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TOTAL SYNTHESIS OF 3-DEOXY AND 3,6-DIDEOXY-DL-HEXOSES

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Abstract—Synthesis of stereoisomeric 3-deoxy-hexoses **24–27** and 3,6-dideoxy-hexoses **28–31** is reported. Butyl (*E*)-2,6-dihydroxy-hex-4-enoate (**2**) was used as the starting material for the synthesis of 3-deoxy-hexoses. For the synthesis of 3,6-dideoxy-hexoses, butyl (*E*)-2-acetoxy-hex-4-enoate (**7**) was employed. The synthesis involved the following successive steps: *cis* or *trans* hydroxylation of the double bond in **2** or **7**, lactonisation of the resulting aldonic acid esters followed by acetylation and chromatographical separation of γ-lactones, reduction of lactones **16–23** to lactols with disiamylborane, and acetylation of lactols to free sugars. All compounds were obtained as pure diastereomers in racemic form.

Recently a new method for synthesis of 2-deoxy-pentoses[1] and 2,6-dideoxy-hexoses[2] was developed. In this approach butyl (*E*)-2-hydroxy-6-oxo-hex-4-enoate (**1**),[3] employed as substrate is converted by: (i) reduction of the aldehyde group, (ii) *cis* or *trans* hydroxylation of the double bond and (iii) Ruff degradation of the α-hydroxy-acid grouping into deoxy-sugar (Scheme 1).[a] Thus the original C atom C-2 of the substrate became C-1 of the final sugar molecule. It is apparent, however, that substrate **1** offers also an easy access to 3-deoxy and 3,6-dideoxy-hexoses. It is necessary to convert the terminal aldehyde group to the CH_2OH or CH_3 group, functionalise of the double bond as above (according to Scheme 1), and to reduce the butoxycarbonyl group into aldehyde, thus leaving this atom as the anomeric C atom of the sugar molecule.

The aim of the present work is the demonstrating that this concept can be, in fact, applied for the synthesis of 3-deoxy-hexoses and 3,6-dideoxy-hexoses. This work is a logical supplement to the investigations shown in Scheme 1.

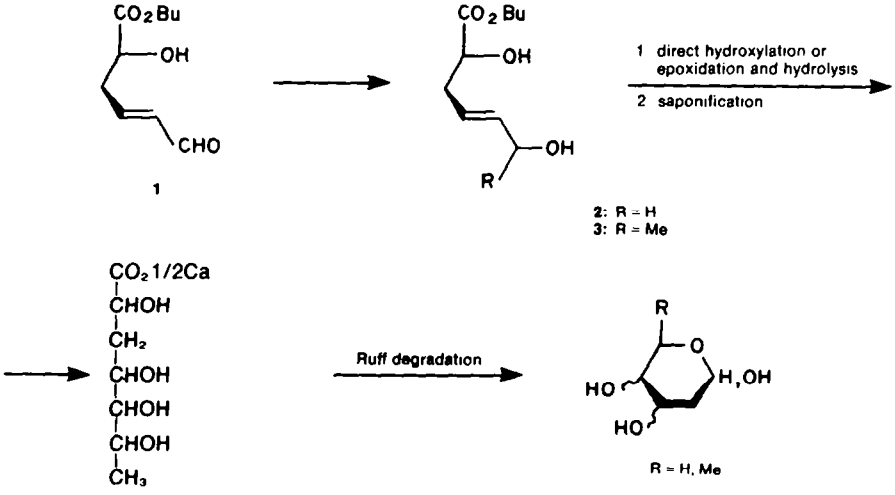
[a]All the compounds in this paper were racemic but for convenience, D-structure are depicted in the formulae.

3-Deoxy-hexoses do not occur in Nature.[4] Some 3,6-dideoxy-hexoses have been found at the nonreducing ends of numerous lypopolisaccharides. They constitute the immunodominant groups of their respective antigenic determinants.[5] In recent years there is an increased interest in the synthesis of this class of dideoxy-sugars.[6–18]

