HYDROXYLATION OF 6-SUBSTITUTED 2,7-DIOXABICYCLO[3.2.0]HEPT-3-ENES. THE SYNTHESIS OF ANALOGS OF 3-DEOXY-DL-STREPTOSE*

Tadeusz KOZLUK and Alexander ZAMOJSKI

Institute of Organic Chemistry,
Polish Academy of Sciences, 01-224 Warszawa, Poland

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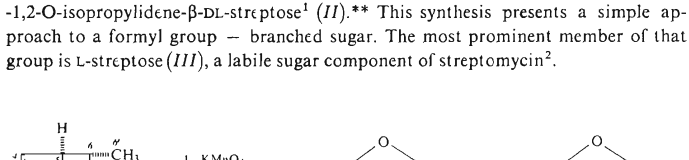
Hydroxylation of 6-substituted 2,7-dioxabicyclc[3.2.0]hept-3-enes (*I*, *XIV* and *XV*) with *m*-chlc roperoxybenzoic acid occurs mainly from the *exo* side and leads to the corresponding 3-*m*-chlorobenzoates of *trans*-3,4-diols (*VI*, *XVIII* and *XXII*). Hydroxylation of substrates *XIV* and *XV* with potassium permanganate leads to 3-deoxy-3-C-formyl-DL-*arabino*-aldofuranoses. Epimerization at the formyl group–bearing carbon atom occurs during the reorganizatcn of dihydroxylated dioxabicycloheptanes in basic medium.

We have shown recently that hydroxylation of the double bond in 6-methyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (*I*) – followed by isopropylidenation – leads to 3-deoxy--1,2-O-isopropylidene-β-DL-streptose[1] (*II*).** This synthesis presents a simple approach to a formyl group – branched sugar. The most prominent member of that group is L-streptose (*III*), a labile sugar component of streptomycin[2].



I *II* *III*

Bicyclic substrate *I* has the 5*RS* : 6*SR* configuration.*** After hydroxylation from the more accessible *exo* side of the double bond the product *V* formed after reorgani-

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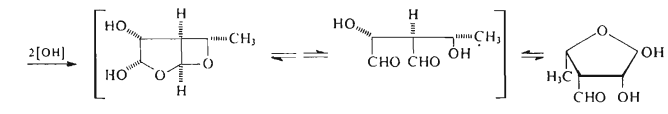
** The formulae in this paper represent sugars belonging to L series in order to facilitate comparison with L-streptose. In reality, all compounds obtained were racemates.

*** Strictly: 1*RS* : 5*RS* : 6*SR*. For our discussion the configuration at $C_{(1)}$ is not important, as the chirality of that atom is lost after conversion into formyl group.

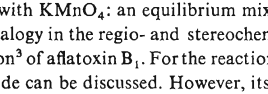
zation of hemiacetal systems should possess the 2*RS* : 3*RS* : 4*SR* configuration.* However, we have shown that a spontaneous epimerization at $C_{(3)}$ of the furanose must occur during the formation of branched-chain sugar[1].



IV *V*

In the present paper a continuation of study of various routes leading to 3-deoxy--3-C-formylaldose system is described. The epimerization reaction is examined and the synthesis of analogs of 3-deoxy-DL-streptose is accomplished.

For the conversion of *I* into 3-deoxy-DL-streptose (*II*) a solution of potassium permanganate in aqueous acetone was employed[1]. We wanted to check the course of hydroxylation of *I* under different conditions. Firstly, a solution of *m*-chloroperoxybenzoic acid in an aprotic solvent was taken. The reaction proceeded readily and furnished two products. The main product *VI*, obtained in *c.* 60% yield, was an ester of *m*-chlorobenzoic acid of a vicinal diol formed directly from *I*. Compound *VI* yielded readily a monoacetyl derivative *VII*. The constitution and configuration of *VI* and *VII* could be deduced from their ^{1}H NMR spectra. The other product of hydroxylation, obtained in only 3% yield, was identical – according to TLC – with that formed[1] from *I* with $KMnO_4$: an equilibrium mixture *IV* ⇌ *V*. The formation of *VI* finds a close analogy in the regio- and stereochemical results of *m*-chloroperbenzoic acid of oxidation[3] of aflatoxin B_1. For the reaction leading to *VI* a transient formation of an *exo* epoxide can be discussed. However, its existence cannot be proved directly.

