperature at 0 °C. The crystalline **10** was filtered off, washed with water and ether and dried to give 38 g (70% calcd from **8**), mp 140–142 °C. A sample was recrystallized from EtOAc, mp 143–144 °C, lit 142–123.5 °C [11]; $[\alpha]_D^{20}$ −25.3° (*c* 1.8, $CHCl_3$), lit −23° [11].

*2-Azido-2,3-dideoxy-5,6-*O*-isopropylidene-*D-ribo*-hexono-1,4-lactone* (**17**).—The mesylate **10** (10 g, 35.7 mmol) and $NaN_3$ (16 g, 146 mmol) in MeCN (100 mL) were boiled for 3 h. Most of the solvent was then removed in vacuum and $CH_2Cl_2$ (50 mL) and water (50 mL) was added. The organic phase was separated and washed with water, dried ($MgSO_4$) and concd leaving 8.1 g ( ~ 100%) of the crude azide **17**. Recrystallization from ether–pentane gave 6.7 g (83%) of a product with mp 60–61 °C, lit 60–61.5 °C [11]; $[\alpha]_D^{20}$ +131.5° (*c* 1.9, MeOH), lit +134° [11].

*2-Amino-2,3-dideoxy-5,6-*O*-isopropylidene-*D-erythro*-hex-2-enono-1,4-lactone* (**15**).—The azide **17** (8.5 g) was dissolved in $CH_2Cl_2$ (30 mL) and MeONa in MeOH (1 M, 10–15 drops) was added in the course of 15 min until $N_2$-evolution ceased. After 0.5 h at 20 °C the mixture was neutralized with dry ice, washed twice with water, dried ($MgSO_4$) and concd leaving 4.0 g (91%) of yellow **15**, mp 131–133 °C, pure as seen from a $^{13}C$ NMR spectrum. Recrystallization from $CH_2Cl_2$–pentane and from $Et_2O$–pentane gave colorless crystals, mp 133–134 °C, $[\alpha]_D^{20}$ −75.0° (c 0.7, $CHCl_3$). $^1H$ NMR ($CDCl_3$): $\delta$ 6.0 (d, 1H, $J_{3,4}$ 2.0 Hz, H-3), 4.72 (dd, 1H, $J_{4,5}$ 7,8 Hz, H-4), 4.09 (dd, 1H, $J_{6,6'}$ 9.0 Hz, H-6), 3.99 (dd, 1H, H-6′), 3.86 (ddd, 1H, $J_{5,6}$ 6.1 Hz, $J_{5,6'}$ 4.2, H-5), 3.81 (br s, ~2H, $NH_2$), 1.45,1.33 (isoprop-$CH_3$). $^{13}C$ NMR: $\delta$ 170.2 (C-1), 133.9 (C-2), 112.4 (C-3), 109.9 (isoprop-C), 79.7, 77.2 (C-4,5), 66.5 (C-6), 26.6, 24.9 (isoprop-$CH_3$). Anal. Calcd for $C_9H_{13}NO_4$: C, 53.99; H, 6.54; N, 6.70. Found: C, 54.21; H, 6.58; N, 7.04.

*2-Acetamido-2,3-dideoxy-5,6-*O*-isopropylidene-*D-erythro*-hex-2-enono-1,4-lactone* (**16**).—To a solution of **15** (3.0 g) in pyridine (10 mL) was added $Ac_2O$ (3 mL) and the mixture was kept overnight at 5 °C. Water was then added and after 0.5 h $CH_2Cl_2$ (15 mL). The organic phase was washed with water, dried and concd The residue was crystallized from $Et_2O$–pentane yielding **16** (2.62 g, 72%), mp 126–128 °C. Recrystallization from EtOH gave a product with mp 127–128 °C, lit 128–129 °C [12], 124–125 °C [16]; $[\alpha]_D^{20}$ −26.9° (*c* 1.8, $CHCl_3$), lit −57° [12], −29.1° [16]. $^1H$ and $^{13}C$ NMR spectra were identical with those reported [12]. Anal. Calcd for $C_{11}H_{15}NO_5$: C, 54.77; H, 6.25; N, 5.81. Found: C, 54.80; H, 6.26; N, 5.93.

*2-Acetamido-2,3-dideoxy-*D-erythro*-hex-2-enono-1,4-lactone* (Leptosphaerin) (**14**).—A suspension of the isopropylidene derivative **16** (1.0 g) in water (10 mL) containing 10 drops of $CF_3COOH$ was stirred until the mixture was homogeneous ( ~ 1 h). The soln was then concd and the crystalline residue was recrystallized from EtOH–pentane to give **14** (0.67 g, 80%), mp 187–189 °C, lit 185–187 °C [12], 186–188 °C [16]; $[\alpha]_D^{20}$ +41.6° (*c* 0.7, $H_2O$), lit +40° [12], +41.1° [16]. $^1H$ and $^{13}C$ NMR spectra were in agreement with those reported [12].

*2,5-Anhydro-3-deoxy-*D-ribo*-hexonic acid* (**12**).—A suspension of the mesylate **10** (10.0 g) in water (25 mL) and $CF_3COOH$ (0.5 mL) was boiled for 3 h. The soln was then concd and the residue was heated under reflux in MeOH (50 mL) for 6 h. Neutralization with Amberlite-67 (OH) ion-exchange resin, to remove the $MeSO_3H$, and concentration gave methyl 2,5-anhydro-3-deoxy-D-*ribo*-hexonate **13** (6.3 g, 100%) as a syrup. $^{13}C$ NMR ($D_2O$): $\delta$ 174.2 (CO), 87.1 (C-5), 75.6, 71.3 (C-2, 4), 61.3 C-6, 52.3 (OMe), 37.2 C-3). Attempts to purify the ester by vacuum distillation [22] resulted in loss of MeOH and formation of a polymeric material.

The methyl ester **13** was dissolved in water (25 mL), $CF_3COOH$ (1 mL) was added and the soln was boiled for 4 h. Concentration and crystallization from dioxane gave the title compound (5.1 g 88%), mp 124–126 °C. Recrystallization from EtOH gave the pure product, mp 132–133 °C, lit 109–111 °C [23]; $[\alpha]_D^{20}$ +34.1° (*c* 0.4, MeOH), lit $[\alpha]_D^{20}$ +30.3° [23]. The reported values [23] were measured on a crude product, obtained by concentration of the reaction mixture. $^{13}C$ NMR ($D_2O$): $\delta$ 175.9 (CO), 87.1 (C-5), 75.5, 71.4 (C-2, 4), 61.2 (C-6), 37.4 (C-3).

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