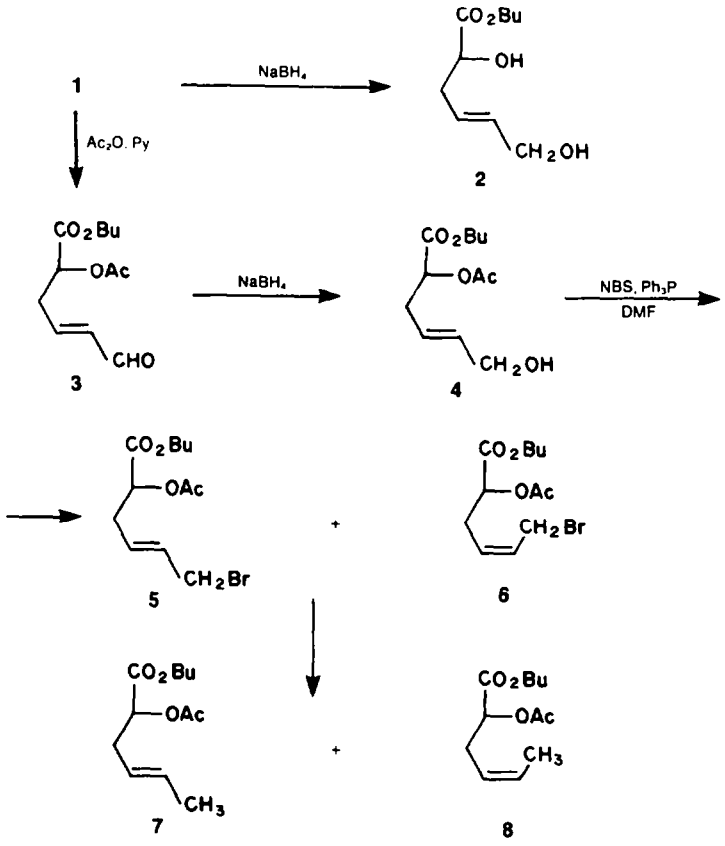
RESULTS

Syntheses leading to 3-deoxy-hexoses and 3,6-dideoxy-hexoses were based essentially on reactions showed in Scheme 3.

Diol **2**, obtained by $NaBH_4$ reduction of the aldehyde group in **1** was used as the starting material for the synthesis of 3-deoxy-hexoses. For the synthesis of 3,6-dideoxy-hexoses butyl (*E*)-2-acetoxy-hex-4-enoate (**7**) was employed. It could be expected that **7** would be obtained from **1** (Scheme 2) with retention of the *E*-configuration of the double bond. However, treatment of **4** with triphenylphosphine and N-bromosuccinimide in DMF (the third step of the transformation **1** into **7**) furnished the bromo compound as a mixture of *Z*- and *E*-isomers (**5** and **6**). According to ^{13}C NMR spectrum **5**, the prevailing component, was contaminated with *ca* 20% of *Z*-isomer **6**. Compounds **5** and **6** could not be



Scheme 1.



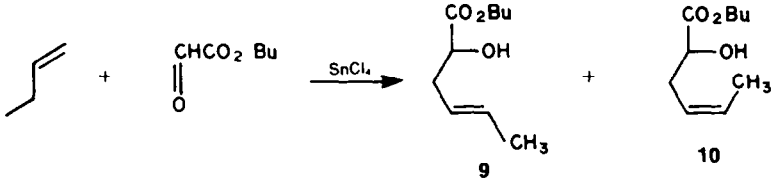
Scheme 2.

separated by chromatography, therefore a mixture of both was used as substrate in further steps. Purification of compounds derived from **5** was achieved at a later step of the synthesis (see separation of lactones **20–23**). Reductive removal of the Br atom from compounds **5** and **6** was achieved with sodium cyanoborohydride in HMPA.

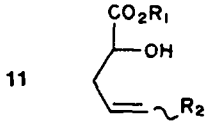
Olefin **7** in non-acetylated form can be, obtained by another, simpler route consisting in an ene reaction between alkyl glyoxylate and but-1-ene.[b,19,20]

Butyl glyoxylate reacts with but-1-ene in the presence of tin tetrachloride furnishing **9** and **10** in 80% total yield. The mixture contains *E* and *Z* isomers in a ratio of about 8.6:1.4. It is obvious that the synthesis of **7** via ene reaction offers advantages over the one depicted in Scheme 2.

The sequence of the reaction leading to 3-deoxy-hexoses and 3,6-dideoxy-hexoses is presented in Scheme 3. Hydroxylation of the double bond in **2** and **7** can be achieved by direct *cis*-hydroxylation, or by epoxidation



[b] Achmatowicz *et al.*[19,20] have found that alkyl glyoxylates in the presence of 1 equiv of stannic chloride at room temp react with a number of olefins to afford in 80–90% yield ene-adducts **11**. The ratio of *trans* and *cis* isomers of **11** was found to vary from 6:4 to 9:1 (vpc).

