EXPERIMENTAL
EXPERIMENTAL DETAILS

All reagents were purified by appropriate methods just before use. Solvents were dried using appropriate drying agents. Solvents used for chromatography were of commercial grade and were fractionally distilled before use. All organic extracts were dried over MgSO₄. Column chromatography was performed using ACME silica gel (100-200 mesh) and eluted with appropriate mixtures of hexane and ethyl acetate. Thin layer chromatography (tlc) was performed on home made plates coated with ACME silica gel GF 254 (with 13% calcium sulphate as binder) and were visualised by shining UV light or exposing to iodine vapours. Melting points were determined on a SUPERFIT melting point apparatus and are uncorrected. Optical rotations were measured on a SHIMADZU polarimeter at 25°. Infrared spectra were recorded on a JASCO FT-IR 5300 instrument. ¹H and ¹³C NMR spectra were recorded on a BRUKER AF 200 NMR Spectrometer operating at 4.7 Tesla magnetic field strength in chloroform-d, with tetramethylsilane (TMS) as internal standard, unless otherwise mentioned. DEPT and 2D NMR data were processed using standard software provided with the instrument. The ¹H NMR spectral data are listed as follows: signals are reported in parts per million (ppm) downfield of TMS. Signal multiplicity is denoted as s = singlet, d = doublet, dd = doublet of a doublet, t = triplet, dt = doublet of a triplet, q = quartet, br = broad and m = multiplet. Number of protons integrated for assignments; coupling constant (J) measured in Hertz. Wherever possible, elemental analyses were obtained using PERKIN-ELMER model 240C-CHN analyser.
FURANOSES:

5,6-Dideoxy-1,2-O-isopropylidene-α-D-xylo-hex-5-enofuranose (207) was prepared from 1,2-O-isopropylidene-α-D-glucofuranose according to literature procedure.90

Attempted oxidation of 5,6-dideoxy-1,2-O-isopropylidene-α-D-xylo-hex-5-enofuranose (207):

\( \text{CrO}_3 \cdot 2\text{Py}/\text{Ac}_2\text{O}/\text{CH}_2\text{Cl}_2 \): To a stirred solution of pyridine (0.65 ml, 8 mmol) in dichloromethane (2 ml) was added chromium trioxide (400 mg, 4 mmol). After 15 min, a solution of 207 (186 mg, 1 mmol) in dichloromethane (4 ml) was added. To the resultant tarry deposit, acetic anhydride (0.37 ml, 4 mmol) was added. The reaction mixture was stirred at room temperature for 10 min. It was then filtered through a short column of silica gel using ethyl acetate. The residue after solvent evaporation contained only starting material.

\( \text{PCC}/\text{NaOAc}/\text{CH}_2\text{Cl}_2 \): A solution of the alcohol 207 (50 mg, 0.27 mmol) in dichloromethane (1 ml) was added to a stirred suspension of pyridinium chlorochromate (87 mg, 0.40 mmol) and sodium acetate (5 mg) in dichloromethane (1.5 ml). After 3 h, the reaction mixture was diluted with ether (20 ml) and filtered through a short column of Florisil. The ether solution was concentrated. The crude concentrate showed no carbonyl band in the IR spectrum.

Silver carbonate on celite: To a stirred suspension of silver carbonate on celite (1.53 g, 5.55 mmol) in benzene (20 ml) was added the alcohol 207 (50 mg, 0.27 mmol) in benzene (1 ml). The reaction mixture was heated under reflux for 14 h. No reaction was observed as indicated by TLC analysis.
Attempted preparation of 5,6-dideoxy-1,2-O-isopropylidene-3-O-pyruvyl-α-D-xylo-hex-5-enofuranose (210):

To a stirred solution of the alcohol 207 (186 mg, 1.0 mmol) in dichloromethane (4 ml) at 0° was added a solution of pyruvic acid (105 mg, 1.2 mmol) in dichloromethane (2 ml) followed by DCC (79 mg, 0.4 mmol) and DMAP (122 mg, 1.0 mmol). After stirring overnight at room temperature, the reaction mixture was poured into water (25 ml), the layers separated and the aqueous phase extracted with dichloromethane (3 x 20 ml). The combined organic layers were washed with aqueous sodium bicarbonate and dried. The reaction mixture was concentrated and chromatographed on a silica gel column. No tractable material was obtained.

5,6-Dideoxy-1,2-O-isopropylidene-3-O-phenylglyoxyl-α-D-xylo-hex-5-enofuranose (211):

To a stirred solution of the alcohol 207 (250 mg, 1.34 mmol) in dichloromethane (5 ml) at 0° were added sequentially phenylglyoxyl chloride (271 mg, 1.61 mmol) and DMAP (409 mg, 3.35 mmol). The reaction mixture was stirred for 1 h at 0° and for 5 h at room temperature. The reaction mixture was quenched with aqueous potassium carbonate and extracted with dichloromethane (3 x 20 ml). The dichloromethane solution was dried and concentrated. The residue after purification by column chromatography gave the ester 211 (125 mg, 29%) as a colourless syrup.

IR (neat): 3000, 2950, 1740, 1680, 1600, 1170, 1020, 740 cm⁻¹.

¹H NMR: 1.28 (s, 3H, CH₃), 1.49 (s, 3H, CH₃), 4.64-4.66 (d, 1H, H-2, J=3.9 Hz), 4.75-4.85 (m, 1H, H-4), 5.16-5.49 (m, 1H, H-3), 5.71-5.98 (m,
\[
5H, \text{ H-1, H-5 and CH}=\text{CH}_2, 7.32-7.65 \ (\text{m, 3H, ArH}). \ 7.87-7.96 \ (\text{m, 2H, ArH})
\]

Attempted photolysis of the phenylglyoxylate 211:

A solution of the phenylglyoxylate 211 (32 mg, 0.1 mmol) in deoxygenated benzene (20 ml) was photolyzed for 3 h with a 450-W medium pressure Hanovia mercury lamp. The solvent was then evaporated under reduced pressure. TLC analysis at this stage showed recovery of starting material.

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\text{1,2,5,6-Di-0-cyclohexylidene-3-C-vinyl-\alpha-D-allofuranose (212) was prepared as reported in the literature}\]

\[
\text{1,2-0-Cyclohexylidene-3-C-vinyl-\alpha-D-allofuranose (213):}
\]

The reaction mixture containing alcohol 212 (800 mg, 2.18 mmol) and aqueous acetic acid (6.67 ml, 75\% v/v) was heated to 80° for 2 h. The reaction mixture was allowed to cool to room temperature and acetic acid was removed under reduced pressure. The residue was purified by column chromatography to furnish the triol 213 (463 mg, 74\%) as a white solid.

\[\text{M.p: 78° (ether/hexane).}\]

\[\text{[\alpha]^{25}_D = +31.4° (c 1.0, CHCl}_3).\]

\[\text{IR (KBr): 3449, 2937, 2876, 1128, 1010.931 cm}^{-1}\].

\[\text{^1H NMR: 5 1.35-1.88 (m, 10H, cyclohexyl). 3.09 (s, 1H, OH). 3.65-3.87 (m, 4H, H-4, H-5, H-6 and H-6'), 4.22-4.24 (d, 1H, H-2, J=4.0 Hz), 5.36-6.00 (m, 4H, H-1 and CH=CH}_2)\]

\[\text{^13C NMR: 134.48, 116.54, 113.84, 103.26, 83.03, 80.51, 79.54, 70.53, 64.16, 36.04, 24.83, 23.91, 23 ppm}\]
Anal Calcd for C₁₄H₂₂O₆: C:58.72; H 7.74
Found C:58.65; H:7.75.

1,2-O-Cyclohexylidene-3-C-vinyl-α-D-ribo-pentodialdo-1,4-furanose (214):
A solution of sodium metapentenodate (214 mg. 1 mmol) in water (5 ml) was added dropwise to a stirred solution of the triol 213 (286 mg. 1 mmol) in water (6 ml) at room temperature. After 1 h, water was removed under reduced pressure. The residue was diluted with chloroform and filtered. The filtrate after solvent evaporation was chromatographed on a silica gel column to yield 214 (236 mg. 93%) as a colourless syrup.

\[\alpha\]D = +24.4° (c 0.59, CHCl₃)
IR (neat): 3450, 2980, 1720, 1356, 1010, 722 cm⁻¹

1H NMR: 8 1.25-1.80 (m, 10H, cyclohexyl), 3.20 (s, 1H, OH), 4.27-4.29 (d, 1H, H-2, J=3.8 Hz), 4.33 (s, 1H, H-4), 5.30-5.85 (m, 3H, CH=CH₂), 5.97-5.99 (d, 1H, H-1, J=3.8 Hz), 9.56 (s, 1H, CHO).

Attempted methylenation of the aldehyde 214:
Ph₃PCH₂I, n-BuLi, THF, 0°: To a stirred suspension of methyltriphenylphosphonium iodide (889 mg, 2.20 mmol) in THF (15 ml) at 0° was added a 1M solution of n-butyllithium in hexane (2 ml, 2 mmol). The slurry was stirred at 0° for 15 min after which the aldehyde 214 (254 mg, 1 mmol) was added in THF (4 ml) and the mixture was stirred at 0° for 4h. The reaction was quenched with saturated ammonium chloride (4 ml) and the mixture was allowed to warm to room temperature. The reaction mixture was diluted with ether (100 ml) and washed with water. The ether layer was dried and concentrated. TLC of the crude mixture was very complex. No characterizable product was isolated from this mixture.
**Ph₃PCH₂I, K₂CO₃, dioxane-water, reflux:** The reaction mixture containing methyltriphenylphosphonium iodide (125 mg, 0.31 mmol), potassium carbonate (55 mg, 0.40 mmol), aldehyde 214 (80 mg, 0.30 mmol) and water (1 drop) in dioxane (0.31 ml) was heated under reflux for 4h. The mixture was then filtered and the solvent evaporated under reduced pressure. TLC analysis of the reaction mixture at this stage showed the presence of a complex mixture. No attempts were made to purify this mixture.

**CH₂I₂,Zn-Ti(OPr-i)₄, THF, rt, 36h:** To a stirred suspension of zinc dust (206 mg, 3.15 mmol) in THF (3 ml) was added diiodomethane (468 mg, 1.75 mmol). After 30 min, a 1M solution of Ti(OPr-i)₄ (99 mg, 0.35 mmol) in THF was added and stirred at room temperature for 30 min. A solution of the aldehyde 214 (89 mg, 0.35 mmol) in THF (2 ml) was then added and stirred at room temperature for 36 h. The reaction mixture was diluted with hexane, poured into 1N HCl (10 ml), and extracted with hexane (3 × 10 ml). The organic extracts were washed with brine, dried and concentrated. TLC of the reaction mixture showed that no reaction had taken place.

**1,2-Cyclohexylidene-6-O-(p-toluenesulfonyl)-3-C-vinyl-α-D-allofuranose (215):**

To a stirred solution of the triol 213 (100 mg, 0.35 mmol) in pyridine (0.5 ml) at 0° was added p-toluenesulfonyl chloride (73 mg, 0.38 mmol) in chloroform (2 ml). The reaction mixture was stirred at room temperature for 24h, then quenched with water (1 ml) and diluted with chloroform (30 ml). The organic layer was washed with water, brine, dried and concentrated. The residue was purified by
chromatography on a silica gel column to afford 215 (60 mg, 39%) as a colourless syrup.

IR (neat): 3514, 2937, 1599, 1359, 1176, 1020, 850 cm⁻¹

^1^H NMR: δ 1.25-1.80 (m, 10H, cyclohexyl), 2.44 (s, 3H, CH₃), 2.97 (s, 1H, OH).

