Synthesis of Lewis X and three Lewis X trisaccharide analogues in which glucose and rhamnose replace N-acetylglucosarnine and fucose, respectively

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Abstract	Three analogues of the Le(x) trisaccharide: alpha-L-Fucp-(1 -> 3)-[beta-D-Galp-(1 -> 4)]-D-GlcNAcp as well as the Le(x) trisaccharide itself were synthesized as methyl glycosides. In the analogues, either only the fucose residue is replaced by rhamnose or both the N-acetylglucosamine and the fucosyl residues are replaced by glucose and rhamnose, respectively. Our synthetic strategy relied on the use of lactoside and 2-azido lactoside derivatives as disaccharide acceptors, which were submitted to either fucosylation or rhamnosylation. Our results confirm that the reactivity of lactose in protection and glycosylation reactions is greatly affected by (1) the structure of the aglycone and (2) the presence of an azido substituent at C-2 of the glucose moiety. Thus, a methyl lactoside acceptor was easily glycosylated at O-3 with perbenzylated P-thiophenyl fucoside and rhamnoside to give anomerically pure alpha-fucosylated and alpha-rhamnosylated trisaccharides, respectively. In contrast, the same reactions on a 2-azido methyl lactoside acceptor led to the formation of anomeric mixtures. While the alpha- and beta-fucosylated 2-azido trisaccharides could be separated by RP-HPLC, such separation was not possible for the rharmnosylated anomers. The desired rhamnosylated trisaccharide was finally obtained anomerically pure using an isopropylidene-protected rhanmosyl donor. The deprotection sequences also showed that the presence of a 2-azido substituent at C-2 of the glucose residue conferred stability to the vicinal facosidic linkage at C-3. To test their relative affinity for anti-Le(x) Abs the Lex analogues will be used as competitive inhibitors against methyl Le(x). In addition, their conformational behavior will be studied by NMR spectroscopy and molecular modeling experiments. (C) 2008 Elsevier Ltd. All rights reserved.
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