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Xylitol and Its Derivatives

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The literature data on the pentahydric alcohol xylitol are reviewed. The methods for the preparation of xylitol, its ethers, esters, nitrogen-, halogen-, and sulphur-containing derivatives, acetals, ketals, anhydroxylitols, and their various derivatives are examined and the spectroscopic methods for demonstrating the structures of certain xylitol derivatives are discussed. The therapeutic and diagnostic, dietary, and industrial applications of xylitol and its derivatives are briefly considered. The bibliography includes 553 references.

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I. INTRODUCTION

Until recently xylitol was manufactured on an industrial scale only in the Soviet Union, which has adequate reserves of pentosan-containing raw material. The introduction of xylitol as a commercial product, its physiological activity, and its high reactivity (due to the presence of five free hydroxy-groups) led to its being investigated by chemists, biochemists, and pharmacologists. It rapidly became popular in the food industry, where it began to be used directly, and as a sugar substitute in food products for diabetics. An extensive literature on the chemistry of xylitol, the synthesis of its derivatives, the methods for its analysis, and therapeutic properties exists in various journals, compilations, conference proceedings, and patents. However, so far there has not been even a brief survey of this research.

In the present review the authors attempt to survey the literature data published up to 1974, which makes it possible to assess the advances achieved in the study of the chemistry of xylitol and to outline new promising applications of this polyol.

II. METHODS FOR THE PREPARATION OF XYLITOL

The laboratory and industrial methods for the synthesis of xylitol are based on several of the usual methods in the chemistry of polyols.

The Reduction of Xylose

Syrupy xylitol was obtained for the first time by Bertrand [1] and Fisher [2,3] by the reduction of D- and L-xyloses with sodium amalgam. Aqueous solutions of D-xylose were also hydrogenated in the presence of platinum oxide [4], Raney nickel [5-8], nickel [9] and nickel–cobalt–chromium catalysts on calcium triphosphate [10], nickel on kieselguhr [11,12], nickel–iron carbonate [13] and nickel–copper catalysts on bentonite [14], and titanium–niobium or vanadium–nickel catalysts [15]. Ashida reduced monoses on an aluminium–nickel alloy [16] in non-aqueous solvents: cyclohexanol [15,17,18] and tetrahydrofuryl alcohol [16]. The hydrogenation of aqueous methanol solutions of xylose [19-30] in the presence of Raney nickel and its reduction with aqueous solutions of sodium tetrahydroborate [31,32] and lithium tetrahydroaluminate [33] has been described. Under these conditions, the pentitol was obtained quantitatively from D-xylo-γ-lactone and D-xylityl pentanitrate [34,35].

Karabinos and Ballun [36] developed a convenient method for the preparative synthesis of polyols by the reduction of aldoses and ketoses with Raney nickel. Greighton [10] described an electrochemical reduction of xylose to xylitol. D-Xylitol has also been obtained from 4-*O*-methylglucuronoxylan [37].

Other Methods

Multistage syntheses of xylitol from divinylmethanol [38] and acrolein [39-42] have been described. The oxidation of the terminal glycol group of a hexose or a hexitol followed by reduction yields monoses [43,44] with a smaller number of carbon atoms. 2,4 : 3,5-Di-*O*-ethylidene-L-xylitol was synthesised in this way from industrial D-sorbitol [45]. Hydrogenolysis of sorbitol [46] yielded a mixture of polyols containing xylitol. Xylitol has been obtained by a microbiological procedure [47-53] and has been isolated from plant material [54-59] and from peat [60,61].

In solutions of anhydrous hydrogen fluoride other pentitols isomerise to xylitol [62,63]. Xylitol derivatives can be obtained by benzoate exchange from sulphonyl derivatives of other pentitols [64].

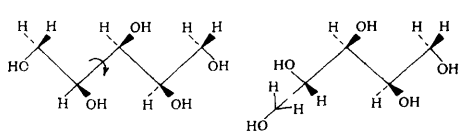
III. THE STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF XYLITOL, THE STEREOCHEMISTRY OF XYLITOL AND ITS DERIVATIVES, AND COMPLEX FORMATION

The structure of xylitol was demonstrated by Bertrand [65], Fischer [2,3], and Neuberg [66]. Bertrand obtained 2-iodopentane from xylitol and thus demonstrated the linearity of the hydrocarbon chain and the fact that it

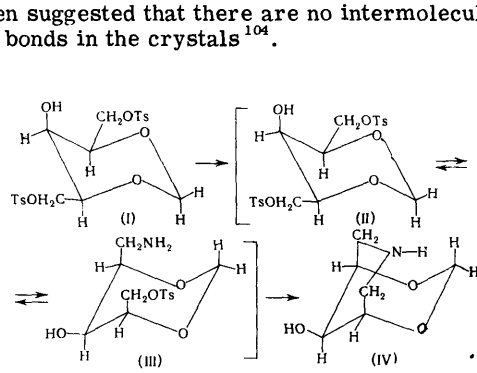
consists of five atoms. Fischer and Neuberg oxidised xylitol to DL-xylose and established that this does not entail isomerisation, so that the configurations of the hydroxy-groups of xylitol and xylose are identical. Two crystalline forms of xylitol have been described: a metastable monoclinic form melting at 61–61.5°C,[11,12] which is spontaneously converted into the stable orthorhombic form melting at 94–94.5°C.[12,19,67,68] Apart from two studies[11,12], other instances of the synthesis of the xylitol melting at 61–61.5°C have not been described.

Like other polyols, xylitol is soluble in a limited number of polar solvents: in concentrated sulphuric and hydrochloric acids, water, pyridine, dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and hexamethylphosphoramide and to a limited extent in methanol and ethanol. The temperature variation of its solubility in 96% ethanol and water has been studied[69,70], which is important for the technological processes involved in the synthesis of xylitol[7,71-82]. The thermal[83,84], radiation-induced[85], and photochemical[86] degradation of xylitol has been studied. Mai[87] calculated the dissociation constants of the OH groups; the Taft constants and the transport numbers of xylitol in a membrane and in solutions have also been evaluated[88]. The conductometric titration[89] and the cathodic overvoltage in the electrolysis[90] of aqueous xylitol solutions have been investigated.

The reactivities of individual OH groups of unsubstituted xylitol have been scarcely characterised. The synthesis of 1,5-di-*O*-tritylxylitol confirmed the higher reactivity of the primary OH groups[13,91], which is characteristic of all monoses and polyols. Esterification of xylitol by aliphatic C_6–C_{30} acids in the presence of acid and basic catalysts leads to mixtures of monoesters (60–75%) and diesters (20–35%).[92-96] An increase of the temperature of duration of esterification is accompanied by the formation of anhydro-derivatives[93,97,98]. The kinetics and mechanism of the sulphonation reaction have been studied by Yamazaki[99]. It has been found by X-ray diffraction[100] that the xylitol molecule is an asymmetric conformer with a non-planar zig-zag chain owing to the interaction between C_n–O and C_{n+2}–O bonds. Indeed, the study of models showed that interactions via 1,3-bonds lead to rotation about the $C_{(3)}$–$C_{(4)}$ bond with displacement of $C_{(5)}$ from the zig-zag plane[57,101,102]. The distortions of the planar conformer are manifested particularly clearly in the presence of bulky charged substituents, as confirmed by NMR.[103]



It has been suggested that there are no intermolecular hydrogen bonds in the crystals[104].



Some information about the structure of xylitol is provided by the study of complex formation. Xylitol forms complexes with acids, bases and salts. The stable crystalline complex $C_5H_{12}O_5.Ca(OH)_2.4H_2O$ has been described[105]. Copper(II) complexes[106] are used for the analysis and separation of mixtures of polyols. Xylitol forms complexes with boric acid[107,108], with alkali and alkaline earth metal borates[109-111], with cerium(IV) salts[112-114], with pyridine, and with nicotinic and other organic acids[115]. The complexes with iron(III) salts and with citrate[116] are physiologically active. It is believed that the complexes are formed via adjoining OH groups.

The conformations of cyclic acetals of xylitol have been more thoroughly investigated[117]. Danilov and Zarubinskii[118-121] showed that 2,4-*O*-methylenexylitol and its derivatives exist in the *C*-conformations stabilised by the equatorial CH_2OH groups. Presumably the conformation is additionally stabilised by the intramolecular hydrogen bond between the axial $C_{(3)}OH$ group and the oxygen atoms of the acetal ring[122]. The reactivity of the $C_{(3)}OH$ group has been studied and it has been found that in esterification by acid anhydrides the equatorial OH group (*ribo*-configuration) reacts faster, while the axial OH group (*xylo*-configuration) reacts faster with acid chlorides[123].

The formation of an imine when 2,4-*O*-methylene-1,5-di-*O*-tosylxylitol is treated with ammonia[124] should involve an inversion of the conformation. The $C_{(3)}OH$ group in the imine forms part of two rings simultaneously: in one of these it is axial and in the other equatorial, which makes it difficult to interpret the NMR spectra of these compounds.

IV. DERIVATIVES OF XYLITOL

1. Esters (Table 1)

Esters[125-145] are obtained by the usual methods: (1) By esterifying the polyol with an excess of acid, acid anhydride, or an acid chloride in the presence of a catalyst or a base. The first xylitol derivative, the pentaacetate, was synthesised in this way[1,11,32,125-129]. Esterification may be accompanied by the formation of anhydro-derivatives[13,130-133]. For a 1 : 1 ratio of the polyol and the acid, the reaction proceeds with formation of a mixture of a monoester and diesters in proportions of 2 : 1–3 : 1.[92-96,134] (2) By the reduction of the corresponding xylitol derivatives; 2,3,5-tri-*O*-benzoyl-D-[135] and 5-deoxy-5-fluoro-L-xylitols[136] were obtained in this way. (3) With intermediate protection of some of the OH groups. For example, 1-*O*-esters have been obtained by the esterification of di-*O*-isopropylidenexylitol with subsequent hydrolysis of the ketal protecting group[137,138]. Trifluoroacetic acid has been suggested as the hydrolysing agent[144].