3.72-4.30 (m, 6H, H-2, H-4, H-5 and H-6), 5.29-5.89 (m, 6H, H-1, CH=CH₂, CH₃Ph), 7.31-7.35 (d, 2H, ArH), 7.77-7.82 (d, 2H, ArH)

5,6-Anhydro-1,2-Ọ-cyclohexyldiene-3-C-vinyl-Ọ-D-allofuranose (216):

Sodium (catalytic amount) was added to the tosylate 215 (60 mg, 0.14 mmol) in n-methylacetone (2 ml) and the reaction mixture was allowed to stand at room temperature for 3h. Methanol was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The organic layer was dried and concentrated. The crude product was purified by column chromatography to furnish 216 (33 mg, 91%) as a colourless syrup.

^1^H NMR: δ 1.22-1.81 (m, 10H, cyclohexyl), 2.77-2.78 (d, 2H, H-6, J=3.3 Hz), 2.87 (s, 1H, OH), 3.01-3.07 (m, 1H, H-5), 3.75-3.77 (d, 1H, H-4, J=4.8 Hz), 4.23-4.25 (d, 1H, H-2, J=4.0 Hz), 5.30-5.94 (m, 4H, H-1 and CH=CH₂)

Attempted deoxygenation of the epoxide 216:

To a solution of the epoxide 216 (67 mg, 0.25 mmol) in benzene (4 ml) was added a freshly prepared colourless solution of magnesium iodide in diethyl ether (1.4 ml, 0.5 mmol) (prepared by refluxing 200 mg of magnesium and 1 g of iodine in diethyl ether (10 ml) for 2h). The reaction mixture was refluxed for 3h. TLC analysis at this stage showed a complex mixture.
1,2-O-Cyclohexylidene-5,6-dideoxy-3-C-vinyl-α-D-ribo-hept-5(E)-enodialdo-1,4-furanose (218):

The aldehyde 214 (200 mg, 0.79 mmol) was dissolved in toluene (10 ml) and formylmethylenetriphenylphosphorane (240 mg, 0.79 mmol) was added to the stirred solution. The reaction mixture was heated at 80° for 5h, after which it was cooled and the solvent evaporated in vacuum. The residue was purified by column chromatography to furnish the aldehyde 218 (172 mg, 78%) as a pale yellow syrup

$[\alpha]_D^{25} = +41.4^0$ (c 1.45, CHCl$_3$).

IR(neat) : 3470, 2935, 1718, 1624, 1124, 711 cm$^{-1}$.

$^1$HNMR: 1.21-1.81 (m, 10H, cyclohexyl). 3.08 (s, 1H, OH). 4.27-4.29 (d, 1H, H-2, J=3.8 Hz), 4.56-4.54 (dd, 1H, H-4, J=3.8 and 1.3 Hz). 5.23-5.70 (m, 3H, CH=CH$_2$). 5.88-5.90 (d, 1H, H-1, J=3.6 Hz). 6.26-6.40 (m, 1H, H-6), 6.60-6.73 (dd, 1H, H-5, J=14.0 Hz and J=4.0 Hz). 9.51-9.54 (d, 1H, CHO, J=7.8 Hz)

$^{13}$C NMR : 193.12, 150.31, 133.72, 13261. 116.93, 113.98, 10331. 8281. 81.19, 36.13, 24.77, 23.90, 23.49 ppm.

Anal Calcd for C$_{15}$H$_{22}$O$_5$: C:64.27; H:7.19

Found: C:64.35; H:7.22.

1,2-O-Cyclohexylidene-5,6-dideoxy-3-C-vinyl-α-D-ribo-hex-5-enofuranose (217):

To a stirred solution of the unsaturated aldehyde 218 (280 mg, 1 mmol) in deoxygenated benzene (15 ml) was added tns(triphenylphosphine)rhodium(l) chloride (1.50 g, 1.6 mmol). The reaction mixture was heated under reflux for 2h and the solvent was evaporated. The residue was purified by column chromatography to give 217 (222 mg, 82%) as a white solid.
M.p 90-92° (hexane)

$[\alpha]^{25}_{D} = +53.0^\circ$ (c 0.35, CHCl$_3$).

IR (KBr) : 3466, 2932, 1275, 1122, 923, 734 cm$^{-1}$.

$^1$H NMR : 5.1 40-1.88 (m, 10H, cyclohexyl). 2.82 (s, 1H, OH). 4.26-4.28 (d, 1H, H-2, J=3.8 Hz). 4.31 (br s, 1H, H-4). 5.23-5.51 (m, 4H, 2 x CH=CH$_2$). 5.67-5.83 (m, 2H, 2 x CH=CH$_2$). 5.86-5.88 (d, 1H, H-1, J=3.8 Hz)

$^1$C NMR : 134.84, 132.04, 118.50, 116.07, 113.53, 103.23, 83.30, 82.99, 80.75, 36.23, 24.97, 24.03, 23.63 ppm

Anal Calcd for C$_{4}$H$_{20}$O$_{4}$: C:66.64; H:7.99.

 Found: C:66.54; H:7.93.

General procedure for attempted anionic oxy-Cope rearrangement of 217:

To a stirred suspension of potassium hydride (35% suspension in oil, washed with hexane to remove oil) (5 eq.) in the desired solvent was added the diene 217 (1 eq.) in the same solvent and the stirring was continued for the desired period at the specified temperature. The reaction mixture was quenched with absolute ethanol at -78°. The reaction mixture was diluted with ether, washed with water, brine and dried. The residue after solvent evaporation was analysed by tlc and IR.

Following the above procedure, heating the reaction mixture containing 217 and potassium hydride in i) THF to 60° for 10h and ii) THF to 60° for 12h yielded the starting material. Similarly, heating the reaction mixture containing 217 and potassium hydride at increased temperatures in i) dioxane to 100° for 8h. ii) dioxane to 100° for 10h and iii) diglyme to 140° for 15h. also afforded only starting material.
Attempted anionic oxy-Cope rearrangement of 217 with KH/I₂:

To a stirred suspension of mineral oil free potassium hydride (20 mg, 0.5 mmol) in THF (1 ml) was added iodine (13 mg, 0.05 mmol) in THF (0.5 ml). To the resultant suspension, the diene 217 (25 mg, 0.1 mmol) was added in THF (0.5 ml). After refluxing for 4 h, the reaction mixture was worked up as described above. Tlc, IR and "H NMR spectra of the crude material indicated the presence of the starting compound.

Attempted anionic oxy-Cope rearrangement of 217 with KH/18-C-6:

The diene 217 (25 mg, 0.1 mmol) and 18-C-6 (132 mg, 0.5 mmol) in diglyme (5 ml) were added to a stirred suspension of mineral oil free potassium hydride (20 mg, 0.5 mmol) in THF (1 ml). The reaction mixture was refluxed for 4 h and worked up as usual. Recovery of starting material was indicated by tlc and was further confirmed from IR and "H NMR spectral data.

Attempted anionic oxy-Cope rearrangement of 217 with KH/n-Bu₄NI:

To a stirred suspension of mineral oil free potassium hydride (20 mg, 0.5 mmol) in THF (1 ml) was added the diene 217 (25 mg, 0.1 mmol) and tetra-n-butylammonium iodide (185 mg, 0.5 mmol) in THF (4 ml). After refluxing for 10 h, the reaction mixture was worked up as usual. No rearranged product was obtained as indicated by tlc and spectral data.

Reaction of the aldehyde 214 with carbethoxymethylenetriphenyl phosphorane:

A solution of the aldehyde 214 (254 mg, 1 mmol) in benzene (5 ml) was heated to reflux in the presence of carbethoxymethylenetriphenyl phosphorane (383 mg, 1.1 mmol) for 4 h. The solvent was evaporated under reduced pressure and the
residue was chromatographed on a silica gel column to yield the cis ester 220a (127 mg) as a white solid and the trans ester 220b (126 mg) as a light yellow syrup which solidified on standing (overall yield 78%).

Ethyl 1,2-O-cyclohexylidene-5,6-dideoxy-3-C-vinyl-α-D-ribo-hept-5(Z)-eno-furanuronate (220a):
M.p. 84-88 (hexane/ethyl acetate)  
[α]D = -71.2° (c 1.0, CHCl₃)  
IR (KBr): 3485, 2943, 1722, 1660, 1190, 935 cm⁻¹  
¹H NMR: 1.26-1.33 (t. 3H, CH₂,). 1.40-1.90 (m. 10H, cyclohexyl). 3.85-3.86 (br s. 1H, 7H-4). 4.14-4.24 (q. 2H, CH₂CH₃). 4.29-4.31 (d. 1H, H-2, J=3.8 Hz). 5.26-5.32 (dd. 1H, H-6, J=10.7 and 1.4 Hz). 5.47-6.12 (m, 5H, H-1, H-5 and CH=CH₂).  
¹³C NMR: 166.45. 144.02. 134.36. 123.01. 116.85. 113.58. 103.54. 83.32. 83.08. 60.79. 36.26. 36.12. 24.92. 23.92. 23.53. 14.09 ppm.  
Anal Calcd for C₇H₉₂O₈: C:62.94; H 7.46  
Found C:62.90; H:7.45.

Ethyl 1,2-O-cyclohexylidene-5,6-dideoxy-3-C-vinyl-α-D-ribo-hept-5(E)-eno-furanuronate (220b):
M.p. 56-58° (hexane/ethyl acetate)  
[α]D = +56.9° (c 0.45, CHCl₃)  
IR (KBr): 3485, 2943, 1720, 1662, 1178, 939 cm⁻¹  
¹H NMR: 1.20-1.26 (t. 3H, CH₂CH₃). 1.40-1.86 (m. 10H, cyclohexyl). 3.09 (br s. 1H, OH). 4.07-4.18 (q. 2H, CH₂CH₃). 4.22-4.24 (d. 1H, H-2, J=3.6 Hz). 4.43-4.45 (m. 1H, H-4), 5.18-5.69 (m. 3H, CH=CH₂),
5.82-5.84 (d, 1H, H-1, J=3.8 Hz), 5.98-6.07 (dd, 1H, H-6, J=15.6 and 1.4 Hz), 6.72-6.82 (dd, 1H, H-5, J=15.7 and 4.0 Hz).

$^{13}$C NMR: 166.10, 141.23, 134 14, 122.68, 116 64, 113 77, 103 30, 83 01, 81.43, 81.00, 60.30, 36.20, 24.82, 23.92, 23.51, 14 13.

Anal. Calcd for C$_{12}$H$_{20}$O$_{5}$: C 62.94; H: 7.46.  
Found: C: 62.85; H: 7.45.

Attempted selective reduction of the conjugated double bond in 220a:

A mixture of the cis ester 220a (32 mg, 0.1 mmol) and magnesium turnings (24 mg, 1 mmol) in methanol (1 ml) was stirred at room temperature for 5h. The reaction was quenched by adding 3N HCl to dissolve excess magnesium and the reaction mixture was extracted with ether (2 x 5 ml). The combined organic extracts were washed with brine and dried. Evaporation of the solvent afforded only starting material as indicated by tlc and IR.

Ethyl 1,2-O-cyclohexylidene-5,6-dideoxy-3-C-ethyl-α-D-ribo-heptofuranuronate (221):

5% Pd/C (9 mg) was added to a solution of the cis ester 220a (30 mg, 0.09 mmol) in deoxygenated ethyl acetate (2 ml). The reaction mixture was stirred in a H; atmosphere (balloon) for 30min. The catalyst was removed by filtration and the filtrate was concentrated to yield 221 (30 mg) in quantitative yield as a colourless syrup, which crystallized on standing.

M.p: 64° (hexane).

$[\alpha]_{D}^{25}$ = -91.7° (c 0.6, CHCl$_3$).

IR(neat): 3518, 2937, 1736, 1371, 1109, 1012, 943 cm$^{-1}$.  


H NMR  0.96-1.03 (t, 3H, CH₂CH₃), 1.21-1.28 (t, 3H, COOCH₂CH₃), 1.33-1.82 (m, 12H, H-5 and cyclohexyl), 2.41-2.57 (m, 4H, CH₂CH₂ and H-6), 3.69-3.76 (q, 1H, H-4), 4.07-4.18 (q, 2H, COOCH₂CH₃), 4.27-4.29 (d, 1H, H-2, J=4.0 Hz), 5.70-5.72 (d, 1H, H-1, J=4.0 Hz).

