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Glycolipids and glycopeptides: Minimally competent Lewis acid catalysis produces surfactants for use *ex vivo* and *in vivo*

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Use of minimally competent main group Lewis acids such as InBr3 and Bi (OSO2CF3)3 permit the formation of glycosides in high yield and purity from simple sugar per-acetates at room temperature or above with remarkable α/β-selectivity. Classical reactions rely on very reactive glycosyl donors in conjunction with metal promoters (Hg^{++}, Ag^{+} etc). Newer methods have used trichloroacetimidates and strong Bronsted or Lewis acids or thioglycosides in conjunction with oxidative or thiophilic activators. Use of the more stable glycosyl per acetates in conjunction with stoichiometric amounts of strong Lewis acids (BF_3.Et_2O, $FeBr_3$ etc) has been explored with limited success. The use of "minimally competent" Lewis acids has allowed us to perform glycosidation reactions with catalytic amounts of $InBr_3$ or Bi $(OTfl)_3$ well above room temperature and without significant decomposition of the glycoside products. We will discuss the exploitation of these methods to produce glycolipid surfactants from renewable resources as well as glycopeptide drugs that penetrate the blood-brain barrier (BBB). These "biousian glycopeptides" are not subject to "Lipinski's rules" that would otherwise eliminate them as CNS drug candidates. Glycosylated amphipathic helices or "address segments" have been used to target G-protein coupled receptors (GPCRs) in the brain after intravenous administration. The addition of glycosides to endogenous peptide neurotransmitters and peptide hormones imparts favorable pharmacokinetic and pharmacodynamics (PK/PD) properties and enables penetration of the BBB which is not constrained by molecular weight.

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Altered glycosylation in cancer

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Altered glycosylation is one of the hallmarks of tumor cells and it is involved in each and every aspect of tumor progression. It affects cell surface carbohydrates and cellular and secreted glycoproteins, some of which may reach the bloodstream and be used as tumor markers. Our group has focused on the altered glycosylation of serum proteins in prostate and pancreatic cancer as potential tumor markers. We have described glycosylation changes of Prostate Specific Antigen (PSA) glycans related to sialylation and fucosylation in prostate cancer compared to Benign Prostate Hyperplasia and seminal plasma from healthy controls. In pancreatic cancer, we have described glycosylation changes on human pancreatic ribonuclease (RNase 1) and acute-phase proteins. An increase in core fucosylated structures in the N-glycan chains of RNase 1 and an increase of sialyl-Lewis x (SLe^x) and fucosylation of the acute-phase proteins ceruloplasmin and alpha-1-acid glycoprotein respectively were described and were found in advanced pancreatic cancer patients. These tumor associated glycan changes are currently being investigated in larger cohort of patients as cancer diagnostic or prognostic tools. The expression of the glycosyltransferases responsible for the synthesis of the tumor associated carbohydrate antigens such as SLe^x has been found deregulated in cancer. In particular, our group has focused on the study of sialyltransferases which have received much attention recently as they are frequently up-regulated in cancer cells. We have described using *in vitro* and *in vivo* models the involvement of the α2, 3-sialyltransferases ST3Gal III and ST3Gal IV in key steps of pancreatic tumor progression processes and have found that they are highly expressed in most pancreatic adenocarcinoma tissues.

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