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A SYNTHESIS OF 2-DEOXY-3-*O*-METHYL-1,4-ALDONOLACTONES

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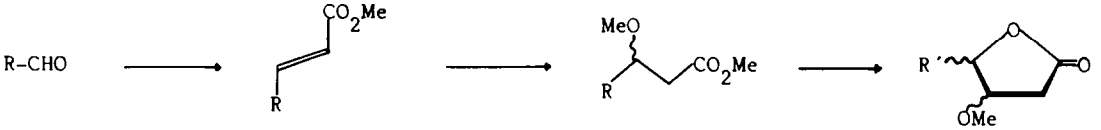
Abstract - A practical synthetic route to 2-deoxy-3-*O*-methyl-1,4-aldonolactones is achieved. Isopropylidene derivatives of aldehyde sugars 1, (free or in lactol form), reacted with methyl hydrogen malonate to give α,β-unsaturated esters 2. In the case of lactols, the R group in 2 is not identical to the R in 1 (epimerisation occurs). Base-catalysed addition of methanol to the esters 2 afforded the epimeric ethers 3, acid hydrolisis of which yielded the 2-deoxy-3-*O*-methyl-1,4-aldonolactones 4. Degradation of the sugar chain permitted the assignment of the absolute configuration on C-3.

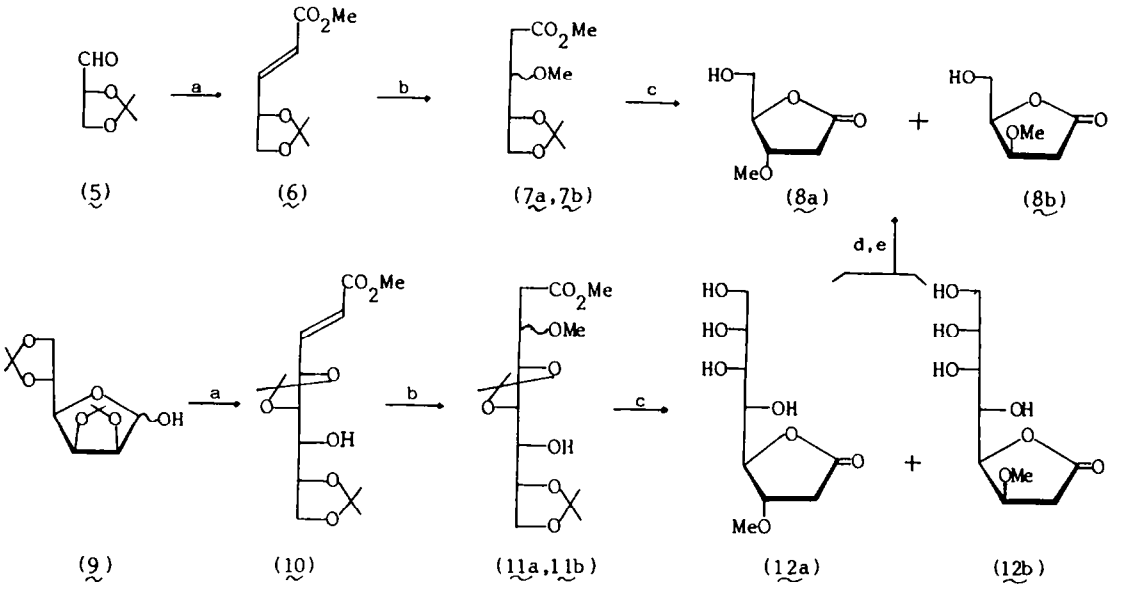
As reported in a preceding paper[1], reaction of α,β-unsaturated esters of type 2, with methanolic sodium methoxide yields a mixture of 3-epimers: 2-deoxy-3-*O*-methyl-D-aldonates 3. The present paper reports a more detailed and extensive study of these compounds and their transformation into 2-deoxy-3-*O*-methyl-1,4-aldonolactones 4.



