SYNTHESIS AND ^{1}H NMR AND ^{13}C SPECTROSCOPY OF L-ARABINOPYRANOSYL BIOSIDES

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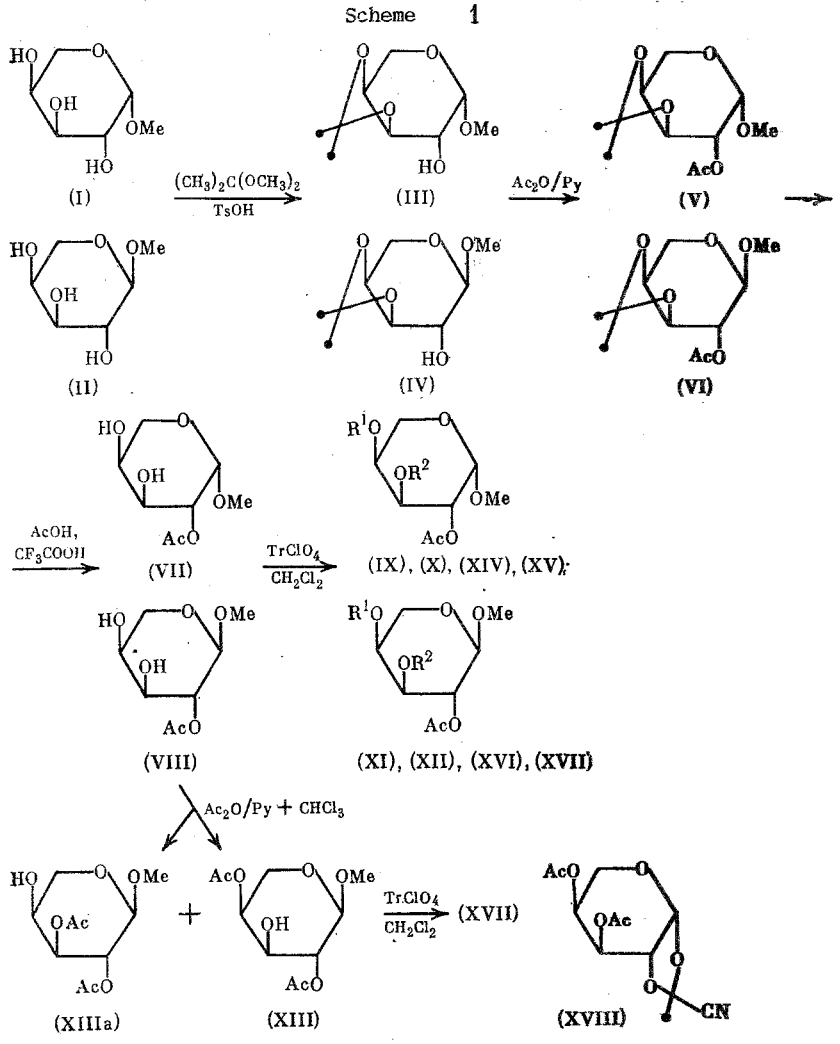
The absence of literature data on the NMR spectroscopy of oligo- and polysaccharides containing arabinopyranose residues presented the requirement to carry out a series of proposals for the assignment of the signals in the ^{13}C NMR spectra of synthetic arabinans [1]. The aim of the present work was the isolation of a series of arabinopyranosyl biosides which could serve as models for the interpretation of the ^{13}C NMR spectra of oligo- and polysaccharides containing arabinopyranose residues. The result of the polycondensation reaction of the acetates of 1,2-O-cyanoethylidene-β-L-arabinopyranoses with the O-trityl group at C^3 or C^4 [1] permits the assumption that the 1,2-cis linked disaccharides will also be formed together with the 1,2-trans compounds during the glycosylation reaction of the 3-O- and 4-O-trityl ethers of the methyl α- and methyl β-L-arabinopyranoside acetates with the aid

Scheme 1



R^1 = Tr, R^2 = H (IX), (XI); R^1 = H, R^2 = Tr (X), (XII);
R^1 = Tr, R^2 = Ac (XIV), (XVI); R^1 = Ac, R^2 = Tr (XV), (XVII).

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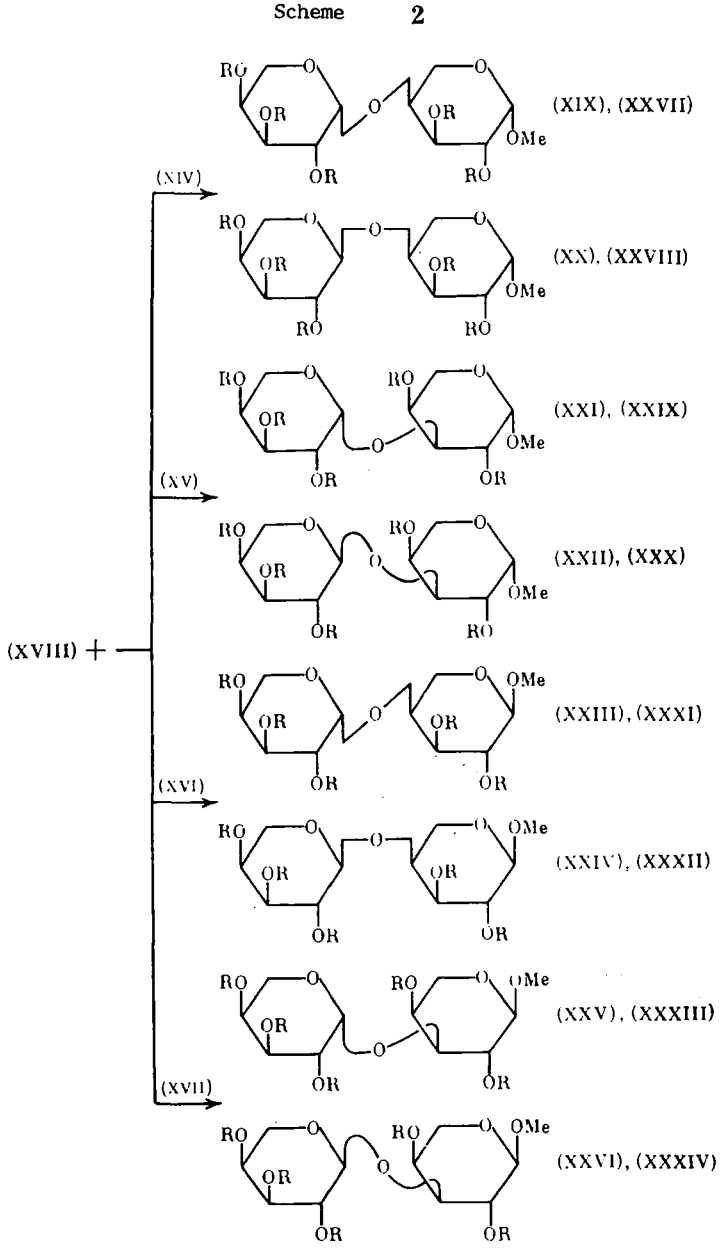
of the acetates of 1,2-O-cyanoethylidene-β-L-arabinopyranose. At the same time, the presence of the 1,2-cyanoethylidene and O-trityl groups in the different molecules participating in the glycosylation reaction (and not in one as in the conditions of the polycondensation reaction) can also lead to another result.