C NMR 173.21, 112.69, 103.04, 81.76, 79.79, 78.91, 60.34, 36.07, 31.39, 24.89, 23.92, 23.54, 23.24, 23.07, 14.21, 7.24 ppm.

Found: C 62.25; H 8.64.

Ethyl 1,2-0-cyclohexylidene-5,6-dideoxy-3-C-vinyl-α-D-ribo-heptofuranuronate (221):

Repeating the above procedure with the trans ester 220b (30 mg, 0.09 mmol), with the same quantity of 5% Pd/C also furnished 221 (30 mg) in quantitative yield.

Reaction of the aldehyde 214 with acetylmethylenetriphenylphosphorane:

To a stirred solution of 214 (254 mg, 1 mmol), in benzene (11 ml) was added acetylmethylenetriphenylphosphorane (350 mg, 1.1 mmol) and the resultant solution heated under reflux. After 4 h, the reaction mixture was worked up as described for 220. Chromatographic purification over a column of silica gel gave the cis ketone 222a (11 mg) as a colourless solid and the trans ketone 222b (218 mg) as a colourless solid (overall yield 78%).

1,2-0-Cyclohexylidene-5,6,8-trideoxy-3-C-vinyl-α-D-ribo-oct-5(Z)-enofuranose-7-ulose (222a):

M.p.: 72° (hexane/ethyl acetate)
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[\alpha]_{D}^{25} = -157.1^\circ (c 0.07, \text{CHCl}_3).
\]
\[
\text{IR (KBr):} \quad 3470, 2935, 1697, 1624, 1124, 925 \text{ cm}^{-1}.
\]
\[
^1\text{H NMR:} \quad 5 \quad 1.40-1.90 (m, 10H, cyclohexyl), 2.27 (s, 3H, COCH). 2.95 (s, 1H, OH). 4.29-4.31 (d, 1H, H-2, J=3.8 Hz), 4.43 (br s, 1H, H-4), 5.25-6.00 (m, 5H, H-1, H-6 and \text{CH=CH}_2), 6.37-6.43 (m, 1H, H-5, J=10.8 Hz).
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^{13}\text{C NMR:} \quad 199.72, 142.60, 134.83, 130.21, 116.87, 113.66, 103.60, 83.24, 36.29, 36.09, 30.77, 24.94, 23.95, 23.54 \text{ ppm}.
\]
\text{Anal. Calcd for C}_{19}H_{32}O}_{5}: \quad \text{C :65.29; H:7.53.}
\text{Found:} \quad \text{C:65.32; H:7.55.}

1,2-O-Cyclohexylidene-5,6,8-trideoxy-3-C-vinyl-\alpha-D-ribo-oct-5(\E)-eno furanos-7-ulose (222b):

M.p: \quad 98^\circ (\text{hexane/ethyl acetate}).
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[\alpha]_{D}^{25} = +79.6^\circ (c 0.47, \text{CHCl}_3).
\]
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\text{IR (KBr):} \quad 3531, 2999, 2930, 1700, 1624, 1024, 727 \text{ cm}^{-1}.
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^1\text{H NMR:} \quad 5 \quad 1.40-1.83 (m, 10H, cyclohexyl), 2.24 (s, 3H, COCH). 2.95 (s, 1H, OH). 4.28-4.30 (d, 1H, H-2, J=3.7 Hz), 4.48-4.51 (m, 1H, H-4), 5.26-5.69 (m, 3H, \text{CH=CH}_2), 5.89-5.91 (d, 1H, H-1, J=3.8 Hz), 6.28-6.36 (dd, 1H, H-6, J=16.0 and 1.4 Hz), 6.58-6.69 (dd, 1H, H-5, J=16.0 and J=4.0 Hz).
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\[
^{13}\text{C NMR:} \quad 197.87, 140.41, 134.14, 131.44, 116.90, 114.05, 103.49, 83.05, 81.50, 81.26, 36.34, 27.37, 24.98, 24.10, 23.70 \text{ ppm}.
\]
\text{Anal. Calcd for C}_{19}H_{32}O}_{5}: \quad \text{C:65.29; H:7.53}
\text{Found:} \quad \text{C:65.18; H:7.66.}
1,2-\(\alpha\)-Cyclohexylidene-5,6,8-trideoxy-3-C-vinyl-\(\alpha\)-D-ribo-oct-5(\(Z\))-eno furanos-7-ulose (222a):

A solution of 214 (200 mg, 0.79 mmol) in methanol (1.5 ml) was added to a solution of acetylmethylenebenzylphosphorane (290 mg, 0.95 mmol) at -78°. The reaction mixture was stirred at -78° for 1 h and then at room temperature for 5 h. After which the solvent was evaporated under reduced pressure. Upon chromatographic purification over a column of silica gel, the cis ketone 222a (55 mg) as a colourless solid and the trans ketone 222b (100 mg) as a colourless syrup (overall yield 67%) were obtained. The spectral properties of 222a and 222b were identical with the earlier prepared samples.

Reaction of the aldehyde 214 with cyanomethylenebenzylphosphorane:

To a stirred solution of 214 (165 mg, 0.65 mmol) in benzene (5 ml) was added cyanomethylenebenzylphosphorane (294 mg, 0.97 mmol) and heated under reflux. After 4 h, the reaction mixture was worked up as described earlier in the case of 220. The residue after purification by column chromatography afforded the nitrile 223a (142 mg) as a white solid and the trans nitrile 223b (24 mg) as a colourless syrup (overall yield 93%).

1,2-\(\alpha\)-Cyclohexylidene-5,6-dideoxy-3-C-vinyl-\(\alpha\)-D-ribo-hept-5(\(Z\))-enofuranuronitrile (223a):

M.p: 106° (hexane/ether).

\([\alpha]_{D}^{25} = -4.6°\) (c 1.0, CHCl₃).

IR (KBr): 3433, 3059, 2224, 1444, 1116, 991 cm⁻¹.

\(^1\)H NMR: 8 1.41-1.90 (m, 10H, cyclohexyl), 3.0 (s, 1H, OH), 4.28-4.30 (d, 1H, H-2, J=3.8 Hz), 4.73-4.77 (d, 1H, H-4, J=7.8 Hz), 5.30-5.82 (m, 4H,
\[ \text{CH}=\text{CH}_2 \text{ and H-6), 5.91-5.93 (d, 1H, H-1, } J=3.8 \text{ Hz), 6.25-6.34 (dd. 1H, H-5, } J=117 \text{ and 7.8 Hz).} \]

\[ ^{13}\text{C NMR: 147.56, 133.05, 117.38, 115.21, 114.16, 103.72, 102.38, 82.46, 80.95, 36.13, 24.81, 23.95, 23.53 ppm.} \]

\[ \text{Anal. Calcd for } C_{10}H_{19}O_4N: C64.96; H6.91; N5.05.} \]

\[ \text{Found: C65.14; H7.04; N5.03.} \]

\[ \text{1,2-O-Cyclohexylidene-5,6-dideoxy-3-C-vinyl-\( \alpha \)-D-ribo-hept-5(E)-enofuranuronitrile (22Jb):} \]

\[ [\alpha]^{25}_D = +64.0^\circ \text{ (c 0.65, CHCl}_3).} \]

\[ \text{IR (neat): 3537, 2939, 2227, 1641, 1111, 736 cm}^{-1}.} \]

\[ ^1\text{H NMR: 5.13-1.80 (m, 10H, cyclohexyl), 2.97 (s, 1H, OH), 4.28-4.30 (d, 1H, H-2, } J=3.8 \text{ Hz), 4.44-4.47 (m, 1H, H-4), 5.30-5.68 (m, 4H, H-6 and \text{CH} = \text{CH}_2), 5.88-5.90 (d, 1H, H-1, } J=3.8 \text{ Hz), 6.56-6.67 (dd, 1H, H-5, } J=16.0 \text{ and 4.0 Hz).} \]

\[ ^{13}\text{C NMR: 148.24, 133.36, 117.19, 116.88, 114.16, 103.30, 100.70, 82.79, 81.22, 80.96, 36.17, 36.12, 24.75, 23.90, 23.49 ppm.} \]

\[ \text{Anal. Calcd for } C_{10}H_{19}O_4N: C64.96; H6.91; N5.05.} \]

\[ \text{Found: C65.12; H6.97; N5.12.} \]

\[ \text{1,2-O-Cyclohexylidene-5,6-dideoxy-3-C-vinyl-\( \alpha \)-D-ribo-hept-5(E)-enofuranuronitrile (223b):} \]

\[ \text{A solution of } 223a \text{ (50 mg, 0.18 mmol) and diphenyl disulphide (10 mg, 0.05 mmol) in deoxygenated benzene (25 ml) was photolysed for 1h using a high pressure mercury lamp and Pyrex filter. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography to afford the trans} \]
nitrile 223b (18 mg. 36%) (recovered starting material 32 mg) as a colourless syrup. The spectral properties of 223b and 223a obtained from this experiment were identical with those of earlier prepared samples.

1,2-O-Cyclohexylidene-5,6-dideoxy-3-C-vinyl-α-D-ribo-hept-5(E)-enofuranose (224):

Cenum(III) chloride heptahydrate (256 mg. 0.72 mmol) in methanol (1.9 ml) was added to a stirred solution of the unsaturated aldehyde 218 (190 mg. 0.68 mmol) in THF (0.80 ml) at 0°. To the reaction mixture, sodium borohydride (50 mg. 1.33 mmol) was added portionwise and was stirred at 0° for 1h and at room temperature for 2h. The residue was partitioned between ethyl acetate (50 ml) and water (50 ml). The aqueous layer was extracted with ethyl acetate (2 x 60 ml) and the combined organic layers were dried and evaporated. The crude product was purified by chromatography to yield 224 (139 mg. 73%) as a colourless syrup.

IR (neat): 3350, 2900, 1360, 1120, 1010, 720 cm⁻¹.

¹H NMR: 5 1.40-1.82 (m, 10H, cyclohexyl). 4.09-4.12 (d, 2H, H-7, J=5.5 Hz). 4.22-4.24 (d, 1H, H-2, J=3.8 Hz). 4.26-4.30 (m, 1H, H-4). 5.23-6.02 (m, 6H, H-1, CH=CH, H-5 and H-6).

1,2-O-Cyclohexylidene-5,6-dideoxy-7-O-(t-butyldiphenylsilyl)-3-C-vinyl-α-D-ribo-hept-5(E)-enofuranose (225):

To a stirred solution of the unsaturated alcohol 224 (150 mg. 0.53 mmol) in DMF (3 ml) at 0° was added imidazole (79 mg. 1.17 mmol) and t-butyldichlorodiphenylsilane (160 mg. 0.58 mmol). The reaction mixture was stirred at 0° for 1h and for 12h at room temperature. The reaction mixture was diluted with ethyl acetate (20 ml), washed with water (2 x 20 ml), dried and concentrated. The
Residue on column chromatography afforded the silyl ether 225 as a colourless syrup in quantitative yield.

IR (neat): 3425, 3072, 2932, 1427, 1113, 740 cm$^{-1}$.

$^1$H NMR 5 1 OS (s, 9H, t-butyl), 1.40-1.85 (m, 10H, cyclohexyl), 4.20-4.22 (m, 1H, H-4), 4.27-4.29 (d, 1H, H-2, J=3.8 Hz), 5.27-5.80 (m, 6H, CH=CH₂, H-5, H-6 and H-7), 5.87-5.89 (d, 1H, H-1, J=4.0 Hz), 7.38-7.42 (m, 6H, ArH), 7.69-7.74 (m, 4H, ArH)

Attempted anionic oxy-Cope rearrangement on the silyl ether 225:

To a stirred suspension of potassium hydride (36 mg, 0.89 mmol) in THF (1 ml) was added the silyl ether 225 (50 mg, 0.18 mmol) in THF (1 ml) and heated under reflux. After 6h, the reaction mixture was cooled to -78°, quenched with ethanol and extracted with ether. The ether solution was dried and concentrated. Purification on a silica gel column gave only starting material.

