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A Total, Asymmetric Synthesis of 2-Deoxy-L-fucose from Furan

Jean-Marc Durgnat [a], Alexander Warm [a b] & Pierre Vogel [a]

[a] Section de Chimie de l'Université de Lausanne, 2, rue de la Barre, CH 1005, Lausanne, Switzerland

[b] Lonza, CH-3930 Visp, Switzerland

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A TOTAL, ASYMMETRIC SYNTHESIS OF 2-DEOXY-L-FUCOSE FROM FURAN

Jean-Marc Durgnat, Alexander Warm*, and Pierre Vogel*

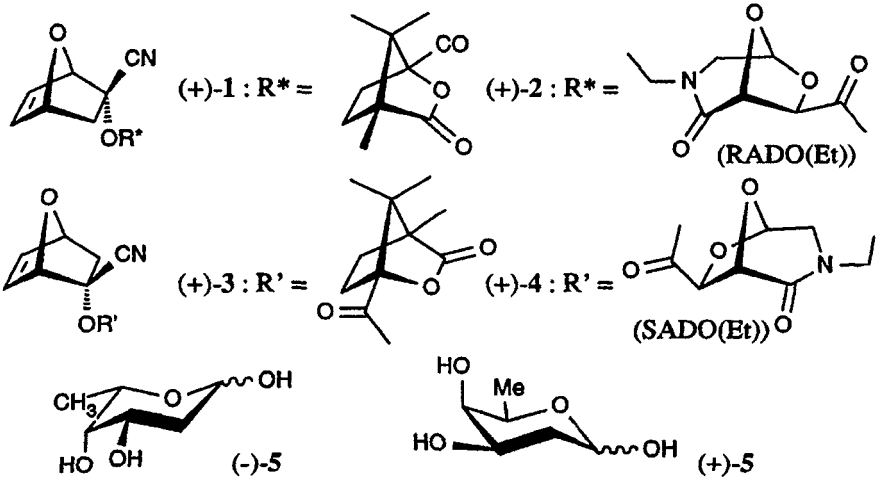
Section de Chimie de l'Université de Lausanne, 2, rue de la Barre, CH 1005 Lausanne, Switzerland

Abstract: The Diels-Alder adduct (+)-1 of furan to 1-cyanovinyl (1'S)-camphanate was converted to methyl 3,5-O-diacetyl-2,6-dideoxy-β-L-*lyxo*-hexofuranoside ((+)-12), a protected form of 2-deoxy-L-fucose, in 8 steps and 16.6% overall yield.

Optically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives 1 - 4 ("naked sugars") obtained by zinc halide-catalysed Diels-Alder additions of furan to optically pure 1-cyanovinyl esters[1,2] have been shown to be useful "chirons" in the total synthesis of natural products and compounds of biological interest.[3,4] We present here a further application of (+)-1 in the total, asymmetric synthesis of 2-deoxy-L-fucose ((-)-5) an important carbohydrate found in a variety of antibiotics.[5,6,7]

