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Caffeic Acid-Derived Biopolyether from Medicinal Plants as Anticancer Agent

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A new series of linear and regular caffeic acid-derived polyether, namely poly[3-(3,4-dihydroxyphenyl)glyceric acid] (PDPGA) was isolated and identified in the water-soluble, high molecular weight fractions obtained from *Symphytum asperum*, *S. caucasicum*, *S. officinale*, *S. grandiflorum* and *Anchusa italica* (Boraginaceae). According to data of ¹³C, ¹H NMR, 2D ¹H/¹³C HSQC experiment the polyoxyethylene chain is the backbone of the polymer molecule. The 3,4-dihydroxyphenyl and carboxyl groups are regular substituents at two carbon atoms in the chain. The repeating unit of this polymer is 3-(3,4-dihydroxyphenyl)glyceric acid residue. Most of the carboxylic groups of PDPGA from *A. italica* and *S. grandiflorum* unlike the polymer of *S. asperum*, *S. caucasicum* and *S. officinale* are methylated. The 2D DOSY experiment gave the similar diffusion coefficient for the methylated and non-methylated signals of *A. italica* PDPGA. Both sets of signals fell in the same horizontal. This would imply a similar molecular weight for methylated and non-methylated polymers. The synthesis of racemic monomer of PDPGA was carried out via asymmetric dihydroxylation of *trans*-caffeic acid derivatives using a potassium osmate catalyst and cinchona alkaloid derivatives as chiral auxiliaries. PDPGA and monomer exerted anti-cancer efficacy *in vitro* and *in vivo* against 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, our results showed that anticancer efficacy of PDPGA is more effective compared to its synthetic monomer. Overall, this study identifies PDPGA as a potent agent against PCA without any toxicity, and supports its clinical application.

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