General procedure for sealed tube reactions:

A solution of the diene in o-dichlorobenzene was heated in a sealed tube to 200-220° for 12h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography.

(3'aR*,10'aS*)-3'a,8',9',10'a-Tetrahydro-spirocyclohexane-1,2'-[1,3]dioxolo[4,5-b]oxoninl-10'-(7'H)-one(219):

As described above, heating the diene 217 (100 mg, 0.40 mmol) at 200-220° for 12h and purification of the reaction mixture gave the rearranged product 219 [16 mg, recovered starting material 60 mg, yield: 40% (based on recovered starting material)] as a colourless syrup.
\([\alpha]_{D}^{25} = -36.2^\circ \text{ (c 0.63, CHCl}_3\).\\
IR (neat) 2937, 1738, 1651, 1095, 1053, 754 cm\(^{-1}\).

\(^1\)H NMR: 5 1 40-2.12 (m, 12H, H-5 and cyclohexyl). 2 36-2.37 (m, 3H, H-6 and H-5). 2.70-2.82 (m, 2H, H-4). 4 60-4.62 (d, 1H, H-2, \(J=4.0\) Hz). 4 74-4.86 (m, 1H, H-7). 5.58-5.60 (d, 1H, H-1, \(J=4.0\) Hz). 6 16-6.19 (d, 1H, H-8, \(J=5.5\) Hz).

\(^{13}\)C NMR: 206.56, 142.70, 114.40, 113.98, 101.29, 84.57, 37.23, 37.02, 36.18, 35.87, 24.92, 23.93, 23.76, 23.37, 22.63 ppm.

Anal Calcd for C\(_{20}\)H\(_{20}\)O\(_4\): C 66.64; H 7.99.

Found: C 66.40; H 8.08.

Note: For \(^1\)H and \(^{13}\)C NMR spectral assignment purposes, the numbering of compounds 219, 227, 228 and 229 has been done as shown on page 54 of results and discussion and not as in the systematic names given here.

Ethyl \((3'aR^*,10'aS^*)-3'a,7',8',9',10',10'a\)-hexahydro-spiro[cyclohexane-1,2'-|l,3|dioxolo[4,5-b]oxonin]--10'-oxo-7'-carboxylate (227): The cis ester 220a (50 mg, 0.15 mmol) on thermal oxy-Cope rearrangement under above mentioned conditions furnished the rearranged product 227 (4 mg, recovered starting material 40 mg) yield: 40% (based on recovered starting material) as a colourless syrup.

Heating the trans ester 220b (50 mg, 0.15 mmol) at 200-220\(^\circ\) for 12h gave no rearranged product.

\([\alpha]_{D}^{25} = -1.12^\circ \text{ (c 1.15, CHCl}_3\).\\
IR(neat): 2935, 1736, 1657, 1114, 1049, 760 cm\(^{-1}\).
$^1$H NMR: δ 1.20-1.28 (t, 3H, COOCH$_2$CH$_3$), 1.29-1.76 (m, 11H, H-5 and cyclohexyl), 2.31-2.40 (m, 2H, H-4'), and H-5), 2.72-2.78 (m, 1H, H-4), 3.44-3.56 (m, 1H, H-6), 4.06-4.19 (q, 2H, COOCH$_2$CH$_3$). 4.63-4.65 (d, 1H, H-2, J=4.0 Hz), 4.96-5.32 (m, 1H, H-7), 5.57-5.59 (d, 1H, H-1, J=4.0 Hz), 6.21-6.24 (d, 1H, H-8, J=5.5 Hz).

$^{13}$C NMR: 210.0, 173.76, 143.24, 115.12, 111.72, 101.34, 84.34, 60.82, 40.12, 37.43, 36.17, 36.06, 26.38, 24.80, 23.83, 23.73, 14.16 ppm.

Anal Calcd for C$_{13}$H$_{24}$O$_6$: C: 62.94; H: 7.46.
Found: C: 62.75; H: 7.43

(3'aR*,10'aS*)-3'a,8',9',10'-Tetrahydro-spiro[cyclohexane-1,2'-|l,3|dioxolo-(4,5-bloxoninl-7'-acetyl-10'-(7'H)-one(228):

As mentioned above for the diene 217, heating the cis ketone 222a (60 mg, 0.20 mmol), in a sealed tube furnished the rearranged product 228 [1 mg. recovered starting material 40 mg, yield: < 5% (based on recovered starting material)] as a colourless syrup.

The trans ketone 222b (60 mg, 0.20 mmol), underwent oxy-Cope rearrangement to furnish 228 [6 mg, recovered starting material 30 mg, yield: 20% (based on recovered starting material)] as a colourless syrup. Its spectral properties were identical with those of the earlier prepared sample.

$[\alpha]$$^{23}_D$ = +50.0° (c 0.1, CHCl$_3$).

IR (neat): 3452, 2937, 1740, 1712, 1369, 1114, 736 cm$^{-1}$.

$^1$H NMR: δ 1.39-2.75 (m, 17H, H-4, H-5, COCH$_3$ and cyclohexyl), 3.51-3.64 (m, 1H, H-6), 4.68-4.70 (d, 1H, H-2, J=4.0 Hz), 4.88-4.96 (m, 1H, H-7), 5.59-5.61 (d, 1H, H-1, J=4.0 Hz), 6.32-6.35 (d, 1H, H-8, J=5.6 Hz)
(3'-aR*,10'aS*)-3',7',8',9',10',10'a-Hexahydro-spiro[cyclohexane-1,2']-1,3-dioxolo[4,5-b]oxonin]-10'-oxo-7'-carbonitrile (228):

Subjecting the cis nitrile 223a (100 mg. 0.36 mmol) to thermolysis at 200-220° for 12h yielded the rearranged product 229 [24 mg. recovered starting material 60 mg. yield: 60% (based on recovered starting material)] as a white solid.

The trans nitrile 223b (100 mg. 0.36 mmol) under similar conditions as those for 223a furnished 229 [2 mg. recovered starting material 60 mg. yield: 5% (based on recovered starting material)] as a white solid. Spectral features of the rearranged products obtained from 223a and 223b were identical.

M.p: 110-112° (hexane).

[α]_D^25 = -157.3° (c 0.1, CHCl₃).

IR (KBr) 3418, 2935, 2243, 1718, 1660, 1053, 760 cm⁻¹.

'H NMR: 6 1.29-1.86 (m, 14H. H-4, H-5 and cyclohexyl), 3.54-3.68 (m, 1H. H-6), 4.64-4.66 (d, 1H, H-2, J=4.0 Hz), 4.83-4.93 (m, 1H, H-7), 5.57-5.59 (d, 1H, H-1, J=4.0 Hz), 6 24-6 27 (d, 1H, H-8, J=5.5 Hz)

'T NMR: 203.58, 144.65, 120.87, 115.69, 108.48, 101.38, 85.96, 84.05, 37.39, 35.96, 35.63, 29.67, 27.34, 25 47, 24.71, 23.78, 23.68, 22.67 ppm

Anal. Calcd for C₁₆H₂₂O₄N: C:64.96; H:6.91; N:5.05.

Found: C:65.00, H:6.93; N:5.08.
Attempted oxy-Cope rearrangement of 220a in the presence of bis(benzonitrile)dichloropalladium(II):

A solution of the unsaturated ester 220a (20 mg, 0.06 mmol) and bis(benzonitrile)dichloropalladium(II) (12 mg, 0.06 mmol) in benzene (1.5 ml) was stirred at room temperature for 12 h. Benzene was removed in vacuum and DMSO was added to quench the complex. The reaction mixture was diluted with dichloromethane, washed with water and the organic layer was dried and evaporated. The residue contained only starting material as indicated by the H NMR spectrum.

Attempted oxy-Cope rearrangement of 220a in the presence of mercuric trifluoroacetate:

To a stirred solution of 220a (20 mg, 0.06 mmol) in dichloromethane (2 ml) was added mercuric trifluoroacetate (26 mg, 0.06 mmol). The reaction mixture was stirred at room temperature for 36 h, after which solid sodium borohydride (2 mg, 0.06 mmol) was added. The organic layer was dried and evaporated to yield recovered starting material.

Attempted oxy-Cope rearrangement of 220a in the presence of lithium perchlorate:

To a stirred solution of lithium perchlorate (532 mg, 5 mmol) in ether (1 ml) was added the unsaturated ester 220a (50 mg, 0.15 mmol) and stirred at room temperature for 36 h. The reaction mixture was diluted with dichloromethane and washed with water. The organic layer was dried and on evaporation only starting material was obtained.
The above experiment was conducted in diglyme (1.5 ml) and heated at 120° for 24h. After the usual workup, TLC showed decomposition of 220a.

**PYRANOSES:**

Methyl 4,6-O-benzylidene-2-O-(p-toluenesulfonyl)-α-D-ribo-hexopyranosid-3-ulose (230) was prepared from D-glucose following literature procedure 71.

Attempted addition of vinylmagnesium bromide to methyl 4,6-O-benzylidene-2-O-(p-toluenesulfonyl)-α-D-ribo-hexopyranosid-3-ulose (230):

To a solution of vinylmagnesium bromide (generated from 89 mg of Mg and an excess of vinyl bromide in THF) was added the ketone 230 (400 mg, 0.92 ml) in THF (7 ml) and the contents were heated under reflux for 5h. The reaction mixture was quenched with saturated ammonium chloride and partitioned between water and ether. The organic layer was dried, concentrated and purified on a silica gel column. No characterizable product was obtained.

Methyl 2,3-anhydro-4,6-O-benzylidene-α-D-mannopyranoside (232) was prepared as reported in the literature 72.

Attempted reaction of methyl 2,3-anhydro-4,6-O-benzylidene-α-D-mannopyranoside (232) with DMSO and oxalyl chloride:

To a stirred solution of DMSO (0.13 ml, 1.9 mmol) in dichloromethane (0.5 ml) at -60° was added oxalyl chloride (0.17 ml, 1.9 mmol) in dichloromethane (0.2 ml). After 15 minutes, the epoxide 232 (200 mg, 0.76 mmol) in dichloromethane (3 ml) and dry methanol (3 ml) were added and stirred at -60°. After 30 min, triethylamine (0.53 ml, 3.8 mmol) was added and the reaction mixture was
allowed to come to room temperature. The reaction mixture was diluted with dichloromethane (50 ml), washed with water, brine and dried. Only a complex mixture was obtained as indicated by tlc.

Methyl 6-\(O\)-benzoyl-2,3-di-\(O\)-benzyl-\(\alpha\)-D-glucopyranoside (234) was prepared from methyl 2,3-di-\(O\)-benzyl-\(\alpha\)-D-glucopyranoside following reported procedure.

Methyl 6-\(O\)-benzoyl-2,3-di-\(O\)-benzyl-\(\alpha\)-D-xylo-hexopyranosid-4-ulose (235):

A solution of methyl 6-\(O\)-benzoyl-2,3-di-\(O\)-benzyl-\(\alpha\)-D-glucopyranoside (234) (96 mg, 0.20 mmol) in benzene (1.5 ml) was added to a stirred suspension of pyridinium chlorochromate (73 mg, 0.34 mmol) in benzene (2 ml) after heating under reflux for 2h, the reaction mixture was cooled, diluted with ether (20 ml) and filtered through a short column of florisil. The ether solution was concentrated and purified by chromatography to give 235 (29 mg, 31%) as a colourless syrup.

\[\text{IR (neat): } 3063, 3032, 2926, 1724, 1602, 1275, 1097, 736 \text{ cm}^{-1}.\]

Attempted addition of vinylmagnesium bromide to 235:

Vinylmagnesium bromide (generated from 15 mg of Mg and a solution of vinyl bromide in THF) was added to the ketone 235 (70 mg, 0.15 mmol) in THF (1.5 ml) and refluxed for 24h. The reaction mixture was worked up as described for 230. Tlc analysis at this stage showed a complex mixture. No purification was attempted.
Following reported procedure, methyl 6-O-acetyl-2,3-di-O-benzyl-α-D-glucopyranoside (237) was prepared from methyl 2,3-di-O-benzyl-α-D-glucopyranoside.