The synthesis of the 3- and 4-O-trityl ethers of methyl α- and methyl β-L-arabinopyranosides was accomplished according to Scheme 1.

Proceeding from the free methyl β- (I) and methyl α-L-arabinopyranosides (II) [2, 3], we obtained (dimethoxypropane in the presence of TsOH [4]) the 3,4-O-isopropylidene derivatives (III) and (IV) which were acetylated to the acetates (V) and (VI) by Ac_2O in pyridine. The removal of the isopropylidene protecting groups with 60% AcOH and 90% CF_3COOH gave the corresponding acetyl derivatives (VII) and (VIII), the tritylation [5] of which by 1 equivalent of $TrClO_4$ in CH_2Cl_2 led to the ethers (IX)-(XII) containing one free hydroxyl. The acetylation of the last led to the requisite trityl-substituted ethers of methyl L-arabinopyranosides (XIV)-(XVII). The high selectivity of the tritylation of the diol (VIII) led mainly to (XI); the yield of the isomer (XII) comprised less than 5%. Therefore, for the isolation of (XVII), the diol (VIII) was initially monoacetylated [6] to (XIII) by 1 equivalent of Ac_2O in pyridine + $CHCl_3$ and then tritylated by $TrClO_4$.

Scheme 2



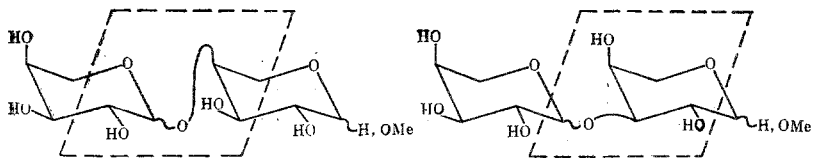
R = Ac (XIX)—(XXVI); R = H (XXVII)—(XXXIV).

The glycosylation [5] of the obtained O-trityl ethers (XIV)-(XVII) by 1,2-O-exo-cyanoethylidene-3,4-di-O-acetyl-β-L-arabinopyranose (XVIII) [1] gave the disaccharides (XIX)-(XXVI), the Zemplen deacetylation of which afforded the free methyl β- and methyl α-L-arabinopyranosyl biosides (XXVII)-(XXXIV) (Scheme 2).

The mixture of the 1,2-trans and 1,2-cis-linked disaccharides was obtained in all the performed glycosylation reactions, whereby the relative content of the latter comprised from 6% for the glycosylation of (XV) to 20% for the glycosylation of (XVII). In the case of the utilization of $TrBF_4$ as the catalyst in the glycosylation of the ether (XV), the 7:1 mixture of the 1,2-trans- and the 1,2-cis-linked disaccharides was obtained.

The structure of the resulting monosaccharide (III)-(XVII) and disaccharide (XIX)-(XXXIV) derivatives was shown on the basis of the combination of the ^1H and ^{13}C NMR data presented in Tables 1-4. The PMR spectra were interpreted with the aid of selective homonuclear double resonance. The signals in the ^{13}C NMR spectra were, in turn, assigned with the utilization of selective heteronuclear double resonance. The ^{13}C NMR spectrum of compound (XXIX), which was present as a mixture with (XXX) as a minor component, constitutes an exception. The signals pertaining to (XXIX) in the spectrum of the mixture were assigned from the general considerations of the influence of structural factors on the chemical shifts (CSs) in the ^{13}C NMR spectra [8] and by comparison with the spectrum of methyl β-L-arabinopyranoside. The complete assignment of the signals in the ^{13}C NMR spectra of the disaccharides (XXVII)-(XXXIV) presents practical interest from the point of view of the interpretation of the spectra of oligo- and polysaccharides containing arabinopyranose residues, since the CSs of the carbon atoms of the arabinopyranosyl biosides, isolated on the Scheme 3, should agree sufficiently closely with the CSs of the corresponding carbon atoms in the chain of the polysaccharides [9].

Scheme 3



1→4-disaccharides 1→3-disaccharides

The configuration of the glycosidic bond of the nonreducing residue can be judged with definiteness from the position of the signals of C^3 and C^5 of this residue: and the position of the signal of the methoxyl carbon depends on the configuration of the reducing end of the oligomeric chain.

