

Antioxidant Properties of Bee Products

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Bee products have been used since ancient times both for their nutritional value and for a broad spectrum of therapeutic purposes. They are deemed to be a potential source of natural antioxidants that can counteract the effects of oxidative stress underlying the pathogenesis of many diseases.

Bee Products

Antioxidant Activity

Honey

Propolis

Pollen

Royal Jelly

Beeswax

Bee Venom

1. Introduction

Since ancient times, beekeeping products as honey, propolis, pollen, royal jelly, beeswax and bee venom have been among the most commonly used natural products in folk medicine by virtue of their powerful healing properties and high bioactive molecule content ^[1]. This branch of traditional medicine, with its scientific foundations, is now called apitherapy and is used to prevent or heal a number of different conditions, as wounds, rheumatic diseases, immune and neurologic conditions, and alimentary tract disorders, among others ^{[2][3]}. Nowadays, diet and a balanced life style are widely acknowledged to play an important role in the prevention and treatment of diseases. To improve their quality of life, modern consumers increasingly seek and use so-called natural functional foods containing bioactive substances of natural origin, thanks in part to their greater safety compared to synthetic drugs ^{[4][5]}. Scientific studies attribute to bee products a broad range of beneficial health effects, including antioxidant, antibacterial, anti-inflammatory, antitumor, antiviral properties, and many others ^{[6][7]}. One of the most important properties is their antioxidant capacity, which contributes to the prevention of certain illnesses, protecting cells against damage by oxidative agents such as free radicals. These are highly unstable, and therefore very reactive atoms, molecules or compounds due to their atomic or molecular structure, which has one or more unpaired electrons. They attempt to pair up with other molecules, atoms, or even individual electrons to create a stable compound, receiving electrons from other atoms. This generates reactive oxygen species (ROS), and free radicals bring about molecular transformations and gene mutations in many types of organisms. This is called oxidative stress and is deemed to contribute to the development of chronic and degenerative diseases such as cancer, autoimmune disorders, aging, cataracts, rheumatoid arthritis, and cardiovascular and neurodegenerative diseases ^[8]. ROS are produced naturally by metabolism or result from poor living conditions and environmental pollution ^[9]. The radical theory in human physiology claims that active free radicals are involved in almost all cellular degradation processes and lead to cell death. Antioxidants are molecules capable of slowing or inhibiting the oxidation of other molecules, thereby preventing such changes. Plant antioxidants display great bioactivity and molecular diversity and are present in honey and other bee products ^[10]. For example, since honey

is produced by bees from nectar or plant secretions, various substances are transferred from plants and accumulated in this food. Consequently, the composition of honey, including its physical, chemical, organoleptic, and nutraceutical properties, is directly linked to the geographical, climatic and environmental characteristics of the areas where it is produced [11]. These differences represent a useful discriminatory tool for the classification and identification of honey.

2. Antioxidant Compounds in Bee Products

Plant antioxidants are synthesized by plants to counteract biotic (pathogenic, predatory, competitive species) and abiotic (UV radiation, desiccation, thermal shock) stresses and favor the attraction of pollinators, the dispersion of seeds and allelopathic phenomena [9]. Secondly, they affect the health of people who consume them through food, including honeybee products produced by bees from floral nectar, pollen, or plant secretions. Plant antioxidants are highly bioactive and present great molecular diversity, but phenolics (phenolic acids, flavonoids) are the most abundant and have the highest antiradical activity [12]. Phenolic compounds range from simple, low molecular-weight, single aromatic-ringed compounds to large, complex tannins and derived polyphenols [13]. Phenolic acids can be divided by chemical structure into hydroxybenzoic acids, with a C1–C6 nuclear structure derived from benzoic acid, with different methylation and hydroxylation of the aromatic ring (e.g., gallic acid, benzoic acid and vanillic acid); and hydroxycinnamic acids, with a C3–C6 general structure and differences in the originating ring substituents (e.g., caffeic acid, p-coumaric acid, ferulic acid, and cinnamic acid). Flavonoids have a C6–C3–C6 general structure, linking two benzene rings connected by a pyran ring, and can be classified into flavones, flavanones, and flavonols according to the type of substituent present on the ring (e.g., catechin, myricetin, quercetin, apigenin, kaempferol, luteolin, rutin, isorhamnetin, pinocembrin, or gallochatechin) [14]. The consulted literature refers only to active substances present in bee products and does not consider possible metabolites derived from honeybee metabolism. Furthermore, the assays used to determine the antioxidant compounds and AOA identify groups of compounds with similar chemical properties and not the single active substances. Different mechanisms underlie the antioxidant capacity of phenols, such as free-radical scavenging, donation of hydrogen, metal ion chelation, single oxygen quenching, and action as a substrate for superoxide and hydroxyl radicals [15][16]. These mechanisms are strictly linked to the metabolites and their molecular structure, e.g., the readiness of hydrogen donation may be affected by the steric hindrance of the carboxyl group, located next to the hydroxyl group. This indicates that the number and position of hydroxyl groups in phenolic compounds are paramount to the scavenging capacity of antioxidants [17]. AOA is highly correlated with phenolic compounds, but bee products are multicomponent natural substances and therefore also contain other substances presenting AOA, including minerals, amino acids, peptides, proteins, organic acids, and enzymes, but at lower concentrations than phenols [14]. Type and concentration are primarily influenced by the bee product in question, followed by botanical source, geographical and entomological origin, and climatic conditions [18].