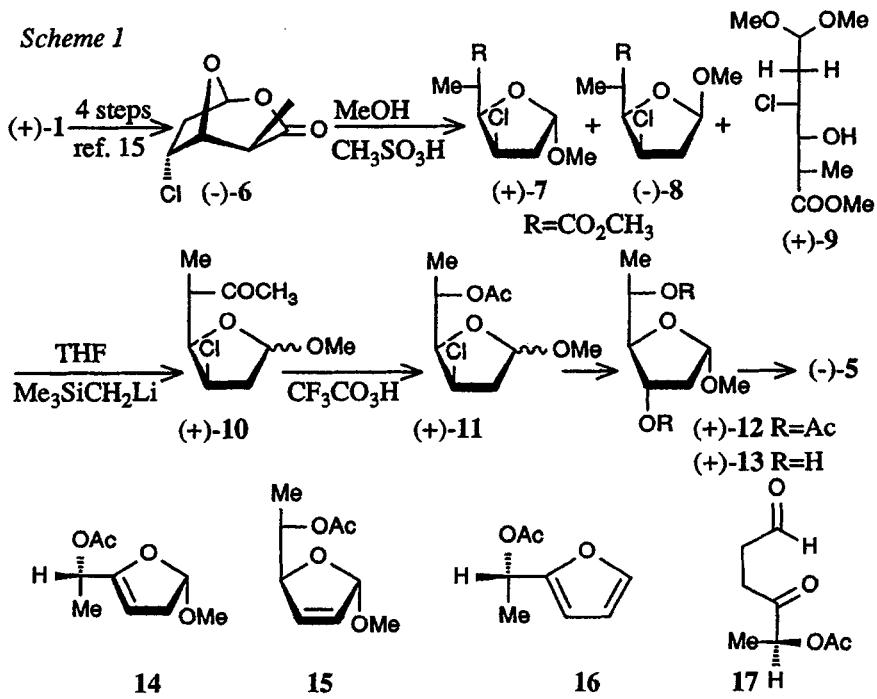
In 1944, Iselin and Reichstein[8] derived (-)-5 from L-fucose (6-deoxy-L--galactose) in 5 synthetic steps. Since then, several other syntheses of (-)-5 star-

* Present address: Lonza, CH-3930 Visp, Switzerland.
* To whom correspondence should be addressed.



ting with natural carbohydrates have been reported.[9] In 1979, Chmielewski[10] obtained a mixture of DL-*ribo*- and DL-*lyxo*-2,6-dideoxyhexoses via the cycloaddition of t-butyl glyoxalate to (E)-1-methoxybutadiene. An efficient, enantioselective synthesis of (+)-oliose ((+-5: enantiomer of 2-deoxy-L-fucose) based on the Katsuki-Sharpless asymmetric epoxidation[11] has been reported in 1983 by Roush and Brown.[12] In 1984, Fronza et al.[13] described a stereo- and enantioselective preparation of (-)-5 applying a baker's yeast mediated reduction of an α-acetoxyketone.[14] Our synthesis of (-)-5 (Scheme 1) makes use of reactions we had developed in the convertion of (+)-1 into L-daunosamine (3-amino-2,3,6-trideoxy-L-*lyxo*-hexose).[15]

Treatment of urono-6,1-lactone (-)-6[15] with anhydrous MeOH and 1 equivalent of $MeSO_3H$ (-15° - 20°C) led to a 78:8:6 mixture of (+)-7, (-)-8 and (+)-9 that could be separated by flash chromatography on silica gel. Reaction of this mixture in THF with Me_3SiCH_2Li in pentane[16] (-55°C, 4 h) afforded (+)-10 in 47% yield (mostly the methyl α-furanoside). Baeyer-Villiger oxidation of



(+)-**10** with CF_3CO_3H/Na_2HPO_4 in CH_2Cl_2 afforded (+)-**11** (85%). No reaction was observed when the chloride (+)-**11** was heated (80 - 85°C) in CH_3CN with a large excess of AcOK or AcOAg. However, when a mixture of 0.15 - 0.3 M of (+)-**11** in CH_3CN of DMF was heated to 90°C (1 hour) with 6 equivalents of AcOK and 6 equivalents of 18-crown-6 ether, a 2:1:1 mixture of (+)-**12**, **14** and **15** was formed. Heating to 110 - 115°C led to lower yields in (+)-**12** and concurrent formation of **16** and **17**. We finally found that the S_N2 displacement product (+)-**12** could be obtained in 43% isolated yield on treating **11** with 1.1 equivalent of $Bu_4N^+AcO^-$ in DMF (80°C, 64 h). The reaction was accompanied by the formation of ca. 14% of products of elimination **14** + **15** under these conditions. Deacetylation (KCN/MeOH) afforded methyl 2-deoxy-β-L-fucoside

((+)-13) in 94% yield. Acidic hydrolysis (AcOH/H_2O 1:3, 100°C) provided 2-deoxy-L-fucose ((-)-5, in 95%) which could be crystallized into its α-pyranose form from ether (74%).