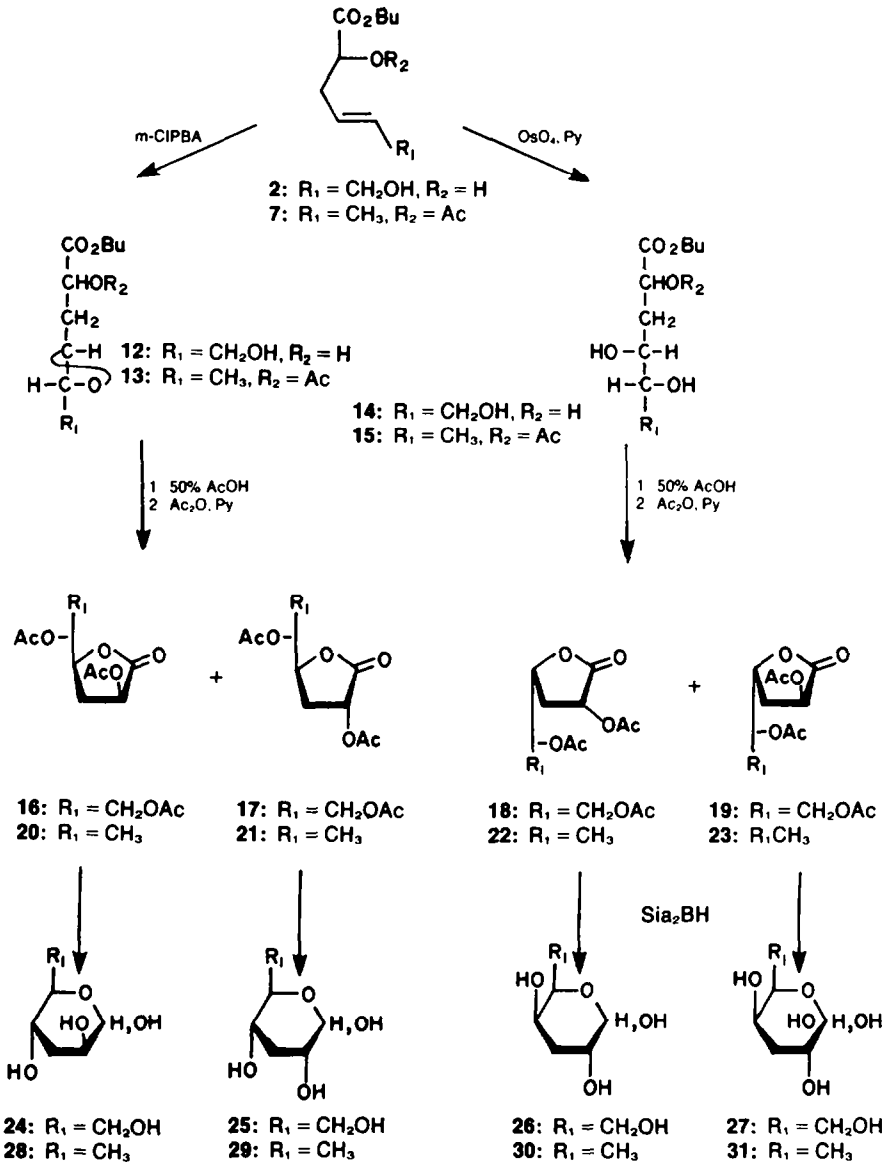


11

R_1 = Bu, Mentyl
R_2 = alkyl

and hydrolytic opening of the oxirane ring. *E* configuration of the double bond in substrates **2** and **7** predetermines the results of *cis*-hydroxylation: threo diol must be obtained. From epoxidation and hydrolysis of the epoxide under acidic conditions erythro diol will result. It was expected therefore that ribo and arabino 3-deoxy- or 3,6-dideoxy-hexoses would be obtained via epoxidation and subsequent hydrolysis, whereas lyxo and xylo-stereoisomers would be produced via direct *cis* hydroxylation of **2** or **7**.

Epoxidation of the double bond in **2** or **7** with *m*-chloroperbenzoic acid afforded mixtures containing two stereoisomeric epoxides in each case, **12** and **13**, respec-



Scheme 3.

tively. Mixtures **12** and **13** were not separated into pure compounds. The ratios of components were determined from their ^{13}NMR spectra. (Table 1).[2]

Opening of the oxirane ring in **12** and **13** and lactonisation of the resulting aldonic acids on treatment with aqueous acetic acid, followed by acetylation, yielded mixtures of acetates of arabino **16**, **20** and ribo **17**, **21** configuration in total about 80% yield. The mixtures **16**, **17** and **20**, **21** were separated into pure components using flash chromatography.[2] The less polar (tlc) products **16** and **20** were assigned the arabino configuration. The proof of the structure of lactones **16**, **17**, **20** and **21** is based on ^{1}H NMR (Table 2), ^{13}C NMR (Table 3), IR and MS data, and will be analysed below (Discussion).

Direct *cis* hydroxylation of the double bond in **3** and **7** with osmium tetroxide in pyridine followed by lactonisation and acetylation led to mixtures of two isomeric γ-lactones of xylo **18**, **19** and lyxo **22**, **23** configuration respectively. The mixtures were separated into pure components. The γ-lactone structure of compounds **18**, **19**, **22** and **23** was deduced from IR and MS data (Discussion). To less polar (tlc) products **18**, **22** xylo configuration was ascribed on the basis of ^{1}H NMR (Table 2), ^{13}C NMR (Table 3).

Lactones **16–23** were reduced to lactols with disiamyl borane according to typical procedure.[22,23] Lactols were deacetylated with triethylamine in methanol–water solution to give corresponding 3-deoxy (**24–27**) and 3,6-dideoxyhexoses (**28–31**). Compounds **28** and **30** were compared with original sample of 3,6-dideoxy-DL-arabinohexose (ascarylose)[9] and 3,6-dideoxy-DL-xylohexose (abequose)[9] by means of tlc and were found to exhibit identical R_f values: Sugars **28–30** display different R_f values (tlc chloroform–methanol 8.5:1.5). Proof of identity of the synthetic material and sample could not be based on comparison of IR spectra, because these spectra of all sugars **28–31** taken as films are very similar.

