of two catalyst systems are in progress and will be reported in the future.

In conclusion, this work describes the catalytic redistribution/dehydrocoupling of 2-phenyl-1,3-disilapropane by Cp_2MCl_2/Red-Al (M=Ti, Zr, Hf). Unlike Cp_2MCl_2/*n*-BuLi (M=Ti, Hf) catalyst system yielding a cross-linked insouble polymer via simple dehydrocoupling process, the Cp_2MCl_2/Red-Al catalyst system produced an uncross-linked soluble polymer *via* redistribution/dehydrocoupling process. A plausible mechanism for the formation of soluble polymers was provided.

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An Effective Synthesis of 4-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-L-threose and erythrose: Useful Chiral Building Blocks in Synthesis

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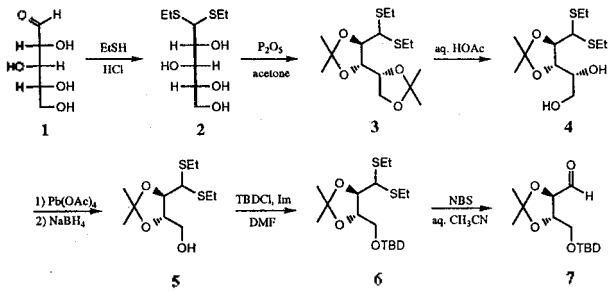
Polyfunctional building blocks from the chiral pool are highly useful in natural product synthesis. Various mono or oligosaccharides used to be converted into valuable intermediates, chiral synthons, or chiral auxiliaries. Both enantiomers of glyceraldehyde derivatives have been widely applied for those purpose. The chemistry of various pentose, hexose, heptose, and disaccharide like sucrose have been deeply investigated, and their results ensured the value of carbohydrates as organic raw materials.[1]

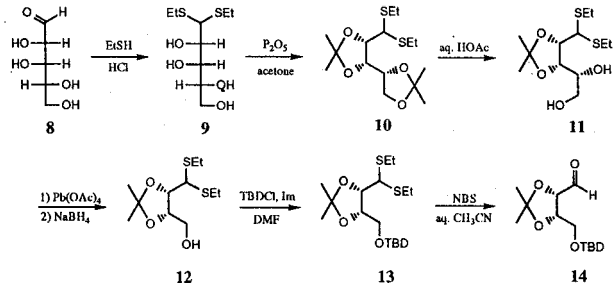
However, relatively few reports about tetrose have been found in spite of their synthetic potentials. Tetrose: D, L-threose and D, L-erythrose: are classified as rare carbohydrates. Although some of them are accessible in chemical market, they are still expensive materials. Recently, synthetic chemists took their interests in tetrose derivatives, and diverse applications have been published.[2] In general, properly protected derivatives are more useful for synthetic purpose rather than tetrose itself. Because of rareness and high price, most tetrose derivatives have been usually prepared from other raw molecules. D, L-Threose from L-ascorbic acid,[3] D, L-arabinitol,[4] D, L-tartaric acid,[5] L-glyceraldehyde[6] were reported. L-Rhamnose,[7] 6-deoxy-L-mannose,[4] D-gulono-1,4-lactone[8] and D-ribono-1,4-lactone[9] were employed as starting materials for the synthesis of L-erythrose. D-Erythrose derivatives were usually prepared starting from D-erythronolacton.[10]

We needed properly protected all four stereoisomers of tetrose for our alkaloid synthesis. Although reported preparations of individual tetrose derivatives are reasonable enough, it was still inconvenient for us to prepare four stereoisomers through four different synthetic schemes. It was necessary to develop more general and convenient way to get properly protected D, L-threose and erythrose.

Starting from D-xylose (**1**), 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-L-threose (**7**) was prepared effectively. When the starting sugar changes to D-lyxose (**8**), with same procedure, 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-L-



Scheme 1.



Scheme 2.

erythrose (**14**) can be produced instead. We expect D-threose and erythrose derivatives can be also prepared with same scheme by changing starting hexose. Therefore, one advantage of our synthesis might be the capability of preparing all possible four stereoisomers of protected tetrose through same synthetic scheme depending on the choice of the starting sugar, and this methodology might be an attractive alternative for whom needs various tetrose building blocks.

1,1-Dithioethyl-2,3;4,5-di-*O*-isopropylidene-D-xylose (**3**)[12] is well known compound easily prepared from 1,1-dithioethyl-D-xylose (**2**)[11] by treating with acetone and P_2O_5. (Scheme 1) Terminal isopropylidene protection group was selectively hydrolyzed in aqueous acetic acid to yield **4**. The diol group of compound **4** was subjected to $Pb(OAc)_4$ oxidation, and the resulting aldehyde was subsequently reduced to alcohol **5** by $NaBH_4$. The primary OH of compound **5** was protected by tert-butyldimethylsilyl group. The resulting compound **6** was stable enough to be stored for a long term, and readily converted into 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-L-threose (**7**) before use by adding NBS in aqueous acetonitrile. The synthesis of 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-L-erythrose (**14**) was also performed through exactly same procedure except that the starting sugar was changed to D-lyxose (Scheme 2).