Since the "naked sugar" (-)-3 or (-)-4 can be obtained as readily as (+)-1 (or (+)-2), our approach to the total synthesis of 2-deoxy-L-fucose can be applied with the same ease to the synthesis of D-oliose ((+)-5), a carbohydrate found in many antibiotics also.[5]

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Experimental Section

General remarks: see ref. 17.

Methyl (methyl 3-chloro-2,3,5-trideoxy-5-*C*-methyl-α-D-*arabino*-hexofuranosid)uronate ((+)-7), methyl (methyl 3-chloro-2,3,5-trideoxy-5-*C*-methyl-β-D-*arabino*-hexofuranosid)uronate ((-)-8) and methyl 3-chloro-2,3,5-trideoxy--5-*C*-methyl-*arabino*-hexouronate dimethyl acetal ((+)-9). $MeSO_3H$ (0.55 mL, 8.7 mmol) was added dropwise to a stirred solution of (-)-6 (1.5 g, 8.5 mmol) in anhydrous MeOH (150 mL) cooled to -15°C for 20 min., the mixture was allowed to warm to 20°C and stirred for 15 h. AcONa (1 g) was added and the

mixture stirred at 20°C for 10 min. The precipitate was filtered off, washed with CH_2Cl_2 (50 mL, 3 times). The org. solutions were combined and washed with a saturated aqueous solution of $NaHCO_3$ (50 mL), then with brine (50 mL). The solvent was evaporated and the residue purified by flash chromatography on silica gel (60 g, light petroleum/AcOEt 4:1). The first fraction (R_f (light-petroleum/AcOEt 2:1) = 0.6) afforded 1.472 g (78%) of (+)-7, the second (R_f = 0.4) 0.15 g (8%) of (-)-8 and the third (R_f = 0.3) gave 136 mg (6.3%) of (+)-9. Characteristics of (+)-7: colourless crystals, m.p. 46-47°C. $[\alpha]_{589}^{21}$ = +114, $[\alpha]_{578}^{21}$ = +119, $[\alpha]_{546}^{21}$ = +134, $[\alpha]_{436}^{21}$ = +220, $[\alpha]_{365}^{21}$ = +332 (c = 0.85g/100 mL, CH_2Cl_2). IR (KBr): ν: 3060, 3040, 3000, 2940, 2840, 1735, 1460, 1435, 1340, 1275, 1195, 1070, 1030, 1005, 950 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.17 (dd, *J* = 5.7, 3.9, H-C(1)); 4.42 (ddd, *J* = 6.1, 3.2, 0.9, H-C(3)); 4.16 (dd, *J* = 10.0, 3.2, H-C(4)); 3.71 (s, ($COOCH_3$); 3.29 (s, MeO); 2.85 (dq, *J* = 10.0, 7.0, H-C(5)); 2.55 (ddd, *J* = 14.6, 5.7, 0.9, H_s-C(2) *syn* with respect to Cl); 2.34 (ddd, *J* = 14.6, 6.1, 3.9, H_a-C(2)); 1.16 (d, *J* = 7.0, CH_3-C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 174.8 (s, CO); 103.7 (d, ^1J(C,H) = 175, C(1)); 81.3 (d, ^1J(C,H) = 145, C(4)); 60.1 (d, ^1J(C,H) = 160, C(3)); 53.8, 52.0 (2q, ^1J(C,H) ≅ 145, 2 MeO), 44.4 (t, ^1J(C,H) = 135, C(2)); 41.2 (d, ^1J(C,H) = 140, C(5)); 13.8 (q, ^1J(C,H) = 128, CH_3-C(5)). MS (IC, NH_3) m/z: 240 ($M^{+\cdot}$ +18, 8.4), 223 (4, $M^{+\cdot}$ +1), 191 (15), 155 (19), 127 (24), 117 (113), 106 (13), 99 (30), 85 (14), 71 (100). Anal. calc. for $C_9H_{15}O_4Cl$ (222.67): C 48.55, H 6.79; found: C 48.75, H 6.89.