DISCUSSION

The NMR spectra of 3-deoxy (**24–27**) and 3,6-dideoxyhexoses (**28–31**) could not be used for assignment

Table 1. ^{13}C NMR spectral data for compounds **2**, **4–10**, **13** in $CDCl_3$. In brackets relative intensities are given. Resonance of AcO and Bu occurred in the spectra given below at 20.5 ± 1.5, 169.5 ± 0.5 and 13.6, 19.1, 30.6, 65.6 ± 0.5 ppm respectively

	C - 1	C - 2	C - 3	C - 4	C - 5	C - 6
2	174.35	70.35	37.25	126.04	133.41	62.71
4	170.49 *	72.00	34.05	125.17	133.48	62.84
5	170.26 *	71.41	33.83	129.01	130.46	31.92
6	—— * *	71.18	28.76	128.76	129.10	33.64
7	170.31*	72.35	34.51	124.71	129.20	17.89
8	—— **	72.15	28.86	123.72	127.71	—— **
9	174.69	70.66	37.82	125.46	128.92	17.96
10	174.78	70.51	32.07	124.50	127.16	18.34
13	170.06 *	70.02 (56) 70.10 (38)	34.06	55.37 (38) 55.44*(29)	54.84*(30) 54.19*(25)	17.39

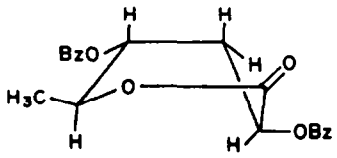
* Assignments uncertain

** Not visible

of their configuration, due to the fact that these sugars exist as mixtures of pyranose and furanose forms. The proof their configuration had to be based on assignments made for lactones **16–23**. Therefore it was necessary to determine precisely the constitution (γ- or δ-lactones) and configuration of these compounds.

Unequivocal proof of the γ-lactone structure of all components **16–27** could be obtained from their IR spectra (1797–1800 cm^{-1} C=O absorption of 5-membered ring lactone) and MS data.[c]

[c]Recently Varela *et al.*[17] have reported on the synthesis of 3,6-dideoxy-L-arabino-hexose (ascarylose) starting from L-rhamnono-1,5-lactone. Benzoylation and elimination of the benzoyloxy group to the lactone CO group followed by catalytic hydrogenation gave 3,6-dideoxylactone to which the δ-lactone structure and arabino configuration was assigned. The ^1H NMR spectrum of this lactone showed $J_{2,3}$ and $J_{2,3'}$ values of ~9 Hz. On the basis of this data authors have assigned the distorted-boat conformation for this compound. $J_{2,3}$ and $J_{2,3'}$ values observed by the authors are close to that found in this paper for 5-membered ring lactones. For this reason we think that the lactone obtained by Varela *et al.*[17] has rather a 5-membered ring structure.



The mass spectra of lactones **16–23** contained M + 1 ions.

The most readily occuring fragmentation involves the cleavage of C-4–C-5 bond. Thus, mass spectra of all compounds displayed peak *m/e* 143 attributable to cation **I**. **I** splits off a molecule of acetic acid to form **II**. The spectra did not show any signal which could be attributed to the ion **III** (*m/e* 215) indicative of δ-lactones structure.

Deduction of the configuration of lactones **16–23** was based on the interpretation of their ^1H and ^{13}C NMR spectra.

Coupling constants between ring protons in ^1H NMR spectra of lactones **16–23** allowed to divide the data into two groups. Less-polar (in tlc) lactones **16**, **18**, **20** and **22** showed coupling constants: $J_{2,3} = 9.0$, $J_{2,3'} = 7.5–8.0$, $J_{3',4} = 3.2–4.5$ and $J_{3,4} = 7.3–9.3$ Hz, whereas their more polar partners **17**, **19**, **21** and **23** showed $J_{2,3} = 8.5–8.7$, $J_{2,3'} = 10.1–10.5$, $J_{3',4} = 5.7–6.0$ and $J_{3,4} = 9.4–9.8$ Hz. These similarities pointed at stereochemical analogy between both groups; they demonstrated the relative *cis* or *trans* configuration of substituents at C-2 and C-4. The configuration at C-5 of the side chain did not influence significantly the magnitude of coupling constants of the ring protons. Large, and similar in value, coupling constants $J_{2,3}$ and $J_{2,3'}$ for all lactones testify that C-2 and C-3 C atoms are positioned on the flat part of the ring. Only such an arrangement causes that $J_{2,3}$ and $J_{2,3'}$ do not depend significantly on configuration at C-2. For

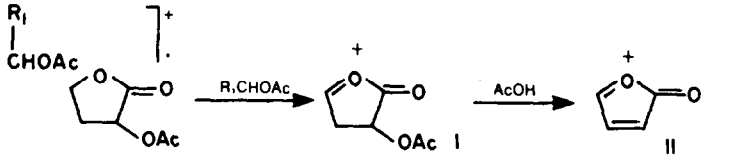
Table 2. ^{1}H NMR chemical shifts and coupling constants of lactones **16–23** in $CDCl_3$

