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Synthesis and antioxidant activity of star-shape phenolic antioxidants catalyzed by acidic nanocatalyst based on reduced graphene oxide

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ABSTRACT

Phenolic antioxidants play important role in prevention of oxidation in different industrials. The research objective in the current study was synthesis and evaluate of antioxidant activity of star-shape phenolic antioxidants. The synthetic compounds were prepared in the presence of sulfonated reduced graphene oxide. The antioxidant activity of synthesized compounds was investigated by spectrophotometrically method according to the DPPH assay. Overall, these compounds are potentially important antioxidant and also to limit activity of reactive oxygen species.

1. Introduction

There are three types of antioxidants including phytochemicals, vitamins, and enzymes that they found in nature [1]. Enzymes are one type of antioxidant that comes from the protein and mineral. These enzymes are synthesized in the human body. The human body does not produce antioxidant vitamins naturally; therefore, it is essential to provide human body. Common vitamins based on antioxidant are vitamins A, C, E, folic acid and beta-carotene. Phytochemicals are the antioxidants that are naturally used by plant to protect themselves against free radicals [2]. They are broken down into the four categories; i) carotenoids ii) flavonoids iii) allyl sulfides and iv) polyphenols. The polyphenol antioxidants are applied in the different sciences (Fig. 1).

Phenolic compounds including polyphenols, phenolic acids, tocopherols, and lignans are widely distributed in plants, foods, animals and so on [3,4]. Synthetic phenolic antioxidants were originally developed for the protection of oxidation in petroleum, food, rubber, polymer, and plastic industrials [5,6]. Some structures of the phenolic antioxidants as food additive are shown in Fig. 2.

The discovery of new synthetic antioxidants is important in the field of organic transformations and antioxidant synthesis that open efficient and simple approaches for the synthesis of robust and convenient antioxidants. The application of efficient approach for the synthesis of phenolic antioxidants is of great importance that can be used to prevent oxidation process in different area of science. The phenolic antioxidants are an important class of organic compounds because of their uses in food, plastic, rubber, polymer, medicine, and pharmacy [7–9]. Traditional methods are manually manufactured by an acid catalyzed condensation reaction of phenol derivatives and carbonyl compounds [10–20]. Despite of simplicity of such methods, they often suffer from several limitations including long reaction times, the use of organic solvent, excess amount of catalyst, and non-reusable and non-environmental

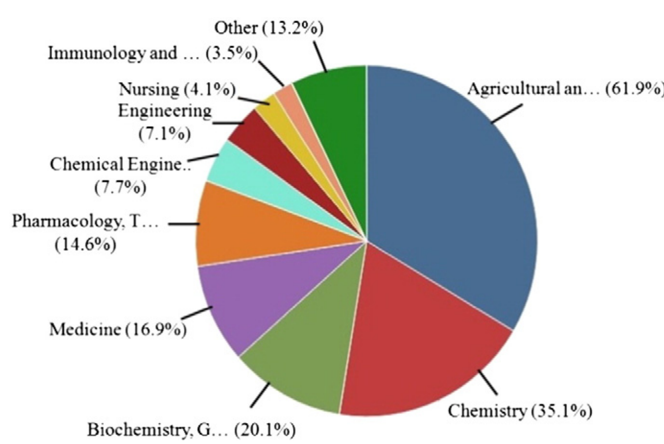

Fig. 1. Importance of phenolic antioxidants in the world science (Results extracted from Scopus web site).

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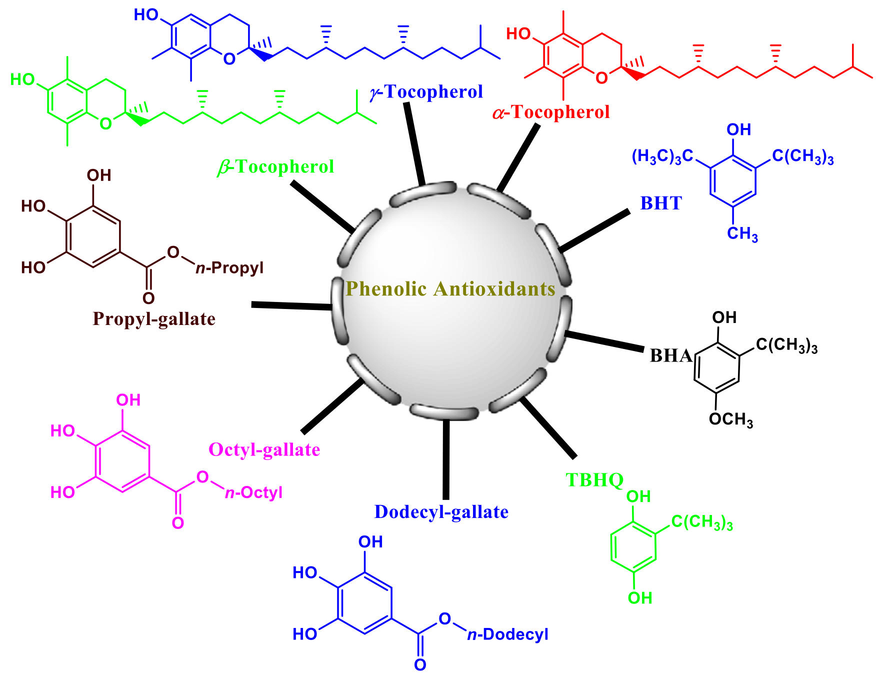

