The Base Catalyzed Rearrangement of Some 6-Bromo-2,6-dideoxyaldono-1,4-lactones. Preparation of L-Digitoxose *

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Treatment of 2,6-dibromo-2,6-dideoxy-D-mannono-1,4-lactone (1) with hydrazine followed by bromine gives 6-bromo-2,6-dideoxy-D-arabino-hexono-1,4-lactone (5). Reaction of 5 with excess aqueous potassium hydroxide leads to inversion at C-4 and C-5 giving 2-deoxy-L-ribo-hexono-1,4-lactone (4a). With aqueous potassium carbonate 5 gives 2-deoxy-L-xylo-hexono-1,4-lactone (3a), inverted only at C-5. Reaction of 4a with hydrogen bromide in acetic acid gives 6-bromo-2,6-dideoxy-L-ribo-hexono-1,4-lactone (8), which is reduced to 2,6-dideoxy-L-ribo-hexono-1,4-lactone (7a) and, subsequently, to L-digitoxose. The reaction of 8 with potassium hydroxide also leads to inversion at C-4 and C-5 giving 2-deoxy-D-arabino-hexonic acid. The mechanism of the base induced rearrangement of 5 has been studied.

In previous papers it was shown that a number of bromodeoxyaldonolactones can be prepared by treatment of aldono lactones with hydrogen bromide in acetic acid. such bromodeoxy lactones may be converted into deoxy lactones and deoxy sugars by debromination and reduction. Besides, bromodeoxy lactones can react with a variety of nucleophiles; in the present paper the behaviour of 6-bromo-2,6-dideoxy-D-arabino-hexono-1,4-lactone (5) and of the L-ribo-isomer (8), towards aqueous base, is described.

The lactone (5) was previously obtained from 2,6-dibromo-2,6-dideoxy-D-mannono-1,4-lactone (1) by debromination with sodium iodide.

* Reaction of Aldonic Acids with Hydrogen Bromide, Part V. For Part IV see Ref. 4.
\( \text{L-ribo-hexonate (11), was formed, converted on} \)
\( \text{acidification and evaporation into 2-deoxy-L-} \)
\( \text{ribo-hexono-1,4-lactone (4a). The latter could} \)
\( \text{not be induced to crystallize, but its tri-O-acetate} \)
\( \text{(4b) was obtained in a pure, crystalline state.} \)
\( \text{Hence, replacement of the bromide of 5 in strong} \)
\( \text{base is accompanied by inversions at both C-4} \)
\( \text{and C-5. Alternatively, 5 was boiled with excess} \)
\( \text{aqueous potassium carbonate until the bromide} \)
\( \text{had been replaced by a hydroxy group. A } {^1} \text{H} \)
\( \text{NMR spectrum of the product revealed that no} \)
\( \text{11 was present, but that a mixture of 2-deoxy-L-} \)
\( \text{xylo-hexonate (16) and 2-deoxy-D-arabino} \)
\( \text{hexonate (15) was formed. Acidification and} \)
\( \text{evaporation followed by acetylation and separation} \)
\( \text{by chromatography gave two crystalline} \)
\( \text{products, namely tri-O-acetyl-2-deoxy-L-xylo} \)
\( \text{hexono-1,4-lactone (3b) (39 % yield) and the} \)
\( \text{corresponding D-arabino-isomer (6b) (8 %).} \)
\( \text{Treatment of the crude L-ribo-lactone (4a)} \)
\( \text{with hydrogen bromide in acetic acid followed by} \)
\( \text{deacetylation with methanol gave the 6-bromeo} \)
\( \text{lactone (8), hydrogenolysis of which yielded the} \)
\( \text{2,6-dideoxy-lactone (7a), which could be isolated} \)
\( \text{as its crystalline diacetate (7b). When the latter} \)
\( \text{was prepared from 1 without isolating any of the} \)
\( \text{intermediates, 5, 4a and 8, the yield was 60 %}. \)
\( \text{The structure of 7, and hence of 8 and 4, was} \)
\( \text{proved by its reduction with diisooamyloborane to} \)
\( \text{the known 2,6-dideoxy-L-ribo-hexose.} \)
\( \text{Treatment of 7a with phenylhydrazine gave the crystalline} \)
\( \text{phenylhydrazide of 2,6-dideoxy-L-ribo-hexonic acid. Both} \)
\( \text{7a and its phenylhydrazide had properties in agreement with those of the D-} \)
\( \text{enantiomers.} \)