-	H - 2	H - 3	H - 3'	H - 4	H - 5	H - 6	H - 6	$J_{2,3}$	$J_{2,3'}$	$J_{3,3'}$	$J_{3,4}$	$J_{3,4'}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
16	5.39	2.72	2.40	4.82	5.21	4.27	4.18	9.0	7.5	13.5	3.7	8.1	4.3	4.2	5.2	12.0
17	5.47	2.76	~3.3	4.66	5.26	4.40	4.18	8.3	10.1	12.5	6.0	9.7	5.1	3.3	5.3	12.0
18	5.35	2.2 —	2.7	4.85	5.17	4.32	4,16	9.0	8.0	— *	4.5	7.6	3.0	5.0	6.5	11.5
19	5.48	2.76	—*	4.70	5.26	4.35	4.17	8.7	10.3	12.5	5.7	9.5	4.0	4.3	6.4	12.0
20	5.42	2.70	2.37	4.62	5.09	1.31		9.0	7.7	13.0	3.2	9.3	3.2	6.5		
21	5.48	2.76	—*	4.48	5.13	1.31		8.6	10.2	12.8	6.0	9.4	4.2	6.3		
22	5.38	—*	—*	4.66	4.97	1.35		9.0	8.0	—*	3.9	7.3	3.2	6.3		
23	5.30	2.72	—*	4.51	4.99	1.33		8.7	10.5	12.0	6.0	9.8	5.0	6.3		

*The signal is overlapped with that of acetyl group.

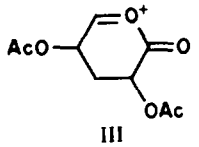
Table 3. ^{13}C NMR chemical shifts of lactones **16–23** in $CDCl_3$

	C - 1	C - 2	C - 3	C - 4	C - 5	C - 6
16	171.90	71.22	29.68	75.62	67.46	61.55
17	171.49	70.71	30.39	74.40	68.00	61.60
18	171.97	71.68	30.76	75.50	67.03	61.93
19	171.23	70.69	30.47	74.46	67.76	61.93
20	172.19	70.53	29.09	78.50	67.61	15.46
21	171.57	69.54	30.04	77.39	68.12	15.13
22	172.39	71.29	31.19	78.81	67.35	16.03
23	171.65	70.11	30.74	77.52	68.14	15.66



16–19: $R_1 = CH_2OAc$, M + 1 *m/e* 289
20–23: $R_1 = CH_3$, M + 1 *m/e* 231

I *m/e* 143 II *m/e* 83

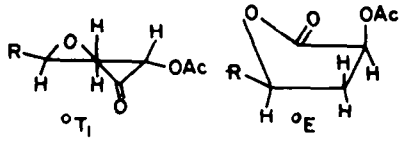


III
m/e 215

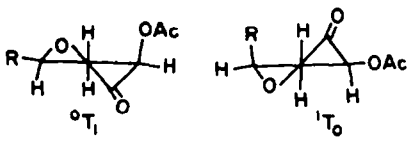
more polar compounds **17**, **19**, **21** and **23** all vicinal coupling constants between ring protons (Table 2) are large; it means that the respective dihedral angles should be close to 20° or 140°. Such an array is possible for lactones having *trans* substituents at C-2 and C-4 in $^0T_1$ conformation. Accordingly, ribo configuration was assigned to **17** and **21** and lyxo configuration to **19** and **23**.

In the spectra of less polar lactones **16**, **18**, **20** and **22** the sum of coupling constants $J_{2,3} + J_{2,3'}$ and $J_{3,4} + J_{3',4}$ is smaller than that of their more polar partners (**17**, **19**, **21** and **23**). *cis* Configuration of ring substituents causes that the energy minimum along the pseudorotational cycle corresponds probably to ^0E, $^0T_1$ and $^1T_0$ conformations. On this basis compounds **16**, **20**, were assigned the arabino configuration and **18** and **22** the xylo configuration.

Additional proof for the structure of lactones **16–23** was provided by the ^{13}C NMR spectra (Table 3). Differentiation between signals of C-2, C-4 and C-5 C atoms was based on relations already known, the assumption that opposite configurations at C-2 does not change significantly the chemical shift of C-5 and *vice versa*,[2,24] and that in 6-deoxy compounds C-4 signal is shifted downfield (*ca* 4 ppm). Lactones **17**, **10**, **21** and **23**



17, 19, 21, 23



16, 18, 20, 22

having substituents *trans* positioned reveal an upfield shift at C-2 and C-4 in comparison with the respective signals of their *cis* partners. The observed shift is caused by the *cis* 1,3-effect of substituent of C-2 and C-4 with H atom at C-4 and C-2 respectively and is in agreement with the well known phenomenon.[25]

CONCLUSION

The synthesis of stereoisomeric 3-deoxy-DL-hexoses (**24–27**) and 3,6-dideoxy-DL-hexoses (**28–31**) presented in this paper offers preparative simplicity and usually moderate to good yields of individual steps. It is of particular importance that the final product was prepared from **2** and **7** in three steps only. It should be underlined that the resolution of **1**, the starting material in the presented synthesis, into diastereoisomeric esters with ω-camphanic acid has been recently realised and will be reported elsewhere.[26] A simple method of obtaining enantiomeric **2** opens the possibility for the preparation of optically pure sugars of both D and L configurational series.