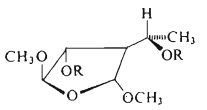


VI: R = H
VII: R = CH_3CO

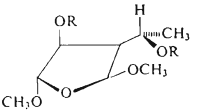
Hydroxylation of 2,3-dihydrofuran with *m*-chloroperbenzoic acid in alcoholic solution leads to *trans*-2-alkoxy-3-hydroxytetrahydrofurans[4]. An analogous reaction performed in methanol led in the case of *I* to three products obtained in 79% overall

* Note the change of numbering system on passing from the bicyclo[3.2.0]hept-3-ene to furanose. Carbon atom No 4 of the bicyclic system becomes No 2 in the furanose. Similarly No 5 becomes No 3 and No 6 – No 4.

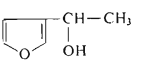
yield. Compounds *VIII* and *IX*, formed in a proportion of 4 : 1, were the main products; the third, obtained in trace amount only, was identified as 1-(3'-furyl) ethanol (*X*). Compounds *VIII* and *IX* gave diacetyl derivatives *XI* and *XII*, respectively. On the basis of analytical and ^{1}H NMR data the structures shown below could be assigned.



VIII: R = H
XI: R = CH_3CO



IX: R = H
XII: R = CH_3CO

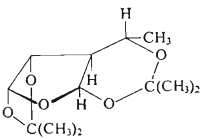


X

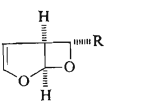
It is clear that the preponderant product *VIII* resulted from the *exo* attack of *m*-chloroperbenzoic acid on *I*. The transient, unstable epoxide was immediately opened with methanol. That reaction was subsequently followed by opening of the oxetane ring. The other product *IX* stemmed from the more hindered *endo* attack of the peroxyacid on the double bond, followed by similar openings of the three- and four-membered rings. The third compound *X* was a product of the acid-catalyzed isomerization of the substrate *I* (ref.[5]). The amount of *X* points at the negligible importance of that process. It is worth of noting here that isomerization of bicyclic substrates with *p*-toluenesulfonic or hydrochloric acid presents a convenient method of preparing 3-furylmethanols in good yield[5].

Acid hydrolysis of *VIII* followed by a reaction with acetone gave a diisopropylidene derivative *XIII* in 26% yield. This compound was obtained earlier[1] as a side-product during the synthesis of *II*.

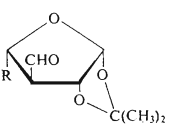
The relative configuration of all chiral centers of *XIII* is the same as in the substrate *VIII*. This demonstrates that no epimerization at the branching occurs under conditions of acid catalysis.



XIII



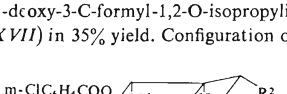
XIV: R = C_6H_5
XV: R = CH_2OCH_3



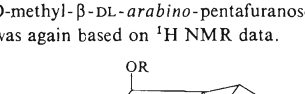
XVI: R = C_6H_5
XVII: R = CH_2OCH_3

Successful transformation of *I* into 3,5-dideoxy-3-C-formyl-DL-pentose system opened the possibility of synthesizing analogs of *II* (or *V*) *via* the hydroxylation

