

## Mini-review

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# Phenolic antioxidants from herbs and spices

Nobuji Nakatani

*Department of Food and Nutrition, Faculty of Human Life Science, Osaka City University, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan*

*Tel.: +81 6 6605 2812; Fax: +81 6 6605 3086; E-mail: nakatani@life.osaka-cu.ac.jp*

**Abstract.** Spices and herbs are recognized as sources of natural antioxidants and thus play an important role in the chemoprevention of diseases resulting from lipid peroxidation. Our studies on spices and herbs have given us over a hundred compounds, known and new, having high antioxidant activity. From the Labiatae family, *Rosmarinus officinalis*, *Thymus vulgaris*, *Origanum vulgare* and *O. majorana* gave 26 active compounds. Over 40 antioxidative compounds from *Zingiber officinale*, 26 compounds from *Curcuma domestica* = *C. longa*, *C. xanthorrhiza* and *Z. cassumunar* were determined, these belonging to the family Zingiberaceae. From the family Myrtaceae, 25 compounds from the berries of *Pimenta dioica* were determined and 3 carbazoles were isolated from *Murraya koenigii*.

Structure-activity relationships of some of the isolated compounds were also discussed.

## 1. Introduction

Lipid peroxidation, a radical chain oxidation of unsaturated fatty acids, causes not only food deterioration but also DNA, cell membrane and tissue damages in human body. Antioxidants have been widely used to delay or prevent oxidation of fats and oils. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), the most commonly used synthetic antioxidants, show high efficacy, but their use in food has been partially restricted due to their undesirable effect on the enzymes of human organs. Natural antioxidants, such as tocopherols and ascorbic acid, are also practically used but less active than synthetic ones. Consequently, there is currently a strong worldwide interest in searching for new and safe antioxidants from natural sources. This prompted us to isolate new antioxidants and elucidate their chemistry and functionality for further study concerning chemoprevention of inflammation, tumor, atherosclerosis and aging. Our major target for effective antioxidants has been focused on edible plants, particularly spices and herbs.

Since the prehistoric time, spices and herbs have been used not only for flavoring foods but also for antiseptic or medicinal purposes. Their preservative effects suggest the presence of antioxidative and antimicrobial compounds. Preliminary studies revealed that rosemary, sage, oregano, thyme, nutmeg, mace, clove, allspice, ginger, turmeric and paprika possessed high antioxidant activity [1–3].

## 2. Antioxidants from the Labiatae

### 2.1. Less polar antioxidants

The extract of rosemary (*Rosmarinus officinalis*) leaves exhibited the most effective activity among the herbs tested. From the weakly acidic fraction of the nonvolatile part of the hexane extract, four