**Methyl 6-O-acetyl-2,3-di-O-benzyl-α-D-xylo-hexopyranosid-4-ulose (238):**

A solution of the methyl 6-O-acetyl-2,3-di-O-benzyl-α-D-glucopyranoside (237) (170 mg, 0.41 mmol) in benzene (3 ml) was added to a stirred suspension of pyridinium chlorochromate (150 mg, 0.70 mmol) in benzene (3 ml). After heating under reflux for 3h, the reaction mixture was worked up as described for 235. The residue was chromatographed to furnish 238 (43 mg, 25%) as a colourless syrup. 

\[ \text{IR (neat): } 3032, 2928, 1724, 1740, 1099, 734 \text{ cm}^{-1}. \]

Attempted addition of vinylmagnesium bromide to 238:

To a stirred solution of vinylmagnesium bromide (generated from 45 mg of Mg and a solution of vinyl bromide in THF) was added a solution of the ketone 238 (190 mg, 0.46 mmol) in THF (4 ml). After stirring the reaction mixture at room temperature for 24h, the usual workup was done. Tlc of the crude product showed it to be a complex mixture.

**Methyl 2,3-di-O-benzyl-6-O-triphenylmethyl-α-D-glucopyranoside** was oxidised to methyl 2,3-di-O-benzyl-6-O-triphenylmethyl-α-D-xylo-hexopyranosid-4-ulose (239) using DMSO and Ac₂O as reported in the literature.

Attempted addition of vinylmagnesium bromide to 239:

Vinylmagnesium bromide (generated from 46 mg of Mg and a solution of vinyl bromide in THF) was added to the ketone 239 (120 mg, 0.19 mmol) in THF.
ml) and refluxed for 1 Oh. The reaction mixture was then worked up as described for 230. Only starting material was recovered.

Methyl 2,3-di-O-benzyl-4-C-ethynyl-6-O-triphenylmethyl-α-D-gluco- and galactopyranosides (240):

A solution of methyl 2,3-di-O-benzyl-6-O-triphenylmethyl-α-D-xylol-hexopyranosid-4-ulose (239) (6.15 g, 10 mmol) in THF (50 ml) was added to a stirred solution of ethynylmagnesium bromide (generated from 2.43 g of Mg, 100 mmol and excess acetylene) in THF (20 ml) at -20°. The reaction mixture was warmed to room temperature and stirred for 4 h. Saturated aqueous ammonium chloride was added to the reaction mixture and the solvent was evaporated under reduced pressure. The residue was diluted with ether, washed with water, brine and dried. The resultant crude product was purified by chromatography to give an epimeric mixture of the alcohols 240 (4.5 g, 70%) as a colourless syrup.

IR (neat): 3474, 3298, 3061, 2935, 1450, 1053, 738 cm⁻¹.

¹H NMR: 2.26 (s, 1H, acetylene), 2.39 (s, 1H, acetylene), 3.26–4.00 (m, 8H, H-2, H-3, H-5. H-6, OMe), 4.56–4.94 (m, 5H, H-1 and -OCH₂Ph), 7.19–7.54 (m, 25H, ArH).

¹³C NMR: 144.01, 143.60, 138.99, 138.36, 138.21, 128.84, 128.73, 128.44, 128.08, 127.99, 127.86, 127.26, 127.02, 98.30, 98.17, 87.93, 87.14, 83.27, 82.49, 81.34, 81.12, 78.55. 75.78, 75.61, 74.21, 74.06, 73.74, 73.62, 72.33, 71.22, 70.15. 64.06, 63.49, 55.34 ppm.
Attempted partial hydrogenation of the propargyl alcohols 240 with **Lindlar's** catalyst:

A suspension of the propargyl alcohols 240 (1 eq.) and Lindlar's catalyst (0.1 eq.) in hexane:benzene (2:1) was subjected to hydrogen atmosphere (balloon) for 8h. The reaction mixture was filtered and evaporated to give back **unreacted** starting material. Carrying out the partial hydrogenation at increased pressures, i) 40 psi for 8h and ii) 55 psi for 5h in a Parr hydrogenation set-up also resulted in recovery of starting material.

Attempted partial hydrogenation of the propargyl alcohols 240 with **Pdc**:

**Preparation of Pdc**:

To a stirred suspension of sodium hydride (1.44 g, 60 mmol) and palladium acetate (2.24 g, 10 mmol) in THF (40 ml) at 40° was carefully added a solution of \( t-\text{amy} \)l alcohol (1.76 g, 20 mmol) in THF (10 ml) so that the reaction temperature did not exceed 45°. After stirring for 3h at 45°, \( t-\text{amy} \)l alcohol (2.82 g, 32 mmol) was added to neutralise the remaining sodium hydride, and the mixture was allowed to come to rt. The resultant non pyrophoric black suspension is **Pdc**.

To a suspension of Pdc in THF (0.2 ml) and quinoline (0.2 ml) exposed to a hydrogen atmosphere for 30 nun. the propargyl alcohols 240 (50 mg, 0.08 mmol) was added and stirred under hydrogen atmosphere (balloon) for 48h. The reaction mixture was then filtered and evaporated. The residue contained only starting material. The partial hydrogenation of propargyl alcohols 240 was attempted at increased pressures, in a Parr hydrogenation set up i) 40 psi for 6h and ii) 50 psi for 4h. In both the cases after usual workup only starting material was recovered.
Methyl 2,3-di-O-benzyl-6-O-triphenylmethyl-4-C'-vinyl-α-D-gluco- and galactopyranosides (241):

To a stirred suspension of lithium aluminium hydride (237 mg, 6.24 mmol) in THF (4 ml) was added the alcohols 240 (1.0 g, 1.56 mmol) in THF (12 ml). After heating under reflux for 6 h, the reaction mixture was cooled in ice and quenched by careful addition of saturated aqueous sodium sulfate. The salts were filtered and washed several times with THF. The filtrate was dried and concentrated. The residue on chromatographic purification furnished 241 (520 mg, 52%) as a colourless syrup.

IR (neat) 3497, 3061, 2935, 1450, 1051, 740, 700 cm⁻¹

H NMR 5 3.41-3.93 (m, 8H, H-2, H-3, H-5, H-6, OMe), 4.59-4.86 (m, 4H, -OCH₂Ph), 4.97 (s, 1H, H-1), 5.03 (s, 1H, H-1), 5.35-5.57 (m, 2H, CH=CH₂), 5.74-6.09 (m, 1H, CH=CH₂), 7.22-7.50 (m, 25H, ArH).

13C NMR: 144.17, 143.85, 139.27, 139.01, 138.52, 138.34, 135.02, 128.85, 128.75, 128.48, 128.33, 128.07, 127.94, 127.86, 127.62, 127.21, 127.02, 117.17, 116.40, 98.26, 87.66, 87.12, 83.55, 80.11, 78.46, 77.89, 77.39, 76.06, 75.63, 73.50, 71.71, 71.10, 63.67, 62.99, 55.27, 55.18 ppm.

Detritylation of methyl 2,3-di-O-benzyl-6-O-triphenylmethyl-4-C'-vinyl-α-D-gluco- and galactopyranosides (241):

A solution of the alcohols 241 (650 mg, 1.01 mmol) and 98% formic acid (93 mg, 2.02 mmol) in ether (2.0 ml) was stirred at room temperature for 1 h. Formic acid and ether were evaporated under reduced pressure. The residue was purified by column chromatography to yield the diols 243 (120 mg) and the corresponding C-6 formates 242 (254 mg) as colourless syrups.
Methyl 2,3-di-O-benzyl-4-C-vinyl-α-D-gluco- and galactopyranosides (243):

**IR (neat):** 3474. 3032. 2932. 1454. 1051, 738, 698 cm⁻¹

**H NMR**
- 2.90 (s, 1H, 2 x OH).
- 3.43-3.90 (m, 8H, H-2, H-3, H-5, H-6, OMe).
- 4.60-4.86 (m, 5H, H-1 and -OCH₃Ph).
- 5.35-5.57 (m, 2H, CH=CH₂).
- 5.75-5.89 (m, 1H, CH=CH₂).
- 7.28-7.35 (m, 10H, ArH)

**C NMR**
- 143.87, 139.03, 138.36, 138.09, 128.72, 128.47, 128.34, 128.05.
- 127.90, 127.05, 116.91, 98.39, 79.70, 77.99, 76.06, 73.38, 71.20, 61.22, 55.42 ppm

Methyl 2,3-di-O-benzyl-6-O-formyl-4-C-vinyl-α-D-gluco- and galactopyranosides (242):

**IR (neat):** 3539, 2914, 1726, 1454, 1186, 1055.736 cm⁻¹.

**H NMR**
- 3.40-4.25 (m, 8H, H-2, H-3, H-5, H-6, OMe).
- 4.61-4.84 (m, 4H, -OCH₃Ph).
- 4.95 (s, 1H, H-1).
- 5.05 (s, 1H, H-1).
- 5.36-5.44 (m, 2H, CH=CH₂).
- 5.99-6.10 (m, 1H, CH=CH₂).
- 7.28-7.43 (m, 10H, ArH).
- 8.03 (s, 1H, OCOH)

**C NMR:**
- 160.66, 134.19, 128.67, 128.46, 127.96, 127.80, 117.36, 98.10.
- 83.26, 78.78, 75.69, 75.54, 73.30, 71.03, 62.68, 55.11 ppm.

Methyl 2,3-di-O-benzyl-4-C-vinyl-α-D-gluco- and galactopyranosides (243):

A catalytic amount of sodium was added to the formates 242 (50 mg, 0.12 mmol) in methanol (1.5 ml) and the contents were allowed to stand at room temperature for 6h. The solvent was removed under reduced pressure and the residue was partitioned between ethyl acetate and water. The organic layer was dried and evaporated to yield 243 (33 mg, 69%) as a colourless syrup. H and C NMR spectra of 243 obtained from both the expennicnts were identical.
Attempted oxidation of 243 with DMSO and trifluoroacetic anhydride:

To a solution of DMSO (10 mg, 0.13 mmol) in dichloromethane (1 ml) at 
-78°, trifluoroacetic anhydride (21 mg, 0.10 mmol) in dichloromethane (1 ml) was 
slowly added and stirred for 30 min. The alcohols 243 (27 mg, 0.07 mmol) in 
dichloromethane (1 ml) were then added. After 1 h, N,N-diisopropylethylamine (26 
mg, 0.20 mmol) was added and the reaction mixture was allowed to come to room 
temperature. The contents were diluted with dichloromethane (50 ml), washed with 
water, brine and dried. The IR spectrum of the residue indicated that no oxidation 
had taken place.

Methyl 2,3-di-O-benzyl-4-C-vinyl-α-D-glucopyranosides (244):

A solution of the alcohols 243 (200 mg, 0.50 mmol) in dichloromethane 
(5 ml) was added to a suspension of pyridinium chlorochromate (323 mg, 1.5 mmol) 
in dichloromethane (6 ml). After stirring at room temperature for 18 h, the reaction 
mixture was filtered and the filtrate was evaporated. The resultant residue was 
column chromatographed to give 244 (40 mg, 20%) as a colourless syrup.

IR (neat): 3472, 2926, 1730, 1454, 1053, 736, 700 cm⁻¹.