Experimental

General

^1H NMR spectra were recorded with Varian VXR-200 spectrometer in $CDCl_3$ or DMSO-d_6 solutions. Because the procedures for 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-L-erythrose (**14**) are almost same, only those for 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-L-threose (**7**) were reported.

1,1-Dithioethyl-D-xylose (2). To the mixture of D-xylose (24 g, 0.160 mol) and ethanethiol (200 mL) was added conc. HCl (5 mL). After stirring for 2 days at room temperature, aqueous Na_2CO_3 sol. was added to neutralize excess HCl. After filtering, the filtrate was collected and excess ethanethiol was evaporated. Water was removed by azeotropic distillation with toluene. The resulting solid was crystallized with toluene to yield white solid (**2**) (33.06 g, 129 mmol, 80.7%, mp 63-65 ℃). ^1H NMR (DMSO-d_6, ppm): 1.17 (dd, J=8, 5.4 Hz, 6H, CH_3), 2.56-2.73 (m, 4H, SCH_2), 3.30-3.60 (m, 5H), 3.65-3.80 (m, 2H), 4.00 (d, J=10.0 Hz, 1H, H-1), 4.50 (brs, 4H, OH).

1,1-Dithioethyl-2,3;4,5-di-*O*-isopropylidene-D-xylose (3). Compound **2** (30 g, 117 mmol) was mixed with P_2O_5 (40 g, 282 mmol) in acetone (600 mL). After stirring for 7h at room temperature, the mixture was filtered. The collected filtrate was neutralized with aqueous Na_2CO_3 solution. After evaporating acetone, the residue was dissolved in CH_2Cl_2 and washed with water. The collected organic layer was dried, filtered, and evaporated. The remaining red syrup was purified by column chromatography to give compound **3** (36.7 g, 109 mmol, 93%). ^1H NMR ($CDCl_3$, ppm): 1.21 (dd, J=7.66, 7.36 Hz, 6H, CH_3), 1.31-1.40 (m, 12H, C$(CH_3)_2$), 2.64-2.75 (m, 4H, SCH_2), 3.83-4.31 (m, 6H).

1,1-Dithioethyl-2,3-*O*-isopropylidene-D-xylose (4). Compound **3** (31 g, 92 mmol) was dissolved in 75% aqueous acetic acid (250 mL) and stirred for 12h at room temperature. Aqueous Na_2CO_3 was added to neutralize, and the mixture was extracted with CH_2Cl_2. The organic layer were collected, dried, filtered, and evaporated. The resulting yellow syrup was purified with chromatography to yield **4**. (24.8 g, 84 mmol, 90.7%) ^1H NMR ($CDCl_3$, ppm): 1.21 (dd, J=7.38, 7.52 Hz, 6H, CH_3), 1.38-1.40 (m, 6H, C$(CH_3)_2$), 2.62-2.75 (m, 4H, SCH_2), 2.99-3.02 (br, 2H, OH), 3.66-3.88 (m, 4H), 4.06 (dd, J=1.9, 5.5 Hz, 1H, H-3), 4.30 (dd, J=6.66, 6.52 Hz, 1H, H-2).

1,1-Dithioethyl-2,3-*O*-isopropylidene-L-threose (5). To the solution of **4** (25 g, 84 mmol) in dry toluene (300 mL) was added $Pb(OAc)_4$ (35 g). After stirring 7h in ice-water bath, the mixture was filtered through a celite pad. The filtrate was washed with $NaHCO_3$ and the collected organic layer were dried, filtered and evaporated. The remaining yellow syrup was dissolved in methanol, and $NaBH_4$ (3.3 g, 87 mmol) was added. After stirring 1h at room temperature, methanol solvent was evaporated, and the residue was dissolved in CH_2Cl_2. The mixture was washed with water, and the collected organic layer was dried, filtered, and evaporated. The residue was purified by chromatography to yield **5** (15.54 g, 56 mmol, 66.2%). ^1H NMR ($CDCl_3$, ppm): 1.28 (dd, J=7.32, 7.56 Hz, 6H, CH_3), 1.44-1.47 (m, 6H, C$(CH_3)_2$), 2.47-2.48 (brs, 1H, OH), 2.67-2.83 (m, 4H, SCH_2), 3.78-3.95 (m, 3H, H-1, 2), 4.17 (m, 2H, H-2, 3).