\( \text{Reaction of the bromolactone (8) with aqueous} \)

potassium hydroxide led to inversion at C-4 and C-5, as described above for 5, and gave, after acidification and acetylation, the known, crystalline triacetate of 2-deoxy-D-arabino-hexono-1,4-lactone (6b). When the latter was prepared from 1 without isolating any intermediates it was obtained in 44% yield. On the other hand, when 8 was treated with the weaker base potassium carbonate the reaction took a different course, again analogous to the behaviour of 5. After acidification and acetylation a mixture of 4b and tri-O-acetyl-D-lyxo-hexono-1,4-lactone (9b) was obtained; 6b could not be detected in the mixture.

The structure of 6b has been confirmed through its synthesis from 2-deoxy-D-arabino-hexose, and that of 9b was similarly proven by its preparation from 2-deoxy-D-lyxo-hexose. The structure of the L-lyxo isomer (3b) has been established in the course of a different investigation.

In order to study more closely the reaction of 5 with aqueous base, the lactone was treated at room temperature with varying amounts of potassium hydroxide or potassium carbonate in water-deuterium oxide mixtures while monitoring the reactions by $^{13}$C NMR spectroscopy. When 5 was treated with 4 molar equivalents of potassium hydroxide it was completely converted into the salt of 2-deoxy-D-ribo-hexonic acid (11) within 30 min. A spectrum measured after 5 min showed the presence of 70% of 11 and 30% of an intermediate, believed to be the 4,5-epoxide (14) with the 2-deoxy-D-xylo-configuration. Its $^{13}$C NMR spectrum (Table 1) shows, inter alia, signals at 61.7, 59.2 and 58.1 ppm, indicating that it contains a primary alcohol group (61.7) and a di-secondary epoxide ring. $^{10,11}$ The conversion of 14 into 11 may take place by intramolecular attack of the carboxylate anion on C-4, resulting in inversion of this carbon and formation of a 1,4-lactone (4a), which subsequently reacts with the base to yield 11.

Reaction of 5 with 2.5 molar equivalents of potassium hydroxide also gave 11 as the only product after 3–4 h reaction. However, in this experiment two intermediates were observed. A spectrum measured after 5 min showed 11% of the 4,5-epoxide (14) and 89% of a different epoxide, believed to have the structure 13 on the basis of its $^{13}$C NMR spectrum (Table 1). The absence of a signal at 62–64 ppm shows that 13 does not contain a primary alcohol group, and the signals at 46.3 and 53.4 suggest a 5,6-epoxide. $^{10,11}$ A spectrum recorded after 18 min showed the presence of 28% of 13, 25% of 14, and 48% of the final product (11).

When 5 was reacted with only two molar equivalents of potassium hydroxide several days were required for the reaction to go to completion and the final product consisted mainly of the salt of 2-deoxy-D-xylo-hexonic acid (16), the corresponding lactone (3a), and smaller amounts of the D-arabino isomer (15). Complete reaction

<table>
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<th>Compound</th>
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<td>15</td>
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$^a$ Assignments may be reversed.

of 5 with two molar equivalents of potassium carbonate also required several days at room temperature and gave only 15 and 16; 11 and 14 were not observed. However, under the less alkaline conditions used in the last two experiments, two other intermediates were observed in addition to 13, in the initial stages of the reactions. One of these (12) is a 1,4-lactone (C-4 at 83.7) with a 5,6-epoxide group (C-6 at 46.3; C-5 at 53.4 ppm). The second intermediate is the anion (10), corresponding to 5, as seen from the chemical shift values (Table).

From these experiments it is concluded that the first step in the reaction of 5 with aqueous base is the simultaneous formation of the epoxide (12) and the 6-bromo-aldonate (10); both of these, on further reaction, yield the 5,6-epoxide (13). Under relatively mild alkaline conditions 13 subsequently opens to the L-xylo-anion (16) as the main product, together with some 15. The preferential formation of 16 from 13 may be explained through an intramolecular attack of the carboxylate anion on C-5 of 13 to give 16 via a six-membered lactone. In strong base (excess potassium hydroxide) the 5,6-epoxide (13) rearranges to the 4,5-epoxide (14), which subsequently yields the L-ribo-carboxylate (11) as described above. The rearrangement of 13 into 14 is analogous to the results of Payne, who studied epoxide migration in epoxy alcohols and found that the isomer with the highest degree of substitutution at the epoxide ring was favoured in aqueous sodium hydroxide.