¹H NMR: 5
3.42 (s, 3H, OMe), 3.86-3.88 (m, 2H, H-2 and H-3), 4.12-4.13 (m, 1H, H-5), 4.61-4.90 (m, 5H, H-1 and -OCH₂Ph), 5.44-5.58 (m, 2H, 
CH=CH₂), 5.91-6.05 (m, 1H, CH=CH₂), 7.29-7.37 (m, 10H, ArH), 
9.58 (s, 1H, CHO)
Methyl 2,3-di-O-benzyl-4-C-vinyl-α-D-glucopyranosides (244):

To a stirred suspension of Dess-Martin periodinane (1.6 g. 3.75 mmol) in dichloromethane (10 ml) was added the diols 243 (500 mg. 1.25 mmol) in dichloromethane (8 ml). After stirring at room temperature for 3 h, the reaction mixture was diluted with dichloromethane. The dichloromethane layer was washed with aqueous sodium thiosulfate, aqueous sodium bicarbonate and water. The organic layer was dried, concentrated and purified by column chromatography to yield 244 (250 mg. 50%) as a colourless syrup. Its spectral features were identical with those of the sample prepared earlier.

Methyl 2,3-di-O-benzyl-6,7-dideoxy-4-C-vinyl-α-D-glucopyranosides (245):

Sodamide (66 mg. 1.65 mmol) was added to a suspension of methyl triphenylphosphonium iodide (728 mg. 1.8 mmol) in ether (12 ml) and the mixture stirred at room temperature for 6 h. The thus formed methylenetriphenylphosphorane was added to a solution of the aldehydes 244 (600 mg. 1.5 mmol) in ether (15 ml). After 30 min, the reaction mixture was quenched with saturated ammonium chloride and worked up as usual. Chromatographic purification of the crude mixture on a silica gel column afforded 245 (300 mg. 50%) as a pale yellow syrup.

IR (neat): 3499, 2928, 1660, 1280, 1049, 700 cm⁻¹.

¹H NMR: δ 3.38-3.40 (s, 3H, OMe), 3.84 (m, 2H, H-2, H-3), 4.094.12 (m, 1H, H-5), 4.60-4.84 (m, 5H, H-1 and -OCH₃Ph), 5.16-5.46 (m, 4H, 2 x CH=CH₂), 5.69-6.08 (m, 2H, 2 x CH=CH₂), 7.25-7.33 (m, 10H, ArH)
Reaction of the aldehydes 244 with carbethoxymethylenetriphenylphosphorane:

To a stirred solution of the aldehydes 244 (60 mg, 0.15 mmol) in benzene (3 ml) was added carbethoxymethylenetriphenylphosphorane (63 mg, 0.18 mmol). After heating the reaction mixture under reflux for 4 h, benzene was removed under reduced pressure. The residue was column chromatographed to yield the cis esters 246a (9 mg) and the trans esters 246b (39 mg) (overall yield 68%) as colourless syrups.

Ethyl [methyl 2,3-di-O-benzyl-6,7-dideoxy-4-C-vinyl-α-D-glucopyranosiduronates (246a):

IR (neat): 3449, 2930, 1720, 1655, 1095, 698 cm⁻¹.

$^1$H NMR: δ 1.23-1.30 (t, 3H, CH₂CH₃), 3.40 (s, 3H, OMe), 3.62-3.83 (m, 2H), 4.0-4.04 (d, 1H), 4.16-4.28 (q, 2H, CH₂CH₃), 4.60-5.0 (m, 5H, H-1 and -OCH₂Ph), 5.24-5.63 (m, 3H, CH=CH₂), 5.96-6.10 (m, 2H, H-6 and H-7).

Ethyl [methyl 2,3-di-O-benzyl-6,7-dideoxy-4-C-vinyl-α-D-galactopyranosiduronates (246b):

IR (neat): 3499.2930. 1718, 1662, 1280, 1049.738 cm⁻¹.

$^1$H NMR: δ 1.23-1.30 (t, 3H, CH₂CH₃), 3.40 (s, 3H, OMe), 3.68-3.87 (m, 2H, H-2 and H-3), 4.12-4.23 (q, 2H, CH₂CH₃), 4.32-4.34 (m, 1H, H-5), 4.62-4.87 (m, 5H, H-1 and -OCH₂Ph), 5.38-5.56 (m, 2H, CH=CH₂,
J=6.8 and 17.4 Hz). 5.76-5.90 (m, 1H. CH=CH. J=10.6 and 17.4 Hz). 6.10-6.18 (d, 1H. H-7, J=15.7 Hz). 6.37-6.47 (dd, 1H. H-6. J=15.7 and 4.3 Hz). 7.31-7.34 (m, 10H, ArH).

\begin{align*}
\text{13C NMR} & : 166.12. 141.57. 138.46, 138.20, 137.94, 128.48, 128.33, 128.07, 127.95, 123.23, 118.0, 98.49, 79.72, 77.70, 76.09, 73.50, 70.53, 60.34, 55.68, 14.21 \text{ ppm}
\end{align*}

Methyl 2,3-di-O-benzyl-6,7,9-trideoxy-4-C-vinyl-α-D-glucopyranosid-8-uloses (247):

A solution of the aldehydes 244 (200 mg, 0.50 mmol) in benzene (5 ml) was added to acetylmethylenetriphenylphosphorane (206 mg, 0.65 mmol) in benzene (5 ml). The reaction mixture was heated under reflux for 4h. and the solvent was removed under reduced pressure. Purification of the crude material by column chromatography furnished the trans ketones 247 (158 mg, 72%) as a colourless syrup.

\begin{align*}
\text{IR (neat)} & : 3462, 3070, 1722, 1633, 1275, 1113, 706 \text{ cm}^{-1}.
\end{align*}

\begin{align*}
\text{1H NMR} & : 5.22 (s, 3H. COCH$_3$), 3.41 (s, 3H, OMe). 3.77-3.98 (m, 2H H-2 and H-3). 4.32-4.34 (m, 1H. H-5), 4.58-4.87 (m, 5H. H-1 and -OCH$_3$Ph), 5.38-5.54 (m, 2H. CH=CH$_2$. J=6.8 and 17.3 Hz). 5.75-5.89 (m, 1H. CH=CH$_2$. J=10.6 and 17.3 Hz), 6.29-6.37 (dd, 1H. H-7. J=15.7 and 16 Hz), 6.70-6.81 (m, 1H, H-6, J=15.7 and 4.4 Hz), 7.31-7.34 (m, 10H, ArH)
\end{align*}

\begin{align*}
\text{13C NMR} & : 198.04, 140.36, 138.66, 138.18, 137.92, 132.20, 128.47, 128.32, 128.03, 127.96, 117.85, 98.58, 79.67, 77.70, 76.08, 73.49, 70.74, 55.74, 27.23 \text{ ppm}
\end{align*}
General procedure for attempted anionic oxy-Cope rearrangement of 245, 246a, 246b and 247:

To a stirred suspension of potassium hydride (5 eq) in the desired solvent was added the dienes (1 eq) in the same solvent and the stirring was continued at the temperatures and time periods as given below. The reaction mixture was then quenched with absolute ethanol at -78°. The reaction mixture was diluted with ether, washed with water, brine and dried. The residue after solvent evaporation was analysed by tlc and IR.

According to the general procedure, heating potassium hydride and the dienes 245 in i) THF at 60° for 10h, ii) diglyme at 120° for 24h and iii) toluene at 110° for 24h led to decomposition. Carrying out the above reaction with 246a in i) dioxane to 80° for 12h, ii) diglyme to 100° for 4h and iii) THF to 60° for 10h led to decomposition. Similarly, heating potassium hydride and 246b in i) diglyme to 120° for 6h and ii) dioxane to 100° for 5h also led to decomposition. Heating a mixture of 247 and potassium hydride in THF at 60° for 12h as described in the general procedure, gave a complex mixture which could not be purified.

General procedure for attempted anionic oxy-Cope rearrangement of 245, 246b and 247 with KH/n-Bu₄NI:

To a stirred suspension of mineral oil free potassium hydride (5 eq) in the desired solvent was added the diene (1 eq) and tetra-n-butylammonium iodide (5 eq) in the same solvent. After stirring for the required time, the reaction mixture was worked up in the usual manner. No rearranged product could be obtained.

Carrying out the above reaction with 245 in THF at 60° for 10h led to decomposition, while 246b under similar conditions yielded a complex mixture. The
reaction with 247 in diglyme at 80° for 2h also was not fruitful, leading to extensive decomposition.

General procedure for attempted thermal oxy-Cope rearrangement of 245, 246a and 246b:

A solution of the substrate in α-dichlorobenzene was heated in a sealed tube. Evaporation of the solvent afforded the crude residue. Heating 245 in α-dichlorobenzene to 180° for 12h gave the starting material as the major component along with slight decomposition. The thermal oxy-Cope rearrangements of 245 at 240-260° for 1h led to extensive decomposition. While at lower temperatures, (<200°) the starting material was recovered. Heating 246a in α-dichlorobenzene to 180° for 12h, resulted in recovery of starting material. Thermal oxy-Cope rearrangement of 246b was attempted by following the above procedure at 220° for 5h led to a complex mixture.

PSEUDO-SUGARS:

1,5-Anhydro-3,4-di-O-benzyl-2-deoxy-D-arabino-hex-5-enitol (250) was prepared from tri-O-acetyl-D-glucal following literature procedure. 7

2,6-Anhydro-3,4-di-O-benzyl-5-deoxy-D-arabinohex-5-enose (251):

A solution of 1,5-anhydro-3,4-di-O-benzyl-2-deoxy-D-arabinohex-1-enitol (250) (2.4 g, 7.35 mmol) in dichloromethane (100 ml) was added to a stirred suspension of pyridinium dichromate (9.7 g, 25.73 mmol) and 4A molecular sieves (9.7 g) in dichloromethane (50 ml). After 10h, the reaction mixture was diluted with ether and filtered through a short column of silica gel. The ether solution was
concentrated and the crude aldehyde 251 was used in the next step without further purification.

Attempted Wittig reaction on 2,6-anhydro-3,4-di-O-benzyl-5-deoxy-D-arabino-
hex-5-enose (251):

To an ice cooled suspension of methyltriphenylphosphonium iodide (75 mg, 0.18 mmol) in THF (2 ml) was slowly added 1M n-BuLi (0.17 ml, 0.17 mmol) and the reaction mixture was allowed to stir at the same temperature for 30 min. The aldehyde 251 (40 mg, 0.12 mmol) in THF (1 ml) was then added and the contents were allowed to come to room temperature before quenching it with saturated ammonium chloride. The compound was extracted into ether (3 x 10 ml) and the combined organic layers were dried and evaporated. TLC analysis showed a complex mixture.

4,8-Anhydro-5,6-di-O-benzyl-2,3,7-trideoxy-D-arabino-oct-2(E),7-dienose (252):

The aldehyde 251 (100 mg, 0.31 mmol) and formylmethylnetriphenylphosphorane (94 mg, 0.31 mmol) in toluene (4 ml) were heated to 80° for 2h. Toluene was removed under reduced pressure and the crude mixture was chromatographed on a silica gel column to give the unsaturated aldehyde 252 (60 mg, 56%) as a pale yellow syrup.

IR (neat) : 2928, 2854, 1730, 1435, 1265, 740 cm⁻¹

¹HNMR : 5 3.67-3.73 (m, 1H), 3.88-3.96 (m, 1H), 4.20-4.29 (m, 1H), 4.41-4.80 (m, 4H, -OCH₂Ph), 5 00-5.09 (m, 1H), 6 27-6 69 (m, 2H, H-1 and H-7), 6.80-6.90 (dd, 1H, H-6, J=16.0 Hz and 4.0 Hz), 7 30-7.37 (m, 10H, ArH), 9.44-9 48 (d, 1H, CHO, J=8 0 Hz)
1,5-Anhydro-3,4-di-O-benzyl-2,6,7-trIDEOxy-D-arabino-hept-1,6-dienitol (253):

To a stirred solution of the unsaturated aldehyde 252 (60 mg, 0.17 mmol) in deoxygenated benzene (5 ml) was added tns(triphenylphosphine)rhodium(I) chloride (252 mg, 0.27 mmol). The reaction mixture was heated under reflux for 4h and the solvent evaporated. The residue was purified by column chromatography to give 253 (15 mg, 27%) as a pale yellow syrup.