EXPERIMENTAL

^{1}H NMR spectra were recorded for solns in $CDCl_3$ a Jeol JNM-4H-100 spectrometer (δ scale, TMS = 0 ppm) and ^{13}C NMR spectra with Varian CFT-20 instrument for solns in $CDCl_3$ with TMS as the internal standard. IR spectra were recorded on a Unicam SP-200 spectrophotometer. Mass spectra were recorded with a LKB GCMS 2091 mass spectrometer. Tlc was performed with silica gel Merck, and column chromatography with MN-Kieselgel (100–200 mesh, Machery Nagel & Co.). Flash chromatography was carried out according to Ref. 21 with silica gel Merck (230–400 mesh).

B.ps are uncorrected. B.ps denoted with asterisk refer to air-bath temperature.

Compound **1** was prepared according to Ref. 3. Butyl (*E*)-2,6-dihydroxy-hex-4-enoate (**2**) was obtained from **1** by the known procedure.[1] Compound **12** was performed according to Ref. 1.

Butyl (E)-*2-acetoxy-6-oxo-hex-4-enoate* (**3**). 20.0 g (0.1 mol) of **1** was cooled to 0° and treated with Ac_2O (30 ml) and pyridine (20 ml). The mixture was stirred overnight at +5°, then poured into ice-water and extracted with ether. The extract was carefully washed with $NaHCO_3$ and with water, dried and evaporated to dryness. The oily residue was evaporated three times with toluene to remove traces of acetylating reagents and distilled at 119–120°/0.5 mm Hg producing **3** (14.0 g, 58%). IR (film): 1745, 1220 (ester), 1690 (aldehyde), 1640 cm^{-1} (olefin). ^{1}H NMR: 0.8–1.9 (m, 7H, C_3H_7), 2.12 (s, 3H, OAc), 2.88 (m, 2H, H-3,3'), 4.15 (t, 2H, OCH_2), 5.19 (t, 1H, ΣJ = 12.0 Hz, H-2), 6.19 (pd, 1H, $J_{5,6}$ = 7.4, $J_{4,5}$ = 15.5 Hz, H-5), 6.74 (pt, 1H, $J_{3',4} + J_{3,4}$ = 13.2 Hz, H-4), 9.63 (d, 1H, H-1). (Found: C, 59.5; H, 7.7. Calc. for $C_{12}H_{18}O_5$: C, 59.5; H, 7.5%.)

Butyl (E)-*2-acetoxy-6-hydroxy-hex-4-enoate* (**4**). A soln of **3** (10.0 g, 0.041 mol) in THF–water (2:1, 150 ml) was stirred with $NaBH_4$ (2.0 g) for 1 hr at room temp. The mixture was dried and concentrated *in vacuo* to give **4** (6.0 g 59%), b.p. 132–134/0.3 mm Hg. IR (film): 3500 (OH), 1745, 1230 cm^{-1} (ester). ^{1}H NMR: 0.8–1.8 (m, 7H, C_3H_7), 2.13 (s, 3H, OAc), 2.57 (m, 2H, H-3,3'), 4.08 (m, 2H, H-6, 6'), 4.15 (t, 2H, OCH_2), 5.00 (t, 1H, ΣJ = 12.3 Hz, H-2), 5.4–5.9 (m, 2H, $J_{4,5}$ = 15.5 Hz, H-4,5). (Found: C, 58.8; H, 8.2. Calc. for $C_{12}H_{20}O_5$: C, 59.0; H, 8.2%.)

Butyl (E)-*2-acetoxy-6-bromo-hex-4-enoate* (**5**). To a soln of **4** (5.0 g, 0.02 mol) and triphenylphosphine (10.5 g, 0.04 mol) in DMF (30 ml) cooled to +5° N-bromosuccinimide (7.1 g, 0.04 mol) was slowly added. The mixture was stirred for 2 hr, poured into water and extracted with ether. The extracted was dried, evaporated and distilled producing **5** 6.0 g, 95%, b.p. 119–120/0.3 mm Hg. IR (film): 1750, 1230 cm^{-1} (ester). ^{1}H NMR: 0.8–1.9 (m, 7H, C_3H_7), 2.15 (s, 3H, OAc), 2.61 (m, 2H, H-3,3'), 3.7–4.2 (m, 2H, H-6,6'), 4.17 (t, 2H, OCH_2), 5.05 (t, 1H, ΣJ = 12.4 Hz, H-2), 5.5–6, (m, 2H, $J_{4,5}$ = 15.4 Hz, H-4,5). (Found: C, 46.2; H, 6.2. Calc. for $C_{12}H_{19}O_4Br$: C, 46.9; H, 6.2%.)

Compound **5** was contaminated with 20% of *Z*-isomer **6**, according to ^{13}C NMR (Table 1).