Direct interaction with inorganic acids yielded xylityl pentanitrate[32,139-141] (stable below 5°C) and sulphate esters[119,120]. When xylitol is heated with concentrated hydrochloric acid, the product is a mixture of 5-chloro-5-deoxyxylitan as the main component[74]. The interaction of xylitol with phosphorous, hypophosphorous, and phosphonous acid[97,143,145,146] results in the formation of a mixture of xylitol and xylitan derivatives. The structure of cyclic xylitol phosphotriesters[147] has been determined with the aid of the Arbuzov reaction.

2. Ethers

Xylityl ethers are also obtained by standard methods. Interaction with alkyl and aryl halides in the presence of bases yielded 1,5-di-*O*-tritylxylitol[13,91,148], penta-*O*-allylxylitol[149], and trimethylsilyl[150,151] and β-cyanoethyl ethers[152].

Table 1. Esters, ethers, and mixed ether-esters of xylitol.

Name	M.p. (b.p.)/mmHg, °C	References
1-*O*-Octanoylxylitol	59-60	137
1-*O*-Decanoylxylitol	60-64	137
1-*O*-Myristoylxylitol	75-78	137
1-*O*-Palmitoylxylitol	86-88	137
1,2,3,4,5-Penta-*O*-acetylxylitol	62.5-63	11,32,125-129
1,2,3,4,5-Penta-*O*-propionylxylitol	Syrup	132
1,2,3,4,5-Penta-*O*-butyrylxylitol	Syrup	132
1,2,3,4,5-Penta-*O*-lauroylxylitol	33.5-35	132
1,2,3,4,5-Penta-*O*-myristoylxylitol	45.5-47	132
1,2,3,4,5-Penta-*O*-palmitoylxylitol	56-59	132
1,2,3,4,5-Penta-*O*-stearoylxylitol	66-68	132
2,3,5-Tri-*O*-benzoyl-D-xylitol, $[\alpha]_D$ = 8.5° (chloroform)	141-142	135
Penta-*O*-benzoylxylitol	105-106	13,64,135
Tetra-*O*-benzoylxylitol	162-163	13
Penta-*O*-nicotinoylxylitol	185-190	133,481
1-*O*-Methylxylitol	167-169/0.5	119,157
2-*O*-Methylxylitol	Syrup	155
3-*O*-Methylxylitol	Syrup	154
1,4,5-Tri-*O*-methylxylitol	97-99/0.5	157
2,3,4-Tri-*O*-methylxylitol	Syrup	158
1-*O*-Methyl-5-*O*-tritylxylitol	87-88.5	119
2,3-Di-*O*-ethylxylitol	67-68	156
Penta-*O*-allylxylitol	125-127/0.01	149
1,5-Di-*O*-tritylxylitol	152-156	13,91
1,5-Di-*O*-acetyl-2,3,4-tri-*O*-methylxylitol	Not stated	158
2,3,4-Tri-*O*-acetyl-1,5-di-*O*-tritylxylitol	204-206	13,91
2,3,4-Tri-*O*-benzoyl-1,5-di-*O*-tritylxylitol	197-198	13
2,3,4,5-Tetra-*O*-benzoyl-1-*O*-methylxylitol	121-122	157
1,2,3,4,5-Pentakis-*O*-trimethylsilylxylitol	112-113/1	160,162
2,3,4-Tri-*O*-benzyl-1,5-bis-*O*-*p*-nitrobenzoylxylitol	98	153

2,3,4-Tri-*O*-benzylxylitol[153], 2- and 3-*O*-methyl-D-xylitol[154,155], and 2,3-di-*O*-ethyl-D-xylitol[156] were synthesised by reducing xylose derivatives. 1-*O*-Methylxylitol was synthesised from the di-*O*-isopropylidene ketal[119,120,157]. Kochetkov et al.[158] synthesised 2,3,4-tri-*O*-methylxylitol by shortening the chain of D-glucopyranosidouronamide with subsequent reduction of the product. 2-*O*-(4-*O*-Methyl-α-D-glucopyranosyl)-D-xylitol has been isolated from natural products[46] and other similar derivatives have been identified[47,48].

3. Amino-derivatives (Table 2)

1-Amino-1-deoxy-D-xylitol has been synthesised by the reductive amination of D-xylose[159,160] and by the hydrogenation of D-xylose phenylhydrazone[161] or oxime[162]. The bis(phenylhydrazone) of D-threopentulose was reduced similarly to 1,2-diamino-1,2-dideoxy-D-xylitol[163]. Ammonolysis of 2,3-anhydroribose yielded 3-amino-3-deoxyxylitol[164]. Hydrogenation of *N*-amino-D-xylopiperidinose or its dimer, obtained by the acid hydrolysis of 5-deoxy-5-hydrazino-1,2-*O*-isopropylidene-D-xylofuranose, leads to 1,5-imino-1,5-dideoxy-D-xylitol[165,166]. Haskell and Hanessian[167,168] synthesised 5-acetamido-5-deoxy-D- and -L-xylitols from derivatives of iditol mercaptals.

Deamination of 1-deoxy-1-methylaminoxylitol with nitrous acid[169-171] led to 1-deoxy-1-methylnitrosamino-D-xylitol instead of the expected xylitan[172]. Veksler and coworkers[173-176] obtained the quaternary ammonium salts $R\overset{+}{N}(CH_3)_2Alk\overline{Br}$ (R is a xylitol or xylitan residue and Alk is a long-chain C_{10}–C_{18} alkyl group) from 1-deoxy-1-dimethylaminoxylitol by alkylation with alkyl bromides.

Table 2. Nitrogen-containing derivatives of xylitol.

Name; $[\alpha]_D$	M.p., °C	References
1-Amino-1-deoxy-D-xylitol (HBr salt); $[\alpha]_D^{23}$ = 13°	167-168	159-162
" (HCl salt)	128-129	159-162
1-Methylamino-	Syrup	172
1-Dimethylamino-	102-104	173
1-Salicylideneamino-	131-133	160,162
1-Decyldimethylammonium (HBr salt)	Amorphous	173
1-Dodecyldimethylammonium- (HBr salt)	145-147	173
1-Dimethylpentadecylammonium (HBr salt)	125	173
1-Hexadecyldimethylammonium- (HBr salt)	88-89	173
1-Dimethyloctadecylammonium- (HBr salt)	89-93	173
5-Acetamido-5-deoxy-D-xylitol; $[\alpha]_D^{23}$ = +73.2°	Syrup	168
5-Acetamido-5-deoxy-L-xylitol; $[\alpha]_D^{23}$ = -41.4°	Syrup	168
5-Acetamido-5-deoxytetra-*O*-acetylxylitol	Syrup	168
1-Deoxy-1-(methylnitrosamino)xylitol	121-122	169,170,172
1,2-Dideoxy-1,2-bis-salicylideneamino-D-xylitol; $[\alpha]_D^{22}$ = -106°	140	163
1,5-Dideoxy-1,5-iminoxylitol (HCl salt)	Syrup	165,166
1,5-Acetimido-1,5-dideoxyxylitol	192-194	165, 166
2,3,4-Tri-*O*-acetyl-1,5-dideoxy-1,5-iminoxylitol	119.5-121	165
Tetra-*O*-acetyl-1-deoxy-1-deoxy-1-methylamino-*N*-nitrosoxylitol	75-76	172
N-Methyl-*N*-tetrahydroxyxylopentylhydrazine- (HCl salt)	116-117	172
N-Benzylidene-*N*-methyl-*N*-tetrahydroxyxylopentylhydrazine	126-127	172
[4-Bis-(2'-chloroethyl)aminobenzylidene]-*N*-methyl-*N*-tetrahydroxyxylopentylhydrazine	143-144	172

4. Deoxy-derivatives (Table 3)

Deoxy-derivatives have also been synthesised by the usual methods of carbohydrate chemistry. Hydrogenation of xylose derivatives yielded 3-acetamido-3,5-dideoxy-D-xylitol[164]. A series of consecutive reactions $RCH_2OH \rightarrow RCH_2OTs \rightarrow RCH_2I \rightarrow RCH_3$ [177] or the elimination of sulphur from diethyl mercaptal[178] (R is a xylitol residue) have been used to synthesise 1-deoxyxylitol.

Table 3. Deoxy-derivatives of xylitol.

Name	M.p., °C	References
1-Deoxyxylitol	Syrup	177,178
Tetra-*O*-acetyl-1-deoxy-D-xylitol	62-63	177,178
2-Deoxy-D-xylitol	Syrup	180,181
2-Deoxy-D-tetraphenylcarbamoylxylitol	200-201	180,181
3-Deoxy-D-xylitol	70-71	182,184
3-Deoxy-D-tetraphenylcarbamoylxylitol	205-206	181
Tetra-*O*-benzoyl-3-deoxy-D-xylitol	104	184
3-Acetamido-1,2,4-tri-*O*-acetyl-3,5-dideoxy-D-xylitol	Syrup	164

By shortening the chain of 3-deoxy-D-galactose, a 2-deoxyxylitol derivative was synthesised[179-181]. 3-Deoxyxylitol has been obtained from the epoxides of L-arabinose and D-ribose[182-184].

Hurd and Bonner [185-187] and then Gertsev and Makarov-Zemlyanskii [188] obtained 1,1-deoxy-1,1-di-*C*-phenyl-D-xylitol and its analogues by the *C*-glycosylation of acetyl-β-D-xylose using benzene in the presence of aluminium chloride. Zhdanov and coworkers [189-196] used the organomagnesium synthesis for the same purpose.

Table 4. Thio-derivatives of xylitol.