Characteristics of (-)-8. Colourless oil. $[\alpha]_{589}^{21}$ = -58, $[\alpha]_{578}^{21}$ = -60, $[\alpha]_{546}^{21}$ = -67, $[\alpha]_{436}^{21}$ = -113, $[\alpha]_{365}^{21}$ = -173 (c = 0.7, CH_2Cl_2). IR ($CHCl_3$) ν:

3620, 3260, 3060, 3000, 2880, 2840, 1730, 1460, 1435, 1320, 1275, 1170, 1100, 1070, 1030 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.02 (dd, J = 6.1, 1.0, H-C(1)); 4.36 (ddd, J = 6.0, 3.9, 0.8, H-C(3)); 4.13 (dd, J = 9.9, 3.9, H-C(4)); 3.57 (s, $COOCH_3$); 3.34 (s, OMe); 2.94 (dq, J = 9.9, 6.8, H-C(5)); 2.53 (ddd, J = 14.5, 6.1, 6.0, H_a-C(2) *anti* with respect to Cl); 2.43 (ddd, J = 14.5, 1.0, 0.8, H_s-C(2)); 1.15 (d, J = 6.8, CH_3-C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 175 (s, CO); 104.5 (d, ^1J(C,H) = 173, C(1)); 83.7 (d, ^1J(C,H) = 147, C(4)); 57.5 (d, ^1J(C,H) = 160, C(3)); 55.4, 51.6 (2q, ^1J(C,H) = 145, 2 MeO); 42.8 (t, ^1J(C,H) = 136, C(2)); 42.7 (d, ^1J(C,H) = 140, C(5)); 13.6 (q, ^1J(C,H) = 130, CH_3-C(5)). MS (IC, NH_3) m/z: 221 ($M^{+\cdot}$ -1, 0.65), 193 (0.9), 186 (4), 162 (2), 155 (23), 135 (5), 127 (25), 117 (16), 106 (11.5), 99 (29), 95 (77), 71 (100). Anal. calc. for $C_9H_{15}O_4Cl$ (222.67): C 48.55, H 6.79; found: C 48.60, H 6.76.

Characteristics of (+)-9: colourless oil. $[\alpha]^{21}_{589}$ = +32, $[\alpha]^{21}_{578}$ = +32.5, $[\alpha]^{21}_{546}$ = +37, $[\alpha]^{21}_{436}$ = +60, $[\alpha]^{21}_{365}$ = +91 (c = 0.8, CH_2Cl_2). IR ($CHCl_3$) ν: 3620, 3260, 3060, 2980, 2840, 1730, 1510, 1435, 1170, 1125, 1050, 870, 700 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.58 (dd, J = 7.6, 3.6, H-C(1)); 4.13 (ddd, J = 9.2, 4.4, 1.7, H-C(3)); 3.77 (dd, J = 8.8, 1.7, H-C(4)); 3.66 (s, $COOCH_3$), 3.36, 3.32 (2s, 2 MeO); 2.8 (dq, J = 8.8, 7.5, H-C(5)); 2.21 (ddd, J = 14.5, 9.2, 3.6), 2.06 (ddd, J = 14.5, 7.6, 4.4, 2 H-C(2)); 1.16 (d, J = 7.5, CH_3-C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 175.6 (s, CO); 102.5 (d, ^1J(C,H) = 164, C(1)); 75.5 (d, ^1J(C,H) = 127, C(4)); 57.5 (d, ^1J(C,H) = 151, C(3)); 54.2, 53.1, 51.8 (3q, ^1J(C,H) = 145, 3 MeO); 43.9 (d, ^1J(C,H) = 132, C(5)); 42.7 (t, ^1J(C,H) = 130, C(2)); 13.8 (q, ^1J(C,H) = 128, C(6)). MS (70 eV) m/z: 254 ($M^{+\cdot}$, 0.2), 193 (2), 191 (2), 187 (1), 156 (2.5), 155 (16), 117 (12), 99 (14), 75 (100).