The comparison of the effects of glycosylation in the ^{13}C NMR spectra of arabinobiosides with those in the spectra of galactobioses presents interest since the α-L-arabinopyranose fragment is homomorphous with the β-D-galactopyranose fragment, and the β-L-arabinopyranose fragment is homomorphous with the α-D-galactopyranose fragment. As is evident from Table 5, the effects of glycosylation for the 1 → 3-linked biosides are comparable for the α-L-arabino and the β-D-galacto series, or the β-L-arabino and the α-D-galacto series. From the viewpoint of the concept of the role of the steric proton—proton interactions in shaping the CSs of the carbon atoms near the glycosidic bond [14], this indicates that the conformational properties of the glycosidic bonds of the α,L 1 → 3 L,β,α-arabino and the β,D 1 → 3 D,α,β-galactopyranosylbiose fragments (or the β,L 1 → 3 L,α-β-arabino and the α,D 1 → 3 D, α,β-galactopyranosylbiose fragments) are similar. On the basis of the similarity of the effects of glycosylation in the 1 → 4-linked bioside fragments of the α,L-arabino and the β,D-galacto series, the similarity of these fragments can be indicated. However, a significant difference in the magnitude of the effects of glycosylation is observed in the series of the 1 → 4-linked β,L-arabino and α,D-galactopyranosylbioses for the corresponding carbon atoms. The α-effects of the glycosylation for C^1 and C^4 are considerably less, in the absolute value, in the series of arabinobiosides than in the series of galactobioses. On the other hand, the β-effects for C^5 in the arabinobiosides considerably exceed in absolute value the β-effects on the same atom of carbon in the galactobioses. From the above-mentioned viewpoint [14], this indicates that the conformational properties of the investigated fragments differ significantly. The qualitative explanation of the divergence in the effects of glycosylation comprises the fact that the rotation around the C^1—C^4 bond, guaranteeing the drawing together of the H^5_e and $H^{1'}$ protons, is facilitated due to the absence of a bulky equatorial substituent at C^5 in the 1 → 4-linked β,L → L-arabinobiosides. The drawing together of the protons at the 1,4-carbon

TABLE 1. The PMR Spectra of the Monosaccharide Derivatives (I)-(XVII) (solutions in $CDCl_3$, internal standard TMS, and CSs* δ, ppm)

Compound	H¹	H²	H³	H⁴	H⁵	H⁶′	OCH_3	OAc	OH	$(CH_3)_2C$
(I)†	4,82	3,83		3,98	3,86	3,64	3,41	–	4,66	–
(II) †	4,29	3,58	3,69	3,96		3,69	3,57	–	–	–
(III)	4,71	3,77	4,22		3,93		3,44	–	3,03	1,38; 1,54
(IV)	4,13	3,60	4,08	4,24	4,14	3,79	3,50	–	3,28	1,36; 1,53
(V)	4,81	4,94	4,30	4,26	4,04	3,92	3,39	2,14	–	1,38; 1,56
(VI)	4,28	5,00	4,14	4,27	3,79	4,09	3,42	2,10	–	1,35; 1,54
(VII)	4,85	5,03	4,01	4,00	3,84	3,74	3,39	2,16	3,30	–
(VIII)	4,43	5,02	3,97		3,83	3,64	3,51	2,18	3,79	–
(IX)	4,96	5,31	3,59	3,65	4,65		3,34	2,12	2,28	–
(X)	4,83	5,40	4,18	3,37	3,37	3,37	3,26	2,07	2,46	–
(XI)	4,37	4,83	3,03	3,10	3,84		3,36	1,95	2,80	–
(XII)	4,07	5,30	3,72	2,86	3,78	3,11	3,41	1,95	–	–
(XIII)	4,46	4,98	3,92	5,09	4,00	3,62	3,48	2,13 2,14	2,92	–
(XIV)	5,05	5,58	5,07	3,92	3,36	2,97	3,33	2,11 1,96	–	–
(XV)	4,84	5,38	4,04	3,94	3,49	3,30	3,23	2,00 2,20	–	–
(XVI)	4,30	5,08	4,61	3,93	3,61	2,84	3,38	2,09; 2,00	–	–
(XVII)	3,98	5,29	3,52	4,23	3,94	3,06	3,42	2,21; 1,90	–	–
(XIIIa)	4,35	5,17	4,96	4,08	4,00	3,61	3,48	2,11; 2,07	2,53	–

*The signals of aromatic protons are present at 7.25-7.52 ppm in the compounds (IX)-(XII) and (XIV)-(XVII).
†The solution in D_2O.

TABLE 2. Spin-Spin Coupling Constants in the PMR Spectra of the Monosaccharide Derivatives (I)-(XVII) (J, Hz)

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,5'}$	$J_{4,5'}$	$J_{OH,H}$
(I)	3,0	*	*	*	13,0	1,6	
(II)	7,6	9,7	3,8	*	*	*	
(III)	3,6	6,4	*	*	*	*	
(IV)	7,4	7,5	6,1	3,4	13,2	3,5	
(V)	3,5	8,0	5,5	1,1	13,0	2,7	
(VI)	6,8	6,8	6,8	5,7	12,8	4,1	
(VII)	3,5	9,2	6,0	1,5	12,5	1,8	
(VIII)	5,3	7,2	*	*	11,6	2,2	
(IX)	3,2	8,6	3,8	*	*	*	8,3
(X)	3,4	9,8	2,8	*	*	*	
(XI)	2,3	4,4	*	*	*	*	7,1
(XII)	7,1	9,0	3,3	3,5	12,6	2,2	
(XIII)	5,0	7,0	3,7	6,3	12,2	*	9,0
(XIIIa)	6,5	8,8	3,5	*	12,0	1,9	
(XIV)	3,4	10,0	3,5	1,6	12,2	2,6	
(XV)	3,6	10,0	3,5	*	12,5	1,5	
(XVI)	3,7	6,1	3,4	7,3	11,8	3,1	
(XVII)	7,1	9,4	3,3	3,2	13,2	1,5	

