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Review

Structural implications of polyphenolic antioxidants

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ABSTRACT

Natural polyphenols have been used in foods, cosmetics, and medicines to exploit their functional properties, including antioxidant, anti-inflammatory, antiviral, antidepressant, analgesic, anti-mutation, and antitumor activities. Because of their protective property against reactive oxygen species in the human body, which are associated with aging-related chronic diseases, polyphenols have been considered as useful building blocks for biomaterials development. Here, recent studies on common polyphenols are summarized and their structural implications are discussed, providing insights into their molecular structure and related properties and evaluating the effect of structural modifications such as functional rearrangements, substitution reactions, and polymeric conjugations. The fundamental understanding of the chemical structure of polyphenols could diversify the strategy for the development of biomimetic, eco-friendly, and biocompatible materials.

Contents

Introduction

Recently, natural antioxidants such as polyphenols have become the subject of active investigation for the development of future biomaterials because of their beneficial properties [1–14]. These structures have been used as valuable building blocks with outstanding functionality and biocompatibility. Polyphenols belong to the large group of flavonoids, which are well-known for their antioxidant activity; they are found in a wide variety of food sources and are the most common active ingredients of phenolic-based plant constituents [15,16]. Polyphenols exhibit various beneficial effects such as anti-inflammatory, anticancer, and antioxidant activities [6–8]. Because of their characteristic phenolic OH groups, they have the ability to chelate highly redox-active metal ions, which strengthens their protective effect against oxidative damage [16].

Polyphenols are the most effective functional ingredients with biological activities [17,18]. Polyphenolic-based compounds are useful to mitigate oxidative stress and prevent or delay oxidation processes by scavenging reactive radicals and by chelating iron [19–24]. Numerous studies have revealed various functions, such as skin protection against biological stressors, ultraviolet (UV)

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radiation, viruses, bacteria, and fungi, and assistance for the adaptation process to environmental conditions and cellular signal transduction. These useful properties can be altered by chemical and enzymatic treatments [25]. Dietary polyphenols play a considerable role in age-related human diseases and their prevention. Although these compounds have been extensively studied, their complex relation with diseases has not yet been thoroughly defined. Their importance is mainly based on their positive contribution to cellular processes in the human body and protective activity against oxidative damage by suppression of reactive radicals [26]. These advantageous properties make polyphenols attractive building blocks for the development of novel biomaterials.

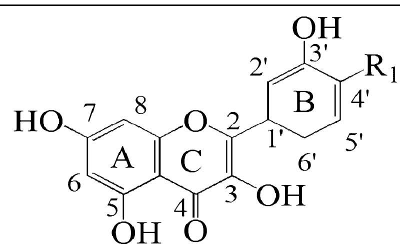
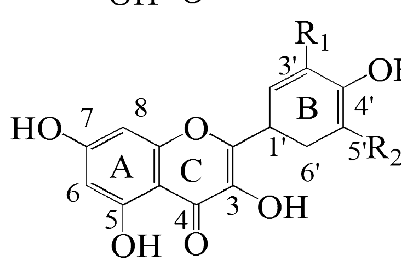
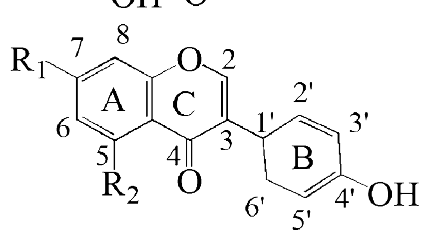
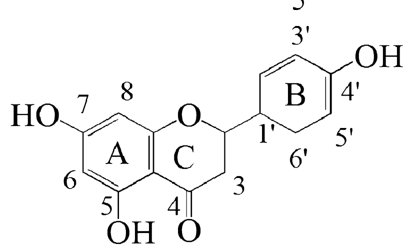
Commercial uses of polyphenols are based on their numerous properties and include functional food ingredients, antioxidants for preservation, cosmetic applications, etc. [27–29]. Plant-derived polyphenols have been receiving increasing attention as compared with synthetic antioxidants such as butylated hydroxyanisole, butylated hydroxytoluene, and *tert*-butyl hydroquinone, widely used in the food industry. Presently, the use of synthetic antioxidants is limited because of their carcinogenicity and liver toxicity, and the development and utilization of more beneficial and biocompatible antioxidants of natural origin significantly increased [30].

Polyphenolic-based secondary metabolites of plants, which are the most commonly used antioxidants in humans, are abundant in a wide variety of plant-derived foods, especially fruits, leaves, and seeds [27,29]. Their content in a regular diet is associated with a good antioxidant performance, and their intake could be as high as 1 g/day, which is much higher than that of all other classes of phytochemicals and known dietary antioxidants, 10 times higher than the intake of vitamin C, and 100 times higher than the intakes of vitamin E and carotenoids. This clearly proves the biocompatibility of polyphenols.

The present review article focuses on polyphenolic-based antioxidants and the dependence of their properties on their chemical structures. More specifically, hydroxyl groups and their modification by glycosylation, acylation, conjugation with macromolecules, and substitution reactions will be extensively discussed to highlight the possible relationship between the presence of a C3 hydroxyl group and the antioxidant capacity. For simplicity, this article will discuss only four representative polyphenolic classes, i.e., flavanones, flavonols, isoflavones, and flavones, and their molecular structures, which are represented in Table 1. Attachment of a sugar moiety to these natural products is under development as one of the most promising tools for the design of novel compounds with potential biological applications.

In the last decade, since aging-linked chronic diseases were associated with oxidative stress, the use of polyphenolic compounds in materials science and engineering, particularly in biomaterials, has become more popular because of the preventive effects of natural polyphenols against reactive oxygen species

Table 1
Basic structures of polyphenols and their numbering.

Classes	Skeleton and carbon numbering of flavonoids	Common examples
Flavones		R_1 = H (Apigenin) R_1 = OH (Luteolin)
Flavonols		R_1 = OH, R_2 = H (Quercetin) R_1 = R_2 = H (Kaempferol) R_1 = R_2 = OH (Myricetin) R_1 = OMe, R_2 = H (Isorhamnetin)
Isoflavones		R_1 = R_2 = OH (Genistein) R_1 = OH, R_2 = H (Daidzein) R_1 = OH, R_2 = H (Glycitein)
Flavanone		R_1 = OH, R_2 = OMe (Hesperetin) R_1 = H, R_2 = OH (Naringenin)