Butyl (E)-*2-acetoxy-hex-4-enoate* (**7**). To a soln of **5** (20.0 g, 0.065 mol) in HMPA (50 ml) sodium cyanoborohydride (4.2 g) was added and the mixture was stirred and heated to 70° for 5 hr. Then the mixture was poured into water and extracted with ether. The extract was dried and evaporated to dryness yielding **7** (7.8 g, 53%), b.p. 100°*/0.5 mm Hg. IR (film): 1745, 1230 cm^{-1} (ester). ^{1}H NMR. 0.8–1.9 (m, 7H, C_3H_7), 1.69 (d, 3H, J_{5,CH_3} = 5.3 Hz, CH_3), 2.15 (s, 3H, OAc), 2.53 (m, 2H, H-3,3'), 4.18 (t, 2H, OCH_2), 5.02 (t, 1H, ΣJ = 12.0 Hz, H-2), 5.2–5.8 (m, 2H, H-4, 5). (Found: C, 63.0; H, 8.9. Calcd. for $C_{12}H_{20}O_4$: C, 63.1; H, 8.8%).

Compound **7** was contaminated with 20% of *Z*-isomer **8**, according to ^{13}C NMR (Table).

Butyl (E)-*2-hydroxy-hex-4-enoate* (**9**). To a stirred soln of butyl glyoxylate (6.1 g, 0.047 mol) in CH_2Cl_2 (50 ml) at 0° soln of 12.1 g (0.047 mol) of stannic tetrachloride in 50 ml of CH_2Cl_2 was added and then but-1-ene (5.35 g, 0.095 mol) was passed slowly through the flask. The reaction was stirred for 24 hr at 0°, and then Et_3N (5.0 g) was added to neutralise the soln. The mixture was diluted with 100 ml CH_2Cl_2, washed, dried and concentrated giving **9** (7.0 g, 80%), b.p. 110°*/0.1 mm Hg. IR (film): 3500 (OH), 1745, 1190 cm^{-1} (ester). ^{1}H NMR: 0.8–1.9 (m, 7H, C_3H_7), 1.69 (d, 3H, J_{5,CH_3} = 4.3 Hz, CH_3), 2.2–2.7 (m, 2H, H-3,3'), 3.9–4.4 (m, 3H, H-2, OCH_2), 5.1–5.8 (m, 2H, H-4,5). (Found: C, 64.2; H, 10.0. Calc. for $C_{10}H_{18}O_3$: C, 64.5; H, 9.7%.)

Alcohol **9** was contaminated with 14.0% of *Z*-isomer **10**. Acetylation of **9** afforded **7** contaminated with 14.0% of **8** (according to ^{13}C NMR spectra).

2,5,6-Tri-O-acetyl-3-deoxy-DL-xylo and lyxo-aldonolactone (**18** and **19**). To a soln of **2** (2.0 g, 0.01 mol) in pyridine 20 ml osmium tetroxide 2.8 g was added with cooling. After storage at room temp for 2 hr the mixture was treated with sat $NaHSO_3$aq, stirred for 1 hr and extracted 10 times with EtOAc. The extract was dried and evaporated to dryness. The oily residue was dissolved in 50% aqueous AcOH (10 ml), heated under reflux for 2 hr and then concentrated to dryness under diminished pressure. The residue was acetylated with Ac_2O and pyridine. The solvents were removed under pressure and the crude residue was separated on a silica gel column using $CHCl_3$ as eluent (flash chromatography). Two fractions were obtained: less polar, **18** (1.0 g), b.p. 160°*/0.2 mm Hg; m.p. 102–104°, IR nujol 1800 (γ-lactone), 1740 cm^{-1} (acetates). more polar, **19** (0.6 g), b.p. 160°/0.2 mm Hg; IR (film): 1803 (γ-lactone), 1750 cm^{-1} (acetates). (Found for the mixture **18** and **19**: C, 50.0; H, 5.8. Calc. for $C_{12}H_{16}O_8$: C, 50.0; H, 5.6%.)

2,5,6-Tri-O-acetyl-3-deoxy-DL-arabino and ribo-aldono-lactone (**16** and **17**). A soln of **12** (20 g, 0.009 mol) in 50% aqueous AcOH 10 ml was boiled under reflex for 6 hr and then evaporated to dryness under diminished pressure. The oily residue was acetylated with Ac_2O and pyridine. The solvent were removed under pressure and the residue was separated on a silica gel column using $CHCl_3$ as eluent flash chromatography. Two following fractions were obtained: less polar, **16** (1.1 g, 38%) b.p. 160°*/0.2 mm Hg, IR (film): 1800 (γ-lactone), 1750 cm^{-1} (acetates), more polar **17** (0.6 g 21%) b.p. 160°*/0.2 mm Hg, IR (film): 1800 (γ-lactone) 1748 cm^{-1} (acetates), (Found for the mixture **16** and **17**: C, 49.7; H, 5.6. Calc. for $C_{12}H_{16}O_8$: C, 50.0; 5.6%.)

