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SYNTHESIS OF SOME DISACCHARIDES CONTAINING PENT-2-ENOPYRANOSE RESIDUES

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ABSTRACT

Two methods of linking racemic 2,3-dideoxypent-2-enopyranos-4-ulose to suitably protected monosaccharide derivatives have been evaluated. The resulting diastereoisomeric mixtures containing D-glucose, D-galactose, and L-rhamnose derivatives in the "aglycon" part were fractionated, and configurations were assigned to ten disaccharide precursors. Disaccharides containing non-reducing 2,3-dideoxy-α-D- and -α-L-pent-2-enopyranose residues and their saturated analogues have been obtained by lithium aluminum hydride reduction of selected pentosylulose-monosaccharides. Inversion of configuration at the allylic position (C-4) in some unsaturated disaccharides is also described.

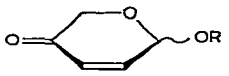
INTRODUCTION

Disaccharides are usually synthesised chemically by glycosylation of a partially protected monosaccharide with another protected monosaccharide having an appropriately activated anomeric position[1]. A fundamentally different approach, involving preparation of a dienyl-sugar ether, followed by Diels–Alder condensation with a glyoxylic ester, and subsequent functionalisation of the resulting dihydropyran ring, has recently been elaborated by David *et al.*[2].

In this paper, two ways of linking a racemic dihydropyran derivative[3] with suitably protected monosaccharide derivatives are described.

RESULTS AND DISCUSSION

We have reported on two methods of preparing complex glycosides from 2,3-dideoxy-D,L-pent-2-enopyranos-4-ulose (**1**), the key intermediate in the total synthesis of pentoses from furfuryl alcohol[4]. One method[5] is based on the use of the diethyl azodicarboxylate–triphenylphosphine–mercuric halide glycosylating system developed by Szarek[6]; the other makes use of the facile displacement of a hemiacetal acyloxy group (*e.g.*, OBz in **2**) in the presence of stannic chloride[7].



1 R = H
2 R = Bz
9 – 20 R = monosaccharide derivative

The aim of this work has been to assess the utility of both methods for the synthesis of disaccharide precursors containing a 2,3-dideoxypent-2-enopyranos-4-ulose residue. Easily available **1** is well-suited for such a purpose because, upon its attachment to a chiral monosaccharide residue, only two diastereoisomers result, and the pentulose moiety can be easily transformed into a pentopyranose residue. Additionally, this approach to the synthesis of disaccharides offers a wide range of possibilities for structural modification of the non-reducing part of the molecule. Moreover, following separation of the diastereoisomeric pentosiduloses, the series of disaccharides containing D- and L-pentopyranose residues would both become available.

The coupling of **1** with the following, easily available, protected sugar derivatives was studied: 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**3**), 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**4**), benzyl and methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranosides (**5** and **6**), 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**7**), and ethyl 4-*O*-*p*-bromophenyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (**8**). Treatment of **1** with the diethyl azodicarboxylate–triphenylphosphine–mercuric bromide reagent, followed by addition, severally, of the monosaccharide derivatives **3**–**8**, gave the unsaturated disaccharides **9**–**20** in modest yields (Table I, Method A).

We noticed earlier that **1** decomposes very quickly upon treatment with azodicarboxylic ester–phosphine betaine reagents. The addition of a mercuric halide to the betaine component slows down decomposition of **1** considerably, but when equimolar proportions of **1** and a protected monosaccharide derivative were treated with the condensing reagent, much of the monosaccharide derivative remained after all of the pentulose had been consumed. Therefore, an excess of the condensing reagent was used with respect to the monosaccharide derivative. A similar excess of **1** was introduced to the reaction mixture in several portions. Compounds **9**–**18** were obtained in appreciably higher yields when the appropriate monosaccharide derivative was treated with 1-*O*-benzoyl-2,3-dideoxy-DL-pent-2-enopyranos-4-ulose (**2**) in the presence of ~10 mol% of stannic chloride in 1,2-dichloroethane (Table I, Method B).