reaction of other 6-substituted 2,7-dioxabicyclo[3.2.0]hept-3-enes. For that purpose we employed 6-phenyl and 6-methoxymethyl derivatives *XIV* and *XV*. Hydroxylation of *XIV* with water–acetone solution of potassium permanganate followed by conversion of the product into a 1,2-O-isopropylidene derivative led to a single compound *XVI* in 36% yield. ^{1}H NMR spectrum of that product was strikingly similar to that of *II* and on that basis the structure of 3-deoxy-3-C-formyl-1,2-O-isopropylidene--4-C-phenyl-β-DL-*arabino*-tetrafuranose was assigned. Hydroxylation of *XV* and isopropylidenation of the product followed a fully analogous course and furnished 3-deoxy-3-C-formyl-1,2-O-isopropylidene-5-O-methyl-β-DL-*arabino*-pentafuranose *XVII*) in 35% yield. Configuration of *XVII* was again based on ^{1}H NMR data.



XVIII: $R^1 = H$, $R^2 = C_6H_5$
XX: $R^1 = CH_3CO$, $R^2 = C_6H_5$
XXII: $R^1 = H$, $R^2 = CH_2OCH_3$



XIX: R = H
XXI: R = CH_3CH

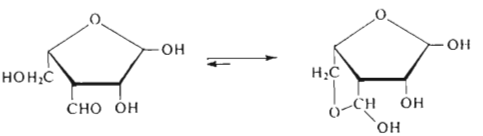
Hydroxylation of *XIV* with *m*-chloroperbenzoic acid in dichloromethane afforded two isomeric products *XVIII* and *XIX* in *c.* 68% overall yield in a proportion of *c.* 20 : 1. Both compounds were mono-*m*-chlorobenzoates of vicinal diols. The ^{1}H NMR spectrum of *XVIII* displayed a close analogy with the spectrum of *VI* and on that basis a similar structure was assigned to *XVIII*. Compound *XVIII* formed readily a monoacetyl derivative *XX*. The minor product *XIX* gave a monoacetyl derivative *XXI*. The ^{1}H NMR spectra of *XIX* and *XXI* permitted the assignment of the alternative monoester *trans*-1,2-diol structure to *XIX*, thus confirming the *endo*-attack of *m*-chloroperbenzoic acid on the substrate.

Deesterification of *XVIII* followed by isopropylidenation led to *XVI* in 37% yield. This experiment showed that epimerization of the formyl group occurs most probably during reorganization of the hemiacetal systems in basic medium.

The reaction of *XV* with *m*-chloroperbenzoic acid in dichloromethane led to a single product *XXII* to which a configuration analogous to *XVIII* was ascribed. Removal of the ester residue in *XXII* and acetonation of the product furnished furanose *XVII*.

Thus, for the synthesis of analogs of 3-deoxy-DL-streptose two routes can be envisaged. One of them consists in $KMnO_4$ hydroxylation of 6-substituted 2,7-dioxabicyclo[3.2.0] hept-3-enes, the other in *m*-chloroperbenzoic acid oxidation of the substrates followed by deesterification of the ester–diol formed. In both cases epimerization occurs at the carbon atom bearing the liberated formyl group. The spontaneous inversion of configuration finds analogy in a similar process described in literature[6]. We had shown[1] that if there is a chance of stabilization of the original configuration in the hydroxylated, bond-reorganized product, *e.g.* by formation

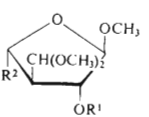
of an additional hemiacetal ring (as in *XXIII*), the epimerization process is fully restrained.



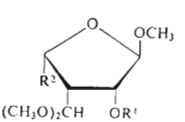
XXIII

In *XV* the hydroxyl group is converted into a methyl ether and, consequently, *XV* is transformed after hydroxylation into the epimerized product *XVII*.