*The SSCCs were not measured due to the overlapping and multiplicity of the signals.

atoms (i.e., at $C^{1'}$ and C^5 in arabinobiosides) leads to a highfield shift of the $C^{1'}$ and C^5 signals in the ^{13}C NMR spectra by comparison with the signals of $C^{1'}$ and C^5 in the galactobioses where such a rotation is hampered, and the equatorial proton is absent at C^5. The drawing together of the $H^{1'}$ and H^5_e protons in the conformation $^4C_1$, which is considered preferred for the β,L → L-arabinobiosides, indicates the separation of the H^1 and H^4 protons, i.e., the protons at the 1,3-carbons. The influence of the interaction of the protons at the 1,3-carbon atoms on the CSs in the ^{13}C NMR spectra has an opposite trent compared with the interaction of the protons at the 1,4-atoms [14]. Therefore, the large separation of the $H^{1'}$ and H^4 protons is the reason for the lower value of the low-field shift of the C^4 signal in the spectra of the 1-4-arabinobiosides compared with the position of the signal in the spectra of galactobioses. This qualitative explanation is now going through experimental verification.

TABLE 3. PMR Spectra of Arabinopyranosyl Biosides (the solutions of the acetates (XIX)-(XXVI) in $CDCl_3$, the solutions of the free (XXVII)-(XXXIV) in D_2O, and the internal standards of TMS and MeOH respectively)*

Compound	H^{1}	H^{2}	H^{3}	H^{4}	H^{5}_{A}	H^{5}_{B}	$H^{1'}$	$H^{2'}$	$H^{3'}$	$H^{4'}$	$H^{5'}_{A}$	$H^{5'}_{B}$	OAc †	OCH_3
(XIX)	4,98	5,16	5,30	4,06	4,14	3,53	5,27	5,07	5,34	5,39	3,75	3,66	2,16–2,04	3,39
(XX)	4,90	5,19		4,11	3,84		4,48	5,19	5,06	5,25	4,06	3,61	2,14–2,09	3,40
(XXI)	5,00	5,15	4,23	4,27	3,83	3,68	5,24	5,24	5,24	5,34	4,14	3,68	2,17–2,00	3,40
(XXII)	4,88	5,21	4,18	5,24	3,83	3,70	4,63	5,09	5,00	5,21	3,98	3,58	2,03–2,17	3,40
(XXIII)	4,34	5,15	5,01	4,02	3,92	3,44	5,29	5,05	5,30	5,38	4,09	3,66	2,17–2,03	3,45
(XXIV)	4,50	5,19	5,04	4,04		3,61	4,35	5,07	4,97	4,04	4,09	3,61	2,14–2,07	3,45
(XXV)	4,34	5,14	3,90	5,19	4,05	3,56	5,19		5,26	5,33	4,05	3,67	2,14–2,00	3,48
(XXVI)	4,29	5,11	3,87	5,11	4,05	3,54	4,56	5,11	5,00	5,22	3,97	3,58	2,13–2,03	3,44
(XXVII)	4,89	4,07		4,15	3,91	3,95	5,20	3,99	4,09	4,07	4,26	3,77	–	3,56
(XXVIII)	4,84	3,76		4,10	3,88	3,84	4,50	3,66	3,63	3,94	3,92	3,65	–	3,42
(XXX)	4,84	4,00	3,92	4,17	3,87	3,65	4,53	3,62	3,67	3,85	3,95	3,68	–	3,43
(XXXI)	4,33	3,62	3,80	4,00	4,17	3,65	5,08	3,87	3,98	4,04	4,11	3,60	–	3,57
(XXXII)	4,31	3,63	3,76	4,08	4,17	3,67	4,54	3,65	3,68	3,97	3,94	3,72	–	3,57
(XXXIII)	4,32	3,67	3,75	4,19	4,00	3,65	5,14	3,89	3,98	4,04	4,16	3,65	–	3,58
(XXXIV)	4,34	3,72	3,82	4,17	3,97	3,69	4,57	3,65	3,71	3,97	3,94	3,68	–	3,57

*The SSCCs between the corresponding protons in the disaccharides (XIX)-(XXXIV) have close values and lie in the intervals: $J_{1,2}$ = 6.0-7.5 Hz (α-anomers), $J_{1,2}$ = 3.0-3.6 Hz (β-anomers), $J_{2,3}$ = 8.3-10.5 Hz, $J_{3,4}$ = 3.0-3.6 Hz, $J_{4,5A}$ = 4.4-5.0 Hz, $J_{4,5B}$ = 1.5-2.0 Hz, and $J_{5A,5B}$ = 12.6-13.0 Hz.

†The signals of the OAc groups in the spectra of the compounds (XIX)-(XXVI) are present in the form of five singlets in the specified interval.

TABLE 4. Chemical Shifts in the ^{13}C NMR Spectra of β-,α-L-arabinopyranoses [7], Methyl β- and α-L-arabinopyranosides (I) and (II), and Methyl β- and α-L-Arabinopyranosyl Biosides (XXVII)-(XXXIV) (the solutions in D_2O, the internal standard CH_3OH, 50.15 ppm from TMS)