Name	$[\alpha]_D^0$	M.p. (b.p.)/mmHg, °C	References
1-Thio-L-xylitol	-2.9 (methanol)	170/0.01	199
1-Thio-D-xylitol	+2.4 (methanol)	170/0.01	199
S-Benzyl-1-thio-L-xylitol	+32 (chloroform)	46-59	199
S-Benzyl-1-thio-D-xylitol	-35 (chloroform)	52-63	199
2,3,4,5-Tetra-*O*-acetyl-*S*-benzyl-1-thio-L-xylitol	+11.5 (chloroform)	180/0.01	199
2,3,4,5-Tetra-*O*-acetyl-*S*-benzyl-1-thio-D-xylitol	-12 (chloroform)	180/0.01	199
2,3,4,5-Tetra-*O*-acetyl-*S*-acetyl-1-thio-L-xylitol	+34 (chloroform)	–	199
2,3,4,5-Tetra-*O*-acetyl-*S*-acetyl-1-thio-D-xylitol	-35 (chloroform)	–	199
S-Auro-1-thio-L-xylitol	–	180 (decomp.)	199
S-Auro-1-thio-D-xylitol	–	180 (decomp.)	199
Bis(tetra-*O*-acetyl-*S*-dehydro-1-thio-L-xylitol)	+28 (chloroform)	97-98	199
Bis(tetra-*O*-acetyl-*S*-dehydro-1-thio-D-xylitol)	-28 (chloroform)	97-98	199

5. Thio-derivatives (Table 4)

Stanek and coworkers [199] obtained tetra-*O*-acetyl-1-benzylthio-1-deoxy-L-xylitol from 1,2-*O*-isopropylidene-5-*O*-tosyl-D-xylofuranose, debenzylated it to 1-deoxy-1-thio-L-xylitol, and characterised it in the form of the octaacetyldisulphide and *S*-auro-1-deoxy-1-thio-L-xylitol. Derivatives of the D-series were obtained similarly.

Table 5. Cyclic xylitol acetals and their derivatives. Di- and mono-methylene acetals of xylitol. 2,4 : 3,5-Di-*O*-methylenexylitols.

Name; $[\alpha]_D$	M.p., °C	References
2,4 : 3,5-Di-*O*-methylene-DL-xylitol	201-202	216,217,220
1-Deoxy-D-; +16.5° (chloroform)	154-155	178
1-Deoxy-DL-	155-156	178,216,221
1-*O*-Methyl-	148	286
1-*O*-Acetyl-	156-157	216
1-*O*-Benzoyl-	164-165	216
1-*O*-Tosyl-	145-146	121,216
1-*O*-Methanesulphonyl-	127.5-129	121,216
1-*O*-Chloromethanesulphonyl-	135.5-137.5	121
1-*O*-Phenylcarbamoyl-	196-197	216
Bis-(2,4 : 3,5-di-*O*-methylene-DL-xylit-1-yl)amine	234-240	224
1-Dimethylamino-1-deoxy-	112-113	173-176
1-Amino-1-deoxy-	120-121	224
1-Deoxy-1-dimethyldodecylammonium-1- (bromide salt)	95-94	176
1-Deoxy-1-dimethyloctadecylammonium- (bromide salt)	102-103	176
1-Deoxy-1-dimethylpentadecylammonium- (bromide salt)	116-118	173
1-Deoxy-1-phenylamino-	133	224
1-Benzamido-1-deoxy-	214-215	224
1-Deoxy-1-(*N*-phenyl)toluenesulphonamido-	176	224
1-Deoxy-1-(*N*-phenyl)benzamido-	178	224
1-Deoxy-1-thiocyanato-	147-148	221
1-Chloro-1-deoxy-	129	224
1-Deoxy-1-iodo-	144-145	216
1-*O*-Naphthylcarbamoyl-	211-212	221
Bis-(2,4 : 3,5-dimethylene-DI-xylityl disulphide	192-193	221
NN-Bis(2,4 : 3,5-di-*O*-methylene-DL-xylit-1-yl)benzamide	261-262	224
NN-Bis(2,4 : 3,5-di-*O*-methylene-DL-xylit-1-yl)toluene-*p*-sulphonamide	211-212	224
1-*O*-Allyl-	146	220
1-*O*-Methylallyl-	133-135	220
1-*O*-Methacryloyl-	157	225,237
1-Deoxy-1-methacrylamido-	198	225
1-Deoxy-1-(*N*-phenyl)methacrylamido-	193	224
NN-Bis-(2,4 : 3,5-di-*O*-methylene-DL-xylit-1-yl)-acrylamide	206	225
NN-Bis-(2,4 : 3,5-di-*O*-methylene-DL-ylit-1-yl)-methacrylamide	217	224,225
1-Cinnamamido-1-deoxy-	197-198	225
1-Deoxy-1-α-methylcinnamamido-	193	225
1-*O*-(1'-naphthylcarbamoyl)-	211-212	221
2,4 : 3,5-Di-*O*-methylene-L-xylitol; -25.3°	217-219	43
1-*O*-acetyl-L-; +2.8° (chloroform)	153-154	43
1-*O*-Benzoyl-L-; -23.8° (chloroform)	170-177	215
1-*O*-Tosyl-L-; -2.7° (chloroform)	146-147	176,215
1-Deoxy-1-iodo-L-; -35.9° (chloroform)	166-167	215
2,4-*O*-Methylene-DL-xylitol	108-109	43,119,216
1-*O*-Methyl-	58.5-59	223
1,3,5-Tri-*O*-methyl	84-86	119
1,5-Di-*O*-trityl-	207.5-209	120,124
3-*O*-Methyl-	109-111	124,217
3-*O*-Methyl-1,5-di-*O*-trityl-	230-231	119,124
3-*O*-Acetyl-1,5-di-*O*-trityl	204-206	217
1,3,5-tri-*O*-acetyl-	87-88	216
1,5-Di-*O*-acetyl-3-*O*-methyl-	121-123	217
3-*O*-Acetoxymethyl-1,5-di-*O*-acetyl-	138-139	119,216,226
	139-140	43
3-*O*-Acetoxymethyl-5-*O*-acetyl-1-*O*-methyl-	83-84	223
1-*O*-Tosyl-	128-129	121,221
3-*O*-Tosyl-	134-135	121
1,3-Di-*O*-tosyl	75.5-77.5	121
1,5-Di-*O*-tosyl	122-124	121
1,3,5-Tri-*O*-tosyl	198-199	121,216
3-*O*-Methyl-1-*O*-tosyl	84-85	121
1-*O*-Tosyl-5-*O*-trityl-	146-147	121
3-*O*-Methyl-1,5-di-*O*-tosyl-	137-138	121,124,223
1-*O*-Methyl-3,5-di-*O*-tosyl	114-115	223
3-*O*-Methyl-1-*O*-tosyl-5-*O*-trityl-	162-163	121
3-*O*-Tosyl-1,5-di-*O*-trityl-	89-90	124
3-*O*-Acetyl-1-*O*-tosyl-5-*O*-trityl-	160-162	121
3-*O*-Benzoyl-1-*O*-tosyl-5-*O*-trityl-	194-196	121
3-*O*-Benzoyl-1,5-di-*O*-tosyl-	128-129	223
1,5-Di-*O*-benzoyl-	140.5-141	
3-*O*-Acetyl-1,5-di-*O*-benzoyl-	174-175	121
1,3,5-Tri-*O*-benzoyl	117-118	216
1,5-Di-*O*-benzoyl-3-*O*-methanesulphonyl-	130-132	121
1,5-Di-*O*-benzoyl-3-*O*-tosyl-	140-141.5	121
3-*O*-Acetoxymethyl-5-*O*-acetyl-1-*O*-methane-sulphonyl-	112-118	221
1,5-Di-*O*-methanesulphonyl-	109-110	121
3-*O*-Acetyl-1,5-di-*O*-methanesulphonyl-	134-136	121
1,3,5-Tri-*O*-methanesulphonyl-	152.5-153.5	121
1,3,5-Tri-*O*-chloromethanesulphonyl-	115-117	121
3-*O*-Acetyl-1,5-di-*O*-methanesulphonyl-	134-136	121
1-Deoxy-	52-53	221
1-Deoxy-5-*O*-tosyl-	145-146	221
1-Deoxy-D-; +5.9° (chloroform)	70-72	178
3-*O*-Acetyl-1-deoxy-D-; -5.3° (chloroform)	101-102	178
3-*O*-Acetoxymethyl-5-*O*-acetyl-1-deoxy-D-; -18° (chloroform)	110-111	178
1-Deoxy-5-*O*-tosyl-D-; -2.1° (chloroform)	62-68	178
1-Deoxy-3,5-di-*O*-tosyl-D-; -18.8° (chloroform)	99-100	178
1,5-Dideoxy-5-iodo-3-*O*-tosyl-	123-125	178
3-*O*-Acetyl-1,5-dideoxy-5-iodo-	51-52	178
3,5-Di-*O*-acetyl-1-*O*-chloromethanesulphonyl-	101-109	121
1-Chloro-1-deoxy-3-*O*-methyl-	104-105	217
1-Chloro-1-deoxy-5-*O*-trityl-	203-204	217
3-Acetylmethyl-5-*O*-acetyl-1-chloro-1-deoxy-	141-143	217
1,2,5-Trichloro-1,2,5-trideoxy-3-*O*-methyl-	67-68	217
1-Chloro-1-deoxy-3-*O*-methyl-5-*O*-trityl-	156-157	217
1-Chloro-1-deoxy-3,5-di-*O*-tosyl-	124-125	221
3,5-*O*-Benzylidene-	187-188	221
1-*O*-Acetyl-3,5-*O*-benzylidene-	155-156	221
1-*O*-Benzoyl-3,5-*O*-benzylidene-	173-174	221
3,5-*O*-Benzylidene-1-*O*-tosyl-	149-150	221
3,5-*O*-Benzylidene-1-iodo-1-deoxy-	165-166	221
3,5-*O*-Benzylidene-1-deoxy-	140-141	221
1-Deoxy-3,5-di-*O*-tosyl-	112-113	221
1,3-Anhydro-	104-105	221
1,3-Anhydro-5-*O*-tosyl-	82-83	221
1,3-Anhydro-5-deoxy-5-iodo-	99-100	221
1,3-Anhydro-5-deoxy-	64-65	221
1,5-Dideoxy-1,5-imino-3-*O*-methylxylityl oxalate	159-161	124
1,5-Dideoxy-1,5-imino-3-*O*-methylxylityltoluene-*p*-sulphonate	152-153	124
1,5-Dideoxy-1,5-imino-3-*O*-methylxylityl picrate	230-231	124
1,5-Diamino-1,5-dideoxy-3-*O*-methylxylitol	120	124
1,5-Dideoxy-1,5-diphthalimido-3-*O*-methylxylitol	279-280	124
1,3,5-Tris-*O*-(trimethylsilyl)xylitol	15-16	150
3,5-Anhydro-1-deoxy-2,4-*O*-methylene-D-xylitol; +28.6° (water)	84-85	178
3,5-*O*-Benzylidene-1-deoxy-2,4-*O*-methylene-D-xylitol; +26.3° (chloroform)	160-162	178
3,5-*O*-Methylene-D-xylitol; -16.5° (water)	119-120	218
1,5-Di-*O*-Benzoyl-2,4-*O*-methylene-3-xylulose	115-116	226
2,4-*O*-Methylene-3-xylulose	95.5-97	226

6. Acetals and Ketals (Tables 5–11)

The methods for the synthesis of cyclic acetals and ketals of xylitol and for the demonstration of their structure are well known. Simple empirical rules have been formulated for the formation of acetals[43,200–207], based on the fact that the rings must cause the minimum distortion of the zig-zag polyol chain. It is necessary to consider the stereochemical stability of the molecule as a whole, when the differences between the eclipsed groups C–C/C–H and C–H/C–H and the electrostatic repulsion between the *gauche* C–O/C–O bonds begin to play the main role[208]. The structures of pentitol ketals agree fairly well with these conclusions[209].