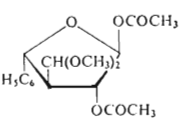
We wanted, however, to obtain a direct proof of the epimerization process by obtaining both products with retained and inverted configuration in a single transformation. For that purpose *m*-chlorobenzoate *XVIII* was deacylated with sodium methoxide in methanol under controlled conditions and the product was immediately, *in situ*, methylated in the presence of acidic resin. Two main products, *XXIV* and *XXV*, resulted. Both of them formed monoacetyl derivatives *XXVII* and *XXVIII*, respectively. Analytical data and ^{1}H NMR spectra of these products permitted the assignment of structures.



XXIV: $R^1 = H$, $R^2 = C_6H_5$
XXVII: $R^1 = Ac$, $R^2 = C_6H_5$
XXIX: $R^1 = H$, $R = CH_3$
XXXI: $R^1 = Ac$, $R^2 = CH_3$



XXV: $R^1 = H$, $R^2 = C_6H_5$
XXVIII: $R^1 = Ac$, $R^2 = C_6H_5$
XXX: $R^1 = H$, $R^2 = CH_3$
XXXII, $R^1 = Ac$, $R = CH_3$



XXVI

A third, low-yield product was also separated from the postreaction mixture and structure *XXVI* was ascribed to it on the basis of ^{1}H NMR spectrum.

It is evident that epimerization is a fast process occurring during reorganization of bond system in the basic medium. Methanolysis converting the formyl group into the dimethoxymethyl group stops the process of isomerization and both products can be isolated.

Similar "freezing out" of both epimers was performed for the *m*-chlorobenzoate *VI*. Repetition of the process described for *XVIII* gave two products *XXIX* and *XXX* in low yield. They were identified as methyl glycosides of 3,5-dideoxy-3-C-dimethoxymethyl-β-DL-pentofuranosides of the *arabino* and *lyxo* configuration.

Reactions described in this paper demonstrate a simple, synthetic approach to formyl group-branched sugars and to 3-deoxy-DL-streptose system in particular. This stresses the value of substituted 2,7-dioxabicyclo[3.2.0]hept-3-enes as useful synthons in chemistry.

EXPERIMENTAL

^{1}H NMR spectra were recorded with Jeol JNM-4H-100 (100 MHz) spectrometer. Mass spectra were obtained with a LKB 2091 mass spectrometer. For column chromatography silica gel 230–400 mesh Merck and for thin layer chromatography silica gel H Merck were employed.

6-Methyl and 6-phenyl-2,7-dioxabicyclo[3.2.0]hept-3-enes (*I* and *XIV*) were prepared according to ref.[7]. Methyl ether *XV* was obtained by methylation (NaH, CH_3I; 94% yield) of 6-hydroxymethyl-2,7-dioxabicyclo-[3.2.0]hept-3-ene[1–6].

(3*SR*)-(*m*-Chlorobenzoyloxy)-(4*RS*)-hydroxy-(6*SR*)-methyl-(1*SR*,5*RS*)-2,7-bicyclo[3.2.0]-heptane (*VI*)

In a solution of *I* (1·2 g) in 20 ml of dichloromethane sodium hydrogen carbonate (2 g) was suspended and a solution of *m*-chloroperoxybenzoic acid (1·9 g) in dichloromethane (5 ml) was slowly at 0° under stirring. After 2 h the mixture was filtered and the solvent was evaporated.

TABLE I

^{1}H NMR spectra ($CDCl_3$) of compounds *VI*–*XII*, *XIV*, *XV* and *XVIII*–*XXII*