Methyl 3-chloro-2,3,5,7-tetradeoxy-5-*C*-methyl-*arabino*-D-α-hept-6-ulofuranoside ((+)-**10**). A 1 M solution of $LiCH_2TMS$ in anhydrous pentane (4 mL, 4 mmol) was added dropwise to a stirred solution of (+)-7 (0.41 g, 1.84 mmol) in anhydrous THF (50 mL) cooled to -55°C under Ar atmosphere. After stirring at -50°C for 3 h, the solution was added to a stirred solution of HCl 0.2 N (100 mL) cooled to 0°C. The pH was adjusted to 6.5 with NaOH 0.1 N. The org. phase was extracted with ether (70 mL, 3 times) washed with a saturated aqueous solution of $NaHCO_3$ (70 mL), water (50 mL), brine (50 mL), dried ($MgSO_4$) then concentrated in vacuo. The residue was purified by flash chromatography (60 g of SiO_2, 230-400 mesh ASTM, AcOEt/CH_2Cl_2 1:19) yielding 179 mg (47%) of yellowish oil unstable at 20°C, must be stored in CH_2Cl_2 at -20°C.

Same characteristics as those reported in the lit.[15]

Methyl 5-*O*-acetyl-3-chloro-2,3,6-trideoxy-β-L-*xylo*-hexofuranoside ((+)-**11**). Obtained following the procedure given in ref. 15, starting with (+)-**10**.

Methyl 3,5-*O*-Diacetyl-2,6-dideoxy-β-L-*lyxo*-hexofuranoside ((+)-**12**). A mixture of (+)-**11** (245 mg, 1.1 mmol), anhydrous DMF (0.5 mL), 1.8 M tetrabutylammonium acetate in DMF (0.6 mL, 1.1 mmol) was stirred at 70°C for 64 h. The mixture was filtered through silica gel (20 g, light petroleum/AcOEt 1:2). After solvent evaporation the residue was purified by flash chromatography on silica gel (20 g, light petroleum/AcOEt 1:2). The two first fractions (R_f = 0.49 and 0.36) contained the products of elimination **14** (11 mg,

6%) and **15** (17 mg, 8%). The third fraction (R_f = 0.27) yielded 116.5 mg (43%) of (+)-**12**, colourless oil. $[\alpha]_{589}^{24}$ = +129, $[\alpha]_{578}^{24}$ = +133, $[\alpha]_{546}^{24}$ = +151, $[\alpha]_{436}^{24}$ = +245, $[\alpha]_{365}^{24}$ = +363 (c = 0.73, $CHCl_3$); lit. $[\alpha]_D^{21}$ = +131 (c = 3.3, $CHCl_3$). IR ($CHCl_3$) ν: 3000, 2950, 2840, 1740, 1440, 1375, 1315, 1245, 1215, 1145, 1130, 1105, 1075, 1040, 965 cm^{-1}. ^{1}H-NMR (360 MHz, $CDCl_3$) δ_H: 5.09 (qd, *J* = 6.2, 4.0, H-C(5)); 5.09 (dd, *J* = 5.1, 1.2, H-C(1)); 4.97 (ddd, *J* = 8.5, 4.5, 2.2, H-C(3)); 4.10 (dd, *J* = 4.5, 4.0, H-C(4)); 3.40 (s, OMe); 2.46 (ddd, *J* = 14.0, 8.5, 5.1, H_a-C(2) *anti* with respect to OAc-C(3)); 2.08, 2.06 (2s, 2 OAc); 1.96 (ddd, *J* = 14.0, 2.2, 1.2, H_s-C(2)); 1.30 (d, *J* = 6.2, CH_3(6)). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 170.7, 170.0 (2s, 2 CO); 104.8 (d, ^1J(C,H) = 170, C(1)); 83.7 (d, ^1J(C,H) = 148, C(4)); 73.8 (d, ^1J(C,H) = 156, C(3)); 69.7 (d, ^1J(C,H) = 148, C(5)); 55.0 (q, ^1J(C,H) = 142, MeO); 39.4 (t, ^1J(C,H) = 154, C(2)); 21.1, 21.0 (2q, ^1J(C,H) = 130, CH_3CO); 16.1 (q, ^1J(C,H) = 128, C(6)). MS (70 eV) m/z: 246 (0.1, $M^{+\cdot}$), 219 (6), 215 (13), 203 (3), 159 (8), 130 (12), 126 (4), 112 (5), 99 (100). Anal. calc. for $C_{11}H_{18}O_6$ (246.26): C 53.65, H 7.37; found: C 53.57, H 7.25.