Table 6. Ethylidenexylitol and its derivatives; 1,3 : 2,4-di-*O*-ethylidenexylitols.

Name; $[\alpha]_D$	M.p., °C	References
1,3 : 2,4-Di-*O*-Ethylidene-D-xylitol; −3.5° (water)	164–165	45
5-*O*-Benzoyl-D-; −5.0° (chloroform)	155–156	45
5-*O*-Phenylcarbamoyl-D-; +15.7° (chloroform)	215–217	45
5-*O*-Tosyl-	71–74	45
1,3 : 2,4-Di-*O*-Ethylidene-L-xylitol; +5.6° (chloroform)	161–162	227

Table 7. Di- and mono-benzylidenexylitols; 2,4 : 3,5-di-*O*-benzylidenexylitols.

Name; $[\alpha]_D$	M.p., °C	References
2,4 : 3,5-Di-*O*-Benzylidene-DL-xylitol	180–190	1,2,11,17 215,229,230
1-*O*-Methyl-	156–157	119
1-*O*-Allyl-	157	220
1-*O*-Methylallyl-	148–149	220
1-*O*-Acetyl-	179.5–180	215,230
1-*O*-Benzoyl-	173–175	119
1-*O*-Tosyl-	155–157	176,215,236
1-*O*-Methacryloyl-	158	225,237
1-Deoxy-	174	215
1-Deoxy-1-iodo-	207–208	215
1-(2′-Cyanoethyl)-1-deoxy-	140–141	236
1-Deoxy-1-dimethylamino-	154–155	176
1-Deoxy-1-decyldimethylammonium- (bromide salt)	122	176
1-Deoxy-1-dimethyldodecylammonium- (bromide salt)	111	176
1-Deoxy-1-dimethylpentadecylammonium- (bromide salt)	109–111	176
1-Deoxy-1-dimethylhexamethylammonium- (bromide salt)	125	176
1-Deoxy-1-dimethyloctadecylammonium- (bromide salt)	121–122	175,176
1-Butylamino-1-deoxy-	146	224
1-Deoxy-1-piperidino-	166	236
1-(2′-Butylacrylamido)-1-deoxy-	146–147	225
1-(*N*-Butyltoluene-*p*-sulphonamido)-1-deoxy-	126–127	224
2,4 : 3,5-Di-*O*-benzilidene-D-xylitol; −36.9° (pyridine)	187–188	238
1-Deoxy-D-; −34.5° (chloroform)	175–176	178
1-Acetamido-1-deoxy-D-; −38.6° (DMF)	250.5–252.5	238
1,1-Dimethyl-D-; −32.7° (chloroform)	170–173	238
1,1-Diphenyl-D-; +98.8° (chloroform)	183	238
1,1-Diethyl-D-; −25.1° (chloroform)	170–173	238
2,4-*O*-Benzylidene-DL-xylitol	144	231,235
3-*O*-Acetyl-1,5-di-*O*-benzoyl-	128–129	239
1,3,5-Tri-*O*-acetyl-	148–149	42
1,5-Di-*O*-benzoyl-3-*O*-(methylthio)methyl-	160–161	239
2,4 : 3,5-Di-*O*-benzylidene-1-deoxy-D-xylit-1-yl-D-xylitol; −22° (pyridine)	179–180	242
(1-*R*)-1,5-Di-*O*-acetyl-2,4-*O*-benzylidenexylitol 1,3-*O*-Methylene-(1-hydroxy-L-xylitol); +51.4° (chloroform)	160–161	241
(1-*S*)-1,5-Di-*O*-acetyl-2,4-*O*-benzylidene-1,3-*O*-methylene-(1-hydroxy-L-xylitol); 64.6° (chloroform)	144–146	241

The bulk of the groups adjoining the carbonyl groups play a decisive role in the formation of ketals. One of the authors of the review failed to obtain the hexachloroisopropylidene ketal of xylitol under the conditions for the synthesis of trifluoroisopropylidene ketals. The influence of temperature on the reaction has been little studied, although it is known that an increase of reaction temperature accelerates the formation of dioxolans[210,211]. There have been no studies of the role of the solvent, which might form hydrogen bonds[212,213] and thus influence the structure of the product.

Table 8. Di- and mono-acetylsalicylideneacetals; 2,4 : 3,5-di-*O*-acetylsalicylidenexylitols, 2,4-*O*-acetylsalicylidenexylitols, and the corresponding salicylidene acetals of xylitol.

Name	M.p., °C	References
2,4 : 3,5-Di-*O*-acetylsalicylidene-DL-xylitol	219–220	243
1-*O*-Trityl-	159–160	243
1-*O*-Acetyl-	209–210	243
1-*O*-Benzoyl-	205–206	243
1-*O*-Tosyl-	206–207	243
1-Deoxy-	222	243
1-Deoxy-1-thiocyanato-	175–176	243
1-Deoxy-1-iodo-	214–216	243
2,4-*O*-Acetylsalicylidene-L-xylitol	218–219	243
1,3,5-Tri-*O*-acetyl-	126–127	243
2,4 : 3,5-Di-*O*-Salicylidene-DL-xylitol	202–204	244
1-*O*-Trityl-	235–236	244
1-Deoxy-	148–150	243
2,4-*O*-Salicylidene-DL-xylitol	155–156	243

Table 9. Xylitol ketals and their derivatives; di- and mono-isopropylidenexylitols; 2,4 : 3,5-di-*O*-isopropylidenexylitols.

Name; $[\alpha]_D$	M.p. (b.p.)/mmHg, °C	References
2,4 : 3,5-Di-*O*-isopropylidene-DL-xylitol	34–36	5,157,177, 250
1-*O*-Methyl-	78–80/0.5	157
1-*O*-Trityl-	73–75	250
1-*O*-Acetyl-	45–75	177
1-*O*-Benzoyl-	61–62	177,250
1-*O*-Tosyl-	77–78	5,105,177
1-*O*-Octanoyl-	124–126/0.03	137
1-*O*-Myristoyl-	29–30	137
1-*O*-Palmitoyl-	46–49	137
1-*O*-Allyl-	106/0.5	220,245,246
1-*O*-Methylallyl-	154/0.8	220
1-*O*-Methacryloyl-	33–33.5	225,237
1-Deoxy-	88–90/6–7	177
1-Deoxy-1-iodo-	57–59	177
1-*O*-Chloroformyl-	120/09	249
1-*O*-Phenylazobenzoyl-	110–114	249
Bis-(1,2 : 3,4-di-*O*-isopropylidene-DL-xylitol) 5,5′-carbonate	204–206/0.5	249
5-*O*-Fluoroformyl-1,2 : 3,4-di-*O*-isopropylidene-Dl-xylitol	41–42 95/05	249
1,2 : 4,5-Di-*O*-isopropylidenexylitol	Syrup	250
3-*O*-Benzoyl	114–116	64,250
2,3-*O*-Isopropylidenexylitol	145–147/0.5	157
1-*O*-Methyl-	109–111/0.5	157
1,4,5-Tri-*O*-methyl-	69–71/0.5	157
2,3 : 4,5-Di-*O*-isopropylidene-L-xylitol; +12.5°	103–104	157
1,4,5-Tri-*O*-benzoyl-; ? (alcohol)	96–98/0.03	252
1-*O*-Tosyl-; +16.3° (alcohol)	65,66	252
5-*O*-Benzoyl-1,4-dideoxy-2,3-*O*-isopropylidene-D-xylitol; −25.6° (chloroform)	–	253

The resistance of the acetal linkage to acid hydrolysis increases with increase of the negative inductive effect in the acetal group. This has been confirmed by the stability series of the acetal linkages as a function of the acetal group: $(CF_3)_2C > CF_3-C-CH_3 > CH_2 > CH_3CH > (CH_3)_2C \geq C_6H_5CH$.

Table 10. Trifluoroisopropylidenexylitols.

Name	M.p. (b.p.)/mmHg, °C	References
2,3:4,5-Di-*O*-Trifluoroisopropylidene-DL-xylitol	83-84/0.4	119
1-*O*-Methyl-	79.5-80/0.5	119
1-*O*-Trityl-	105-106	119
1-*O*-Acetyl-; isomer I	104-106	119
isomer II	116-118	119
3-*O*-Methyl-	75-76/0.5	119

Table 11. Cyclohexylidene-DL-xylitols.