Butyl (E) *4.5-anhydro-3,6-dideoxy-DL-hex-aldonate* (**13**). A soln of **7** (2.0 g, 0.0087 mol) and *m*-chloroperbenzoic acid (3.0 g) in $CHCl_3$ (10 ml) was left at room temp for several days. After disappearance of the substrate (tlc; hexane–EtOH 7:3), the mixture was cooled to 0° and filtered: The soln was washed with 5% NaOHaq cooled to 0° and water, dried and concentrated to dryness. The oily residue was purified by chromatography to produce **13** (2.0 g, 93%), b.p. 140°*/0.4 mm Hg. IR (film): 1740, 1230 cm^{-1} (ester). ^{1}H NMR 0.8–1.9 (m, 7H, C_3H_7), 1.32 (d, 3H, J_{5,CH_3} = 5.2 Hz, CH_3), 1.9–2.3 (m, 2H, H-3,3'), 2.8 m, 2H, epoxide), 4.17 (t, 2H, OCH_2, 5.14 t, 1H, H-2). (Found: C, 58.8; H, 8.4. Calc. for $C_{12}H_{20}O_5$: C, 59.0; H, 8.2%.)

2,5-Di-O-acetyl-3,6-dideoxy-DL-arabino and ribo-aldono-lactones (**20** and **21**) were obtained from **13** by the method described for **16** and **17**. The mixture **20** and **21** was separated by flash

chromatography using $CHCl_3$ as eluent. Two fractions were obtained: less polar **20** (30%) b.p. 160°*/0.2 mm Hg, IR (film): 1797 (γ-lactone), 1747 cm^{-1} (acetates), more polar **21** (20%) b.p. 160°*/0.2 mm Hg, IR (film): 1798 (γ-lactone), 1745 cm^{-1} (acetates). (Found for the mixture **20** and **21**: C, 52.2; H, 6.2. Calc. for $C_{10}H_{14}O_6$: C, 52.2; H, 6.1%.)

2,5-*Di*-O-*acetyl*-3,6-*dideoxy*-DL-*xylo and lyxo-aldonolactones* (**22** and **23**), were obtained from **7** according to the procedure described for **18** and **19**. The mixture **22** and **23** was separated by flash chromatography using $CHCl_3$ as eluant. Two fractions were obtained: less polar **22** (25%) b.p. 160°*/0.2 mm Hg, m.p. 53–58°, IR film: 1792 (γ-lactone), 1745 cm^{-1} (acetates); more polar **23** (22%) b.p. 160°*/0.2 mm Hg, m.p. 50–53°; IR (film): 1796 (γ-lactone), 1745 cm^{-1} (acetates). (Found for the mixture **22** and **23**: C, 52.4; H, 6.2. Calc. for $C_{10}H_{14}O_6$: C, 52.2; H, 6.1%)

3-*Deoxy*-DL-*arabino-hexose* **16**. To a soln containing 1.4 mmol of freshly prepared bis-(3-methyl-2-butyl)borane [to cooled to −10° THF (10 ml) under N_2 BH_3, CH_3SCH_3 complex (0.13 ml) and 2-methyl-but-2-ene (0.29 ml) were added and the mixture was kept for 1 hr at −10°] under N_2 **16** (0.02 g, 0.7 mmol in THF (10 ml) was added dropwise. The mixture was stirred overnight at room temp, then 2 ml of water were slowly added. The soln was stirred for 1 hr then additional 20 ml of water were added. The mixture was extracted 4 times with $CHCl_3$. The extract was dried and evaporated to dryness. The residue was purified on a silica gel column and then was deacetylated with 10% soln of Et_3N in MeOH–water 91 v/v. The solvents were evaporated, the oily residue was purified chromatographically to give **16**' colorless syrup (0.045 g, 40%); $R_f = 0.23$ ($CHCl_3$–MeOH 7:3 v/v).

3-*Deoxy*-DL-*ribo-hexose* **25** was obtained from **17** according to the procedure described for **24**. $R_f = 0.23$ ($CHCl_3$–MeOH 7:3 v/v).

3-*Deoxy*-DL-*xylo-hexose* **26** was obtained from **18** according to the procedure described for **24**. $R_f = 0.23$ ($CHCl_3$–MeOH 7:3 v/v).

3-*Deoxy*-DL-*lyxo-hexose* **27** was obtained from **19** according to the procedure described for **24**. $R_f = 0.23$ ($CHCl_3$–MeOH 7:3 v/v).

3,6-*Dideoxy*-DL-*arabino-hexose* **28** was obtained from **20** by the method described for **24**. $R_f = 0.30$ ($CHCl_3$–MeOH 8.5:1.5 v/v).

3,6-*Dideoxy*-DL-*ribo-hexose* **20** was obtained from **21** by the method described for **24**. $R_f = 0.25$ ($CHCl_3$–MeOH 8.5:1.5 v/v).

3,6-*Dideoxy*-DL-*xylo-hexose* **30** was obtained from **22** by the procedure described for **24**. $R_f = 0.27$ ($CHCl_3$–MeOH 8.5:1.5 v/v).

3,6-*Dideoxy*-DL-*lyxo-hexose* **31** was obtained from **23** by the method described for **24** $R_f = 0.23$ ($CHCl_3$–MeOH 8.5:1.5 v/v).

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