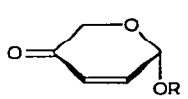
In all cases, ~1:1 diastereoisomeric mixtures of the unsaturated disaccharides were formed, according to chromatographic (h.p.l.c.) and spectral (^{1}H-n.m.r.) examination of the crude reaction products. In five out of the six reactions, these mixtures could be fractionated into pure components by preparative high-performance liquid chromatography (h.p.l.c.) (**9**,**10**; **15**,**16**; and **19**,**20**), or by column chromatography on silica gel (**11**,**12** and **13**,**14**). A comparison of the physical properties of the individual diastereoisomers (Table I) reveals that both the [α] values and the chemical

TABLE I

DATA FOR THE 2,3-DIDEOXY-α-D- AND -α-L-PENT-2-ENOPYRANOSYL-4-ULOSE-MONOSACCHARIDES **9–20**

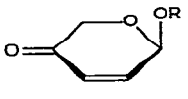
Compound	*Reducing moiety*	*Formula*	*Yield (%)*		*M.p. (degrees)*	$[\alpha]_D$ *(degrees)*	$[\alpha]_{578}$ *(degrees)*	*Chemical shift for H-1 (δ)*	*Configuration at C-1*	*Analysis (%)*			
			Method A	*Method B*						*Calc.*		*Found*	
										C	*H*	*C*	*H*
9					114	−35.0	−34.7	5.31	α-L			56.9	6.9
	3	$C_{17}H_{24}O_8$	36	59						57.3	6.8		
10					oil	−69.0	−73.7	5.25	α-D			57.3	7.0
11					oil	−39.1	−42.5	5.37	α-D			57.2	6.9
	4	$C_{17}H_{24}O_8$	32	53						57.3	6.8		
12					oil	−3.8	−2.1	5.48	α-L			57.1	6.9
12					103	−9.5	−10.0	5.82	α-L			64.6	6.8
	5	$C_{21}H_{26}O_7$	28	57						64.6	6.7		
14					95	−37.4	−43.1	5.31	α-D			64.5	6.7
15					oil	−21.5	−23.8	5.51	α-L			57.3	7.1
	6	$C_{15}H_{22}O_7$	35	61						57.3	7.1		
16					78–79	−65.6	−75.8	5.44	α-D			57.2	6.9
17,18	**7**	$C_{17}H_{24}O_8$	17	32	oil	−48.3	−51.3	5.26,5.32		57.3	6.8	57.3	6.5
19					108	−227.4	−243.2	5.11	α-D				
	8	$C_{19}H_{21}BrO_6$	11	0						53.65	5.0	53.8	5.0
20					149	−138.1	−145.2	5.32	α-L				

shifts of the anomeric protons of the non-reducing part are different for each member of a pair, and that the n.m.r. signal for H-1 of the more laevorotatory isomer always occurs at higher field than that for the more dextrorotatory isomer. The absolute configuration at C-1 of the diastereoisomeric glycosiduloses can be assigned tentatively on the basis of optical rotation differences. Although it has been pointed out that Hudson's rules cannot be used safely for assessment of the configuration of unsaturated glycosides[8], the applicability of Mills' rule[9], which correlates the configuration of epimeric, cyclic, allylic carbinols with their $[\alpha]$ values, has not been invalidated. Applied to this particular case, Mills' rule requires that the compounds containing α-D-pentenulose units (*A*) be more laevorotatory than those containing α-L units (*B*).