(1) (2) (3) (4)

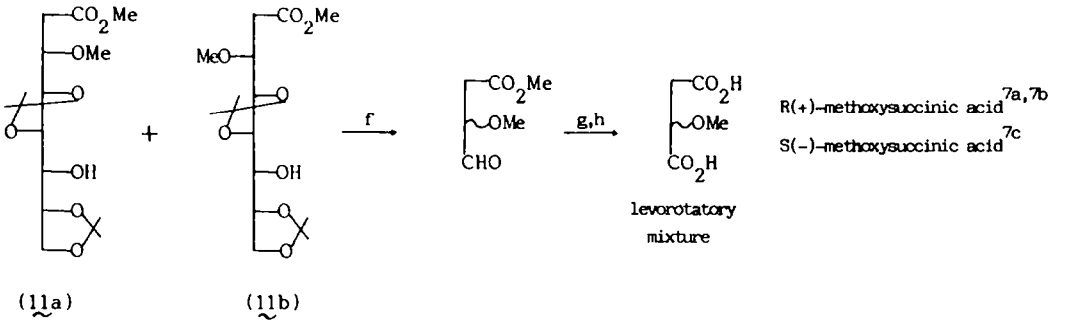
R: Isopropylidene sugar derivatives R': Polyhydroxyalkyl chain
In the case of lactols, the R group in 2 is not identical to the R in 1 (epimerisation occurs)

The reaction of 2,3-*O*-isopropylidene-D-glyceraldehyde (5)[2] with methyl hydrogen malonate in pyridine, with piperidine as the catalyst, gave methyl trans-2,3-dideoxy-4,5-isopropylidene-D-*glycero*-pent-2-enonate (6). Treatment of 6 with methanolic sodium methoxide yielded a mixture of diastereoisomeric methyl 2-deoxy-4,5-*O*-isopropylidene-3-*O*-methyl-D-*erythro*- and -D-*threo*-pentonates (7a,7b). This addition was studied by Mulzer et col.[3], after our preliminary communication[1]. Hydrolysis of 7a and 7b with hot aqueous 20% acetic acid yielded 2-deoxy-3-*O*-methyl-D-*erythro*- and -D-*threo*-pentono-1,4-lactones (8a,8b). The stereochemical assignments agree with the results of Font et al.[4], which were obtained by unequivocal synthesis from chiral natural products.



(a) $MeO_2C-CH_2-CO_2H$; (b) $MeO^-/MeOH$, 0.1M; (c) $AcOH/H_2O$; (d) $NaIO_4/H_2O$; (e) $NaBH_4/H_2O$

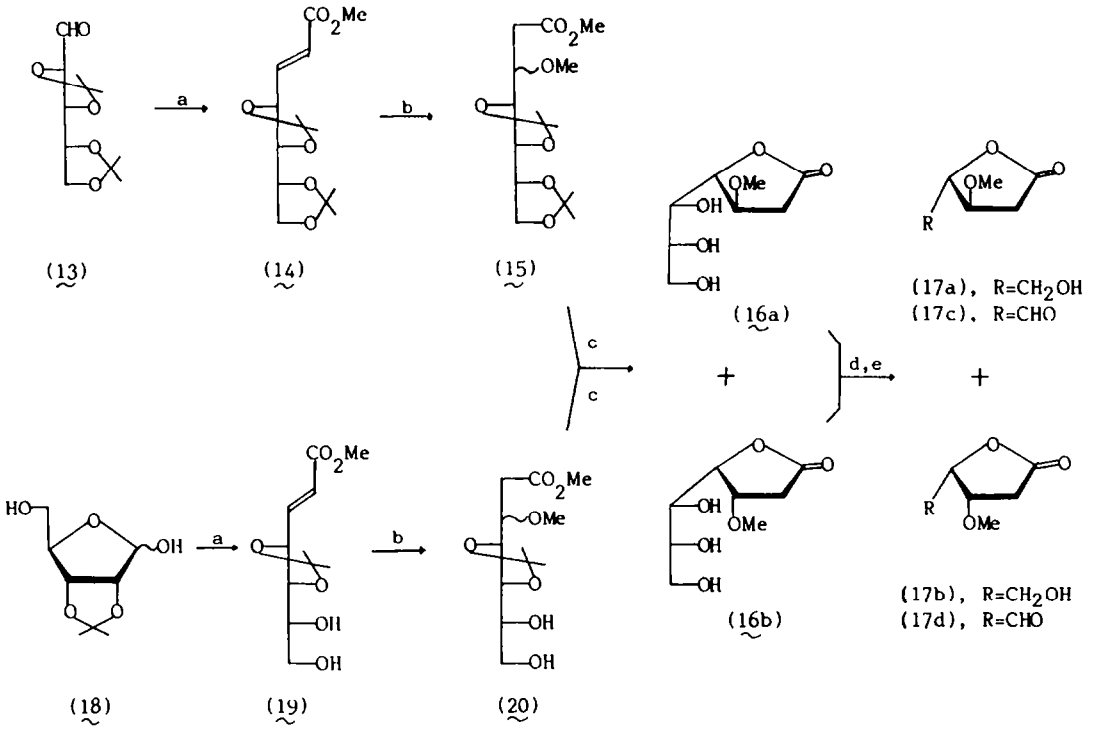
Starting from 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (9), methyl *trans*-2,3-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*gluco*-oct-2-enonate (10)[5] was obtained, because of epimerisation at C-2 of the sugar[5,6]. The Michael adducts 11a and 11b were obtained in a 1.2:1 approximate proportion (GLC analysis). Absolute configuration at C-3 was shown by acid hydrolysis in the presence of periodic acid, followed by Ag_2O oxidation and alkaline hydrolysis, and gave a levorotatory (in aqueous or acetone media) mixture of methoxysuccinic acids [7]. Thus, the preponderant isomer had the D-*glicero*-D-*gulo* configuration 11a.