[α]25D = -70.2° (c 1.3, CHCl3).

IR (neat): 3065, 2862, 1643, 1238, 1095, 696 cm⁻¹.

1H NMR: 6 3.58-3.65 (dd, 1H), 4.21-4.26 (dd, 1H), 4.30-4.40 (t, 1H), 4.61-4.92 (m, 4H), 5.29-5.48 (m, 3H), 5.94-6.14 (m, 1H), 6.40-6.45 (d, 1H), 7.20-7.33 (m, 10H, ArH).

13C NMR: 144.63, 139.90, 139.82, 134.54, 128.47, 128.02, 127.81, 127.71, 118.23, 100.48, 78.50, 78.11, 75.63, 73.87, 70.74 ppm.


Found: C 78.28, H 6.85.

1,5-Anhydro-3,4-di-O-benzyl-2,6,7-trIDEOxy-D-arabino-hept-1,6-dienitol (253):

Sodamide (135 mg, 3.39 mmol) was added to a suspension of methyl triphenylphosphonium iodide (1.5 g, 3.68 mmol) in ether (20 ml) and stirred at room temperature for 6h. The resultant methyltriphenylphosphorane was added to a solution of the aldehyde 251 (1.0 g, 3.08 mmol) in ether (10 ml). After 30 min, the reaction mixture was quenched with saturated ammonium chloride and worked up as usual. Chromatographic purification of the crude mixture on a silica gel column afforded 253 (300 mg, 62%) as a pale yellow syrup. Its spectral properties were identical to that reported earlier.
Attempted Claisen rearrangement of 253 in N, N-diethylaniline:

A solution of 253 (200 mg, 0.62 mmol) in N, N-diethylaniline (3 ml) was heated to 220° in a sealed tube for 8 h. The contents were cooled and diluted with ethyl acetate. The organic layer was washed with 2 N HCl, water, brine and dried. Tlc analysis at this stage showed a complex mixture.

(1S,2R,3R)-2,3-Dibenzyloxy-4-cyclohexene carboxaldehyde (254):

A solution of 253 (200 mg, 0.62 mmol) in o-dichlorobenzene (4 ml) was heated to 240° in a sealed tube. After 1 h, the reaction mixture was cooled and the solvent was removed under reduced pressure to give the crude aldehyde 254.

(3R,4R,5R)-3,4-Dibenzyloxy-5-hydroxymethylcyclohexene (255):

To an ice cooled solution of the crude aldehyde 254 (325 mg, 1.01 mmol) in THF (5 ml) was added sodium borohydride (153 mg, 4.04 mmol) in portions and the reaction mixture stirred for 10 min. The reaction mixture was quenched with 10% aqueous citric acid and the THF was removed under reduced pressure. The residue was diluted with ethyl acetate. It was then washed with water, brine and dried. The crude product was purified by column chromatography to yield the alcohol 255 (292 mg, 90%) as a colourless syrup.

\[ \sigma[^{[D]} = -27.0° \text{ (c 1.75, CHCl}_3) \].

IR (neat): 3445, 2924, 1454, 1093, 1028, 698 cm\(^{-1}\).

\(^1\)H NMR: δ 1.81-2.21 (m, 3H), 2.52-2.66 (br s, 1H, OH), 3.57-3.71 (m, 3H), 4.20-4.27 (m, 1H), 4.67-5.03 (m, 4H, -OCH\(_2\)Ph), 5.74-5.78 (m, 2H), 7.30-7.48 (m, 10H, ArH).

\(^13\)C NMR 138.42, 128.57, 128.48, 128.21, 127.87, 127.72, 125.95, 82.00, 81.15, 74.30, 71.30, 65.53, 40.62, 28.05 ppm.
Anal Calcd for C\textsubscript{21}H\textsubscript{24}O\textsubscript{3}  
\begin{align*}
\text{C} & : 77.7, \text{H} : 7.46 \\
\text{Found:} & \quad \text{C} : 77.8, \text{H} : 7.46.
\end{align*}

Ethyl 4,8-anhydro-5,6-di-O-benzyl-2,3,7-trideoxy-D-arabino-oct-2(E),7-dienuronate (256):

A solution of the aldehyde 251 (200 mg. 0.62 mmol) and carbethox>Thcethylenetnphcnylphosphorane (258 mg. 0.74 mmol) in benzene (7 ml) was heated to reflux for 5h. The solvent was removed and the residue was purified by column chromatography to yield the unsaturated ester 256 (200 mg. 82%) as a pale yellow syrup.

\[
\beta = +26.0^\circ (c 1.9, \text{CHC}l_2).
\]

IR(neat): 2928, 1722, 1188, 1111, 702, 491 cm\textsuperscript{-1}.

\textsuperscript{1}H NMR: 6 1.25-1.32 (t, 3H, CH\textsubscript{3}:CH\textsubscript{3}), 3.60-3.68 (m, 1H, \text{H}-4), 4.13-4.24 (q. 2H, CH\textsubscript{2}CH\textsubscript{2}), 4 47-4.82 (m, 4H), 4.90-4.96 (m, 1H, \text{H}-2, \text{H}-5 and -OCH\textsubscript{2}Ph), 6.09-6.17 (d, 1H, \text{H}-7, J=15.8 Hz), 6 42-6.45 (d, 1H, \text{H}-1, J=6.0 Hz), 7 09-7.16 (dd, 1H, \text{H}-6, J=4.0 and 15.8 Hz), 7.22-7.45 (m, 10H, ArH).

\textsuperscript{13}C NMR: 166.07, 144.26, 143.12, 138 26, 137.68, 128 47, 128.11, 127.70, 122.44, 100.55, 75.72, 74.82, 73 82, 70.62, 60 48, 1423 ppm.

4,8-Anhydro-5,6-di-O-benzyl-2,3,7-trideoxy-D-arabino-oct-2(E),7-dienonitrile (257):

To a stirred solution of the aldehyde 251 (350 mg. 1.08 mmol) in benzene (12 ml) was added cyanomethylenetnphcnylphosphorane (488 mg. 1.62 mmol) and the reaction mixture was maintained at 80° for 10h. The usual workup and
chromatographic purification of the crude product over a column of silica gel gave the required unsaturated nitrile 257 (280. 75%) as a colourless syrup.

$[\alpha]_\text{D}^\text{C}= -5.6^\circ$ (c 1.0. CHCl$_3$)

IR (neat) 3065.2868, 2226, 1651, 1454, 1244, 1091, 698 cm$^{-1}$.

$^1$H NMR: 5.36-3.64 (m, 1H, H-4), 4.20-4.27 (m, 1H, H-3), 4.48-5.01 (m, 6H, H-2. H-5 and -OCH$_2$Ph), 5.62-5.70 (d, 1H, H-7, J=16.4 Hz), 6.42-6.45 (d, 1H, H-1, J=6.1 Hz), 6.79-6.90 (dd, 1H, H-6, J=4.0 and 16.4 Hz), 7.30-7.50 (m, 10H, ArH).

$^{13}$CNMR 149 64. 143 76, 136 21, 137 34. 128 52, 128 17. 128 08, 127.75, 100 84. 100 38 ppm.

General procedure for the Claisen rearrangement of vinyl ethers 256 and 257:

The vinyl ether in o-dichlorobenzene was heated to 240°C in a sealed tube for 1h. After cooling to room temperature, the solvent was removed in vacuum. The crude compound after purification on a silica gel column afforded the pure rearranged product.

(1S,2S,3R,4R)-Ethyl 3,4-dibenzyloxy-2-formyl-5-cyclohexenecarboxylate (258):

IR (neat): 2922, 1730, 1724, 1454, 1099, 688 cm$^{-1}$

$^1$H NMR: 5.122-1.29 (t, 3H, CH$_3$CH$_2$), 3.05-3.11 (t, 1H), 3.61-3.62 (m, 1H), 3.99-4.05 (m, 1H), 4.12-4.23 (q, 2H, CH$_2$CH$_3$), 4.32-4.38 (q, 1H), 4.55-4.85 (m, 4H, -OCH$_2$Ph), 5.85-5.94 (dt, 1H, J=10.3 and 2.6 Hz), 6.14-6.21 (dd, 1H, J=3.1 and 10.3 Hz), 9.73 (s, 1H, CHO)

(1S,2S,3R,4R)-3,4-Dibenzyloxy-2-formyl-5-cyclohexenecarbonitrile (259):

IR (neat) 3032, 2926, 2245, 1730, 1454, 1070, 700 cm$^{-1}$. 

\[ \text{HNMR} \quad \delta 3.57-3.64 \text{ (m, 1H), 4.10-4.94 \text{ (m, 9H). 5.86-5.96 \text{ (m, 2H, H-6 and H-7). 6.42-6.45 \text{ (d, 1H, H-1, J=6 1 Hz).}} } \]

13C NMR: 144.52, 138.70, 133.18, 128.41, 128.05, 127.71, 127.27, 100.34, 78.16, 77.20, 75.35, 73.75, 70.69, 62.87 ppm.

Attempted Claisen rearrangement of 260:

The alcohol 260 (30 mg, 0.09 mmol) in o-dichlorobenzene (2 ml) was heated to 210°C in a sealed tube for 10h. After cooling to room temperature, the solvent was removed in vacuum. Purification of the residue on a silica gel column gave no tractable material.
(IS,2S,3R,4R,5R)-3,4-Dibenzyloxy-5-hydroxymethyl-1,2-cyclohexanediol (262):

To a solution of the alcohol 255 (80 mg, 0.25 mmol) in t-butyl alcohol (1.72 ml) and water (1.72 ml) were added potassium hexacyanoferrate(III) (226 mg, 0.75 mmol), potassium carbonate (95 mg, 0.75 mmol) and a solution of osmium tetroxide in t-butanol (57 µl, 0.003 mmol). The reaction mixture was stirred at room temperature for 24h. after which sodium sulphite was added and stirring continued for several hours. The pale blue solution was concentrated to dryness under reduced pressure and the residue was extracted thoroughly with ethyl acetate. The solvent was removed in vacuum and the crude product was purified by column chromatography to yield the triol 262 (88 mg) in quantitative yield as a colourless syrup.

$\alpha$: $\left\langle \alpha \right\rangle_{D} = +28.0^\circ$ (c 0.15, CHCl$_3$).

IR (KBr): 3408, 3030, 2926, 1454, 1089, 698 cm$^{-1}$.

$^1$H NMR: 1.40-1.80 (m, 3H), 3.40-3.88 (m, 5H), 4.04-4.10 (m, 1H), 4.72-5.04 (m, 4H, -OCH$_2$Ph), 7.26-7.36 (m, 10H, ArH).

Pseudo-α-D-glucopyranose (263):

The triol 262 (27 mg, 0.08 mmol) in MeOH was hydrogenated at 55 Psi pressure for 2h in a Parr apparatus using 20% Pd(OH)$_2$/C (Pearlman’s catalyst, 3 mg). The catalyst was filtered off and the solvent was evaporated to give pure 263 as a colourless syrup in quantitative yield (13 mg).

$\alpha$: $\left\langle \alpha \right\rangle_{D} = +57.0^\circ$ (c 0.65, H$_2$O); lit. $\left\langle \alpha \right\rangle_{D} = +70.0^\circ$ (c 1.02, H$_2$O)$^{57}$

$^1$H NMR (D$_2$O): 5.128-1.36 (br t, 1H), 1.66-1.77 (m, 2H), 3.07-3.58 (m, 5H), 3.92-3.93 (m, 1H).