A, α-D

10, 11, 14, 16, 19



B, α-L

9, 12, 13, 15, 20

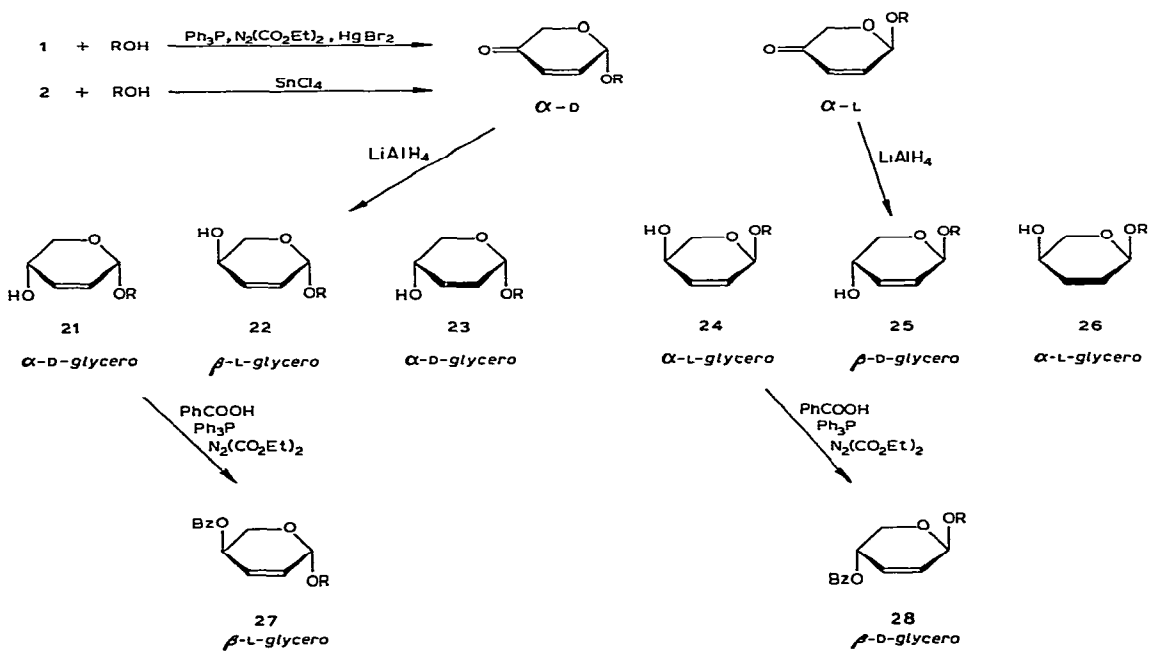
It has been demonstrated that methyl 2,3-dideoxy-DL-pent-2-enopyranosid-4-ulose (**1**, R = Me) can be transformed into methyl α-DL-lyxopyranoside in three steps, with a high degree of selectivity; in fact, no isomeric *ribo*-glycoside was detected after *cis*-hydroxylation of methyl 4-*O*-acetyl-2,3-dideoxy-α-DL-*glycero*-pent-2-enopyranoside[4]. Therefore, we decided to use the same reaction sequence to provide unambiguous proof of the configurational assignment based on optical rotation values. The unsaturated alcohols **30** and **43**, obtained by lithium aluminum hydride reduction of the separated 3-*O*-(pentenosylulose)glucofuranoses **11** and **12**, respectively, were acetylated and then *cis*-hydroxylated with the stoichiometric quantity of osmium tetraoxide in pyridine[10]. In both cases, a single diol (characterized as the corresponding acetate) was formed in good yield. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α-lyxopyranosyl)-α-D-glucofuranose obtained from precursor **11** was dextrorotatory ($[\alpha]_D$ +6.0°) in contrast to the isomeric disaccharide ($[\alpha]_D$ −47.2°) obtained from **12**. Since the α-D-*lyxo* unit must provide a positive contribution to the overall $[\alpha]_D$ value, and the α-L-*lyxo* unit a negative contribution, it follows that the non-reducing part of **11** belongs to the α-D series, and that of **12** to the α-L series.

Reduction of the enone grouping in the methyl glycoside of **1** by complex metal hydrides proceeds[11] with high regio- and stereo-selectivity, due to stereoelectronic control of the approach of the hydride anion. As a result, the unsaturated alcohol having a pseudoequatorial hydroxyl group in the $^{O}H_5$ conformation is formed preponderantly. Having carried out the reduction of the pentenosiduloses **9–14** with lithium aluminum hydride, we found that, in the majority of cases, three compounds (separable by column chromatography) were formed from each diastereoisomerically pure disaccharide-precursor (Scheme 1). The unsaturated alcohols, which were identified, on the basis of ^{1}H-n.m.r. data for their acetates, as having α-D- (**21**) or α-L-*glycero*- (**24**) and β-L- (**22**) or β-D-*glycero* (**25**) configurations, were formed in an

$\alpha\beta$ ratio of ~9:1, and were accompanied by significant amounts of the saturated α-D- (**23**) or α-L-*glycero* (**26**) analogues. For the di-*O*-isopropylidenegalactose derivatives **9** and **10**, the saturated reduction-products actually preponderated (60% yield). For the 3-*O*-(pentenosylulose)glucofuranoses **11** and **12**, the ratio of unsaturated to saturated alcohols obtained during lithium aluminum hydride reduction was 6:4.

Pentenosyluloserhamnosides **13** and **14**, on the other hand, afforded only unsaturated alcohols, the $\alpha\beta$ ratio being 9:1 in each case. Thus, whereas the stereoselectivity of 1,2-hydride addition to the enone system in the disaccharide precursors remains within previously reported limits, the extent of 1,4-addition in the overall reduction process can be surprisingly high in some cases. Admittedly, no further examination of the influence of reaction conditions and aglycon constitution on the distribution of the products has been made.