The reaction of 8 with base to give either 6 or a mixture of 4 and 9 may be explained through an analogous series of intermediates.
EXPERIMENTAL

Melting points are uncorrected. Optical rotations were measured on a Perkin Elmer 141 polarimeter. NMR spectra were obtained on Bruker WH-90 and HX-270 instruments. Dioxane (67.40 ppm) was used as internal reference for $^{13}$C NMR spectra. Column chromatography was done on silica gel 60 (40–63 μm, Merck 9385) using the “flash technique”. Evaporations were performed in vacuum at 50 °C. Microanalyses were performed by NOVO microranalytical laboratory.

In order to observe the course of the base catalyzed hydrolysis of 5 the pure, crystalline product (500 mg) was dissolved in D$_2$O (0.5 ml) in a 10 mm NMR sample tube and the appropriate amounts (see discussion) of potassium hydroxide or carbonate, dissolved in H$_2$O, were added at 0 °C, bringing the total volume of the solution to ~1.5 ml. Besides, a few drops of 1,4-dioxane were added as internal reference. The solutions were kept at room temperature and $^{13}$C NMR spectra were measured at intervals at 22.63 MHz.

6-Bromo-2,6-dideoxy-α-arabinono-hexono-1,4-lactone (5). To a suspension of 2,6-dibromo-2,6-dideoxy-β-mannono-1,4-lactone (I) $^1$ (5.0 g) in water (60 ml) was added 80 % aqueous hydrazine hydrate (2.5 ml, ~3 equiv.) After a few min the nitrogen evolution ceased and a clear solution was obtained which contained the 2-deoxy-hydrazide (2) as the only product as seen from a $^{13}$C NMR spectrum (see below). The solution was cooled in ice and bromine (~3 ml) was added dropwise (vigorous N$_2$ evolution) until a persistent bromine colour was obtained. The solution was evaporated, water was twice added and again evaporated leaving a syrup (4–5 g) which consisted of almost pure 5 as seen from a $^{13}$C NMR spectrum. This crude product was used without further purification in subsequent experiments.

In order to obtain pure 5 the crude product was dissolved in water (30 ml); the solution was saturated with sodium chloride and extracted five times with ethyl acetate. The extract was dried and evaporated leaving ~4 g of a syrup which crystallized on trituration with diethyl ether to give 2.9 g (78 %) of 5, m.p. 62–66 °C. Recrystallization from ethyl acetate gave a product with m.p. 71–73 °C, $[\alpha]_{D}^{20} +65.6^\circ$ (c 2.9, H$_2$O). Anal. C$_8$H$_6$BrO$_4$; C, H, Br. A $^{13}$C NMR spectrum was identical with that described previously.

6-Bromo-2,6-dideoxy-α-arabinono-hexonic acid hydrazide (2). To a solution of the dibromolactone (I) (2.0 g) in methanol (10 ml) was added 1 ml of 80 % aqueous hydrazine hydrate. When kept overnight at +5 °C the solution deposited 1.4 g (83 %) of 2 as colourless crystals with m.p. 123–125 °C. Two recrystallizations from methanol did not change the m.p., $[\alpha]_{D}^{20} +10.6^\circ$ (c 2.6, H$_2$O). Anal. C$_9$H$_{13}$BrN$_2$O$_5$; C, H, Br, N. $^{13}$C NMR (D$_2$O): 173.7 ppm (C-1); 74.3 (C-4); 70.2 and 67.7 (C-3 and C-5); 39.2 and 39.0 (C-2 and C-6).

2-Deoxy-α-ribo-hexono-1,4-lactone (4a). Crude 5, prepared from 5 g of dibromolactone (I) as described above, was dissolved in water (60 ml) and potassium hydroxide (4 g) was added. The strongly basic solution was kept overnight at room temperature and it was then neutralized with hydrochloric acid and evaporated. A $^{13}$C NMR spectrum of the residue showed the signals of the salt of 2-deoxy-α-ribo-hexonic acid (II) (Table 1). When a solution of the salt was acidified with hydrochloric acid the lactone (4a) was formed as seen from a $^{13}$C NMR spectrum (Table). Only traces of other products were present. Evaporation of the acidified solution and extraction of the residue with methanol followed by evaporation gave ~3 g of crude lactone (4a), which could not be induced to crystallize.