Compound	H-1	H-3	H-4	H-5	H-6	$J_{3,4}$	$J_{4,5}$	$J_{1,5}$	$J_{5,6}$	Others
XIV[a]	6·47	6·63	5·38	3·57	5·50	2·9	2·9	4·4	2·9	$J_{1,3}$ = 0·8 $J_{3,5}$ = 0·8
XV	6·29	6·61	5·31	3·63	4·65	2·5	2·5	4·5	3·2	$J_{1,3}$ = 0·8 $J_{3,5}$ = 0·5
VI	6·15	6·65	4·60	3·08	4·66	0	0	3·8	4·0	—
VII	5·96	6·59	5·24	3·00	4·68	0	0	3·8	4·0	—
XVIII	6·26	6·69	4·66	3·26	5·43	0	0	4·0	4·9	—
XXII	6·14	6·65	4·59	3·40	4·59	0	0	4·0	—	—
XIX	6·11	6·63	4·46	3·48	5·84	4·5	8·4	3·6	4·5	—
XXI	6·15	6·93	5·34	3·74	5·56	4·3	8·2	4·2	4·4	—
VIII	4·99	4·84	~3·80	1·93	~3·80	2·0	2·4	2·7	6·4	—
XI	5·02	4·98	4·86	2·19	5·15	1·5	3·0	3·2	6·5	—
IX[b]	5·25	4·70	4·15	2·15	4·15	0	5·4	5·5	3·5	—
XII[b]	5·10	4·70	5·08	2·15	5·06	0	5·2	5·4	8·8	—

[a] From ref.[7]. [b] In order to facilitate comparison of ^{1}H NMR data of compounds *VIII*–*XII* with those of bicyclic compounds the numbering system of the latter is left here. In the Experimental Part compounds *VIII*–*XII* are numbered properly.

The residue was chromatographed on a silica gel column with a mixture of benzene and ether 1 : 1 (v/v). Compound *VI*, oil, 1·86 g (59%). IR spectrum (film): 3 490 (OH), 1 729 (CO), 1 577 (C=C arom.), 1 115 (C—O—C) cm^{-1}. ^1H NMR spectrum: Table I. Acetyl derivative *VII* (obtained from *VI* with acetanhydride and pyridine). IR spectrum (film): 1 738 (CO), 1 576 (C=C arom.), 1 220, 1 160 (C—O—C) cm^1. ^1H NMR spectrum: Table I. For $C_{15}H_{15}ClO_6$ (326·7) calculated: 55·14% C, 4·63% H; found: 55·17% C, 4·63% H. The second compound eluted from the column in 3% yield displayed ^1H NMR spectrum identical with that of the substance (*IV*—*V*) obtained after $KMnO_4$ hydroxylation of *I* (ref.[1]). Also R_F-values of both substances on UC plates were identical.

(3*RS*)-Hydroxy-(4*RS*)-(1′*SR*-hydroxyethyl)-(2*RS*,5*RS*)dimethoxy- and
(3*SR*)-Hydroxy-(4*RS*)-(1′*SR*-hydroxyethyl)-(2*SR*,5*SR*)dimethoxyoxolanes (*VIII* and *IX*)

To a cooled (−10°C) solution of *I* (1·55 g) in methanol (20 ml) *m*-chloroperoxybenzoic acid (2·6 g) in 20 ml of methanol was added dropwise while stirring. After 12 h the solvent was evaporated and products were separated on a column. Three fractions were obtained: 1-(3′-Furyl)-ethanol (*X*) (*c.* 50 mg) identified by comparison of its ^1H NMR and IR spectra with those of an original sample[5] Compound *VIII* oil, 1·59 g (60%), b.p. 105°C/2·5 Pa. IR spectrum (film): 3 480 (OH), 1 095 (C—O—C) cm^{-1}. ^1H NMR spectrum: Table I. For $C_8H_{16}O_5$ (192·2) calculated: 49·99% C, 8·39% H; found: 49·98% C, 8·47% H. Acetyl derivative *XI* was obtained from *VIII* on the conventional way. The product was purified by chromatography. IR spectrum (film): 1 750 (CO), 1 240 (C—O—C acetyl), 1 102 (C—O—C) cm^{-1}. Mass spectrum (electron impact, 15 eV), *m/z* (rel. intensity): 275 (M^+-1,1), 245 (M^+-OCH_3,5), 156 (75), 129 (66), 114 (83), 113 (100). For $C_{12}H_{20}O_7$ (276·3) calculated: 52·16% C, 7·30% H; found: 52·16% C, 7·68% H. Compound *IX*, oil, 0·394 g (15%), b.p. 110°C/2 Pa. IR spectrum ($CHCl_3$): 3 490 (OH), 1 155, 1 105 (C—O—C) cm^{-1}. ^1H NMR spectrum: Table I. Mass spectrum (electron impact, 15 eV), *m/z* (rel. intensity): 161 (M^+-OCH_3,6), 129 (11), 114 (11), 87 (100). Acetyl derivative *XII* was obtained on the conventional way; dist. at 90°C/2·5 Pa. IR (film): 1 750 (CO), 1 215 (C—O—C acetyl), 1 110 (C—O—C) cm^{-1}. For $C_{12}H_{20}O_7$ (276·3) calculated: 52·16% C, 7·30% H; found: 51·99% C, 7·17% H.