4-*O*-*tert*-Buthyldimethylsilyl-1,1-dithioethyl-2,3-*O*-isopropylidene-L-threose (6). To the solution of **5** (15 g, 54 mmol) in dry DMF (200 mL) were added TBDCl (13 g, 81 mmol) and imidazole (9 g, 140 mmol). After stirring 5h at room temperature, solvent was removed and the residue was dissolved in CH_2Cl_2. After washing with water, the organic layer was collected, dried, filtered, and evaporated to give crude **6**. Final purification was done by chromatography to yield **6** (20.2 g, 51 mmol, 95.7%). ^1H NMR ($CDCl_3$,

ppm): 0.03 (s, 6H, $Si(CH_3)_2$), 0.83 (s, 9H, $SiC(CH_3)_3$), 1.18 (dd, J=7.32, 7.56 Hz, 6H, CH_3), 1.35 (d, J=11.47 Hz, 6H, $C(CH_3)_2$), 2.60-2.70 (m, 4H, SCH_2), 3.75 (dd, J=6.34, 4.88 Hz, 2H, H-4), 3.87 (d, J=4.64 Hz 1H, H-1), 4.04-4.10 (m, 1H, H-3), 4.18 (dd, J=4.64, 4.64 Hz, 1H, H-2).

4-*O*-*tert*-Buthyldimethylsilyl-2,3-*O*-isopropylidene-L-threose (7). To the mixture of **6** (200 mg, 0.51 mmol) and 2,6-lutidine (0.35 mL, 3 mmol) in aqueous acetonitrile was added NBS (0.25 g, 1.4 mmol) until yellow color was remaining. The mixture was washed with 1 M Na_2SO_3 solution, and extracted with CH_2Cl_2/hexane (1 : 1) solution. The collected organic layer was dried, filtered, and evaporated to yield crude aldehyde **7** (0.13 g, 0.48 mmol) which can be usually used for the further reaction without purification. ^1H NMR ($CDCl_3$, ppm): 0.03 (s, 6H, $Si(CH_3)_2$), 0.83 (s, 9H, $SiC(CH_3)_3$), 1.35 (d, J=11.47 Hz, 6H, $C(CH_3)_2$), 3.75 (dd, J=6.34, 4.88 Hz, 2H, H-4), 4.04-4.10 (m, 1H, H-3), 4.18 (dd, J=1.8, 4.64 Hz, 1H, H-2), 9.72 (d, J=1.8 Hz, 1H, H-1). IR (cm^{-1}): 3464, 2935, 1710, 1464, 1377, 1259, 1182, 1091.

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Synthesis and Properties of Low Molecular Weight π-Conjugated Poly(2,5-diethynylthiophene)

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Conjugated polymers have received considerable attention as advanced materials in recent years.[1] These polymers could be widely used as electronic, photonic, and optical materials.[2] Conjugated polymeric materials such as polyacetylene, polypyrrole, polyaniline, and polythiophene, etc., have been intensively studied.[3]

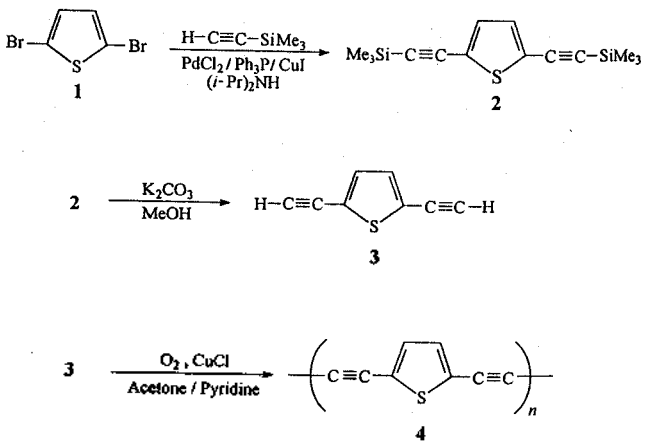
Recently, polymers conjugated with thiophene and diacetylene functionalities were reported.[4] However, the unsubstituted diethynylthiophene polymer prepared by oxidative polymerization in pyridine with copper(I) chloride and oxygen[5,6] turned out to be insoluble in usual organic solvent.[7]

Here we wish to describe the preparation and properties of low molecular weight poly(2,5-diethynylthiophene), which is soluble in organic solvents.

Results and Discussion

The synthetic route for the monomer of 2,5-diethynylthiophene (**3**) is outlined in Scheme 1.

The synthesis of **3** involves two steps: (a) the displacement of 2,5-dibromothiophene (**1**) with trimethylsilylacetylene, and (b) the subsequent cleavage of the trimethylsilyl protecting group to **3**.[8,9] Trimethylsilylacetylene easily displaced the bromines of **1** in the presence of palladium(II) chloride, triphenylphosphine, copper(I) iodide in diisopropylamine to yield 2,5-bis[2′-(trimethylsilyl)ethynyl]thiophene (**2**). The desilylation reaction of **2** was accomplished with potassium carbonate in methanol at ambient temperature to obtain mono-



Scheme 1.

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