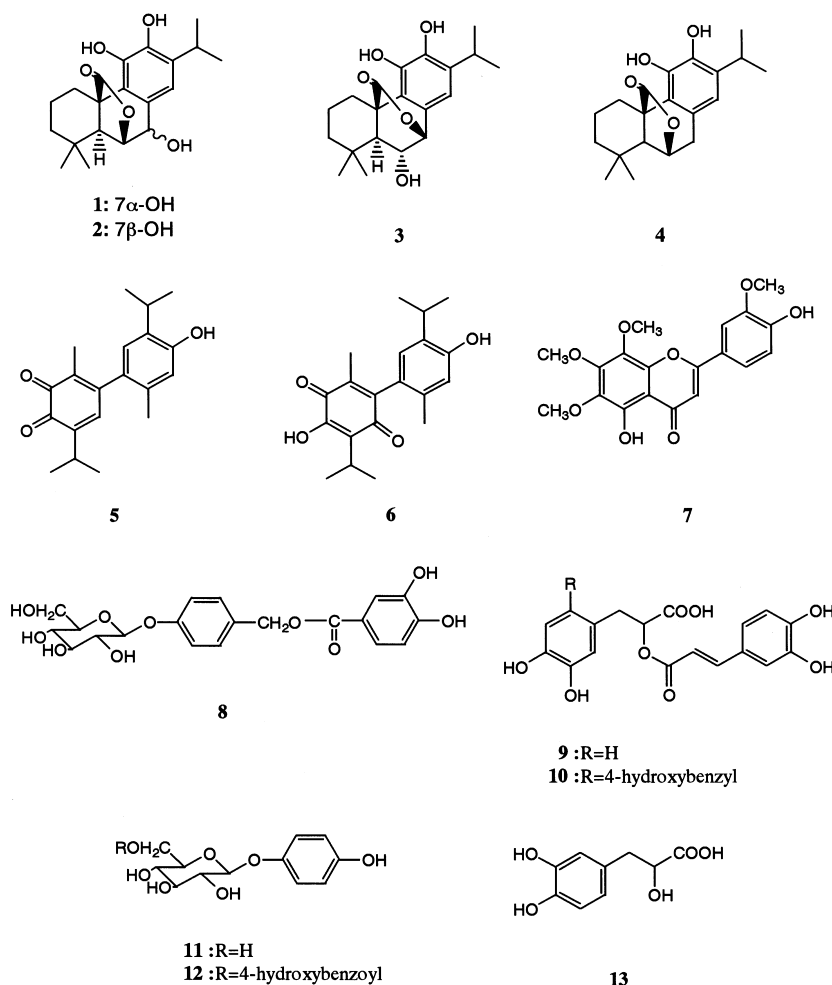


Fig. 1. Major antioxidants isolated from the Labiatae.

antioxidative phenolic diterpenoids (1–4) were isolated and their structures were determined. Rosmanol (1), epirosmanol (2) and isorosmanol (3) exhibited more than 4 times higher activity than BHT, and carnosol (4) showed twice, when evaluated in lard measured by the Active Oxygen Method [4,5].

Thymol and carvacrol, the major essential monoterpenes of thyme (*Thymus vulgaris*) showed high antioxidant activity. Several biphenyl compounds (e.g. 5, 6) which are dimeric compounds of thymol and proved to be efficient antioxidants were isolated from the less polar fraction along with highly methylated flavonoids (e.g. 7) [6].

## 2.2. Polar antioxidants

Several polyhydroxy benzoic and cinnamic acids have been known as antioxidative compounds from the leaves of oregano (*Origanum vulgare*). In our study, both polar and nonpolar fractions of oregano leaves retarded oxidation of linoleic acid. The polar fraction gave a new water soluble glycoside (8), rosmarinic acid (9) and its related compound (10) [7,8]. Because of its closeness to oregano in morphological classification, marjoram (*Origanum majorana*) contains similar phenolic compounds.

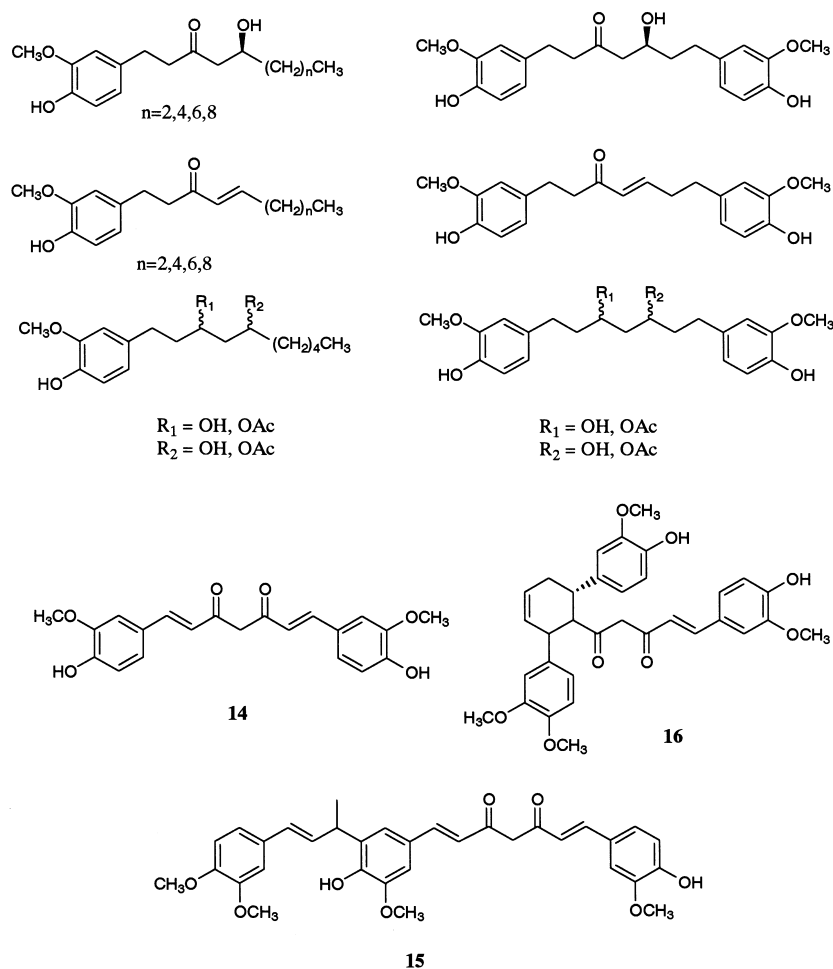


Fig. 2. Major antioxidants from the Zingiberaceae.