(f) TFA, HIO_4; (g) Ag_2O; (h) NaOH

Treatment of the mixture 11(a,b) with hot aqueous 20% acetic acid yielded 12a (major product) and 12b, which were separated by column chromatography, and later recrystallized. Metaperiodate oxidation of 12(a,b) and subsequent reduction with sodium borohydride yielded the pentonolactones 8(a,b). The analytical and spectroscopic data of the latter were the same as the data of the products obtained from 6, which proves the configurational assignment for 12a and 12b.

Similarly, 2,3:4,5-*O*-isopropylidene-aldehydo-D-arabinose (13), was the starting material in the synthesis of the enantiomeric aldonolactones of 8a and 8b, (17a and 17b).



(a) $MeO_2C-CH_2-CO_2H$; (b) $MeO^-/MeOH$, 0.1M; (c) $AcOH/H_2O$; (d) $NaIO_4/H_2O$; (e) $NaBH_4/H_2O$

The same lactones were obtained when the ester 19 was employed. Methyl trans-2,3-dideoxy-4,5-*O*-isopropylidene-D-arabino-hept-2-enonate (19) was prepared by condensation of 2,3-*O*-isopropylidene-D-ribofuranose (18)[9] with methyl hydrogen malonate. In this case, epimerisation was also observed[5]. Addition of methanol yielded the C-3 epimers 20, which gave the lactones 16 by the usual method.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 or 241 polarimeter. I.r. spectra were recorded with a Beckman Aculab IV spectrophotometer. H-n.m.r. spectra (internal Me_4Si or 2,2-dimethyl-2-silapentane-5-sulfonate) with Perkin-Elmer Hitachi R-24B (60 MHz) and a Bruker WP-200 SY (200.13 MHz) spectrometers. U.v. spectra with a Beckman DB-GT spectrophotometer, and mass spectra with a Hewlett-Packard 5930A mass spectrometer. T.l.c. was performed on Silica Gel G (Merck) and column chromatography on Silica Gel 7734 (Merck). Elemental analyses were carried out by the Microanalysis Services of the Universities of Granada and Santiago de Compostela.