7,8-O-Isopropylidene-3,(5*SR*)-trimethyl-(1*RS*,6*RS*)-
-2,4,9-trioxabicyclo[4.3.0]nona-(7*RS*,8*RS*)diol (*XIII*)

Dimethoxyoxolane *VIII* (0·384 g) was refluxed in 1% sulfuric acid (4 ml). After disappearance of the substrate (TlC, 8 h) the solution was evaporated and the residue was dissolved in acetone containing 0·1% sulfuric acid. After standing overnight the mixture was concentrated and the product *XIII* was purified on a silica gel column with benzene and ether 4 : 1 (*v/v*) used for elution, 0·073 g (15%), m.p. 55—56°C. Compound *XIII* was found to be identical (IR, ^1H NMR spectra, TLC) with an original sample[1].

3-Deoxy-3-C-formyl-1,2-O-isopropylidene-4-C-phenyl-β-DL-*arabinose*-tetrafuranose (*XVI*)

To a cooled (0°C) solution of potassium permanganate (1·58 g) and magnesium sulfate (3 g) in 300 ml of a mixture water and acetone 1 : 1 (v/v) bicycloheptene *XIV* (1·74 g) in 20 ml acetone was slowly added under stirring. After 2 h the mixture was filtered and the precipitate was washed with water. The combined filtrate was evaporated under reduced pressure. The residue was dissolved in acetone containing *c.* 5% sulfuric acid and left at room temperature overnight. The solution was thereafter neutralized with triethylamine, filtered and evaporated. The residue was

distilled at 110°C/2·5 Pa. A single product *XVI* was obtained, oil, 0·9 g (36%). IR spectrum (film): 1 722 (CHO), 1 605, (1 500 (C=C arom.) cm^{-1}. ^1H NMR spectrum: Table II. For $C_{14}H_{16}O_4$ (248·2) calculated: 67·72% C, 6·50% H; found: 67·54% C, 6·50% H.

3-Deoxy-3-C-formyl-1,2-O-isopropylidene-5-O-methyl-β-DL-*arabino*-pentofuranose (*XVII*)

The experiment was performed along the procedure described for compound *XVI*. From 0·71 g of *XV* 0·38 g (35%) of *XVII* was obtained, Oil, dist. at 85°/5 Pa. IR spectrum (film): 1 705 (CHO) cm^{-1}. ^1H NMR spectrum: Table II. For $C_{10}H_{16}O_5$ (216·2) calculated: 55·54% C, 7·46% H; found: 54·78% C; 7·62% H.