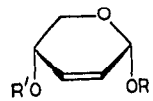
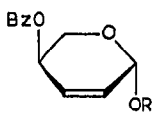
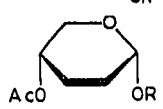
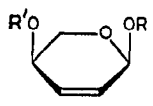
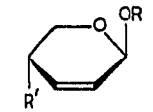
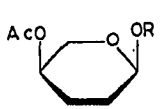
It should be pointed out that efficient separation of the starting pentenosylulose-monosaccharides gives access to all of the corresponding 2,3-unsaturated alcohols, which in turn makes possible the synthesis of disaccharides containing every D- or L-pentopyranose unit. In this connection, it is of interest that a number of reducing disaccharides containing D- or L-pentopyranose residues at the non-reducing end have been isolated from natural sources[12]. Although the amounts of 2,3-unsaturated alcohols having β-D- or β-L-*glycero* configurations available by reduction of the pentenosiduloses **9–14** are too small to be of synthetic significance, they may be obtained from the major reduction products in excellent yield *via* esterification, with inversion of configuration at the allylic (C-4) site, in the presence of diethyl azodicarboxylate and triphenylphosphine, as described earlier[13]. Stereospecific amination[14]



Scheme 1

TABLE II

DATA FOR 2,3-DIDEOXY-D- AND -L-*glycero*-PENTOPYRANOSYL-MONOSACCHARIDES **29–50**

Compound	*"Non-reducing residue"*	*R'*	*"Reducing residue" (R)*	*Composition*	*M.p. (degrees)*	$[\alpha]_D$ *(degrees)*	$[\alpha]_{578}$ *(degrees)*	*Analysis (%)*			
								Calc.		*Found*	
								C	*H*	*C*	*H*
29		H	3	$C_{17}H_{26}O_8$	94	−94.2	−98.9	57.0	7.3		
30		H	4	$C_{17}H_{26}O_8$	85	+29.5	+31.2	57.0	7.3	57.0	7.2
31		H	5	$C_{21}H_{28}O_7$	122	+14.8	+15.1	64.3	7.2	64.0	7.3
32		Ac	3	$C_{19}H_{28}O_9$	103	−99.0	−105.0	57.0	7.05	56.9	7.1
33		Ac	4	$C_{19}H_{28}O_9$	68	+32.3	+34.8	57.0	7.05		
34		Ac	5	$C_{23}H_{30}O_8$	82	+26.0	+26.8	63.6	7.0	63.3	7.0
35		—	3	$C_{24}H_{30}O_9$	79–81	−24.5	−27.1	62.3	6.5	62.2	6.5
36		—	4	$C_{24}H_{30}O_9$	130	−63.5	−68.4	62.3	6.5	62.4	6.5
37		—	3	$C_{19}H_{30}O_9$	107	−54.7	−58.4	56.7	7.5	56.4	7.6
38		—	4	$C_{19}H_{30}O_9$	56	+4.5	+5.1	56.7	7.5	56.3	7.6
39		H	3	$C_{17}H_{26}O_8$	oil	−20.9	−22.3	57.0	7.3		
40		H	4	$C_{17}H_{26}O_8$	70–72	−57.5	−60.3	57.0	7.3	56.7	7.1
41		H	5	$C_{21}H_{28}O_7$	88–89	−77.0	−81.8	64.3	7.2	64.3	7.3
42		Ac	3	$C_{19}H_{28}O_9$	112	−24.5	−25.5	57.0	7.05	56.8	7.2
43		Ac	4	$C_{19}H_{28}O_9$	82–83	−62.8	−66.2	57.0	7.05	56.7	7.1
44		Ac	5	$C_{23}H_{30}O_8$	oil	−81.5	−87.3	63.6	7.0	63.3	7.0
45		Bz	3	$C_{24}H_{30}O_9$	67–69	−102.2	−108.9	62.3	6.5	62.5	6.3
46		Bz	4	$C_{24}H_{30}O_9$	87	+61.4	+65.0	62.3	6.5	62.4	6.5
47		Ac	5	$C_{23}H_{30}O_8$	oil	+13.6	+14.6	63.6	7.0		
48		phthalimido	5	$C_{29}H_{31}NO_8$	145	+59.7	+63.4	66.8	6.0	66.5	6.0
								N = 2.7		N = 2.7	
49		—	3	$C_{19}H_{30}O_9$	oil	−4.8	−5.0	56.7	7.5	56.4	7.4
50		—	4	$C_{19}H_{30}O_9$	oil	+66.0	+70.2	56.7	7.5	56.5	7.6

at the allylic position can also be achieved easily, as exemplified for the pentenopyranosylrhamnoside **48** (see Experimental). The scheme of transformations performed to obtain unsaturated disaccharides containing all four configurational isomers of the pentenopyranose moiety is shown in Scheme 1.