2-Deoxy-α-ribo-hexonic acid hydrazide. A sample of the crude lactone (4a) (1.8 g) was heated for a few min with 80 % aqueous hydrazine hydrate (2 ml) in methanol (10 ml). The solution was then evaporated and methanol (10 ml) was added. On standing crystallization took place to give 1.3 g (68 %) of the hydrazide, m.p. ~130 °C. Recrystallization from methanol gave a product with m.p. 135–136 °C, $[\alpha]_{D}^{20} +26.8^\circ$ (c 1.9, H$_2$O). Anal. C$_8$H$_{13}$N$_2$O$_5$; C, H, N. $^{13}$C NMR (D$_2$O): 174.9 ppm (C-1), 75.7 (C-4); 73.9 and 70.7 (C-3 and C-5); 64.5 (C-6); 38.3 (C-2).

Tri-O-acetyl-2-deoxy-α-ribo-hexono-1,4-lactone (4b). The crude lactone (4a), prepared from 5 g of I as described above, was acetylated with acetic anhydride and 60 % aqueous perchloric acid. Work-up in the usual way gave 3.6 g of product, which could be crystallized from diethyl ether-pentane (seed crystals were obtained after chromatography of a previous sample using diethyl ether as eluant) to give 2.29 g (48 %) of 4b, m.p. 72–74 °C. Recrystallization gave a product with m.p. 74–75 °C, $[\alpha]_{D}^{20} +8.0^\circ$ (c 5.4, CHCl$_3$). Anal. C$_{16}$H$_{19}$O$_8$, C, H. $^{1}$H NMR (CDCl$_3$): 6.25 (H-2a); 2.98 (H-2b); 5.40 (H-3); 4.59 (H-4); 5.20 (H-5); 4.18 (H-6a); 4.41 (H-6b). J$_{22}$ 18.8 Hz; J$_{23}$ 2.2; J$_{24}$ 7.0; J$_{25}$ 1.5; J$_{45}$ 5.3; J$_{56}$ 5.3; J$_{56}$ 4.3; J$_{56}$ 12.0.

6-Bromo-2,6-dideoxy-α-ribo-hexono-1,4-lactone (8). Crude 5, prepared as described above from 5 g of the dibromolactone (I), was dissolved in water (50 ml); potassium hydroxide (3 g) was added and the solution was kept overnight. It was
then acidified with acetic acid and evaporated; acetic acid was twice added and again evaporated. The residue thus obtained (containing II) was stirred with 40 ml of a 30% solution of hydrogen bromide in acetic acid for 3 h at room temperature. Methanol (200 ml) was added and the mixture was kept overnight. It was then evaporated, water (~25 ml) was twice added and again evaporated. The residue thus obtained consisted of crude 8 mixed with potassium bromide. A 13C NMR spectrum gave the following signals (D2O); 179.3 ppm (C-1); 89.0 (C-4); 70.4, 68.2 (C-3, C-5); 38.2 (C-2); 35.2 (C-6). Only traces of other products were observed.

Neither the lactone 8 nor its diacetate or the corresponding hydrazone could be induced to crystallize.

2,6-Dideoxy-1,1-ribo-hexono-1,4-lactone (7a). To crude 8, prepared as described above from 5 g of dibromolactone (I), was added ethyl acetate (50 ml) and triethylamine (10 ml) and the mixture was filtered through activated carbon to remove potassium and triethylammonium bromide. The filtrate was hydrogenolyzed for 24 h at room temperature and 1 atm. hydrogen pressure in the presence of additional triethylamine (10 ml) and 5% palladium on carbon (500 mg). The mixture was filtered and evaporated leaving 3.4 g of crude 7a containing some triethylammonium bromide. Column chromatography using ethyl acetate as eluant gave 1.8 g (75%) of the lactone (7a) as a colourless syrup, [α]D20 +34.9° (c 1.9, acetone), (reported 7 +30°). 13C NMR (D2O): 180.1 ppm (C-1); 92.6 (C-4); 67.4, 67.1 (C-3, C-5); 38.6 (C-2); 17.9 (C-6).