Name	M.p. (b.p.)/mmHg, °C	References
2,4:3,5-Di-*O*-cyclohexylidene-DL-xylitol	193/0.5	220
1-*O*-Methyl-	183/0.5	243
1-*O*-Trityl-	108	220
1-*O*-Allyl-	152/0.6	220
1-*O*-Methylallyl-	144-147/0.5	220
1-*O*-Tosyl-	86	243
1-Deoxy-1-thiocyanato-	74-75	243
1-Deoxy-	102.5/0.02	243
3,5-*O*-Cyclohexylidene-2,4-*O*-methylenexylitol	103-104	243
3,5-*O*-Cyclohexylidene-2,4-*O*-methylene-1-*O*-tritylxylitol	182	243
3,5-*O*-Cyclohexylidene-2,4-*O*-methylene-1-*O*-tosylxylitol	153-154	243

The structures of the acetals have been demonstrated by various methods: by selective hydrolysis, chemical modification, and the study of physicochemical constants; for example, the study of the solvolysis constants [214] helped in confirming the *cis*-decalin structure for di-*O*-benzylidenexylitol. It is interesting to note that in the synthesis of this diacetal the monoacetal could not be isolated from the reaction mixture, although it has been stated in the literature that this is possible [157]. Consequently the rate of formation of the second ring greatly exceeds the rate of formation of the first in dibenzylideneacetals of xylitol.

Methyleneacetals. 2,4:3,5-Di-*O*-methylenexylitol was obtained for the first time by Ness et al. [43,215] from tri-*O*-methylene-D-sorbitol by selective hydrolysis with subsequent shortening of the chain. The acetal was then synthesised by treating xylitol with formaldehyde [216] or paraformaldehyde [217] in the presence of concentrated hydrochloric acid. Acetolysis of the diacetal leads to 2,4-*O*-methylenexylitol, which does not contain α-glycol groups. Schmidt and Nieswandt [218] synthesised 3,5-*O*-methylenexylitol by the selective oxidation of the 1,2-*O*-methylene group in 1,2:3,5-di-*O*-methylene-D-xylofuranose to the carbonate group with its subsequent hydrolysis and reduction of the reaction product. This reaction may be of general applicability [219].

Numerous derivatives of di-*O*-methylenexylitol [173,176,220] and mono-*O*-methylenexylitol [119,124,217,221-225] have been obtained. 1,5-Di-*O*-benzoyl-2,4-*O*-methylenexylitol has been oxidised to the corresponding 3-xylulose derivative; it has been shown [226] that this greatly reduces the resistance of the acetal ring to hydrolysis and the free ketose isomerises to a mixture of erythro- and threo-2-ketoses.

Ethylideneacetals. Ness and Fletcher [45] obtained 2,4:3,5-di-*O*-ethylidene-L-xylitol by shortening the chain of 1,3:2,4-di-*O*-ethylidene-D-sorbitol. Foster et al. [227] synthesised the D-analogue by a similar procedure. The monoacetal derivative has also been obtained [228].

Benzylideneacetals. 2,4:3,5-Di-*O*-benzylidenexylitol was obtained for the first time by condensing xylitol with benzaldehyde in the presence of concentrated hydrochloric acid in order to purify the xylitol [1,2]. Its solubility in organic solvents has been determined [229]; it has been shown that the diacetal contains one free OH group [215,230]. 2,4-*O*-Benzylidenexylitol has been synthesised by shortening the chains of 3,5-*O*-benzylidene-D-gluco-D-*gulo*-heptitol [231], 2,4-*O*-benzylidene-D-sorbitol [232], and 2,4-*O*-benzylidene-D-glucuronomercaptal [233] and by the reduction of the diethyl mercaptal of 2,4:3,5-di-*O*-benzylidene-D-xylose [234,235].

Various derivatives of the diacetal [119,120,175,176,215,225,236-238] and the monoacetal [228,239] have been described and the kinetics of the esterification of the diacetal have been studied [240]. It has been found that the acetylation of 1,5-di-*O*-benzoyl-2,4-*O*-benzylidenexylitol in DMSO [239] proceeds with formation of methylthiomethyl derivatives. Angyal and James [241] obtained (1*R*)- and (1*S*)-1,5-di-*O*-acetyl-2,4-*O*-benzylidene-1,3-*O*-methylene-(1-hydroxy-L-)xylitol from 2,4-*O*-benzylidene-D-sorbitol. On treatment with aluminium isopropoxide, 2,4:3,5-di-*O*-benzylidene-D-aldoxylose gives rise to 2,4:3,5-di-*O*-benzylidene-1-deoxy-D-xylit-1-yl-2′,4′:3′,5′-di-*O*-benzylidene-D-xylonate via the Claisen–Tishchenko reaction [242].

Acetylsalicylidene- and Salicylideneacetals. Rusanova et al. [243,244] obtained acetylsalicylidene- and salicylidene-acetals by condensing xylitol with the corresponding aldehydes and achieved their interconversion.

Isopropylideneketals. Among the methods for the synthesis of ketals, the condensation of xylitol with acetone in the presence of concentrated sulphuric acid is most frequently used [5,157,245,246]. Derivatives formed via the free OH group have been identified [177,220,225,237,247-249]. It was shown later that the crystalline 2,3:4,5-isomer is mainly formed [64,250,251]. An admixture of 10–30% of the 1,2:4,5-diketal has been detected by NMR. The isomers have been separated by preparative gas–liquid chromatography (GLC).

A diketal of the L-series has been obtained by shortening the chain of 1,2:3,4-di-*O*-isopropylidene-L-iditol [252]. Foster and coworkers [64] converted 1,2:4,5-di-*O*-isopropylidene-3-*O*-tosylribitol into 1,2:4,5-di-*O*-isopropylidenexylitol by benzoate substitution. Kochetkov and Usov [253] obtained 5-*O*-benzoyl-1,4-dideoxy-2,3-*O*-isopropylidene-D-xylitol from the diethyl mercaptal of 5-*O*-benzoyl-2,3-*O*-isopropylidene-L-arabinose by treatment with methyltriphenylphosphonium iodide.

Trifluoroisopropylideneketals. Zarubinskii and Danilov[119,222] synthesised 2,3:4,5-bis-*O*-(trifluoroisopropylidene)xylitol by condensing xylitol and trifluoroacetone in concentrated sulphuric acid solution. The presence of 1,3-dioxolan rings was established in the model derivatives which the above workers obtained: 1,2-*O*-(trifluoroisopropylidene)glycerol and 3-*O*-methyl-1,2:4,5-bis-*O*-(trifluoroisopropylidene)xylitol[254]. 1,3-Dioxan rings are characteristic of trifluoroacetone-xylitan derivatives[121]. Thus the condensation of xylitol and trifluoroacetone results in the formation of the 2,3:4,5-diketal, consisting of a mixture of several diastereoisomers owing to the non-equivalence of the substituents at the carbonyl carbon atom[254].

Cyclohexylideneketals. Anikeeva and Zarubinskii[220] obtained a diketal containing a primary OH group by condensing xylitol with cyclohexanone[243]. The reaction of 2,4-*O*-methylenexylitol with cyclohexanone led to the synthesis of 3,5-*O*-cyclohexylidene-2,4-*O*-methylenexylitol, which is formed more slowly than di-*O*-cyclohexylidenexylitol. If it is possible to assign a definite structure of the derivative to the rate of its formation[255], then the last diketal is probably a mixture of the 2,3:4,5- and 1,2:4,5-isomers, by analogy with di-*O*-isopropylidenexylitol.

Table 12. Anhydro-derivatives of xylitol; 1,4-anhydroxylitol and its derivatives.

Name; $[\alpha]_D$	M.p. (b.p.)/mmHg, °C	References
1,4-Anhydro-D-xylitol; −11.2° (water)	160-170/0.02	62
2,3,5-Tri-*O*-acetyl-D-xylitol; +31.5° (dichloroethane)	90-98/0.04	62
2,5-Anhydro-D-xylitol; +10° (water)	150-155/0.2	282
2,5-Anhydro-3,4-di-*O*-tosylxylitol; +33.8° (chloroform)	112-113	281
2,5-Anhydro-1-*O*-benzoyl-3,4-di-*O*-tosylxylitol; +66.6° (chloroform)	141-142	281
2,5-Anhydro-1,3,4-tri-*O*-tosylxylitol; +38.5° (chloroform)	118-119	281
3,4-Di-*O*-acetyl-2,5-anhydro-1-*O*-tritylxylitol; +6° (benzene)	153	282
1,3,4-Tri-*O*-acetyl-2,5-anhydro-D-xylitol; −45.5° (chloroform)	90/0.02	282
1,4-Anhydro-DL-xylitol	140-145/0.01 M.p. 38	259
2-*O*-Methyl-	122/0.8	279
2,3,5-Tri-*O*-ethyl-	Syrup	280
5-*O*-Trityl-	135-137	268
2,3,5-Tri-*O*-allyl-	105-106/0.8	220
2-*O*-Methyl-5-*O*-trityl	124-125	279
3-*O*-Acetoxymethyl-5-*O*-acetyl-2-*O*-methyl-	148-149/2	279
2-*O*-Methyl-5-*O*-tosyl-	71-72	117
2-*O*-Methyl-3,5-di-*O*-tosyl-	104	279
2,3-Di-*O*-acetyl-5-*O*-trityl-	147-148	279
2-*O*-Methyl-3-*O*-tosyl-5-*O*-trityl-	94-95	279
2,3,5-tri-*O*-(trimethylsilyl)-	106	271
2,3-Ethylene-5-*O*-oleoyl-	Syrup	283
3,5-Di-*O*-benzyl-2-*O*-methyl-	58-59	279
2,3-Di-*O*-benzyl-5-*O*-tosyl-	114-116	268
2,3-Di-*O*-benzyl-5-*O*-trityl-	140-142	268
2,3-Di-*O*-acetyl-5-*O*-trityl-	134-135	259
2,3,5-Tri-*O*-benzoyl-	79-80	259
2,3,5-Tri-*O*-(trimethylsilyl)-	90-97/1	150
3,3,5-Triphenylcarbamoyl	193-194	259
3,5-*O*-Thionyl-	83-84	271
2-*O*-Acetyl-3,5-*O*-thionyl-	104-105/0.05	271
2-*O*-Benzoyl-3,5-*O*-thionyl-	96-98	271
3,5-*O*-Thionyl-2-*O*-tosyl-	60-61	271
5-*O*-Hexylphosphonyl-	Syrup	143
5-*O*-Nonylphosphonyl-	Syrup	143
3,5-*O*-Methylene-	83-84.5	271
2-*O*-Methyl-3,5-*O*-methylene-	46-48	286
2-*O*-Ethyl-2,5-*O*-methylene-	90-92/3	287
2-*O*-Hexyl-3,5-*O*-methylene-	84-85/3	287
2-*O*-Decyl-3,5-*O*-methylene-	76-77/3	287
2-*O*-Allyl-3,5-*O*-methylene-	88/1	220
2-*O*-Benzoyl-3,5-*O*-methylene-	113-114	271
3,5-*O*-Methylene-2-*O*-palmitoyl-	61-62	92
3,5-*O*-Methylene-2-*O*-tosyl-	85-86	271

Table 12 (continued).