Methyl *trans*-2,3-dideoxy-4,5-*O*-isopropylidene-D-glycero-pent-2-enonate (6).- A solution of 5 (33.65 g, 0.26 mmol) and monomethyl malonate (32.4 g, 0.3 mmol) in pyridine (25 g), with piperidine (0.35 mL), was left overnight at room temp. Pyridine was eliminated in vacuo and the residue was distilled to give 6 (37.83 g, 78%), (78°C/0.2 mm Hg). Rf 0.76 (Hexane-AcOEt, 1:1). $[\alpha]_D^{20}$ +17.16°(c 0.99, EtOH). UV, λmax(EtOH): 228 nm. IR, ν max(film): 2960, 2925, 1730, 1670, 1440, 1380 and 980 cm^{-1}. H-n.m.r.($CDCl_3$, 200 MHz), δ ppm: 6.80(dd, J 15.6 and 5.5 Hz, H-3), 6.02 (dd, J 15.6 and 1.4 Hz, H-2), 4.58(m, J 6.6, 5.5, 1.4 and 1.2, H-4), 4.10(dd, J 8.3 and 6.6, H-5a), 3.65(s, 3H, MeO), 3.60(dd, J 8.3 and 1.2, H-5b), 1.35 and 1.31(2s, 2x3H, Me_2C). Anal. Calc. for $C_9H_{14}O_4$: C, 58.05; H, 7.57. Found: C, 58.08; H, 7.61%

Methyl 2-deoxy-3-*O*-methyl-4,5-*O*-isopropylidene-D-*erythro*- and -D-*threo*-pentonates (7a and 7b).- 23 g of 6 were dissolved in MeONa/MeOH 0.1M (130 mL). After 30 h, the mixture was eluted with ether (600 mL) and washed with $KHSO_4$ 0.1M (230 mL). The aqueous layer was extracted with ether (60 mL). The ethereal fractions were washed (170 mL, water) and dried (Na_2SO_4 anh.). After elimination of solvent, the resultant syrup was distilled to

give 7a and 7b (19.4 g, 72%, 74°C/0.2mm Hg). Rf 0.82 (Hexane-AcOEt, 1:1). IR, ν max: 3000, 2950, 1755, 1450, 1380, 1110 and 840 cm^{-1}. H-n.m.r. (CCl_4, 60 MHz), δ ppm: 4.5-3.4(m, 4H, H-3,4,5a and 5b), 3.64(s, 3H, MeO_2C), 3.37(s, 3H, MeO), 2.8-2(m, 2H, H-2a and 2b), 1.34 and 1.27(2s, 2x3H, Me_2C). Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.05; H, 8.31. Found: C, 54.85; H, 8.35%.

2-Deoxy-3-*O*-methyl-D-*erythro*-pentono-1,4-lactone (8a) and 2-deoxy-3-*O*-methyl-D-*threo*-pentono-1,4-lactone (8b).- Method A: The distilled mixture of 7a and 7b (1g, 4.5mmol), was refluxed with aqueous 20% acetic acid for 45 min. Solvent was eliminated under vacuo giving a syrup whose H-n.m.r. spectra corresponded to a mixture of 8a and 8b (590 mg, 88%). Purification by column chromatography (Hexane-AcOEt, 10:1, gradient elution to 1:1) gave three fractions: 119 mg of 8a, 104 mg of 8a and 8b, and 95 mg of 8b. Method B: 5 g of 7(a,b) were treated as above, but the resultant syrup was distilled (175°C/0.2mm Hg), to give 8(a,b) (2.04 g, 60.3%). The distillate was dissolved in ether and left overnight at 0°C, crystallizing 8b (987.5 mg, after recrystallization). The ether solution was concentrated to give 8a (687.5 mg after redistillation). 8a had: Rf 0.21 (Hexane-AcOEt, 1:1); $|\alpha|_D^{20}$ -3.2°(c 1, EtOH), $|\alpha|_D^{30}$ +5°(c 0.88, MeOH). UV, λ max (EtOH): 230 nm. IR, νmax (film): 3470, 2950, 2840, 1785, 1465, 1370, 1190, 1100 and 1025 cm^{-1}. H-n.m.r. ($CDCl_3$, 200 MHz), δ ppm: 4.52(ddd, J 3, 3 and 2.3 Hz, H-4), 4.12(m, J 6.8, 2.7 and 2.3 Hz, H-3), 3.98(dd, J 12 and 3 Hz, H-5a), 3.74 (dd, J 12 and 3 Hz, H-5b), 3.37(s, 3H, MeO), 2.92(dd, J 18 and 6.8 Hz, H-2a), 2.54(dd, J 18 and 2.7 Hz, H-2b). Anal. Calc. for $C_6H_{10}O_4$: C, 49.81; H, 6.84. Found: C, 49.61; H, 7.19% 8b had p.f.: 98-100°C. Rf 0.14. $|\alpha|_D^{20}$ -2.1°(c 1, MeOH); +15(c 1, water). UV, λmax(EtOH): 237 nm. IR, ν max (KBr): 3280, 2960, 2940, 2840, 1780, 1460, 1370, 1170, 1100, 1070 and 1020 cm^{-1}. H-n.m.r. ($CDCl_3$, 200 MHz), δppm: 4.62(ddd, J 5, 4.9 and 4.9 Hz, H-4), 4.27(ddd, J 5.9, 4.9 and 4 Hz, H-3), 4.01(dd, J 13 and 5 Hz, H-5b), 3.92(dd, J 13 and 5 Hz, H-5a), 3.37 (s, 3H, MeO), 2.73(d, J 5.9 Hz, H-2a), 2.72(d, J 4 Hz, H-2b). Anal. Calc. for $C_6H_{10}O_4$: C, 49.81; H, 6.84. Found: C, 49.72; H, 6.93%.