A sample was converted into the phenylhydrazone, which was recrystallized from ethanol-diethyl ether, m.p. 122–123 °C, [α]D20 +16.8° (c 1.6, H2O), (reported 9 for the d-isomer m.p. 123–124°, [α]D20 -17.8°).

Di-O-acetyl-2,6-dideoxy-1,1-ribo-hexono-1,4-lactone (7b). The crude lactone (7a), prepared from 5 g of I, was acetylated with acetic anhydride (20 ml) and a few drops of 60% aqueous perchloric acid. Work-up in the usual way gave 3.8 g of a syrup, which crystallized from dichloromethane-diethyl ether-pentane to give 2.2 g (58%) of 7b, m.p. 109–111 °C. Recrystallization from ethanol gave a product with m.p. 111–112.5 °C, [α]D20 +17.1° (c 1.8, CHCl3). Anal. C15H14O6C, H, 1H NMR (CDCl3): δ 2.56 (H-2a); 3.00 (H-2b); 5.40 (H-3); 4.22 (H-4); 5.11 (H-5); 1.24 (H-6). J2,2 18.5 Hz; J2,3a 2.0; J2,3b 7.0; J3,4 1.5; J4,5 3.9; J5,6 6.6.

2,6-Dideoxy-1,1-ribo-hexose. A solution of disoamylborane was prepared under an argon atmosphere from borane-dimethyl sulfide complex (8 ml) in THF (15 ml) and 2-methyl-2-

butene (16.5 ml) in THF (20 ml).14 The solution was cooled in ice and stirred while crude, dried 7a (2.6 g) (prepared from 5 g of I as described above) in THF (15 ml) was added. The resulting mixture was kept overnight at room temperature. Water (10 ml) was then added and the mixture was boiled for 1 h. It was then partially evaporated and extracted with dichloromethane. The aqueous phase was evaporated and methanol was added three times and again evaporated. The residue thus obtained (2.1 g) consisted mainly of 1-digitoxose as seen from a 13C NMR spectrum. Crystallization from ethyl acetate gave 0.76 g (31%) of a product with m.p. 101–104 °C. Further recrystallization from acetone gave a product with m.p. 113–114 °C, [α]D20 -47.1° (final; c 1.4, H2O), (reported 7 m.p. 105–107 °C, [α]D20 -47°). A 13C NMR spectrum (D2O) showed that the β-pyranose form predominated, but smaller amounts, of α-pyranose and α- and β-furanose were also present; β-pyranose: 92.2 ppm (C-1); 73.3 (C-4); 70.2, 68.3 (C-3, C-5); 39.2 (C-2); 18.2 (C-3).

Tri-O-acetyl-2-deoxy-d-arabino-hexono-1,4-lactone (6b). Crude 8, prepared as described above from 5 g of I, was dissolved in water (30 ml) and potassium hydroxide (4 g) was added. The solution was kept overnight. A 13C NMR spectrum showed that the solution contained the salt of 2-deoxy-d-arabino-hexonic acid (15) as the major product (Table). The solution was acidified and evaporated giving a residue which contained mainly the corresponding lactone (6a) as seen from a spectrum (Table). The residue was acetylated with acetic anhydride and perchloric acid to give 3.8 g of a syrup. Crystallization from ethanol-pentane gave 2.1 g (44%) of 6b, m.p. 94–98 °C. Recrystallization from ethanol gave a product with m.p. 103–104 °C, [α]D20 +32.7° (c 3.4, CHCl3), (reported 9 m.p. 103–105 °C, [α]D20 +34°. 1H NMR (CDCl3): δ 2.84 (H-2a); 2.58 (H-2b); 5.59 (H-3); 4.64 (H-4); 5.29 (H-5); 4.58 (H-6a); 4.13 (H-6b). J2,2 18.0 Hz; J2,3a 5.3; J2,3b 1.0; J3,4 3.5; J4,5 9.1; J5,6a 2.2; J5,6b 4.2; J6,6 12.5.

Treatment of 6-bromo-2,6-dideoxy-d-arabino-

hexono-1,4-lactone (5) with potassium carbonate. Crude 5, prepared as described above from 5 g of I was boiled in water (50 ml) for 2 h with anhydrous potassium carbonate (10 g). The mixture was then evaporated. A 13C NMR spectrum of the material in the residue showed two set of signals. The more intense signals corresponded to the salt of 2-deoxy-1,1-xylo-hexonic acid (16) (Table). The less intensive signals arose from the d-arabinos isomer (15).