$^{13}$C NMR (D$_2$O): 74.66, 74.04, 73.44, 68.95, 62.63, 38.15, 30.26 ppm.
(3R,4R,5R)-5-Benzylxymethyl-3,4-dibenzyloxy cyclohexene (264):

To a stirred suspension of mineral oil free NaH (29 mg, 1.2 mmol) in DMF (3 ml) was added a solution of the alcohol 255 (324 mg, 1 mmol) in DMF (4 ml). After 30 min, benzyl bromide (0.24 ml, 2 mmol) was added and the reaction mixture was stirred for 10h. After the usual workup with ethyl acetate (3 x 30 ml), and chromatographic purification of the crude product over a column of silica gel, the required tribenzyl ether 264 (340 mg, 85%) was obtained as a colourless syrup.

$|\alpha|^{2} D = +3.4^\circ$ (c 1.6, CHCl$_3$).

IR (neat): 3030, 1496, 1454, 1155, 1097, 696 cm$^{-1}$

$^1$H NMR: 6 2.02-2.30 (m, 3H, H-5 and H-6), 3.54-3.75 (m, 3H, H-4 and H-7), 4.12-4.24 (m, 1H, H-3), 4.50-5.92 (m, 6H, -OCH$_2$Ph), 5.66-5.85 (m, 2H, H-1 and H-2), 7.24-7.40 (m, 15H, ArH).

$^1$C NMR: 139.14, 138.76, 128.52, 128.34, 127.91, 127.78, 127.51, 126.17, 81.11, 79.62, 74.29, 73.17, 71.44, 70.64, 39.47, 28.81 ppm


Found: C:81.18; H:7.31.

Hydroxylation of (264):

To a stirred dispersion of the tribenzyl ether 264 (84 mg, 0.20 mmol) in deionized water (0.45 ml), m-CPBA (38 mg, 0.22 mmol) was added and was stirred at room temperature for 8h. 10% H$_2$SO$_4$ (0.03 ml) was then added and the mixture was stirred for a further 48h. The aqueous solution was extracted with ethyl acetate (3 x 10 ml) and the combined organic layers were washed with sodium bicarbonate, water, brine and dried. The crude diol was purified by preparative tlc to afford 265 (30 mg, 36%) and 266 (22 mg, 24%) as colourless syrups.
(1S,2R,3R,4R,5R)-5-Benzylxoxymethyl-3,4-dibenzyloxy-1,2-cyclohexanediol (265):

\[
[a]^{25}_{D} = +14.3^\circ \text{ (c 0.7, CHCl}_3)\]

IR (neat): 3425, 3065, 1454, 1267, 1055, 738 cm\(^{-1}\).

\(^1\)H NMR: 5.152-1.86 (m, 3H, H-5 and H-6), 3.56-3.61 (t, 2H, H-7), 3.73-3.84 (m, 2H), 3.88-4.03 (m, 2H). 4.46-4.79 (m, 6H, OCH\(_2\)-Ph). 7.24-7.35 (m, 15H, ArH)

\(^13\)C NMR: 138.40, 128.48, 128.33, 127.84. 127.55, 81.56, 74.12, 73.04, 72.68. 71.95, 70.56, 68.68, 37.28, 30.03 ppm.

(1R,2S,3R,4R,5R)-5-Benzylxoxymethyl-3,4-dibenzyloxy-1,2-cyclohexanediol (266):

\[
[a]^{25}_{D} = +40.4^\circ \text{ (c 0.45, CHCl}_3)\]

IR (neat): 3420, 3062, 1454, 1266, 1055, 738 cm\(^{-1}\).

\(^1\)H NMR: 6.1.50-1.84 (m, 3H, H-5 and H-6), 3.34-3.38 (m, 2H), 3.49-3.63 (m, 4H), 4.48-5.02 (m, 6H, OCH\(_2\)-Ph), 7.23-7.35 (m, 15H, ArH)

\(^13\)C NMR: 138.43, 128.62, 128.36, 127.85, 127.57. 85.78, 81.00, 75.34, 75.09, 74.11, 71.97, 69.81, 39.50, 32.15 ppm.

**General** procedure for the hydrogenation of 265 and 266:

A solution of the alcohol in methanol (3 ml) was taken in a 250 ml Parr hydrogenation flask and Pearlman’s catalyst (3 mg) was added. Hydrogenation was carried out at 55 psi for 2h. The catalyst was filtered off and the solvent evaporated to give the products.
**Pseudo-α-D-mannopyranose (267):**

The alcohol 265 (10 mg, 0.02 mmol) upon hydrogenation gave pseudo-α-D-mannopyranose (267) (4 mg) as a colourless syrup in quantitative yield:

\[ \alpha^\circ_{D} = +1.5^\circ (c 0.4, \text{MeOH}) \]

\[ \text{lit } \alpha^\circ_{D} = +1.9^\circ (c 1.0, \text{MeOH}) \]

\[ ^1\text{H} \text{ NMR (D}_2\text{O) : 8 1.52-1.78 (m, 3H). 3.36-3.68 (m, 4H). 3.88-3.91 (br t, 1H). 3.94-3.98 (q, 1H).} \]

\[ ^13\text{C} \text{ NMR (D}_2\text{O) : 72.59, 72.36, 70.30, 69.0, 62.55, 38.70, 28.28 ppm.} \]

**Pseudo-β-D-glucopyranose (268):**

The alcohol 266 (10 mg, 0.02 mmol) was hydrogenated to furnish pseudo-β-D-glucopyranose (268) (4 mg) as a colourless syrup in quantitative yield:

\[ \alpha^\circ_{D} = +10.0^\circ (c 0.3, \text{H}_2\text{O}) \]

\[ \text{lit } \alpha^{20}\text{D} = +10.9^\circ (c 0.83, \text{H}_2\text{O}) \]

\[ ^1\text{H} \text{ NMR (D}_2\text{O) : 6 1.01-1.20 (m, 2H). 1.37-1.64 (m, 1H), 1.79-1.89 (dt, 1H, J=4.7 Hz). 3.05-3.16 (m, 3H), 3.32-3.64 (m, 3H).} \]

\[ ^13\text{C} \text{ NMR (D}_2\text{O) : 77.12, 76.95, 72.88, 71.22, 62.42, 40.20, 31.79 ppm.} \]

**(1S,2S,3R,4R,5R)-5-Benzylxymethyl-3,4-dibenzyloxy-1,2-cyclohexanediol (269):**

To a solution of the tribenzyl ether 264 (20 mg, 0.05 mmol) in glacial acetic acid (0.2 ml) was added silver acetate (16 mg, 0.09 mmol) and finely powdered iodine (12 mg, 0.05 mmol) over a period of 30 min, at room temperature. After 30 min, aqueous glacial acetic acid (0.02 ml, prepared by dilution of 2.0 ml of water up to 50 ml with glacial acetic acid) was added. The reaction mixture was heated to 90-95° for 3 h. The reaction mixture was then cooled. Excess sodium chloride was added and the insoluble salts were filtered off. The precipitate was washed with ethyl acetate and the solvent was removed in vacuum. The resultant residue was taken in
methanol (2 ml) and sodium (catalytic amount) was added. The reaction mixture was allowed to stand for 12 h at room temperature. The reaction mixture was neutralised by careful addition of dilute HCl at 0°C. The residue was concentrated to dryness and column chromatographed to afford the diol 269 (14 mg, 66%) as a colourless syrup.

\[ \text{\textsuperscript{1}H NMR}: \delta 1.60-1.67 (m, 2H), 1.90-2.02 (m, 1H), 3.47-3.60 (m, 3H), 3.70-3.83 (m, 2H), 4.06-4.09 (m, 1H), 4.47-5.03 (m, 6H, \text{-OCH}_{2}\text{Ph}), 7.27-7.35 (m, 15H, \text{ArH}). \]

\[ \text{\textsuperscript{13}C NMR}: \delta 138.63, 128.69, 128.35, 127.86, 127.57, 83.55, 81.17, 75.25, 74.84, 74.45, 73.10, 69.80, 68.27, 37.45, 30.53 \text{ ppm}. \]

**Pseudo-\(\alpha\)-\(\text{D}\)-glucopyranose (263):**

A solution of the alcohol 269 (10 mg, 0.02 mmol) in methanol (3 ml) was taken in a 250 ml Parr hydrogenation flask and Pearlman’s catalyst (3 mg) was added. Hydrogenation was carried out at 55 psi for 2 h. The catalyst was filtered off and the solvent was evaporated to yield pseudo-\(\alpha\)-\(\text{D}\)-glucopyranose (263) (4 mg) as a colourless syrup in quantitative yield. Its spectral properties were identical with that reported earlier.

Aldehyde (254) on standing at room temperature yielded (1R,2R,3R)-2,3-dibenzylxy-4-cyclohexene-carboxaldehyde (270).

(3R,4R,5S)-3,4-Dibenzylxy-5-hydroxymethylcyclohexene (271): To a solution of the aldehyde 270 (163 mg, 0.5 mmol) in THF (3 ml) at 0°C was added sodium borohydride (76 mg, 2.02 mmol) portionwise and the mixture was stirred for 10 min before quenching with 10% aqueous citric acid. THF was
then removed under reduced pressure. The residue was diluted with ethyl acetate and washed with water. The organic layer was dried and evaporated to give the crude alcohol. Purification by chromatography on a silica gel column gave the pure alcohol 271 (150 mg. 92%) as a colourless syrup.

$^1$H NMR: 6 2.05-2.07 (m, 2H). 2.35-2.42 (m, 1H). 3.40-3.63 (m, 2H). 3.81-3.87 (m, 2H). 4.48-4.60 (m, 4H, -OCH$_2$Ph), 5.70-6.00 (m, 2H). 7.27-7.30 (m, 10H, ArH).

(1S,2S,3R,4R,5S)-3,4-Dibenzyloxy-5-hydroxymethyl-1,2-cyclohexanediol (272):

Potassium hexacyanoferrate(III) (226 mg. 0.75 mmol), potassium carbonate (95 mg. 0.75 mmol) and a solution of osmium tetroxide in t-butyl alcohol (57 µl, 0.003 mmol) were sequentially added to a solution of the alcohol 271 (80 mg. 0.25 mmol) in t-butyl alcohol (1.72 ml) and water (1.72 ml). The reaction mixture was stirred at room temperature for 24 h. Sodium sulphite was then added to the reaction mixture and was stirred for 2 h. The pale blue solution was concentrated to dryness under reduced pressure and the residue was extracted thoroughly with ethyl acetate. The solvent was removed under reduced pressure and the crude product was purified on a silica gel column to furnish the triol 272 (81 mg. 92%) as a colourless syrup.

$[a]^{25}_D$ = +1.5° (c 0.9, CHCl$_3$)

IR (neat): 3412, 2932, 1454, 1072, 1028, 700 cm$^{-1}$.

$^1$H NMR: 5 1.59-1.64 (m, 2H), 2.03-2.21 (m, 1H), 3.61-3.64 (d, 2H, J=6.4 Hz), 3.78-3.85 (m, 1H), 3.86-3.95 (m, 3H), 4.47-4.67 (m, 4H), 7.27-7.38 (m, 10H, ArH).

$^{13}$C NMR: 137.98, 137.14, 128.67, 128.50, 128.29, 127.91, 127.69, 75.34, 73.22, 72.75, 72.62, 67.90, 63.53, 37.91, 27.11 ppm
Pseudo-β-L idopyranose (273):

A solution of the tool 272 (50 mg, 0.15 mmol) in methanol (6 ml) was hydrogenated at 55 psi for 2h in a Parr apparatus using 20% Pd(OH)$_2$/C (Pearlman’s catalyst, 6 mg) to afford 273 (25 mg) as a colourless syrup in quantitative yield

[$\alpha$]$^{D}_{D}$ = $+11.5^\circ$ (c 1.0, H$_2$O), lit. [$\alpha$]$^{D}_{D}$ = $+8.5^\circ$ (c 1.02, H$_2$O)$^{57}$

$^1$HNMR (D$_2$O): 5.1.48-1.69 (m, 2H), 1.86-2.08 (m, 1H), 3.46-3.63 (m, 4H), 3.80-3.84 (m, 2H)