Methyl 2-deoxy-4,5:7,8-di-*O*-isopropylidene-3-*O*-methyl-D-*glycero*-D-*gulo*- and -D-*glycero*-D-*ido*-octanonates (11a and 11b).- 632 mg (2 mmol) of methyl *trans*-2,3-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*gluco*-oct-2-enonate (10)[5], were treated with MeONa/MeOH 0.1M (5 mL). G.l.c. analysis showed the immediate apparition of two new products with RT: 15.8 (major product) and 17.5 min (200°C, column Teknokroma 2515 F, 10% Carbowax-Chromosorb WAW). After 8 h at 36°C, the mixture was eluted with ether (20 mL), washed with $KHSO_4$ 0.1M and with water. The ethereal solution was dried over Na_2SO_4 and concentrated under vacuo. The crude product (0.545 mg) was purified by chromatography over 75 mg of silica gel (Hexane-AcOEt, 1:1; Rf: 0.2 and 0.18), to yield the starting material (80 mg) and two fractions of a mixture of 11a and 11b: 260 mg (2:1, G.l.c. analysis) and 150 mg (67.5%, total yield over 10 consumed). Data for the two isomers: IR, ν max (film): 3500, 2950, 2930, 1750, 1465, 1450, 1385 and 1375 cm^{-1}. H-n.m.r. ($CDCl_3$, 200 MHz), δ ppm: 11a, 3.76(ddd, H-3), 3.40(s, 3H, MeO), 2.66(dd, J 15.5 and 4.5 Hz, H-2a), 2.54(dd, J 15.5 and 7.2 Hz, H-2b); 11b 3.86(m, H-3), 3.37(s, 3H, MeO), 2.58(m, H-2a and 2b); 3.67(s, 6H, two isomers, MeO_2C), 1.37 and 1.32(2s, two isomers, Me_2C). MS, m/e: 333(M^+-Me), 301(M^+-Me-MeOH), 243(M^+-Me-MeOH-Me_2CO), 185(M^+-Me-MeOH-2Me_2CO). Anal. Calc. for $C_{16}H_{28}O_7$: C, 55.16; H, 8.09. Found: C, 55.01; H, 8.06%.

Determination of the absolute configuration on the C-3 of methyl 2-deoxy-3-*O*-methyl-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*gulo*- and -D-*glycero*-D-*ido*-octanonates (11a and 11b).- 60 mg of the fraction (11a:11b, 2:1), obtained above, were heated with trifluoroacetic acid and HIO_4 (102 mg) in water (1 mL) for 1 h (steam bath). After cooling, the oxidation product was extracted with ether, concentrated and treated with Ag_2O/NaOH. After filtering the solution was neutralized and extracted with ether. The combined extracts were concentrated and the resultant mixture of acids showed negative rotation in water and in acetone. In agreement with the bibliography[7], the predominant isomer of the starting mixture, had the D-*glycero*-D-*gulo* configuration (11a).