Compound	C1'	C2'	C3'	C4'	C5'	C1	C2	C3	C4	C5	OMe
β-*L*-Ara						93,7	69,6	69,8	69,8	63,5	
α-*L*-Ara						97,8	73,0	73,5	69,6	67,5	
(I)						101,2	69,4	70,1	70,1	63,8	56,5
(II)						105,1	71,7	73,4	69,3	67,1	58,1
(XXXIV)	105,5	72,3	73,4	69,4	67,2	105,0	71,0	82,7	69,2	66,9	58,1
(XXX)	105,6	72,3	73,4	69,5	67,2	101,1	68,6	79,6	69,9	63,4	56,5
(XXXII)	105,9	72,3	73,5	69,4	67,3	105,1	72,3	78,5	79,2	66,6	58,2
(XXVIII)	105,9	72,4	73,6	69,5	67,3	101,5	69,9	70,3	80,1	63,1	56,6
(XXXIII)	97,3	69,4	70,0	70,2	64,3	105,2	70,4	78,6	66,1	67,2	58,2
(XXIX)	97,0	69,5	70,0	70,2	64,3	101,2	67,9	75,2	66,6	63,4	56,5
(XXXI)	97,85	69,6	70,0	70,1	64,4	105,2	72,0	72,9	74,6	63,4	58,2
(XXVII)	97,65	69,6	70,0	70,1	64,4	101,1	69,5	69,6	75,3	60,4	56,6

TABLE 5. Effects of Glycosylation in the ^{13}C NMR Spectra of the Disaccharides (XXVII)-(XXXIV) and Galactopyranosylbioses [10-13]

Disaccharides	β-Effect	α-Effect	β-Effect	α-Effect
1→3-Linked Disaccharides				
α-*L*-Arap-*L*-Arap, α-Me	−0,75(2)	+9,30(3)	−0,20(4)	+7,70(1)
α-*L*-Arap-*L*-Arap, β-Me	−0,8(2)	+9,75(3)	−0,1(4)	+7,8(1)
β-*D*-Galp-*D*-Galp, α,β-OH	−1,3(2)	+9,9(3)	−0(4)	+7,9(1)
β-*L*-Arap-*L*-Arap, α-Me	−1,4(2)	+5,15(3)	−3,3(4)	+3,6(1)
β-*L*-Arap-*L*-Arap, β-Me	−1,5(2)	+5,3(3)	−3,35(4)	+3,3(1)
α-*D*-Galp-*D*-Galp, α-OH	−1,7(2)	+6,0(3)	−4,4(4)	+3,0(1)
1→4-Linked Disaccharides				
α-*L*-Arap-*L*-Arap, α-Me	+0,1(3)	+9,8(4)	−0,75(5)	+8,1(1)
α-*L*-Arap-*L*-Arap, β-Me	+0,4(3)	+10,1(4)	−0,7(5)	+8,1(1)
β-*D*-Galp-*D*-Galp, α,β-OH	+0,6(3)	+9,0(4)	−1,4(5)	+8,1(1)
β-*L*-Arap-*L*-Arap, α-Me	−0,5(3)	+5,2(4)	−3,85(5)	+4,15(1)
β-*L*-Arap-*L*-Arap, β-Me	−0,1(3)	+5,3(4)	−3,45(5)	+3,95(1)
α-*D*-Galp-*D*-Galp, α,β-OH	−1,3(3)	+8,3(4)	−0,2(5)	+8,7(1)

The data of Table 4 clearly confirm the correctness of the assignment of the signals in the ^{13}C NMR spectra of synthetic arabinans carried out in the preceding work [1]: The C^1 signal of the arabinopyranose residue participating in the 1,2-cis-glycosidic bond is located in the interval of 97.0-97.85 ppm.

EXPERIMENTAL

The PMR and ^{13}C NMR spectra were taken on a Bruker WM-250 (250 MHz, West Germany) instrument. The optical rotation was measured on a Perkin–Elmer-141 polarimeter. The mps were determined on a Kofler stage. The column chromatography was performed on silica gel of type L 100/160 (Czechoslovakia). The TLC was performed on silica gel of type L 5/40 (Czechoslovakia) in the systems: benzene–ether, 1:1 (A), chloroform–methanol, 4:1 (B), and chloroform–acetone, 7:3 (C). The detection of substances on TLC was performed with 5% H_2SO_4 in MeOH with heating to 200°C. The solutions were concentrated in vacuo with a water-jet pump at $\leqslant$45°C. The preparation of the solvents for glycosylation was performed as previously described [15].

Methyl β- (I) and Methyl α-L-Arabinopyranoside (II). The methyl glycoside (I) was obtained by the methanolysis of L-arabinose [2]; after recrystallization from MeOH, it had $[\alpha]_D$ +246, :C 1.5, H_2O) and mp 170°C. The α-L isomer (II) was synthesized under the conditions of the Koenigs–Knorr reaction [3]. We dissolved 5 g of the acetate of L-arabanopyranosyl bromide in the mixture of 50 ml of MeOH and 20 ml of CH_2Cl_2. We added 5 g of drierite $CaSO_4$ and 5 g of Ag_2CO_3. The mixture was stirred for 20 h at ∿20°C and filtered through. The residue on the filter was washed with 50 ml of chloroform; the filtrate was concentrated, and

the residue was dried. It was dissolved in 30 ml of MeOH prior to the addition of 2 ml of 1 N MeONa. After 15 h, the mixture was treated with KU-2 (H^+) and concentrated. The syrup was crystallized from EA. The yield of (II) was 1.89 g (78%), mp 133°C, $[\alpha]_D$ +18° (C 2.0, H_2O).

Methyl β- (III) and Methyl α-3,4-O-Isopropylidene-L-arabinopyranoside (IV). We stirred 5 g of (I) in 20 ml of 2,2-dimethoxypropane for 5 h with 100 mg of TsOH. The mixture was applied to a column with dry silica gel L 100/160 of 2 by 3 cm, and washed with 400 ml of C_6H_6. The solution was concentrated, and the residue was dissolved in ether and filtered through. The filtrate was concentrated. The syrupy product obtained had a yield of 5.95 g (95%). It was discrete on TLC, R_f 0.45 (A), $[\alpha]_D$ +195° (C 5.2, $CHCl_3$) (ef. [16]).

