

Contents

Abbreviations	XV
1. Introduction	1
2. Synthesis of 3-Amino-2,3,6-Trideoxyhexoses from Carbohydrates	7
2.1 Synthesis of 2-deoxyhexose derivatives	7
2.1.1 Preparation of 2-deoxyhexopyranosides from glycals and glycal esters	7
2.1.2 Synthesis of 2-deoxyhexose analogs from oxirane and sulfonate ester derivatives	16
2.1.3 Synthesis of 2-deoxyhexose derivatives by means of the chain-elongation of pentoses	19
2.1.4 Cleavage of the 2-phenyl-1,3-dioxolane-type acetal function of hexose derivatives	20
2.1.5 Miscellaneous methods	22
2.2 Introduction of the C-3 amino function into mono- and dideoxyhexose derivatives	25
2.2.1 Displacement reactions of sulfonate esters and halogeno derivatives with nitrogen nucleophiles	25
2.2.2 Ring opening of anhydro- and epiminohexopyranosides with nitrogen nucleophiles	34
2.2.3 Reduction of 3-oximino-2,3-dideoxyhexopyranosides	37
2.2.4 Synthesis and transformation of 3-deoxy-3-nitrohexopyranosides into 3-amino-3-deoxyhexose derivatives	42
2.2.5 Preparation of 3-amino-3-deoxyhexoses from hex-2-enopyranoside (pseudoglycal) derivatives	46
2.2.6 Synthesis of 3-amino-3-deoxyhexose derivatives by means of the allylic azide rearrangement reaction	50
2.2.7 Miscellaneous methods	57
2.3 Simultaneous generation of the C-3 amino and C-2 deoxy functions	59
2.4 2-Halogeno analogs of 3-amino-3-deoxy-hexopyranosides	60
2.4.1 Syntheses via 2,3-epiminohexopyranoside intermediates	61
2.4.2 Syntheses from 2-hydroxy- and 2-O-sulfonyl derivatives	64
2.4.3 Simultaneous introduction of the 3-amino- and 2-halogeno substituents	66

2.5 Methodologies for the preparation of 3-C-methyl branched-chain 3-amino- and 3-nitrosugars of antibiotic substances	67
2.5.1 Cyclization of dialdehyde derivatives with nitroethane	68
2.5.2 Cyanomesylation of hexopyranosid-3-ulose derivatives	69
2.5.3 The spirooxirane route to 3-C-methyl-branched amino- and nitrosugars	76
2.5.4 Addition of iodine azide to C-3 methylene sugars	79
2.5.5 Introduction of the $\text{CH}_3-\text{C}-\text{NH}_2$ branching by means of [3.3]-sigmatropic rearrangement	80
2.6 Subsequent generation of the 2-deoxy functionality of unbranched- and branched-chain 3-aminosugars	83
2.6.1 Deoxygenation of 3-aminohexoses at C-2 according to the Fischer's glycal procedure	84
2.6.2 Deoxygenation by means of the reductive removal of C-2 thioester- and thioether functions	85
2.6.3 Reductive dehalogenation of 3-amino-2-halogeno-2,3-dideoxyhexose derivatives	88
2.7 Synthetic strategies for the preparation of the 6-deoxy analogs of 3-amino-3-deoxyhexopyranosides	90
2.7.1 Deoxygenation at C-6 via C-6 sulfonate ester derivatives	90
2.7.2 C-6 Deoxygenation of 3-azido- and 3-amino-2,3-dideoxyhexopyranosides with the utilization of the ring opening reactions of 4,6-O-benzylidene acetals	94
2.7.3 Miscellaneous methods for the preparation and dehalogenation of 6-halogeno-3-amino- and 3-azidohexopyranosides	100
2.7.4 Preparation of the 6-deoxy analogs of C-3 nitrogen-substituted 2,3-dideoxyhexopyranosides with concomitant inversion of the configuration at C-5	101
2.8 Interconversion of 3-amino-2,3-dideoxy- and 3-amino-2,3,6-trideoxyhexose derivatives by means of the inversion of the configuration at carbon C-4	111
2.8.1 The <i>arabino</i> → <i>lyxo</i> conversion	111
2.8.2 The <i>lyxo</i> → <i>arabino</i> configurational transformation	116
2.8.3 The <i>ribo</i> → <i>xylo</i> C-4 configurational inversion	117
2.8.4 The <i>xylo</i> → <i>ribo</i> configurational step-over	121
2.8.5 Methods for the configurational interchange at the carbohydrate portion of the intact anthracycline antibiotics	121
3. Synthesis of 3-Amino-2,3,6-Trideoxyhexoses by Using Non-carbohydrate Precursors	123
3.1 Synthesis of 3-amino-2,3,6-trideoxyhexoses from six-carbon substrates	124
3.2 Synthesis of 3-amino-2,3,6-trideoxyhexoses from chiral and achiral precursors by means of carbon-carbon bond formation reactions	132

3.2.1 Construction of the six-carbon framework with a 5C + 1C ascent	133
3.2.2 Synthesis of 3-amino-2,3,6-trideoxyhexoses according to the 4C + 2C chain-lengthening principle	136
3.2.3 Construction of the carbon framework of 3-amino-2,3,6-trideoxyhexoses by means of the [4C + 3C]-1C methodology	146
3.2.4 3C + 3C Type construction of 3-amino-2,3,6-trideoxyhexoses . .	153
3.2.5 Miscellaneous methods	162
4. Miscellaneous Functionalized Derivatives of 3-Amino-3-Deoxyhexoses of Antibiotics and Their Conversion into Other Organic Substances	163
4.1 Thio-, nitrogen- and C-glycosides of 3-amino-2,3,6-trideoxyhexoses	163
4.1.1 1-Thio derivatives	163
4.1.2 Nitrogen-glycoside derivatives of daunosamine	165
4.1.3 C-Glycoside analogs of daunosamine	167
4.2 N-Substituted derivatives of daunosamine-type aminodeoxy hexoses	169
4.3 4-Deoxy-, C-4 branched-chain and other C-4 substituted derivatives of 3-amino-2,3,6-trideoxyhexoses	171
4.3.1 Synthesis of 4-deoxy analogs	171
4.3.2 C-4 Branched-chain derivatives	175
4.3.3 Syntheses of C-4 substituted 3-amino-2,3,6-trideoxyhexoses susceptible of transformations into beta-lactam antibiotic (thienamycin) analogs	177
4.4 Furanose-ring analogs of 3-amino-2,3,6-trideoxyhexoses	181
4.5 Synthesis of the 6-azido- and 6-amino derivatives of 3-amino-di- and trideoxyhexoses	187
4.5.1 6-Azido- and amino analogs of D-ristosamine	187
4.5.2 Approaches to 3,6-diaminohexose precursors for the synthesis of antibiotic negamycin	189
4.6 Synthesis of the uronic acid derivatives of 3-amino-di- and trideoxyhexoses	191
4.7 Conversion of 3-amino- and 3-azido-2,3,6-trideoxyhexose derivatives into carbocyclic compounds	193
5. Concluding Remarks	196
Appendix	198
Note Added in Proof	212
References	221
Subject Index	237