The physical properties and analytical data of the main reduction products obtained from compounds **9–14**, supplemented by the data for compounds resulting from inversion of configuration at C-4 in the unsaturated α-D- and α-L-*glycero* alcohols are listed in Table II.

The ^{1}H-n.m.r. spectra (100 MHz) of the unsaturated disaccharides presented in Table II accord with the spectra[11] of methyl 2,3-dideoxypent-2-enopyranosides. In particular, the spectra of the 4-acetates having the α-D- and α-L-*glycero* configurations contained, besides a doublet at δ ~4.6 (1 H, J 2.5–3.0 Hz, H-1) and 2-proton signals at δ 5.8–6.0 (CH=CH), a characteristic broad-triplet centered at δ ~5.3, corresponding to a pseudoaxial H-4 ($J_{4,5a}$ ~8.5, $J_{4,5e}$ ~7 Hz). In the spectra of the benzoates obtained by inversion of configuration at C-4, on the other hand, the signals for H-4 appear as rather irregular multiplets (ΣJ ~5 Hz) at δ ~5.2. Similarly, the spectra of the acetates of the minor reduction products having β-D- and β-L-*glycero* configurations of the pentenopyranose moiety display broad singlets at δ ~4.9, corresponding to the pseudoequatorial H-4. Other spectral features of the compounds obtained, including i.r. data, also accorded with the structures assigned.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler micro-stage apparatus and are uncorrected. T.l.c. was performed on silica gel (Merck) with light petroleum–ethyl acetate (9:1–2:1), and column chromatography on MN-Kieselgel-60 (Macherey–Nagel). High-pressure liquid chromatography (h.p.l.c.) was carried out on a Siemens S-100 chromatograph equipped with a 30-cm Lichrosorb SI 60 column, using hexane–ethyl acetate (7:3). ^{1}H-N.m.r. spectra (100 MHz) were recorded with a Jeol JNM-4H-100 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). I.r. spectra were recorded with an SP-200 spectrophotometer. Optical rotations were determined with a Perkin–Elmer 141 automatic polarimeter for 1% solutions in dichloromethane at 18 ±2°. Di-*O*-isopropylidene-monosaccharide derivatives **3**, **4**, and **7** were prepared according to standard procedures[15]. *O*-Isopropylidenerhamnopyranosides **5** and **6** were prepared as described in the literature[16]. The unsaturated glycoside **8** was obtained by treatment of the corresponding 4,6-diol with an equimolar proportion of *p*-bromophenol in the presence of diethyl azodicarboxylate and triphenylphosphine[17]. Hexane–ethyl acetate mixtures were used for crystallisation of solid products.

Benzyl 4-O-(2,3-dideoxy-α-L- and -α-D-pent-2-enopyranosyl-4-ulose)-2,3-O-isopropylidene-α-L-rhamnopyranoside (**13** *and* **14**). — (*a*) To a stirred solution of triphenylphosphine (524 mg, 2 mmol) in dry tetrahydrofuran (15 ml) was added diethyl azodicarboxylate (350 mg, ~2 mmol) followed by mercuric bromide (720 mg, 2 mmol). At intervals of 5 min, 2,3-dideoxy-DL-pent-2-enopyranos-4-ulose (**1**; 60 mg,