2-deoxy-3-*O*-methyl-D-*glycero*-D-*gulo*- and -D-*glycero*-D-*ido*-octono-1,4-lactones (12a and 12b).- 1.5 g of the mixture 11(a,b), were refluxed with 12 mL of aqueous 20% acetic acid for 45 min. After removing solvent, the residue was washed with water and repeatedly evaporated to eliminate traces of acid. Chromatography over 100 g of Silica Gel (gradient elution: AcOEt, AcOEt-EtOH 1:1) gave: 125 mg of 12a, 677 mg of a mixture of 12a and 12b, and 40 mg of 12b, (82.64% for 12a + 12b). The second product 12b crystallized (214 mg) from the mixture dissolved in EtOH. 12a had: m.p. 168-169°C (from ethanol). $|\alpha|_D^{20}$ +0.3(c 1, water) IR, ν max (film): 3400, 3320, 3260, 2970, 1760, 1380, 1260, 1190, 1130, 1100, 1080, 1060, 1030, 885, 795 and 700 cm^{-1}. H-n.m.r. (D_2O, 200 MHz, TFA), δ ppm: 4.76(dd, J 5.25 and 2.5 Hz, H-4), 4.26(ddd, J 7, 2.8 and 2.5 Hz, H-3), 4.03(dd, J 5.25 and 2.6 Hz, H-5), 3.9-3.6(m, H-6,7,8a and 8b), 3.39(s, 3H, MeO), 3.07(dd, J 18.7 and 7.7 Hz, H-2a), 2.68(dd, J 18.7 and 2.8 Hz, H-2b). Anal. Calc. for $C_9H_{16}O_7$: C, 45.76; H, 6.82. Found: C, 45.47; H, 6.73%. 12b had: m.p. 193-195°C (from EtOH). $|\alpha|_D^{20}$ 0(c 1, water). IR, ν max (KBr): 3420, 3360, 3310, 2960, 2900, 1775, 1400, 1370, 1215, 1185, 1155, 1130, 1085, 1053, 1035, 998, 910, 790 and 765

cm^{-1}. H-n.m.r. (D_2O, 200 MHz, TFA), δ ppm: 4.77(dd, J 8.7 and 3.8 Hz, H-4), 4.32(ddd, J 3.8 and 1.6 Hz, H-3), 4.28(dd, 8.7 and 1.7 Hz, H-5), 3.66(dd, J 9.25 and 1.7 Hz, H-6), 3.92-3.6 (m, H-7,8a and 8b), 3.35(s, 3H, MeO), 2.99-2.85(m, 2H, H-2a,2b). Anal. Calc. for $C_9H_{16}O_7$: C, 45.76; H, 6.82. Found: C, 45.44; H, 6.78%.

2-Deoxy-3-*O*-methyl-D-*erythro*-pentono-1,4-lactone (8a) and 2-deoxy-3-*O*-methyl-D-*threo*-pentono-1,4-lactone (8b), from 12(a,b).- 816 mg (3.45 mmol) of the mixture of lactones 12(a,b), obtained above, were treated with $NaIO_4$ (2.5 g, 11.68 mmol) in water (6 mL), for 15 min and stirred continuously. Then, 50 mL of ethanol were added. After cooling, the iodates were filtered and the remaining solution concentrated at low temp. More ethanol was added to precipitate the rest of the iodates, and the solution was filtered and concentrated at low temp. The aldehydes obtained (400 mg, 71.6%), were dissolved in water (2 mL), and a solution of 51.4 mg of $NaBH_4$ in water (14 mL), was added carefully (temp below 15ºC). After 2.5 h, the mixture was concentrated at low temp, the residue was extracted with acetone, filtered, concentrated and extracted with warm ether, filtered again, and concentrated to give a syrup (611 mg, 85%). Its H-n.m.r. spectra showed all the signals corresponding to the compounds 8a and 8b. Separation of 8a and 8b was made as described in the obtainment from 7 (Method A).

