Enzymatic synthesis of glycosides and oligosaccharides using glycansucrases and potential applications

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Glucosyltransferases (GTFs) are enzymes that synthesize either dextrans or glucans, using sucrose as a substrate. GTFs can catalyze the transfer of a sucrose-derived glucose to other carbohydrates, thereby, allowing oligosaccharide synthesis. This reaction is an acceptor reaction, where the added carbohydrates are acceptors. Enzymatic transglycosylation, using *L. mesenteroides* glucansucrases, have been also employed in the modification of natural bioactive compounds, improving their physicochemical properties. EGCG (epigallocatechin gallate), which are main polyphenol compound in green tea, and quercetin, which is a widespread flavonoid found in fruits, vegetables, and a variety of other dietary sources, have strong antioxidative activities, anticancer, antimutagenic, antibacterial effects, prevention of dental caries, regulation of plasma cholesterol levels. However, EGCG and quercetin are poorly soluble in water, and degraded easily by light irradiation in water resulting in rapid browning. To solve these problems, the transglucosylation of novel EGCG and quercetin analogues was studied using glucansucrases from *Leuconostoc mesenteroides*. Analogues were synthesized by the reaction of EGCG or quercetin with sucrose and glucansucrases from *L. mesenteroides* B-1299CB. Their structures were assigned as epigallocatechin gallate 7-*O*-a-D-glucopyranoside (EGCG-1), epigallocatechin gallate 7,4"-*O*-a-D-glucopyranoside (EGCG-2), epigallocatechin gallate 4"-*O*-a-D-glucopyranoside (EGCG-4), epigallocatechin gallate 4'-*O*-a-D-glucopyranoside (EGCG-5),

epigallocatechin gallate 7,4'-*O*-a-D-glucopyranoside (EGCG-3), epigallocatechin gallate 4¢,4"-*O*-a-D-glucopyranoside (EGCG-6), quercetin-4′-*O*-α-D-glucopyranoside (Q-G1) and quercetin -3′-*O*-α-D-glucopyranoside (Q-G1′), after ^{1}H, ^{13}C, HSQC, H-H COSY, HMBC analyses. EGCG analogues showed a different antioxidant effects according to their structures (EGCG ³ EGCG-1 > EGCG-4 > EGCG-3 > EGCG-2 > EGCG-5 > EGCG-6). Furthermore, EGCG analogues showed the strong stability in a browning resistance than EGCG, even for 24 h. The solubility of the EGCG analogues was 49, 126, 114, 69, 55 and 122 times higher than that of EGCG, respectively. The primary product (Q-G1) evidenced slower effects on DPPH radical scavenging activity (SC_{50} = 25.2 μM) than was seen with quercetin (SC_{50} = 6.5 μM). The water solubility of Q-G1 was 12.7 mM, whereas the quercetin was barely soluble in water. The K_i value of Q-G1 (674.5 μM) was almost identical to that of quercetin (673.3 μM) with regard to tyrosinase inhibition effects. A method is presented for synthesizing thermo- and acid-stable oligosaccharides (TASO) from sucrose (2.5-4M) using a dextransucrase prepared from *Leuconostoc mesenteroides* B-512FMCM. The DP of oligo-saccharides synthesized was ranged from 2 to 11. TASO resists hydrolysis of its glycosidic linkages at 140℃ and pH 6.0 for 1 h. It was stable at pHs ranging from 2 to 4 at 120℃. These oligosaccharides effectively inhibited the formation of insoluble glucan, the growth and pH production of *Streptococcus sobrinus.* However, it stimulated the growth of probiotic such as *Bifidobaterium* sp. TASO potentially can be used as sweeteners for the food and beverages where thermo- and acid-stable properties are required and as potential inhibitors of dental caries.