Name; $[\alpha]_D$	M.p. (b.p.)/mmHg °C	References
2-*O*-Methacryloyl-3,5-*O*-methylene-	77-78	225,236
2-Deoxy-3,5-*O*-methylene-2-phenylamino-	34-35	224
2-(*N*-Butyltoluene-*p*-sulphonamido)-2-deoxy-3,5-*O*-methylene-	100	224
2-Deoxy-3,5-*O*-methylene-2-phenylamino-	123-124	224
2-Deoxy-3,5-*O*-methylene-2-(*N*-phenylbenzamido)-	128	224
2-Deoxy-3,5-*O*-methylene-2-(*N*-phenylacrylamido)-	103	224
2-Deoxy-3,5-*O*-methylene-2-(*N*-phenylmethacrylamido)-	114	224
3,5-*O*-Ethylidene-	96-97	289
3,5-*O*-Ethylidene-2-*O*-methyl-	73/3	289
2-*O*-Benzoyl-3,5-*O*-ethylidene-	103-104	289
3,5-*O*-Ethylidene-2-*O*-tosyl-	86	289
3,5-*O*-Ethylidene-2-*O*-methacryloyl-	97-98	289
3,5-*O*-Ethylidene-2-*O*-phenylcarbamoyl-	150-151	289
3,5-*O*-Benzylidene-	65-66	271
3,5-*O*-Benzylidene-2-*O*-methyl-	40-41	286
2-*O*-Allyl-3,5-*O*-benzylidene-	157-158/0.8	220
3,5-*O*-Benzylidene-2-*O*-benzoyl-	133	271
3,5-*O*-Benzylidene-2-*O*-tosyl-	110	271
3,5-*O*-Benzylidene-2-*O*-methacryloyl-	138	225,237
3,5-*O*-Benzylidene-2-*O*-phenylcarbamoyl-	197-198	271,225,237
3,5-*O*-Isopropylidene-	65-66	271
3,5-*O*-Isopropylidene-2-*O*-methyl-	69-70/0.2	286
2-*O*-Allyl-3,5-*O*-isopropylidene-	105-106/0.8	220
2-*O*-Benzoyl-3,5-*O*-isopropylidene-	79.5-80	271
3,5-*O*-Isopropylidene-2-*O*-tosyl-	84	271
3,5-*O*-Isopropylidene-2-*O*-methacryloyl-	56-57	225,237
3,5-*O*-Isopropylidene-2-*O*-phenylcarbamoyl-	107-108	271
3,5-*O*-Cyclohexylidene-	155-158/0.5	271
3,5-*O*-Cyclohexylidene-2-*O*-methyl-	103-104/0.5	286
2-*O*-Allyl-3,5-*O*-cyclohexylidene-	105-106/0.8	220
2-*O*-Benzoyl-3,5-*O*-cyclohexylidene-	104-105	271
3,5-*O*-cyclohexylidene-2-*O*-tosyl-	96	271
3,5-*O*-Trifluoroisopropylidene-	102.5-104	120
2-*O*-Methyl-3,5-*O*-trifluoroisopropylidene-	46.5/0.5	120
2-*O*-Methyl-3,5-*O*-trifluoroisopropylidene-	62-62.5/0.6; M.p.32-34°	120
3,5-*O*-Methylene-2-*O*-polymethacryloyl-	172 (softening)	288
3,5-*O*-Isopropylidene-2-*O*-polymethacryloyl-	136 (softening)	288
5-Chloro-5-deoxy-	48-49	176,269,271
5-Chloro-5-deoxy-2-*O*-methyl-	108-109/2	222
5-Chloro-5-deoxy-2-*O*-methyl-3-*O*-tosyl-	76-77	222
5-Chloro-5-deoxy-3-*O*-methyl-2-*O*-tosyl-	88-88.5	117,197
5-Chloro-5-deoxy-2,3-di-*O*-tosyl-	104	271
2,3-Di-*O*-benzoyl-5-chloro-5-deoxy-	114-115	269
5-Chloro-5-deoxy-2-*O*-tosyl-	95-96	222
5-Chloro-5-deoxy-2(3)-phenylcarbamoyl-	137-138	271
5-Chloro-5-deoxy-2,3-diphenylcarbamoyl-	151-152	271
5-Deoxy-5-fluoro-	117-119/0.02	291
2,3-Di-*O*-benzoyl-5-deoxy-5-fluoro-	72-73	291
5-Deoxy-5-fluoro-2,3-di-*O*-tosyl-	112	291
5-Amino-5-deoxy- (HCl salt)	134	283,292
5-Deoxy-5-ethylamino-	130/1	292
5-Deoxy-5-dimethylamino-	162-165/14	176
5-Deoxy-5-dimethylamino- (oxalate)	72-73	176
5-Deoxy-5-diethylamino-	127/1	292
5-Deoxy-5-phenylamino-	134-135	292
5-Deoxy-5-piperidino-	115-116	292
5-Deoxy-5-dimethylhexadecylammonium- (bromide salt)	98-99	176
5-Deoxy-5-decyldimethylammonium- (bromide salt)	Amorphous	176
5-Deoxy-5-dimethyldodecylammonium- (bromide salt)	90-92	176
(2,3-Di-*O*-tosylxylitanyl)toluene-*p*-sulphonamide	146-147	292
N-Ethyl-(2,3-di-*O*-tosylxylitanyl)toluene-*p*-sulphonamide	120-121	292
N-Phenyl-(2,3-di-*O*-tosylxylitanyl)toluene-*p*-sulphonamide	141-142	292
5-Deoxy-5-diethylamino-2,3-di-*O*-tosyl-	154-155	292
5-Deoxy-5-piperidino-2,3-di-*O*-tosyl-	130-132	292
1,5-Anhydroxylitol	116-117	276,277
2,3,4-Tri-*O*-acetyl-	122-123	276,277
1,4:3,5-Dianhydro-DL-xylitol	77	269,271
2-*O*-tosyl-	114-116	269,271
2-*O*-Methyl-	51/2	269,271
2-*O*-Acetyl-	92/4	271
2-*O*-Benzoyl-	84	271
2-Phenylcarbamoyl-	114	271
2-Phenylamino-	77	274

7. Anhydroxylitols (Table 12)

Mono- and di-anhydro-derivatives of xylitol have been synthesised by two main methods.

Synthesis by intramolecular nucleophilic substitution. The reaction is carried out under acid or alkaline conditions. Various acids are used as the acid catalysts[256-263]. The acid-catalysed conversion of

pentitols into anhydro-derivatives leads to the formation of 1,4-anhydro-derivatives, which has been explained by the favourable steric disposition of the OH groups [264]. The anhydro-derivative usually retains the configuration of the initial polyol. However, Hudson and Barker [264] showed that in the presence of acids D-arabitol is converted into the 1,4-anhydro-derivatives of D-arabitol (62.6%), L-ribitol (7.6%), D-ribitol (3.3%), L-xylitol (11.7%), D-xylitol (4.3%), D-lyxitol (6.2%), and L-lyxitol (0.7%). Assuming that the reaction proceeds via an S_N2 mechanism, it is possible to explain the formation of anhydro-derivatives with the D-arabo- and D-lyxo-configurations by the attack of the O^- anionic group at $C_{(2)}$ or $C_{(4)}$ on carbon atoms with primary OH groups and the formation of derivatives with L-xylo- and L-ribo-configurations can be accounted for by the attack of the O^- group at $C_{(1)}$ or $C_{(5)}$ on carbon atoms with secondary OH groups. In the latter case the configuration is inverted. The relative rates of cyclisation increase in the following sequence: lyxitol < arabitol < xylitol < ribitol < 1-deoxy-D-arabitol < 2-deoxy-D-arabitol. Barker [265] determined the rates of conversion of hexitols into 1,4-anhydro-derivatives and arranged them in the following sequence: mannitol < gulitol < galactitol < altritol < sorbitol < iditol < talitol < allitol. In the two series the qualitative dependence of the rate of cyclisation on the configuration of the OH groups at the first four carbon atoms is the same [143,256].

1-Phosphate esters of xylitol readily form xylitans. By treating 1-amino-1-deoxy-ribitol with a mixture of hydrochloric and nitric acids, Kuhn and Wendt obtained ribitan [262]. Similarly 1-deoxy-1-nitrosaminoxylitol can serve as the starting material for the synthesis of xylitan [162]. Similar mechanisms have been proposed for these reactions [258]. Fletcher and coworkers [62] found that ribitan triacetates and tribenzoates form a mixture of ribitan, lyxitan, ribitol, xylitol, and arabitol in liquid HF solution, while the corresponding D-xylitan derivatives give rise to ribitan alone.

A second method for the synthesis of a wide variety of anhydro-derivatives involves intramolecular substitution of sulphonate esters. The reaction proceeds via an S_N2 mechanism and, when the sulphonyl group is attached to a secondary carbon atom, the closure of the oxygen-containing ring proceeds with Walden inversion at this carbon atom. The intramolecular substitution of sulphonates proceeds under the influence of the usual basic agents, although the formation of anhydro-derivatives in an acid medium has also been described [266].

Hartman and Barker [267] determined the characteristics of the formation of anhydro-derivatives for different positions of the tosyl and OH groups. Gray et al. [268] showed that the presence of the benzyloxy-group at the $C_{(4)}$ atom in 1-*O*-tosyl derivatives promotes the substitution of the tosyl group. It is suggested that the reaction involves the formation of an oxonium ion stabilised by the aryl substituent. The rate of cyclisation depends on the configuration of the OH groups responsible for the steric interactions in the transition and ground states.