Under analogous conditions, 6 g of (II) yielded 5.85 g (79%) of (IV) in the form of a crystallized syrup. The recrystallization from the 1:9 mixture of EA–heptane gave the crystalline product with mp 130°C, $[\alpha]_D$ +31.3° (C 6.3, $CHCl_3$). Found: C 52.75; H 7.74. $C_9H_{16}O_5$. Calculated: C 52.95; H 7.84%.

Methyl β- (V) and Methyl α-2-O-Acetyl-3,4-O-isopropylidene-L-arabinose (VI). To 5.95 g of (III) in 20 ml of pyridine was added 5 ml of Ac_2O; the mixture was maintained for 15 h at ∿20°C. We added 5 ml of MeOH, and evaporated the mixture after 30 min. The syrupy (V) was obtained with a yield of 7.2 g (100%), R_f 0.80 (A), crystallized from pentane, mp 75°C, $[\alpha]_D$ +122° (C 1.5, H_2O) (cf. [16]).

Having subjected 5.85 g of (IV) to the analogous conversion, we obtained 7.0 g (99%) of (VI), R_f 0.75, $[\alpha]_D$ +1.3° (C 1.3, $CHCl_3$), mp 57°C (hexane). Found: (VI); C 53.53; H 7.36%. $C_{11}H_{18}O_6$. Calculated: C 53.55; H 7.32%.

Methyl β- (VII) and Methyl α-2-O-Acetyl-L-arabinopyranoside (VIII). We maintained 2.0 g of (V) in 10 ml of 60% AcOH at ∿20°C for 20 h, and concentrated with toluene to dryness. We obtained 1.7 g of the product with R_f 0.65 containing insignificant admixtures with R_f 0.85 [the initial (V)] and R_f 0.30 (I) (B). By means of chromatography on a column 2.5 by 25 cm eluting with EA, we isolated 1.3 g (78.3%) of (VII), a syrup, $[\alpha]_D$ +203° (C 5.1, $CHCl_3$) (cf. [17]), a syrup, $[\alpha]_D$ +197° (C 0.91, $CHCl_3$), and material with mp 172°C, $[\alpha]_D$ +252.2° (C 1.0, H_2O) (cf. [16]).

We maintained 7 g of (VI) in 10 ml of 90% CF_3COOH for 5 min at ∿20°C, and concentrated with toluene. The mixture was chromatographed on a column 5 by 40 cm in EA. We obtained 5.2 g (89%) of (VIII) in the form of a crystallizing syrup, R_f 0.65 (B), mp 110°C (from EA), $[\alpha]_D$ −28° (C 1.5, $CHCl_3$). Found: C 46.61; H 6.78%. $C_8H_{14}O_6$. Calculated: C 46.56; H 6.79%.

Tritylation of the Diols (VII) and (VIII). We dissolved 1.46 g (7 mmoles) of (VII) and 2.4 g (7 mmoles) of $TrClO_4$ in 40 ml of CH_2Cl_2 containing 1.18 ml (9 mmoles) of 2,4,6-collidine, and maintained the mixture at ∿20°C for 10 min (until the disappearance of the yellow color of $TrClO_4$). We diluted the mixture with 50 ml of $CHCl_3$, washed with H_2O (30 ml threefold), dried, and concentrated. The residue was chromatographed on a column 3 by 40 cm in the system benzene–ether with a gradient to 20% ether. We obtained 0.85 g (27%) of methyl 2-O-acetyl-4-O-trityl-β-L-arabinopyranoside (IX), 0.70 g (22%) of methyl 2-O-acetyl-3-O-trityl-β-L arabinopyranoside (X), and 0.2 g (6%) of the 1:1 mixture of (IX) and (X). After crystallization from MeOH, we isolated 0.8 g of (IX) with R_f 0.60 (A), mp 220°C, $[\alpha]_D$ +132° (C 4.3, $CHCl_3$). After crystallization from the 1:1 mixture of benzene–hexane, we obtained 0.5 g of (X) with R_f 0.57 (A), mp 155°C, $[\alpha]_D$ +73.5 (C 2.0, $CHCl_3$). Found: (IX), C 72.23 and H 6.26; (X), C 71.95 and H 6.17%. $C_{27}H_{28}O_6$. Calculated: C 72.25 and H 6.25%.

By analogy to this description, 2.42 g (12 mmoles) of (VIII) and 4 g (11.6 mmoles) of $TrClO_4$ in 70 ml of CH_2Cl_2 with 1.96 ml (15 mmoles) of 2,4,6-collidine yielded 6.34 g of the syrupy product which was chromatographed on a column 3 by 40 cm in the system benzene–ether with the gradient of ether to 10%. We obtained 4.25 g (80%) of methyl 2-O-acetyl-4-O-trityl-α-L-arabinopyranoside (XI) with R_f 0.70 (A), $[\alpha]_D$ −29.6° (C 2.6, $CHCl_3$) and 0.25 g (4.7%) of methyl 2-O-acetyl-3-O-trityl-α-L-arabinopyranoside (XII) with R_f 0.68 (A), $[\alpha]_D$ −22.0° (C 1.1, $CHCl_3$), in the form of syrups.

Methyl 2,4-Di-O-acetyl-α-L-Arabinopyranoside (XIII). To the solution of 650 mg (3.1 mmoles) of (VIII) in 3 ml of pyridine was added 0.3 ml of Ac_2O (3.2 mmoles) in dry $CHCl_3$ (3 ml). After 24 h, we added 1 ml of MeOH and concentrated to a syrup after 30 min. The syrup was chromatographed on a column 2 by 30 cm with benzene → ether–benzene (1:4) → acetone. We obtained 130 mg of (XIII) with R_f 0.70 (B), mp 120°C (ether–petroleum ether, 1:1), $[\alpha]_D$ −6.2° (C 1.3, $CHCl_3$), 140 mg of the 2,3-di-O-acetyl isomer (XIIIa) with R_f 0.67 (B),

syrup, $[\alpha]_D$ −7.5° (C 1.8, $CHCl_3$), 30 mg of the mixture of the di-O-acetates (2:1), and 380 mg (58%) of the initial (VIII). Found: (XIII), C 48.25; H 6.40%. $C_{10}H_{16}O_7$. Calculated: C 48.35; H 6.45%.