Methyl 2-deoxy-4,5:6,7-di-*O*-isopropylidene-3-*O*-methyl-D-*gluco*- and -D-*manno*-heptonates (15a and 15b).- Methyl *trans*-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-D-*arabino*-hept-2-enonate (14) [5,10] (8.35 g, 29.16 mmol), were treated with MeONa/MeOH 0.1M (45 mL). After 68 h of stirring at room temperature, the mixture was dissolved in ether (190 mL) and neutralized with $KHSO_4$ 0.1M (60 mL). The aqueous layer was separated and washed with ether (3x15 mL). The combined ether extracts were washed with water (40 mL), dried (Na_2SO_4 anh) and evaporated. The residue was distilled under vacuum to give a mixture 13(a,b), (7.2 g, 78%), 110ºC/0.5mm Hg). Data for the two epimers: IR, ν max: 3020, 2960, 1755, 1465, 1445, 1380, 1000, 920, 890 and 850 cm^{-1}. H-n.m.r. (CCl_4, 60 MHz), δ ppm: 4.5-3.4(m, 6H), 3.56(s, CO_2Me), 3.3(2s, 2x3H, two isomers, MeO), 2.9-2(m, H-2a,2b), 1.35-1.25(m, Me_2C). MS, m/e: 319(M^++1), 303(M^+-15), 287(M^+-MeO), 286(M^+-MeOH).

2-Deoxy-3-*O*-methyl-D-mannono- and -D-glucono-1,4-lactone (16a and 16b).- A solution of the above mixture 15(a,b), (7 g, 20 mmol) in aqueous 50% acetic acid was refluxed for 50 min. Solvent is eliminated under vacuo and the residue was washed with water and evaporated several times, then finally, evaporated to dryness. The resulting syrup (3.69 g) was dissolved in EtOH, adding ether to precipitate (by cooling) 40 mg of a mixture of no-investigated products. The purified solution was evaporated (3.63 g, 88%) and subjected to separation by column chromatography (EtOH-AcOEt, 1:10), which yielded 78 mg of 16a, 523 mg of 16a contaminated by 16b, 2.76 g of a mixture 16(a,b), and 114 mg of 16b. 16a had Rf 0.67 (EtOH-AcOEt, 1:3), $[\alpha]_D^{20}$ -21.8º(c 0.92, MeOH); UV, λmax(MeOH): 225 nm; IR, ν(film): 3350, 2950, 2820, 1775, 1665, 1405, 1370 and 1190 cm^{-1}. H-n.m.r. (D_2O-TFA, 200 MHz), δppm: 4.92(t, J 1.6 Hz, H-4), 4.29(dt, J 6.9, 2 and 1.6 Hz, H-3), 3.85-3.59(m, 4H, H-5,6,7a and 7b), 3.03(dd, J 18.8 and 6.9 Hz, H-2a), 2.65(dd, J 18.8 and 2 Hz, H-2b). Anal. Calc. for $C_8H_{14}O_6$: C, 46.64; H, 6.85. Found: C, 46.55; H, 6.93%. 16b had: Rf 0.60; UV, λmax(MeOH): 224 nm; IR, ν(film): 3400, 2940, 2820, 2450, 1770, 1680, 1370 and 1190 cm^{-1}. H-n.m.r. (D_2O-TFA, 200 MHz), δppm: 4.82(dd, J 6 and 4 Hz, H-4), 4.50(ddd, J 7.6 and 4 Hz, H-3), 3.92(dd, J 7 and 4 Hz, H-5), 3.75-3.5(m, 3H, H-6,7a and 7b), 2.83(dd, J 18 and 7 Hz, H-2b), 2.67(dd, J 18 and 4 Hz, H-2a).

