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Carbohydrate based biopolyethers: Biologically active poly(sugar acid) – poly[3-(3,4-dihydroxyphenyl)glyceric acid] from medicinal plants of Boraginaceae family and its synthetic analogues

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Abstract

Sugar-based biopolymers from medicinal plants have long been studied and widely used in medicine and pharmaceutics. Novel poly(sugar acid) is the main chemical constituent of high molecular (>1000 kDa) water-soluble preparations from medicinal plants of Symphytum asperum, S.caucasicum, S.officinale, S.grandiflorum, Anchusa italica, Cynoglossum officinale and Borago officinalis. According to data of liquid-state 1 H, 13 C NMR, 2D 1 H/ 13 C HSQC, 2D DOSY and solid-state13 C NMR spectra of this biopolymer was found to be poly[oxy-1-carboxy-2-(3,4-dihydroxyphenyl)ethylene]or poly[3-(3,4-dihydroxyphenyl)glyceric acid] (PDPGA) (1) (Fig. 1). The polyoxyethylene chain is the backbone of this polymer molecule with a residue of 3-(3',4'-dihydroxyphenyl)glyceric acid as the repeating unit (2) (Fig.2). PDPGA as a 3,4-dihydroxyphenyl derivative of poly(2,3-glyceric acid ether) belongs to a rare class of poly(sugar acids) as well. Its basic monomeric moiety glyceric acid is an oxidative form of the aldotriose glyceraldehyde. Poly(2,3-glyceric acid ether) chain is the backbone of this polymer molecule and 3,4-dihydroxyphenyl groups are regular substituents at carbon atoms in the chain. Multifunctionality of PDPGA should be a reason of its wide spectrum of biological activity (Fig. 3). Oligomers of PDPGA was synthesized by "green" enzymatic ring opening polymerization of methyl 3-(3,4- dibenzyloxyphenyl)glycidate using lipase from Candida rugosa and further deprotection. The enzymatic polymerization is a "green" chemistry alternative to classic chemical synthesis as it utilizes processes that minimize the use and generation of hazardous substances. Hyaluronidase degrades high molecular mass of hyaluronic acid into smaller fragments which stimulate inflammation. PDPGA possesses the ability to inhibit the enzymatic activity of hyaluronidase and consequently exhibits anti-inflammatory efficacy. PDPGA exerted anticancer activity in vitro and in vivo against prostate cancer (PCA) cells via targeting androgen receptor, cell cycle arrest and apoptosis together with a strong decrease in prostate specific antigen level in plasma. Thus, PDPGA was identified as a potent agent against PCA without any toxicity.