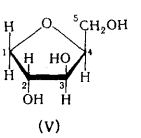
1,3-Anhydro-2,4-*O*-methylenexylitol was obtained by treating 2,4-*O*-methylene-1-*O*-tosylxylitol with an aqueous or aqueous acetone solution of alkali [178,221]. Under the same conditions, the 3-*O*-tosyl derivative remained unchanged [121]. Danilov and Kazimirova [269] and then Wiggins [270] synthesised the 1,4 : 3,5-dianhydroxylitol, the structure of which was established by Ustyuzhanin, Sidorova, and Danilov [197,271,272]. 1,4 : 2,3-Dianhydroxylitol was obtained from 1,4-anhydro-5-chloro-5-deoxy-2-*O*-tosylxylitol [273,274] and 1,4 : 2,5-dianhydroxylitol was synthesised from 2,5-anhydro-3,4-di-*O*-tosyl-D-xylitol [275].

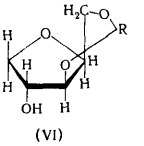
Synthesis by reduction methods. Fletcher and Hudson [276] hydrogenated 2,3,4-tri-*O*-acetyl-D-pyranoxylal or eliminated sulphur from 1-phenylthio-β-D-xylopyranoside triacetate and obtained 1,5-anhydro-2,3,4-tri-*O*-acetylxylitol. The same product was obtained by eliminating sulphur from 1-thio-β-D-xylopyranose [277] or β-D-glucopyranosyl-*NN*-dimethyldithiocarbamate [278] on Raney nickel.

1,4-Anhydroxylitol (xylitan) and its derivatives. Xylitan has been manufactured in the Soviet Union since 1950 and has been studied more thoroughly than other anhydro-derivatives. It was described for the first time by Grandel [260] and Carson and Maclay [259], who isolated crystalline hygroscopic xylitan, melting at 38°C, and showed that it contains one primary and two vicinal secondary OH groups, which confirmed the 1,4-anhydro-structure.

A wide variety of ethers, esters, and thio-derivatives of xylitan are known [62,143,150,163,220,259,268,279-283]. Among the sulphonates of the anhydro-derivative, unsaturated compounds have been synthesised in the presence of DMS solution of KI and zinc dust [281,284,285]. Methylene [92,220,224,225,237,271,286-288], ethylidene [289], and benzylidene [220,225,237,271,286] acetals and isopropylidene [220,224,237,271,286,288], cyclohexylidene [220,271,286], and trifluoroisopropylidene ketals [120] and their derivatives, including polymeric derivatives [289,290], have been described. Halogeno- [117,176,197,222,269,271,291] and amino-derivatives [274,283,292,293] have been obtained.

The structures of cyclic acetals and ketals of 1,4-anhydroxylitol (V) have been studied mainly by the authors of the present review. It has been established [279] that the acetal and ketal groups occupy the same 3,5-positions [compounds (VI)]. Examination of the xylitan model showed that the tetrahydrofuran ring fixes rigidly the *trans*-disposition of the $C_{(2)}-C_{(3)}$ hydroxyls and therefore the formation of acetal and ketal linkages involving these groups is apparently hindered. 1,4-Anhydroribitol, in which there is a *cis*-disposition of the hydroxyls at $C_{(2)}$ and $C_{(3)}$ is known to form 2,3-ketals readily [294].


(V)


(VI)

Danilov and coworkers showed that the second anhydro-ring in 1,4-anhydroxylitol is also formed via the 3- and 5-hydroxyls and the product is therefore 1,4 : 3,5-dianhydroxylitol and not the 1,4 : 2,5-derivative as had been believed previously [269,271,272]. The nucleophilic substitution of the tosyl group at $C_{(2)}$ in dianhydroxylitol proceeds via an S_N2 mechanism with inversion of the configuration at this atom and the formation of lyxitol derivatives [275].

Xylitol derivatives in which the substituent is linked to the polyol molecule via a carbon–carbon bond have been synthesised. These compounds (Table 13), which have been obtained from xylose, do not have an aldehyde group and we have therefore classified them as xylitol derivatives, although in the original studies the authors called them xylose derivatives. For this reason, two names are quoted for these compounds in the Table.

V. PHYSICAL METHODS FOR THE DETERMINATION OF THE STRUCTURES OF CYCLIC ACETALS

The experimental determination of the structures of acetals is usually difficult: in the course of chemical reactions occurring during partial acid hydrolysis, there is a possibility of the isomerisation and migration of the acetal and acyl groups. Hydrolysis is inapplicable to stable rings and the structures of the diastereoisomers of acetals with various groups attached to the carbonyl moiety cannot be determined by purely chemical methods. Numerous studies using model acetals showed that spectroscopic methods are the most promising for the determination of the structures of cyclic acetals. They require small amounts of the test substance, the analysis is carried out under neutral conditions, and both the structure and conformation of the derivative are determined.

Table 13. *C*-Substituted xylitol derivatives.

Name	M.p., °C	References
1-Deoxy-1,1-di-*C*-phenyl-D-xylitol	167-168	185,186
1-Deoxy-α-*C*-phenyl-β-*C*-*p*-tolylxylitol	163.5-164.5	185,186
2,3,4-Tri-*O*-acetyl-1-*C*-anisoyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-*C*-anisoyl-1-deoxy-D-xylitol)	129.5-130.5	189
2,3,4-Tri-*O*-acetyl-1-*C*-chlorophenyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-*C*-chlorophenyl-1-deoxy-D-xylitol)	149.5-150.5	189
2,3,4-Tri-*O*-acetyl-1-*C*-chloroanisoyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-*C*-chloroanisoyl)-1-deoxy-D-xylitol)	151-153	189
2,3,4-Tri-*O*-acetyl-1-*C*-bromoanisoyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-*C*-bromoanisoyl-D-xylitol)	159-160	189
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-nitroanisoyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-nitroanisoylxylitol)	155.5-156.5	189
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-phenethyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-phenethyl-D-xylitol)	130.5-131	189
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-nitrophenethyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-nitrophenethyl-D-xylitol)	165.5-167	189
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-diphenyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-diphenyl-D-xylitol)	191-192	190
2,3,4-Tri-*O*-acetyl-1-*C*-allyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1-*C*-allyl-1,5-anhydro-1-deoxy-D-xylitol)	Syrup	190
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-thienyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-thienyl-D-xylitol)	151-152	190
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-*o*-tolyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-*o*-tolyl-D-xylitol)	110-111	195
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-dibromophenethyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-dibromophenethyl-D-xylitol)	80-81.5	195
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-dichlorophenethyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-dichlorophenethyl-D-xylitol)	Syrup	195
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-dibromoallyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-dibromoallyl-D-xylitol)	123-124	195
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-dithiocyanatoallyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-dithiocyanatoallyl-D-xylitol)	95.5-98	195
1-Deoxy-1-*C*-β-indol-D-xylitol	140-145	194
1-Deoxy-1-*C*-hexachlorocyclohexyl-D-xylitol	Syrup	194
1-Deoxy-1-*C*-phenyl-D-xylitol	168-169	188,196
1,5-Anhydro-1-deoxy-1-*C*-phenyl-D-xylitol	148-148.5	187,196
2,3,4-Tri-*O*-benzoyl-1-deoxy-1-*C*-phenyl-D-xylose (1,5-anhydro-2,3,4-tri-*O*-benzoyl-1-deoxy-1-*C*-phenyl-D-xylitol)	168	196

Infrared spectroscopy [295] of acetals and ketals of aldo- and keto-pentofuranoses, aldo- and keto-hexofuranoses, saccharic and uronic acid salts, lactones, and polyols did not reveal the presence of the characteristic bands of 1,3-dioxolans. Bands at 2820–2830 cm^{-1} [296] and at 2770 and 1030 cm^{-1}, [297] which characterise O–C–O stretching vibrations, have been found for 1,3-dioxans. It has been shown that xylitol derivatives with methylene acetal rings [142,255,298] are also characterised by a band in the region of 2800 cm^{-1}. Infrared spectra are used to demonstrate the presence of various functional groups in xylitol derivatives [109,121,217,299] and for the detection of the formation of hydrogen bonds [300].

NMR is used to determine the structures and stereochemistry of the cyclic acetals of monoses and polyols. Evidently 1,2- and 1,3-acetals should be formed in each case in the form of a mixture of two isomers with respect to the positions of the groups at the carbon atom of the acetal bridge. The possibility of the diastereoisomerism of cyclic benzylidene acetals was suggested for the first time by Fischer [301] and later such isomerism was actually observed [162,302,303]. Model substituted and unsubstituted *trans*- and *cis*-5-hydroxy-2-phenyl-1,3-dioxans (benzylidene glycerols) have been paricularly thoroughly investigated [304-314].

The structures of the mono- and di-*O*-acetals of monoses and polyols have been established by ^1H NMR. [312, 315,316] In particular, the signals of the acetal protons of di-*O*-benzylidenexylitol [317] have been found at $\tau = 4.79$ and 4.85, which confirms the presence of 1,3-dioxan rings with a *cis*-disposition of the groups and the 2,4 : 3,5-structure. The ^1H NMR spectra of monomethylenexylityl acetates made it possible to demonstrate the existence of one axial and two equatorial acetyl groups [318].

The proton signals in the NMR spectra of the methyl groups in ketals depend on the relative positions of these groups [266]. This made it possible to show that di-*O*-isopropylidenexylitol is a mixture of two isomers—one giving rise to signals of methyl protons at $\tau = 8.78$ and 8.73 with an intensity ratio of 1 : 3, which corresponds to the 2,3 : 4,5-structure, and another with signals of equal intensity at $\tau = 8.81$ and 8.73 corresponding to the 1,2 : 4,5-structure.

The relation between the structure of the ketal rings and the chemical shift of the fluorine nuclei in trifluoroisopropylidene derivatives has been described [120,121,254,319]. It has been found that the influence of the steric environment on the chemical shift of the fluorine nuclei in the CF_3 group exceeds by a factor greater than 50 the corresponding value for CH_3 groups. These spectra established the quantitative proportions of the diastereoisomers. The NMR and infrared spectra are usually investigated at the same time [118,217,299]. NMR with Fourier transformation yields more information than the proton spectra [320].

