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Biopolyether from medicinal plants, its synthetic monomer and their anticancer efficacy

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Within the field of pharmacologically active biopolymers the area of stable polyethers seems rather new and attractive. The high-molecular fractions (>1000 kDa) from the several species of two genera Symphytum and Anchusa (Boraginaceae) family were isolated by ultrafiltration. According to 13C and 1H NMR, 1D NOE, 2D heteronuclear 1H/13C HSQC and 2D DOSY esperiments the main structural element of these high-molecular fractions was found to be a new regular polymeric molecule. The polyoxyethylene chain is the backbone of this biopolymer. 3,4-Dihydroxyphenyl and carboxyl groups are regular substituents at two carbon atoms in the chain. The repeating unit of this regular caffeic acid-derived polyether, is 3-(3,4-dihydroxyphenyl)glyceric acid residue. Thus, the structure of natural polymer under study was found to be poly[oxy-1-carboxy-2-(3,4-dihydroxyphenyl) ethylene] or poly[3-(3,4-dihydroxyphenyl)glyceric acid] (PDPGA). This compound represents a new class of natural polyethers. Then the racemic monomer 2,3-dihydroxy-3-(3,4-dihydroxyphenyl)propionic acid (DDPPA) and its enantiomers (+)-(2R,3S)-DDPPA and (-)-(2S,3R)-DDPPA were synthesized via Sharpless asymmetric dihydroxylation of trans-caffeic acid derivatives using a potassium osmiate catalyst and enantiocomplementary catalysts cinchona alkaloid derivatives $(DHQ)_2$-PHAL and $(DHQD)_2$-PHA as chiral auxiliaries. Besides, methylated PDPGA was obtained via ring opening polymerization of 2-methoxycarbonyl-3-(3,4-dimethoxyphenyl)oxirane using a cationic initiator. PDPGA is endowed with intriguing pharmacological activities as anticomplementary, antioxidant, anti-inflammatory, burn and wound healing and anticancer properties. PDPGA and its synthetic monomer exerted anticancer activity *in vitro* and *in vivo* against androgen-dependent and -independent human prostate cancer (PCA) cells via targeting androgen receptor, cell cycle arrest and apoptosis without any toxicity, together with a strong decrease in prostate specific antigen level in plasma. However anticancer efficacy of PDPGA against human PCA cells is more compared to its synthetic monomer. Methylated PDPGA did not show any activity against PCA. Overall, this study identifies PDPGA as a potent agent against PCA without any toxicity, and supports its clinical application.

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