The mixture was acidified with hydrochloric acid and evaporated. A 13C NMR spectrum showed the signals of the corresponding 1,4-

lactones (6a) and (3a), respectively (Table). Acetylation of the product with acetic anhydride and perchloric acid gave 3.7 g of a syrup which crystallized from diethyl ether to give 1.5 g of tri-O-acetyl-2-deoxy-1,4-xylono-hexono-1,4-lactone (3b), m.p. 90–94 °C. The material in the mother liquor was chromatographed on a column using diethyl ether as eluant to give two main fractions. The slow running fraction (730 mg) crystallized from diethyl ether to give 350 mg of 3b, m.p. 96–98 °C, bringing the total yield to 1.85 g (39%). Additional recrystallization from dichloromethane–diethyl ether–pentane gave a product with m.p. 97–98 °C, [α]D20 +4.5° (c 5.3, CHCl3). Anal. C12H16O6; C, H. 1H NMR (CDCl3): δ 2.91 (H-2a); 2.63 (H-2b); 5.51 (H-3); 4.79 (H-4); 5.33 (H-5); 4.36 (H-6a); 4.07 (H-6b). J22 18.0 Hz; J23 7.5; J23 5.3; J34 4.2; J45 6.2; J56a 4.7; J56b 7.1; J66 12.0.

The fast running fraction (830 mg) crystallized from diethyl ether to give 380 mg (8%) of tri-O-acetyl-2-deoxy-γ-arabinono-hexono-1,4-lactone (6b), m.p. 95–97 °C, undepressed in admixture with the product described above.

Treatment of 6-bromo-2,6-dideoxy-1-ribo-hexono-1,4-lactone (8) with potassium carbonate. Crude 8, prepared as described above from 5 g of I, was dissolved in water and anhydrous potassium carbonate (10 g) was added. The solution was boiled for 2 h and it was then evaporated. A 13C NMR spectrum of the material in the residue showed several components; the largest set of signals (Table) arose from the salt of 2-deoxy-α-lyxo-hexonic acid (17). A smaller set of signals corresponded to those of 2-deoxy-α-ribo-hexonic acid (11).

The mixture was then acidified with hydrochloric acid and evaporated. A 13C NMR spectrum of the residue thus obtained showed the signals of the two lactones (4a and 9a), the latter being the major component. Acetylation of the residue with acetic anhydride and perchloric acid gave 3.0 g of crude acetate which was purified by column chromatography using diethyl ether as eluant. The main fraction gave 1.5 g (32%) of tri-O-acetyl-2-deoxy-α-lyxo-hexono-1,4-lactone (9b) as a syrup, which was not quite pure. Repeated chromatography gave a colourless syrup, [α]D20 +5.5° (c 1.3, CHCl3). Anal. C12H16O6; C, H. Its 1H NMR spectrum was identical with that of authentic 9b, described below. A faster moving fraction (500 mg) was crystallized from diethyl ether–pentane to give 150 mg (3%) of 4b, m.p. 71–73 °C.

Tri-O-acetyl-β-lyxo-hexono-1,4-lactone (9b). A solution of 2-deoxy-β-lyxo-hexose (1.0 g) in water (20 ml) was stirred overnight with excess barium carbonate and bromine (0.32 ml). The mixture was then filtered and evaporated leaving 2-deoxy-α-lyxo-hexono-1,4-lactone (9a) and barium bromide. A 13C NMR spectrum (Table) showed only traces of other products. Acetylation with acetic anhydride and perchloric acid gave 1.5 g (85%) of syrup 9b. Column chromatography (diethyl ether–dichloromethane 3:1) gave 1.22 g (69%) of a colourless syrup, [α]D20 +6.4° (c 7.6, CHCl3). 1H NMR (CDCl3): δ 2.58 (H-2a); 2.89 (H-2b); 5.13 (H-3); 4.64 (H-4); 5.33 (H-5); 4.16 (H-6a); 4.29 (H-6b). J22 18.5 Hz; J23 2.0; J23 7.0; J34 1.9; J45 3.0; J56a 6.5; J56b 5.5; J66 12.0.

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