VI. METHODS FOR THE ISOLATION AND IDENTIFICATION OF XYLITOL AND ITS DERIVATIVES

Laboratory methods for the column chromatography of xylitol on neutral sorbents [321,323] and the chromatography in aqueous ethanol on ion-exchange resins in salt-forms [323,324] have been described. Ion-exxhange methods are used much more frequently to remove salts from xylitol solutions both in laboratory practice [58,61,325,326] and in industrial manufacturing processes [75,327]. Complexes of xylitol and its derivatives are chromatographed on ion-exchange resins [20,59,328].

Thin-layer chromatography of xylitol and its derivatives [176,329] and GLC of methyl ethers [330], trimethylsilyl derivatives [331-333], trifluoroacetates [333,334], methylated

acetates [335], acetates [336], methyl ethers [337], acetals, and ketals [338] are widely used. Methods have been developed for GLC of biological media containing xylitol [329] and for quantitative GLC of polyols with automatic integration of peak areas [340]. Paper chromatography of xylitol [60,341-347] and its derivatives [168,348,349] and molybdate [350] and borate [351] complexes has been used and quantitative paper chromatography of xylitol has been developed [352,353].

Xylitol can be identified on the basis of the mobility of germanate [154], phenylboronate [111,154], and copper complexes in paper electrophoresis [106]. Mass-spectrometric techniques have been developed for the acetates [129,354], methylated acetates [355], methyl ethers [356], benzylidene [357,358] and trimethylsilyl derivatives [359,360], cyclic xylityl phenylboronates [110], and trisaccharides containing xylitol [361]. Xylitol can also be identified by colour reactions [362] and Kofler microscopy [363]. Methods have been proposed for the determination of the OH groups [364]. Quantitative and qualitative analytical methods for xylitol [365] include colorimetric and polarimetric techniques whereby the polyol can be determined in preserved food [366,367] and in atmospheric dust [368].

VII. THE USES OF XYLITOL

1. In Medicine

Studies on the metabolism and clinical applications [369-380], biochemistry, and the mechanism of the action of xylitol [381-383] have been published. It has been shown by the tracer atom method that in the organism xylitol may be formed [383] by the decarboxylation of D-glucuronic acid. The pentosephosphate, glucuronoxylulose [384], and glycerophosphate metabolic cycles [385,386] are thus related.

The lethal dose [387-389] and rational norms for the consumption of xylitol have been determined, since the introduction of excessive amounts of xylitol into the organism entails an increase in weight [388,390,391], although the number of calories produced by xylitol is lower than that produced by glucose [392]. The maximum permissible harmless xylitol contents in water have been established [393]. The intravenous injection of an excess amount of a 10% xylitol solution (in excess of 4.4 g kg^{-1}) produces poisoning symptons [394], which vanish when the administration is terminated. It has been established that the elimination of xylitol from blood is a first-order process [395].

Since it has been found that xylitol increases the level of insulin in animals [371,375,396-415], a detailed study has been made of the physiological action of the polyol on the human organism [416]. A scheme has been proposed for the biosynthesis of proinsulin and insulin in the presence of xylitol [417,418]. Its influence on the carbohydrate and lipid metabolisms of healthy [412,419-424] and sick human beings [420,425-430] of different ages has been investigated. It has been found that xylitol is readily assimilated even by premature and newly born infants [431,432]. Peroral and intravenous administration of xylitol lowers the concentration of lactates [433,434], glucose, and acetoacetic acid in blood and increases the insulin content [394,406,413,422,435-441]. At the same time there is an increase in the amount of glycogen in the liver [377,395], a fall of the level of acetone, and a change in the amount of aminoacids in urine [442].

Xylitol stimulates gastrosecretion [441,443], the biosynthesis of uronic acids [388,444], ATP, [445] corticosteroids hormones [372,373,446,447], proteins [446], and growth hormones [448] and chalcogenetic, choleretic, and pancreatic activities [449-452]. Xylitol has a favourable effect on the functioning of healthy [374,376,444,453,454] and cirrhotic liver [408,409,454,455], reduces haemolysis under the influence of primaquine [365], stabilises the level of bilirubin [388,451], lowers the content of aliphatic acids in the blood [433,439,456,457], stimulates the activity of dehydrogenases [415,458,459], and inhibits isomerases [460]. It is used to inhibit the suppression of adrenocortical activity in hormonal treatment [373,447,461-463]. On the other hand, the introduction of adrenalin suppresses the secretion of insulin caused by xylitol [434]. Thus the effect of xylitol presumably depends on its concentration [451].

It has been found that xylitol is assimilated more slowly than glucose [388], since the organism must become adapted to its assimilation [371,464,465]. Xylitol may serve as a source of energy for cardiac muscle [445,466]. Intravenous administration of xylitol during anaesthesia [467] causes smaller shifts in blood composition than the introduction of glucose. It has been noted the xylitol causes caries to a lesser extent [468], since cariogenic streptococci [389] require a considerable time to become adapted to the assimilation of xylitol [469]. It has been shown that it increases the level of aminopeptidase *B* [469,470] and has a favourable effect during stress [471,472] and in parenteral feeding [394,473-475].

Even prolonged administration of xylitol does not alter the frequency and depth of respiration, arterial pressure, and cerebrocortical activity (up to 1 g kg^{-1}) [387] and does not affect the level of uric acid, triglycerides, glycerol, α- and β-lipoproteins, and total cholesterol [424]. D-Xylose or its possible metabolic products, including xylitol, are capable of causing cataract in rats [476].

Xylitol has been recommended for use in gastroenterology [477], in duodenal tubage [450], and in diabetic diets [392,424,478-480]. Cerebral scleroses, hypertonia, and pellagra are treated with xylityl pentanicotinate, which exhibits a vasodilating activity [133,481]. Xylitol derivatives of hydroxycinnamic [482] and 2-hydroxy(acetoxy)-5-iodobenzoic acids [483] exhibit anti-inflammatory activity. Aminoderivatives [228] are analgesics [484].

Xylitol solutions containing hydroxymethylaminomethane are administered intravenously [484] and the xylitol–Fe^{3+}–citrate complex [116], which increases the level of haemoglobin, is administered intramuscularly. Calcium deficiency is compensated by medicinal compositions based on xylitol and calcium carboxylates [485]. The compatibility of xylitol solutions with various combinations of 36 medicinal substances used in infusion has been studied [486]. Quaternary ammonium salts based on xylitol exhibit bacteriostatic activity [173,176]. Xylitol is introduced into ointment bases [487] and into compositions for the pressing of tablets [488].

Methods have been developed for the quantitative determination of xylitol in blood [489,490] and in urine [455], which make it possible to diagnose hepatitis [491] and cirrhosis of the liver [455]. Xylitol is an effective blood preservative, which protects it from haemolysis and the formation of methaemoglobin, reduces methaemoglobin [492-495], and promotes the coagulation of blood [496]. The metabolism of xylitol in erythrocytes has been studied [497]. Xylitol solutions stabilise bacterial cultures in lyophilisation [498] and plant cells in freezing with liquid nitrogen [489,490,499,500]. The latter behaviour is attributed to conformational changes in the plasma–membrane system [501]. Xylitol inhibits [495,502] or promotes [494,503] the germination of various plant seeds.

2. In the Food Industry

Xylitol is being used increasingly to sweeten food products[480,504] together with other synthetic sweetening agents, which are usually employed in low-calorie diets[505]. It is interesting that the maximum sweetness of xylitol is achieved following the addition of 0.06% NaCl; mixtures of xylitol with sodium glutamate, saccharin, and organic acids have been studied[506,507]. Xylitol[504,508] and surfactants based on xylitol and C_{10}–C_{30} aliphatic acids[509], which can be readily blended with dough, are used in the bread baking industry and in preserving fruit[366,510]. Milk with added xylitol has been recommended for the feeding of infants[511]. The taste, colour, bouquet, and stability of alcoholic drinks are improved by the addition of 0.5–3% of xylitol[512].

Xylityl esters of saturated and unsaturated acids[92-96] are relatively non-toxic and can be added in large concentrations (up to 10 wt.%)[509] to food products, in which they serve as dispersing, emulsifying, and surface-active agents. Such esters are soluble in oils, are dispersed in warm water[513], do not cause allergy, and are used as stable non-ionogenic emulsifying agents in cosmetic preparations[131,514-516] and for the stabilisation of food fats[517]. In aqueous solutions xylitol stabilises cysteine[518].

3. In Engineering

Xylitol replaces glycerol as a regulator of foaming[519] and as a plasticiser[520]. In aqueous solutions it protects metals from corrosion[521,522]. Xylitol-containing fluorescent pigments have been prepared[523]. Varnishes, drying oils[524], dyes, adhesives, resins[81,135,182,524-529], wetting and surface-active agents[92-96,134,173-177,228,380,530], non-ionogenic[531] and ionogenic emulsifying agents[173-176], de-emulsifying agents[532-534], polyurethane foam plastics[535,536], film-forming polyurethanes[537,538], polyphthalates[539], and hardening agents for water-soluble polymers[540] are manufactured from xylitol derivatives.

Synthetic tanning agents have been obtained by the condensation of xylityl esters with benzaldehyde and formaldehyde[541] and the condensation of the esters with epoxyethane yielded surfactants with bacteriostatic activity[96]. The product of the electrochemical alcoholysis with xylitol of natural fatty acid triglycerides (linseed oil) is used in the paint and varnish industry[542]. The monoesters of fatty acids and xylitol are employed in dying polyamide fibres[543], in the treatment of viscose staple fibre[544,545], and as deflocculating and flotation agents[137,546,547]. Mixtures of methyl and ethyl ethers of xylitan[548] and mixtures of xylityl esters of resin and tall oil acids[549] have found technical applications. Hardening acrylate oligoesters[550-552], polymethacrylate esters[290], and polycondensation resins[553] have been synthesised on the basis of xylitol.

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