Methyl 2-3-Di-O-acetyl-4-O-trityl-β-L-arabinopyranoside (XIV). We added 1 ml of Ac_2O to 500 mg of (IX) in 2 ml of pyridine, and maintained the mixture at ∿20°C for 20 h. We added 3 ml of MeOH and concentrated with benzene after 30 min. We obtained 520 mg (95%) of (XIV) with R_f 0.80 (A), mp 152°C (MeOH), $[\alpha]_D$ +150°C (C 4.2, $CHCl_3$). Found: C 71.03; H 6.20%. $C_{29}H_{30}O_7$. Calculated: C 70.97; H 6.12%.

Methyl 2,4,-Di-O-acetyl-3-O-trityl-β-L-arabinopyranoside (XV). The solution of 500 mg of (X) in 2 ml of pyridine was treated as described above for (XIV), and we obtained 510 mg (93.5%) of a crystallizing syrup with R_f 0.78 (A). The recrystallization from MeOH gave 410 mg of (XV) with mp 204°C, $[\alpha]_D$ +97° (C 6.8, $CHCl_3$) (cf. [18] for the D-enantiomer: mp 202-203°C, $[\alpha]_D$ −107.6°, $CHCl_3$). Found: C 71.04; H 6.24%. $C_{29}H_{30}O_7$. Calculated: C 70.97; H 6.12%.

Methyl 2,3-Di-O-acetyl-4-O-trityl-α-L-arabinopyranoside (XVI). By means of the acetylation of 1.80 g of (XI) analogously to (IX), we obtained 1.90 g (97%) of (XVI) after the chromatography on a column 3 by 40 cm in the system benzene–ether with the gradient to 6%. Compound (XVI) had R_f 0.80 (A), mp 112°C (ether–heptane, 1:9), $[\alpha]_D$ −2.5° (C 1.5, $CHCl_3$). Found: C 70.83; H 6.27%. $C_{29}H_{30}O_7$. Calculated: C 70.97; H 6.12%.

Methyl 2,4-Di-O-acetyl-3-O-trityl-α-L-arabinopyranoside (XVII). The solution of 250 mg (1 mmole) of (XIII) in 5 ml of CH_2Cl_2 with 0.25 ml (1.9 mmoles) of 2,4,6-collidine was stirred with 0.52 g (1.5 mmoles) of $TrClO_4$ until solution, and left at ∿20°C for 2 h. We added 1 ml of aqueous pyridine and evaporated. After the chromatography on a column 1.5 by 25 cm in the system C_6H_6 → C_6H_6–ether (94:6), we isolated 450 mg (92%) of (XVII) with R_f 0.82 (A), mp 187°C, $[\alpha]_D$ +17° (C 1.1, $CHCl_3$). Found: C 71.04; H 6.25%. $C_{29}H_{30}O_7$. Calculated: C 70.97; H 6.12%.

Glycosylation of the Trityl Ethers (XIV)-(XVII) with the Acetal (XVIII). The solution of 340 mg (0.7 mmole) of (XIV) in 1 ml of C_6H_6 was placed into two Y-shaped ampuls (in one of the outlets). We added 180 mg (0.63 mmole) of (XVIII) in 1 ml of C_6H_6 in equal parts to these outlets; we added 22 mg (0.064 mmole) of $TrClO_4$ in 0.5 ml of CH_3NO_2 to the other outlets. The solutions were lyophilized and dried in vacuo ($4 \cdot 10^{-3}$ mm). After this, 1 ml of CH_2Cl_2 was passed into each of the ampuls. The contents of the outlets were mixed after the complete solution and left at ∿20°C for 20 h. Then we added portions of 0.5 ml of the 1:3 mixture of MeOH–pyridine into each ampul, and 30 ml of $CHCl_3$ was added to each. After mixing the contents of both ampuls, we washed with water (30 ml threefold), and the organic layer was dried and evaporated. The mixture was chromatographed on a column 2 by 30 cm in the system benzene → EA. We obtained 15 mg of methyl 2,3-di-O-acetyl-4-O-(2,3,4-tri-O-acetyl-β-L-arabinopyranosyl)-β-L-arabinopyranoside (XIX), crystallizing on evaporation. Compound (XIX) had mp 193.5° (MeOH), R_f 0.40 (A), $[\alpha]_D$ +302.5° (C 5.0, $CHCl_3$). We also obtained 75 mg of methyl 2,3-di-O-acetyl-4-O-(2,3,4-tri-O-acetyl-α-L-arabinopyranosyl)-β-L-arabinopyranoside (XX), a syrup with R_f 0.38 (A), $[\alpha]_D$ +78.5° (C 1.0, $CHCl_3$) and 100 mg of the mixture of (XIX) and (XX) in the ratio of 5:95. We recovered 60 mg of the initial trityl ether. The total yield of the disaccharide product was 66%, with the ratio of 11.5:88.5. Found: (XIX), C 49.87; H 5.88%. $C_{21}H_{30}O_{14}$. Calculated: C 49.80; H 5.93%.

Methyl 2,4-Di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-β-L-arabinopyranosyl)-β-L-arabinopyranoside (XXI) and Methyl 2,4-Di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-arabinopyranosyl)-β-L-arabinopyranoside (XXII). By the glycosylation of 340 mg of (XV) with the aid of 180 mg (XVIII) in the presence of 22 mg of $TrClO_4$, as described above, we obtained 10 mg of (XXI) with mp 211°C (MeOH), $[\alpha]_D$ +148° (C 0.3, $CHCl_3$), R_f 0.40 (A), 185 mg of (XXII) with mp 154°C (heptane–EA, 2:1), $[\alpha]_D$ +89.3° (C 2.0, $CHCl_3$), and 10 mg of the mixture of (XXI) and (XXII) (1:2). The total yield of the disaccharides was 62%, with the ratio of 3:47. Found: (XXI), C 49.32; H 5.92%; (XXII), C 49.52; H 5.90%.