(3*SR*)-(*m*-chlorobenzoyloxy)-(4*RS*)-hydroxy- and
(3*RS*)-(*m*-chlorobenzoyloxy)-(4*SR*)-hydroxy-(6*RS*)-phenyl-(1*SR*),(5*RS*)-2,7-dioxabicyclo-[3.2.0]heptanes (*XVIII* and *XIX*)

In a solution of bicycloheptane *XIV* (7·0 g) in dichloromethane (80 ml) sodium hydrogen carbonate (10 g) was suspended and 7·7 g of *m*-chloroperoxybenzoic acid dissolved in 40 ml of the same solvent was gradually added at 0°C under stirring. After 24 h the solution was filtered, the precipitate was washed and the filtrate was evaporated under diminished pressure. The residue was chromatographed on a silica gel column with a mixture of benzene and ether 10 : 1 (v/v). Two products were obtained. Compound *XVIII*, oil, 9·05 (66%), non-distillable. ^1H NMR spectrum: Table I. For $C_{18}H_{15}ClO_5$ (346·8) calculated: 62·34% C, 4·36% H; found: 62·89% C, 4·45% H. Acetyl derivative *XX*, IR spectrum ($CHCl_3$): 1 732 (CO), 1 575 (C=C arom.) cm^{-1}. Compound *XIX*, oil, 0·41 g (3%), non-distillable. ^1H NMR spectrum: Table I. For $C_{18}H_{15}ClO_5$ (346·8) calculated: 62·34% C, 4·36% H; found: 62·89% C, 4·42% H. Acetyl derivative *XXI*, ^1H NMR: Table II.

TABLE II
H NMR data ($CDCl_3$) of compounds *XVI*, *XVII*, *XXIV*–*XXXII*[a]

Compound	H-1	H-2	H-3	H-3′	H-4	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{3,3'}$
XVI	5·88	5·07	3·47	9·75	5·34	4·0	2·3	6·2	0
XVII	5·77	5·04	3·40	9·61	4·43	4·0	1·7	4·4	0
XXIV	5·02	4·30	2·42	4·50	4·82	0	3·2	7·5	8·2
XXVII	5·02	5·10	2·52	4·62	4·90	0	1·5	6·0	9·0
XXIX	4·80	4·12	2·02	4·40	4·12	0	—	—	8·5
XXXI	4·79	4·97	2·02	4·45	4·03	0	2·4	6·0	8·8
XXVI	6·35	5·28	2·62	4·66	5·07	0	2·0	6·5	8·5
XXV	4·88	4·25	2·64	4·50	4·85	0	3·5	8·9	6·2
XXVIII	5·05	5·05	3·00	4·42	4·88	1·1	6·2	8·5	8·5
XXX	4·80	4·12	2·75	4·68	4·30	0	4·7	9·0	9·0
XXXII	4·79	5·01	2·95	4·59	4·36	0	4·9	8·5	9·2

[a] All other signals were found at typical δ values, *e.g.* C_6H_5: 7·35, OCH_3: 3·10–3·50.

(3*SR*)-(*m*-Chlorobenzoyloxy)-(4*RS*)-hydroxy-(6*RS*)-methoxymethyl-(1*SR*,5*RS*)-2,7-dioxabicyclo[3.2.0]-heptane (*XXII*)

Compound *XX* was obtained according to the procedure described for *XVIII* and *XIX*. From 1·42 g of *XV* 2·1 g (67%) of *XXII* was obtained, m.p. 114·5°—115·5°C. IR spectrum (nujol): 3 400 (OH), 1 730 (CO), 1 570 (C=C arom) cm^{-1}. ^1H NMR spectrum: Table I. For $C_{14}H_{15}ClO_6$ (314·7) calculated: 53·43% C, 4·80% H; found: 53·41% C, 4·89% H.

Methyl 3-Deoxy-3-C-dimethoxymethyl-4-C-phenyl-α-DL-*arabino*- and *lyxo*-tetrafuranosides (*XXIV* and *XXV*) and 1,2-Di-O-acetyl-3-deoxy-3-C-dimethoxymethyl-4-C-phenyl-α-DL-*arabino*-tetrafuranoside (*XXVI*)