Fig. 2. Some structure of food additives based on phenolic antioxidants.

catalyst. To avoid the mentioned problems associated with these traditional methods and to enable reaction with a broad catalytic systems and substrates for the synthesis of phenolic antioxidants [21–27], a great deal of effort has been made toward the development of new methodologies. Some of the most widely used strategies in the synthesis of phenolic antioxidant are shown in Scheme 1.

As shown in Scheme 1, the most of these approaches for the synthesis of phenolic antioxidants are based on condensation reactions in acidic medium. In work by Scott et al., triethyl orthoformate was used as providing condensation agent in the synthesis of cyclic trisphenolic antioxidants [34]. Recently, Buravlev et al. introduced one interesting method using KSF clay for bisphenolic antioxidants and they evaluated antioxidant properties [35].

Very recently, Gorji et al. reviewed the graphene/nanotube application in thin film solar cells [36]. In 2011, Gao et al. were prepared MnO_2/graphene composites and they used it as electrode materials for supercapacitors and excellent electrocatalytic activity for reduction of oxygen [37,38]. Also, we have previously studied acidic catalyst based on graphene and graphene oxide for the synthesis of phenolic antioxidants [39–41]. In continuation of our interest on antioxidant, and antimicrobial activity of our synthetic compounds [42–44], herein we report the antioxidant properties of bisphenolic compounds.

2. Experimental

2.1. General remarks

2,4-Dimethylphenol, 2,4-di-*tert*-butylphenol, 2,6-di-*tert*-butylhydroxytoluene (BHT), different aldehydes, graphite powder and inorganic materials were purchased from Merck chemical company and used without purification. Also, the 1,1-diphenyl-2-pycril-hydrazyl (DPPH) was purchased from Sigma-Aldrich (USA). The ^{1}H and ^{13}C NMR spectra were recorded on Brucker DRX-400 MHz spectrometer. Chemical shifts δ (ppm) are given relative to DMSO-d_6 as a solvent: references for DMSO-d_6 were 2.47 ppm (^{1}H NMR) and 39.94 ppm (^{13}C NMR). Multiplets in ^{1}H NMR spectra were recognized as m (multiplet), s (singlet), d (doublet), t (triplet), and dd (doublet of doublet). The ^{13}C NMR spectra were acquired on a broad band decoupled mode. FT-IR spectra were recorded in the range of 400–4000 cm^{-1} as potassium bromide pellets on Perkin-Elmer 781 spectrophotometer. Melting points of synthetic compounds were determined in open capillary tubes with a Thermo-scientific micro melting point apparatus and are uncorrected. The progress of the reactions was monitored by thin layer cheomatography (TLC) on silica gel poly Gram SILG/UV 254 plates from Merck chemical company.

2.2. Preparation of the catalyst

The graphene oxide and reduced graphene oxide nanosheets were prepared according to our previous works [41]. Sulfonated reduced graphene oxide nanosheets (RGO-SO_3H) was synthesized *via* the hydrothermal process using sulfuric acid at 180 °C under inert gas conditions. First, 1.0 g of reduced graphene oxide (RGO) was added into 50 mL of sulfuric acid. The mixture was sonicated at 40 W for 15 min. Then, the mixture was moved into round-bottom flask at 180 °C for 24 h under nitrogen atmosphere. After the completion of the reaction, the mixture was washed with a large amount of deionized water over sinter-glass (G-4). The solid materials were dried at 80 °C for 24 h. Finally, the prepared catalyst (RGO-SO_3H) was obtained and employed in the synthesis of star-shape phenolic antioxidants.

2.3. General procedure for RGO-SO_3H-catalyzed star-shape phenolic antioxidants

A mixture of 2,4-dialkylphenol (6 mmol), aromatic and aliphatic aldehydes (2 mmol) and RGO-SO_3H (40 mg) was stirred in a 25 mL round-bottom flask equipped with a condenser at 100 °C for appropriate time according to Results and discussion section. After TLC indicated that the reaction was completed, the reaction mixture was cooled to room temperature and 15 mL acetone (3 × 5 mL) was added. The catalyst was separated under reduced pressure using vacuum pomp over sinter glass (G-4). The organic solution was evaporated on rotary