~0.5 mmol) and benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**5**; 294 mg, 1 mmol) were added, and the resulting suspension was stirred at room temperature. More **1** (6 × 20 mg) was added during 3 h and the mixture was then stirred overnight. After evaporation of the solvent under reduced pressure, the residue was triturated with carbon tetrachloride (25 ml) and the solids were collected and washed several times with carbon tetrachloride. The combined filtrate and washings were concentrated and the residue was eluted from a column (30 ml) of silica gel with light petroleum–ethyl acetate (9:1) to afford, first, **13** (45 mg, 11.5%), m.p. 103°, $[\alpha]_D$ −9.5°; ^{1}H-n.m.r. data: δ 1.28–1.40 (m), 1.57 (s, 9 H, 3 Me), 3.60–4.76 (m, 8 H, CH_2 of the ulose and benzyl group and H-2,3,4,5 of the rhamnoside), 5.05 (s, 1 H, H-1), 5.82 (d, 1 H, *J* 3.5 Hz, H-1′), 6.08 (d, 1 H, *J* 10.7 Hz, H-3′), 6.88 (dd, 1 H, H-2′), and 7.33 (s, 5 H, Ph); ν_{max}^{KBr} 3000, 2920, 1700, 1455, 1385, 1240, 1210, 1135, 1120, 1090, 1080, 1045, 1020, 990, 860, 750, and 700 cm^{-1}.

Eluted second was **14** (45 mg, 11.5%), m.p. 95°, $[\alpha]_D$ −37°; ^{1}H-n.m.r. data: δ 1.25–1.38 (m), 1.55 (s, 9 H, 3 Me), 3.50–4.90 (m, 8 H, CH_2 of the ulose and benzyl group and H-2,3,4,5 of the rhamnoside), 5.04 (s, 1 H, rhamnose H-1), 5.31 (d, 1 H, *J* 3.7 Hz, H-1′), 6.09 (d, 1 H, *J* 10.0 Hz, H-3′), 6.85 (dd, 1 H, H-2′), and 7.33 (s, 5 H, Ph); ν_{max}^{KBr} 2990, 2910, 1700, 1455, 1385, 1370, 1240, 1205, 1130, 1090, 1080, 1040, 1020, 990, 860, 820, 780, 750, and 695 cm^{-1}.

Fractions containing both **13** and **14** (20 mg, 5%) were also obtained.

(*b*) To a solution of **5** (588 mg, 2 mmol) and 1-*O*-benzoyl-2,3-dideoxy-DL-pent-2-enopyranos-4-ulose (**2**; 436 mg, 2 mmol) in dry 1,2-dichloroethane (10 ml) was added stannic chloride (~100 mg), and the solution was kept at room temperature for 3 h. The mixture was then diluted with ether (60 ml), washed quickly with cold, dilute, aqueous sodium hydrogen carbonate and twice with water, dried ($MgSO_4$), and concentrated. The oily residue was eluted from a column of silica gel (25 g) with light petroleum–ethyl acetate (9:1), to give **13** (190 mg, 24%), m.p. 103°, $[\alpha]_D$ −9.5°; a mixture of **13** and **14** (84 mg, 11%); and **14** (170 mg, 22%), m.p. 95°, $[\alpha]_D$ −37°.

*Benzyl 4-*O*-(2,3-dideoxy-α-*L*-glycero-pent-2-enopyranosyl)-2,3-*O*-isopropylidene-α-*L*-rhamnopyranoside* (**41**), *its 4-acetate* **44**, *and benzyl 4-*O*-(4-*O*-acetyl-2,3-dideoxy-β-*D*-glycero-pent-2-enopyranosyl)-2,3-*O*-isopropylidene-α-*L*-rhamnopyranoside* (**47**). — To a solution of **13** (195 mg, 0.5 mmol) in dry ether (40 ml) was added lithium aluminum hydride (20 mg). After 30 min, acetone (0.1 ml) was added to decompose the excess of hydride, and the mixture was diluted with wet ether (60 ml), washed with water, dried ($MgSO_4$), and concentrated. Chromatography of the oily residue on silica gel with light petroleum–ethyl acetate (4:1) afforded, first, **41** (151.5 mg, 77.3%), m.p. 88–90°, $[\alpha]_D$ −77°.

The 4-acetate (**44**) of **41** was an oil, $[\alpha]_D$ −81.5°; ^{1}H-n.m.r. data: δ 1.30–1.43 (m), 1.57 (s, 9 H, 3 Me), 2.09 (s, 3 H, AcO), 3.55–4.00 (m, 4 H, H-2,3,4,5), 4.15–4.35 (m, 2 H, -CH_2-O), 4.64 (ABq, 2 H, CH_2Ph), 5.08 (s, 1 H, H-1), 5.35 (dd, 1 H, $J_{4,5}$ 7, $J_{4,5'}$ 9 Hz, H-4′), 5.52 (bs, 1 H, H-1′), 5.94 (s, 2 H, H-2′,3′), and 7.38 (s, 5 H, Ph); ν_{max}^{KBr} 3000, 2950, 1730, 1460, 1380, 1235, 1090, 1040, 1015, 870, and 700 cm^{-1}.

