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Short Communication

Enzymatic routes for the production of mono- and di-glucosylated derivatives of hydroxytyrosol

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ABSTRACT

In this work, a new eco-friendly procedure for the synthesis of hydroxytyrosol and tyrosol α-glycosidic derivatives was proposed by using the marine α-glucosidase from *Aplysia fasciata*, and a commercial tyrosinase from mushroom for the bioconversion of tyrosol glycosidic derivatives into the corresponding hydroxytyrosol products. New hydroxytyrosol mono- and di-saccharide derivatives were synthesized at final concentrations of 9.35 and 10.8 g/l of reaction, respectively, and their antioxidant activity was evaluated by DPPH test. The best antioxidant agent resulted the (3,4-dihydroxyphenyl) ethyl-α-D-glucopyranoside; it showed a radical scavenging activity similar to that of the hydroxytyrosol, together with an increased hydrosolubility. This molecule could be a good response to many food industry demands, always in search of cheap antioxidants with nutritional properties to improve the nutritional value and the quality of foods.

1. Introduction

Olive biophenols have attracted the attention of food and pharmaceutical industries first of all for their well-acquainted antioxidant activity (Obied et al., 2005). 2-(4-Hydroxyphenyl)ethanol (tyrosol, **1**) and 3,4-dihydroxyphenyl ethanol (hydroxytyrosol, **2**) represent the most abundant oil phenols (Vissers et al., 2004). Hydroxytyrosol, as well as being a powerful antioxidant and scavenger of free radicals, reduces, in fact, the risk of coronary heart disease and atherosclerosis (Visioli et al., 1995, 2002) and it is involved in a mechanism of protection against oxidative DNA damage (Waterman and Lockwood, 2007). Differently, tyrosol shows milder antioxidant properties (Damiani et al., 2003). Nevertheless, it exerts a powerful protective effect against oxidative injuries in cell systems and improves the intracellular antioxidant defence systems (Mateos et al., 2008). In spite of their potential applications in the nutraceutical and pharmaceutical fields, few methods have been developed for synthesizing tyrosol and hydroxytyrosol glycosidic derivatives.

In this paper, we screened the possibility to perform glucosylation reactions of various phenolic compounds, including tyrosol and hydroxytyrosol and their structurally analogous compounds, by using the marine α-glucosidase from *Aplysia fasciata*. Interesting glucosylations at phenolic sites of some selected acceptors were observed, especially considering that phenolic hydroxyls are inefficiently glycosylated by glycosidases (van Rantwijk et al., 1999). Among all molecules tested, tyrosol and hydroxytyrosol glycosylation procedures were more deeply investigated. Tyrosol α-glycosidic derivatives were efficiently produced by direct glucosylation and in a second enzymatic step, these molecules were regioselectively oxidized by a commercial mushroom tyrosinase to give the hydroxytyrosol α-glycosyl derivatives, possessing interesting radical scavenging activities.

These results appeared of great interest when compared to enzymatic synthesis of salidroside, monoglucuronides derivatives of hydroxytyrosol, and tyrosol, previously reported in literature (Tong et al., 2004; Khymenets et al., 2006).

2. Methods

2.1. General

TLC solvent systems: (A) (CH_3CN:H_2O, 8:2, v/v); (B) (CH_3CN:H_2O, 9:2, v/v). Compounds on TLC plates were visualized under UV light or charring with α-naphthol reagent.

Other technical information were reported in Supplementary Section S.1.

2.2. Enzyme source

A clear enzymatic homogenate from *A. fasciata* visceral mass was prepared as previously described by Andreotti et al. (2006). Since the most abundant hydrolytic enzyme in *A. fasciata* visceral mass extract was an α-D-glucosidase activity, this enzymatic solution (8.1 mg total protein/ml; 1.2 U/mg, using *p*-nitro-

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