3. Concluding Remarks

The antioxidant properties of different bee products can be only be compared when the data are obtained using the same methods and units of measurement for the different matrices. Bartkiene et al. [6] compared honey, propolis, and bee bread, ranking TPC and AOA values (measured as % DPPH) in the following order: bee bread > propolis > honey, and bee bread > honey > propolis, respectively. Based on data from the literature, propolis should be the most powerful antioxidant of bee products—having been shown to contain the highest levels of phenols and flavonoids—followed by pollen and royal jelly [3][18]. The results do, however, differ considerably depending on matrix, extraction solvent, and assay. By way of example, Nakajima et al. [19] (using an antioxidant-capacity assay to measure the radicals induced in a rat cell line through application of ROS) observed the rank order of antioxidant effects to be as follows: propolis water extract > propolis ethanol extract > pollen, but neither royal jelly nor 10-hydroxy-2-decenoic acid (10-HDA) had any effect. A comparative study of the AOA of honey and propolis performed by Mouhoubi-Tafinine et al. [20] showed propolis samples to have higher concentrations of polyphenols, flavonoids, vitamin C, and carotenoids, and to display a greater AOA (measured by the reducing power assay). Even compared to pollen, honey clearly appears to have lower phenol and AOA levels, as shown by Duarte et al. [21]. Mohdaly et al. [22] reported that propolis extract had superior scavenging activity (based on DPPH and ABTS assays) compared to pollen extract. The disparity of the results presented in this review is well known to be influenced by considerable botanical, geographical, and other above-mentioned differences among samples. There are many inconsistencies in the information related to AOA analysis of bee products, such as sample dilution, extraction method, and conditions, quantification method, and criteria for reporting the results. All these have a decisive influence on the disparity of results, hindering comparison of the biological properties of different samples of the same bee products, despite being similar. Hence, to determine valid common criteria, the analytical procedures need to be as standardized as possible to accurately classify bee products by composition and commercial value. It is difficult to compare the analytical results reported in this review with each other, because even where the same analytical technique is used (as the Folin-Ciocalteu method), the results may be expressed in different units. Results are calculated by plotting the concentration of a calibration standard against absorbance on a standard curve, but analytical results can only be compared with others when the same reference compounds are used. Furthermore, bee products are chemically very complex, and the use of solvents of different polarity affects the composition of the solutions or extracts to be analyzed. While hydrophilic substances are more soluble in polar solvents such as alcohols, hydrophobic ones show greater affinity for non-polar solvents such as hydrocarbons. The analytical result can therefore also vary according to the solvent used to dissolve the honey or propolis or other hive products being tested. The extract's properties strongly depend on the solvent used but also on extraction conditions, time, and temperature [3]. Accurate standardization of analytical methods is needed to define quality criteria and support estimation of the commercial value of these expensive natural products. Working with standardized methodologies, accepted by researchers and analytical laboratories, with adequate analytical protocols that define the solvents, extraction procedures, and criteria for expressing the results, will allow the collection of reliable, comparable data.

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