Methyl 2,6-dideoxy-β-L-*lyxo*-hexofuranoside ((+)-**13**). A mixture of (+)-**12** (50 mg, 0.2 mmol), anhydrous MeOH (1.5 mL) and KCN (13.2 mg, 0.2 mmol) was stirred at 20°C for 4 days. The solvent was evaporated and the residue purified by filtration on a short column of silica gel (3 g, light petroleum/AcOEt/MeOH 25:25:1, R_f ((+)-**13**) = 0.1), yielding 31 mg (94%), colourless oil. $[\alpha]_{589}^{21}$ = +97, $[\alpha]_{578}^{21}$ = +101, $[\alpha]_{546}^{21}$ = +114, $[\alpha]_{436}^{21}$ = +185, $[\alpha]_{365}^{21}$ = +277 (c = 3, CH_2Cl_2). IR ($CHCl_3$) ν: 3560, 3260, 3250, 2930, 1725, 1445, 1370, 1240, 1090, 1070, 1025, 945, 905, 835 cm^{-1}. ^{1}H-NMR (250 MHz,

$CDCl_3$) δ_H: 5.07 (dd, J = 4.3, 0.8, 1H, H-C(1)); 4.06 (ddd, J = 6.0, 1.8, 1.5, 1H, H-C(3)); 3.85 (dd, J = 5.8, 1.8, 1H, H-C(4)); 3.7 (dq, J = 6.2, 5.8, 1H, H-C(5)); 3.4 (s, 3H, MeO); 2.1 (ddd, J = 13.4, 6.0, 4.3, 1H, H_a-C(2) *anti* with respect to HO-C(3)); 1.96 (ddd, J = 13.4, 1.5, 0.8, 1H, H_s-C(2)); 1.22 (d, J = 6.2, 3H, H-C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 105.2 (d, ^1J(C,H) = 172, C(1)); 91.0 (d, ^1J(C,H) = 147, C(4)); 73.1 (d, ^1J(C,H) = 153, C(5)); 68.1 (d, ^1J(C,H) = 141, C(3)); 54.8 (d, ^1J(C,H) = 125, MeO); 41.4 (t, ^1J(C,H) = 142, C(2)); 19.4 (q, ^1J(C,H) = 129, C(6)). Ms (70 eV) m/z: 162 (0.4, $M^{+\cdot}$), 131 (12), 117 (46), 100 (29), 99 (77), 88 (40), 87 (19), 85 (15), 73 (8), 71 (40), 45 (100). Anal. calc. for $C_7H_{14}O_4$ (162.19): C 51.86, H 8.70; found: C 51.91, H: 8.65.

2-Deoxy-L-fucose (2,6-Dideoxy-L-*lyxo*-hexose: (-)-5). A mixture of (+)-13 (15 mg, 0.1 mmol) and H_2O/AcOH 3:1 (1 mL) was heated to 100°C for 45 min. The solvent was evaporated to dryness in vacuo and the residue dried over P_4O_{10} (20°C, 3 days). The hydroscopic sugar was recrystallized from anhydrous ether under Ar atmosphere: 11 mg (74%), colourless crystals, m.p. 100.5-103°C. Lit.: 102-105[9] $[\alpha]_{589}^{21}$ = -70.3 (after 6 min); -62.8 (12 min); -54.3 (20 min); -51.5 (40 min); -50.3 (60 min) (c = 0.4, H_2O). Lit.: -90.4±2 (90 min. equil.) (c = 1.039, H_2O)[8] typical of a mixture of α-pyranose, β-pyranose, α-furanose and β-furanose forms where the α-pyranose forms dominate.

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