Eluted second was an oil (19 mg, 9.7%), the 4-acetate (**47**) of which was also an oil, $[\alpha]_D$ +14°; ^{1}H-n.m.r. data: δ 1.21–1.35 (m), 1.51 (s, 9 H, Me), 2.07 (s, 3 H, AcO), 3.55–4.23 (m, 6 H, H-2,3,4,5 plus CH_2-O), 4.54 (ABq, 2 H, -CH_2Ph), 4.87 (bs, 1 H, H-4'), 4.98 (s, 1 H, H-1), 5.50 (s, 1 H, H-1'), 5.98 (d, 2 H, H-2',3'), and 7.40 (s, 5 H, Ph); ν_{max}^{KBr} 3000, 2950, 1735, 1460, 1375, 1230, 1080, 1040, 1020, 985, 860, and 690 cm^{-1}.

*Benzyl 2,3-*O*-isopropylidene-4-*O*-(4-*N*-phthalimido-2,3,4-trideoxy-β-*D*-glycero-pent-2-enopyranosyl)-α-*L*-rhamnopyranoside* (**48**). — To a solution of **41** (98 mg, 0.25 mmol) and phthalimide (70 mg, 0.5 mmol) in dry tetrahydrofuran (5 ml) was added diethyl azodicarboxylate (0.1 ml, 0.5 mmol). After 1 h, the solvent was evaporated under reduced pressure and the residue was subjected to chromatography on silica gel (10 ml) with light petroleum–ethyl acetate (9 : 1), to give **48** (118 mg, 91%), m.p. 145°, $[\alpha]_D$ +60°; ^{1}H-n.m.r. data: δ 1.30–1.56 (m, 9 H, 3 Me), 3.57–4.78 (m, 9 H, H-2,3,4,5, H-4',5',5', and CH_2Ph), 5.05 (s, 1 H, H-1), 5.70 (bs, 1 H, H-1'), 5.94–6.25 (m, 2 H, H-2',3'), 7.37 (s, 5 H, Ph), and 7.67–7.90 (m, 4 H, aromatic protons); ν_{max}^{KBr} 3000, 2900, 2800, 1775, 1720, 1390, 1040, 1020, 980, 750, 720, and 690 cm^{-1}.

The compounds in Tables I and II were obtained by the appropriate method described above. The benzoates **35**, **36**, **45**, and **46** were obtained as described for **48**, but using benzoic acid in place of phthalimide.

*1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α-*D*- and -α-*L*-lyxopyranosyl)-α-*D*-glucofuranose* (**51** *and* **52**). — To a solution of **33** (100 mg, 0.25 mmol) in pyridine (5 ml) was added osmium tetraoxide (75 mg, 0.3 mmol), and the solution was stored in a stoppered flask overnight at room temperature. Freshly prepared, saturated, aqueous sodium hydrogen sulphite (5 ml) was added, and the mixture was stirred for 3 h and then extracted with chloroform (5 × 10 ml). The combined extracts were dried ($MgSO_4$), and concentrated under reduced pressure, the residue was acetylated (acetic anhydride–pyridine), and the product was eluted from a short column of silica gel with light petroleum–ethyl acetate (4 : 1), to afford oily **51** (110 mg, 85%), $[\alpha]_D$ +6°; ^{1}H-n.m.r. data: δ 1.30–1.56 (m, 12 H, 4 Me), 2.03–2.11 (3 s, 9 H, 3 AcO), 3.60–4.32 (m, 8 H, H-5',5' and H-2,3,4,5,6,6), 4.62 (d, 1 H, J 3.7 Hz, H-1), 5.00–5.36 (m, 3 H, H-2',3',4'), and 5.91 (d, 1 H, J 3.5 Hz, H-1'); ν_{max}^{KBr} 1740, 1250 (AcO), 1080, 1050, and 1020 cm^{-1} (C-O).

Anal. Calc. for $C_{23}H_{34}O_{13}$: C, 53.3; H, 6.6. Found: C, 53.3; H, 6.7.

In an analogous way, **43** was converted into **52** (82%), $[\alpha]_D$ −47°. The ^{1}H-n.m.r. and i.r. spectra of **52** were almost identical with those of **51**.

Anal. Found: C, 53.6; H, 6.7%.

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