2-Deoxy-3-*O*-methyl-L-*erythro* - (17a) and -L-*threo*-pentono-1,4-lactone (17b).- 2.48 g (12 mmol) of the above resultant mixture 16(a,b), was treated with $NaIO_4$ (5.55 g, 26 mmol) in water (18 mL) for 15 min. The solution was dissolved in ethanol (100 mL), cooled, filtered and evaporated at low temp. the residue was treated with more ethanol and working as above gave 17(c,d), (798 mg, 41%). H-n.m.r. (D_2O, 60 MHz), δppm: 5.10(d, H-5), 4.45(d, H-4), 4.2(d), 2.98(dd, J 18 and 6 Hz), 2.56(dd, J 18 and 3 Hz). A solution of $NaBH_4$ (50 mg) in 25 mg of water was added drop by drop, to the mixture of aldehydes dissolved in 4 mL of water (temp below 20ºC). After 2 h, the solution was concentrated at low temp. The working up as was described for the D-isomers gave a mixture whose H-n.m.r. spectra corresponded to 17(a,b), (625 mg, 87%). Chromatography by column (CH_2Cl_2-Et_2O, 10:1) yielded 17a (550 mg) and a mixture of 17a and 17b (40 mg). 17b could not be isolated analytically pure because of its low proportion. 17a had: $[\alpha]_D^{20}$ +3.8(c 0.9, EtOH), -4.8(c 1.15, MeOH); UV, λmax(MeOH): 228 nm. IR, ν(film): 3400, 2940, 1775, 1380 and 1190 cm^{-1}. H-n.m.r. ($CDCl_3$, 200 MHz), δppm: 4.52(ddd, J 3, 3 and 2.5 Hz, H-4), 4.12(dt, J 7, 2.5 and 2.5 Hz, H-3), 3.9 (dd, J 13 and 3 Hz, H-5a), 3.73(dd, J 13 and 3 Hz, H-5b), 3.34(s, 3H, MeO), 2.89(dd, J 18 and 2.5 Hz, H-2b), 2.53(dd, J 18 and 7 Hz, H-2a). Anal. Calc. for $C_6H_{10}O_4$: C, 49.31; H, 6.89. Found: C, 49.45; H, 7.20%.

Methyl 2-deoxy-4,5-*O*-isopropylidene-3-*O*-methyl-D-*gluco*- and -D-*manno*-heptonates (20a and 20b), and lactonization to 16.- 316 mg (1.28 mmol) of 19 [5], were treated with MeONa /MeOH 0.1M (5 mL). After 36 h of stirring at room temp. the mixture was dissolved in ether (20 mL). The working up as described for 15(a,b) gave a syrup 20(a,b), (218 mg, 0.78

mmol, 61%). H-n.m.r. ($CDCl_3$, 200 MHz), δ ppm: 3.64(s, 2x3H, two isomers, MeO_2C), 3.42(s, 3H, MeO), 3.38(s, 3H, major product, MeO), 2.6(m, 2x2H, H-2a,2b), 1.3(s, 2x6H, two isomers, Me_2C). The syrupy product was dissolved into aqueous 40% acetic acid and refluxed for 40 min. The 1,4-lactones (130 mg, 81%), obtained after usual work up, were identical to 16(a,b).

REFERENCES

1. F. J. López Aparicio and F. J. López Herrera, *An. Quim.*, Ser. C, **78**, 137 (1982).
2. H. O. L. Fisher and E. Baer, *Helv. Chim. Acta*, **17**, 622 (1934).
3. J. Mulzer, M. Kappert, G. Huttner, and I. Jibril, *Angew. Chem. Int.* Ed. Engl. **23**, 704 (1984).
4. J. Font, R. M. Ortuño, O. Ponsati, and F. Sanchez-Ferrando, *Nouv. J. Chim.*, **6**, 305 (1982).
5. F. Jorge López Herrera and M. Soledad Pino González, *Carbohydr. Res.*, **152**, 000 (1986).
6. P. M. Collins, W. G. Overend, and T. S. Shing, *J. Chem. Soc., Chem. Commun.*, 297 (1982).
7. a) T. Purdie and H. W. Bolam, *J. Chem. Soc.*, **67**, 957 (1895).
   b) T. Purdie and S. Williamson, *Ibid.*, **67**, 944 (1895).
   c) G. Fodor and F. Soti, *CA*, **61**, 10725d, (1964).
8. L. F. Wiggins, *J. Chem. Soc.*, 13 (1946).
9. a) P. A. Levene and E. T. Stiller, *J. Biol. Chem.*, **102**, 187 (1933).
   b) N. A. Hughes and P. R. H. Speakman, *Carbohydr. Res.*, **5**, 171 (1965).
10. D. Horton, T. Machinami, and Y. Takagi, *Carbohydr. Res.*, **121**, 135 (1983).