

ABSTRACT

Chapter One reviews the occurrence of branched-chain sugars in nature as well as some theories of their biosynthesis. Several methods for the synthesis of branched-chain sugars are outlined and some methods by which the configuration at the branching-carbon atom of branched-chain sugars may be determined are discussed.

Chapter Two reviews some of the existing data on the selective esterification of alkyl 4,6-O-benzylidene-D-galactopyranosides. An investigation of the phase-transfer method, the acyl chloride-tetrabutylammonium iodide-potassium carbonate system, the use of N-acylimidazoles and acid chloride-pyridine systems for the selective esterification of methyl 4,6-O-benzylidene-D-galactopyranosides is described and discussed.

Chapter Three describes the preparation of a number of 2- and 3-oxo derivatives by the oxidation of 3-O-acyl and 2-O-acyl derivatives of methyl 4,6-O-benzylidene-D-galactopyranosides. The synthesis of singly-branched C-methyl sugars by the reaction of the oxo-derivatives with methylmagnesium iodide is described and discussed. The cleavage of acetals by Grignard reagents is reviewed and the facile cleavage of the benzylidene acetal of two methyl 4,6-O-benzylidene- α -D-taloside derivatives by methylmagnesium iodide is described.

Chapter Four reviews some of the evidence leading to the development of a hypothesis by J. Yoshimura on the factors determining the orientation of the addition of diazomethane to D-hexopyranosid-2-, 3- and 4- uloses. The reaction of diazomethane with some methyl 3-O-acyl-4,6-O-benzylidene-D-lyxo-hexopyranosid-2-uloses and 2-O-acyl-4,6-O-benzylidene-D-xylo-hexopyranosid-3-uloses is described. The observation that the orientation of addition of diazomethane to methyl 4,6-O-benzylidene-3-O-pivaloyl- α -D-lyxo-hexopyranosid-2-ulose is opposite to that expected on the basis of Yoshimura's hypothesis has necessitated a review of the existing data and the suggestion of an alternative interpretation of this data.

Chapter Five describes the methods employed in the determination of the configuration of the C-methyl sugars, the preparation of which is described in Chapters Three and Four. The methods employed were the observation of the hydroxyl stretching of frequencies of tertiary hydroxyl groups, the dehydration of tertiary alcohols using thionyl chloride-pyridine and, in one case, by the synthesis of a known naturally-occurring C-methyl sugar. The observation of the chemical shifts of the tertiary acetoxy protons of a pair of epimeric C-methyl derivatives was investigated but this method did not permit the assignment of configuration to these derivatives.

Chapter Six reviews briefly some synthesis of doubly-branched-chain sugars. The preparation of a 2,3-di-C-methyl sugar from D-galactose is described.