The glycosylation of 130 mg (0.26 mmole) of (XV) by the acetal (XVIII) (63 mg, 0.22 mmole) in the presence of 7.5 mg (0.022 mmole) of $TrBF_4$ as the catalyst led to the formation of 41 mg (30%) of the mixture of the disaccharides (XXI) and (XXII) in the approximate ratio of 1:7. By the chromatography of the mixture, we managed to isolate the individual compounds (XXI) with mp 210.5°C, $[\alpha]_D$ +156° (C 0.3, $CHCl_3$) and (XXII) with mp 154°C, $[\alpha]_D$ +88° (C 2.6, $CHCl_3$).

Methyl 2,3-Di-O-acetyl-4-O-(2,3,4-tri-O-acetyl-β-L-arabinopyranosyl)-α-L-arabinopyranoside (XXIII) and Methyl 2,3-Di-O-acetyl-4-O-(2,3,4-tri-O-acetyl-α-L-arabinopyranosyl)-α-L-arabinopyranoside (XXIV). These compounds were synthesized from 550 mg (1.1 mmoles) of (XVI) in the ampuls with 290 mg (1 mmoles) of (XVIII) and 34 mg (0.1 mmole) of $TrClO_4$. We obtained 420 mg (83%) of the 1:9 mixture of (XXIII) and (XXIV). After chromatography, we obtained the individual compounds (XXIII) (a syrup, $[\alpha]_D$ +147.5° (C 3.9, $CHCl_3$)) and (XXIV) with mp 176.5°C (EA–hexane, 1:1, $[\alpha]_D$ +13.8° (C 1.4, $CHCl_3$). Found (XXIV), C 49.63 H 5.91%.

Methyl 2,4-Di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-β-L-arabinopyranosyl)-α-L-arabinopyranoside (XXV) and Methyl 2,4-Di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-arabinopyranosyl)-α-L-arabinopyranoside (XXVI). These compounds were obtained by the glycosylation of 400 ml of the ether (XVII) by the acetal (XVIII) (240 mg) in the presence of 28 mg of $TrClO_4$. The yield of the 1:4 mixture of the disaccharides (XXV) and (XXVI) was 300 mg (73%). After column chromatography, we isolated the individual compounds (XXV), a syrup with $[\alpha]_D$ +115° (C 2.3, $CHCl_3$) and (XXVI) with mp 70°C (ether–petroleum ether, 1:1), $[\alpha]_D$ +1.78° (C 4.8, $CHCl_3$). Found: (XXVI), C 49.54; H 5.92%.

The Zemplen deacetylation of the disaccharides (XIX)-(XXVI) yielded the arabinopyranosyl biosides: methyl 4-O-(β-L-arabinopyranosyl)-β-L-arabinopyranoside (XXVII), a syrup with $[\alpha]_D$ +225° (C 0.8, MeOH); methyl 4-O-(α-L-arabinopyranosyl)-β-L-arabinopyranoside (XXVIII) with mp 290°C (MeOH), $[\alpha]_D$ +168° (C 2.8, H_2O). Found: C 44.57; H 6.81%. $C_{11}H_{20}O_9$. Calculated: C 44.55; H 6.76%. Methyl 3-O-(α-L-arabinopyranosyl)-β-L-arabinopyranoside (XXX) with mp 194°C (MeOH), $[\alpha]_D$ +156° (C 0.8, H_2O). Found: C 44.61; H 6.78%. Methyl 4-O-(β-L-arabinopyranosyl)-α-L-arabinopyranoside (XXXI) was a syrup with $[\alpha]_D$ +111° (C 3.2, MeOH). Methyl 4-O-(α-L-arabinopyranosyl)-α-L-arabinopyranoside (XXXII) had mp 185°C (EtOH), $[\alpha]_D$ + 37.8° (C 5.2, H_2O). Found: C 44.55; H 6.84%. Methyl 3-O-(β-L-arabinopyranosyl)-α-L-arabinopyranoside (XXXIII) was a syrup with $[\alpha]_D$ +140° (C 2.6, MeOH). Methyl 3-O-(α-L-arabinopyranosyl)-α-L-arabinopyranoside (XXXIV) had mp 211°C (EtOH), $[\alpha]_D$ +34.4° (C 3.9, H_2O). Found: C 44.51; H 6.97%.

CONCLUSIONS

The 3-O- and 4-O-trityl ethers of the acetates of methyl α-L- and methyl β-L-arabinopyranosides were synthesized. The glycosylation of the ethers with the aid of 3,4-di-O-acetyl-1,2-O-(1-exo-cyano)ethylidene-β-L-arabinopyranose and the subsequent deacetylation of the synthesized products yielded the disaccharides: methyl 4-O-(β-L-arabinopyranosyl)-, methyl 4-O-(α-L-arabinopyranosyl)-, and methyl 3-O-(α-L-arabinopyranosyl)-β-L-arabinopyranoside; and methyl 4-O-(β-L-arabinopyranosyl)-, methyl 4-O-(α-L-arabinopyranosyl)-, methyl 3-O-(β-L-arabinopyranosyl)-, and methyl 3-O-(α-L-arabinopyranosyl)-α-L-arabinopyranoside.

The assignment of the signals in the PMR and ^{13}C NMR spectra of the synthesized arabinopyranosyl biosides was carried out, allowing the determination of the type and configuration of the glycosidic bond by means of which the arabinopyranose residues are linked in the oligo- and polysaccharide chains.

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