To a stirred solution of sodium (0·05 g) in methanol (20 ml) compound *XVIII* (1·04 g) was added and the mixture was left for 20 min at room temperature. Thereafter 5 g of IR 120 resin was added and stirring was continued for 24 h. TLC showed the formation of three products. The resin was removed and the solution was evaporated. Separation of the residue on a silica gel column with ligroin–ether 4 : 1 (v/v) gave the following fractions: Compound *XXIV*, oil, 0·396 g (49·2%), b.p. 150°/2·5 Pa. IR spectrum (film): 3 480 (OH), 1 600, 1 500 (C=C arom.) 1 100, 1 060 (C—O—C) cm^{-1}. ^1H NMR spectrum: Table II. Acetyl derivative *XXVII* (prepared from *XXVI* on the conventional way), oil. IR spectrum (film): 1 745 (CO), 1 600, 1 500 (C=w arom.), 1 100 1 060 (C—O—C) cm^{-1}. ^1H NMR spectrum: Table II. For $C_{16}H_{22}O_6$ (310·2) calculated: 61·94% C, 7·10% H; found: 61·98% C, 7·45% H. Compound *XXV*, oil, 0·121 g (15%). IR spectrum (film): 3 500 (OH), 1 610, 1 500 (C=O arom.), 1 100, 1 060 (C—O—C) cm^{-1}. ^1H NMR: Table II. Acetyl derivative *XXVIII* (prepared from *XXV* on the conventional way), oil. IR spectrum (film): 1 740 (CO), 1 600, 1 500 (C=O arom.) 1 100, 1 060 (C—O—C) cm^{-1}. For $C_{16}H_{22}O_6$ (310·2) calculated: 61·94% C, 7·10% H; found: 61·74% C, 7·26% H. During chromatographic purification of *XXVIII* a third product was isolated and identified, as diacetylated derivative *XXVI*, 0·03 g (3%). ^1H NMR spectrum: Table II.

Methyl 3,5-Dideoxy-3-C-dimethoxymethyl-α-DL-*arabino*- and *lyxo*-Pentofuranosides (*XXIX* and *XXX*)

The experiment was performed as described for compounds *XXIV*—*XXVI*. From 0·852 g of *VI* a mixture of two products was obtained. Separation on a silica gel column with ligroin–ether 10 : 1 (v/v) furnished the pure components. Compound *XXX*, oil, 0·067 g (11%). ^1H NMR spectrum: Table II. The acetyl derivative *XXXII* was obtained from *XXX* in the usual manner (^1H NMR spectrum: Table II). For that compound experiments with nuclear Overhauser effect (NOE) were performed. The signal of methyl group at $C_{(4)}$ was irradiated with 20—60% of the power necessary for full decoupling of H-4. A distinct NOE (amounting to *c.* 11%) was observed for H-3′. This experiment confirmed unambiguously the *cis* relation of the methyl group at $C_{(4)}$ and H-3′, supporting the *lyxo* configuration of *XXXII* (and of *XXX*). Compound *XXIX*, oil, 0·031 g (5%), ^1H NMR: spectrum Table II. Acetyl derivative *XXXI* (^1H NMR spectrum: Table II). A similar NOE experiment was negative: irradiation of the methyl group at $C_{(4)}$ did not influence the intensity of the H-3′ signal.

REFERENCES

1. Kozluk T., Zamojski A.: Unpublished results.
2. Lemieux R. U., Wolfrom M. L.: Advan. Carbohyd. Chem. *3*, 337 (1948).

3. Gorst-Allman Ch. P., Steyn P. S., Wessels P. L.; J. Chem. Soc., Perkin Trans. 1, *1977*, 1360.
4. Sweet F., Brown R. K.: Can. J. Chem. *44*, 1571 (1966).
5. Zamojski A., Kozluk T.: J. Org. Chem. *42*, 1089 (1977).
6. Ng Ying Kin N. M. K., Williams J. M., Horsington A.: J. Chem. Soc. *1971 C*, 1578.
7. Toki S., Shima K., Dakurai H.: Bull. Chem. Soc. Jap. *38*, 760 (1965).