Beside these polyphenols, arbutin (11) and 6-*O*-4-hydroxybenzoyl arbutin (12) and 2-hydroxy-3-(3,4-dihydroxyphenyl)propionic acid (13) were isolated as moderate antioxidants [9] (Fig. 1).

### 3. Antioxidants from the Zingiberaceae

Ginger is one of the most common spices. In tropical countries, many species of the Family Zingiberaceae are widely cultivated and their rhizomes are used not only for spices but also for traditional folk medicines. We measured the antioxidative activity of the acetone extracts of 10 species of tropical gingers by the ferric thiocyanate method and the thiobarbituric acid (TBA) method [10]. Among them, ginger (*Zingiber officinale*) showed the most remarkable activity, followed by turmeric (*Curcuma domestica* = *C. longa*), *Alpinia galanga*, *C. xanthorrhiza*, *Z. cassumunar*, *C. manga* and *A. kepulaga*, activities of which were stronger than or comparable to that of  $\alpha$ -tocopherol.

From the rhizomes of ginger (*Z. officinale*), we isolated and determined more than 40 antioxidative compounds together with pungent principles such as gingerol, shogaol and zingerone, which were

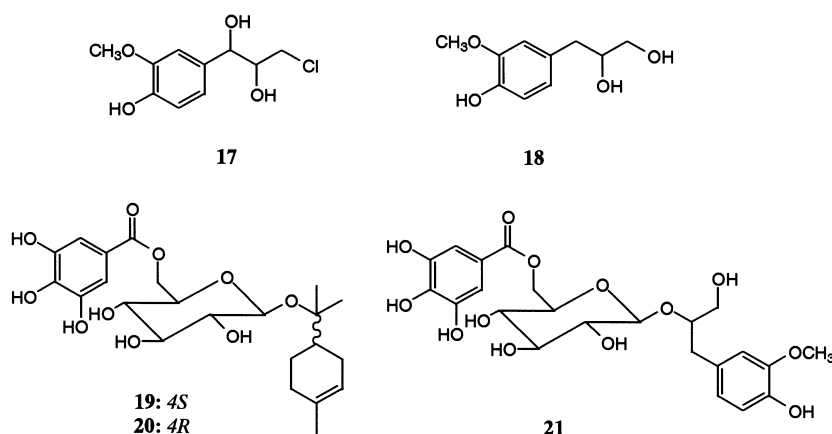


Fig. 3. Major antioxidants isolated from Allspice (*Pimenta dioica*).

reported to show potent antioxidant activity. These compounds can be structurally classified into two types, that is gingerol related compounds and diarylheptanoids as shown in Fig. 2 [11–13]. The structure – antioxidant activity relationship was examined among these compounds, with the structures having differences in side chain length, substituent group and substitution positions. Results suggested that the side chain length, functional group and the substitution pattern on the benzene ring definitely played an important role in the antioxidant activity [14].

Curcumin (14), a major yellow pigment in turmeric (*C. domestica* = *C. longa*), is known to possess important biological activities, such as antioxidant, antiinflammatory, antitumoral promotion effects. Six novel curcuminoids (e.g. 15, 16) having phenylbutane as substituents with were determined from the rhizomes of *Z. cassumunar*. These exhibited not only antioxidant efficiency but also antiinflammatory activity *in vivo* [15,16].

#### 4. Antioxidants from Myrtaceae

In a more recent study, we have investigated the antioxidative components of allspice, the berries of *Pimenta dioica*, which belongs to Myrtaceae. Ground berries of allspice were successively extracted with hexane, dichloromethane and 70% aq. acetone. After evaporation of acetone from the later extract, the resulting aqueous residue was partitioned with ethyl acetate to give the ethyl acetate-soluble and water-soluble fractions. Each fraction was measured for its antioxidant activity by the ferric thiocyanate method and Oil Stability Index method and for radical scavenging activity against DPPH. The dichloromethane extract, ethyl acetate-soluble fraction and water-soluble fraction showed high effectiveness in both evaluation.

From the dichloromethane extract, two new phenylpropanoids (17, 18) were isolated along with eugenol, a major essential oil [17]. Examination of the ethyl acetate-fraction gave five galloyl glucosides, including three new structures (19–21). Compounds 19 and 20 showed very similar  $^1\text{H}$  and  $^{13}\text{C}$  NMR and MS spectra. To determine the aglycone moiety of both compounds, enzymatic technique was used to reveal the structure and stereochemistry which is shown in Fig. 4 [18]. Flavonoids were isolated from the same fraction and three gallotannins were obtained from the water soluble fraction.

Recently, we isolated antioxidative carbazoles, such as euchrestine-B, its dimer and maharnine, from curry leaves (*Murraya koenigii*), which are commonly used for Malaysian dishes.

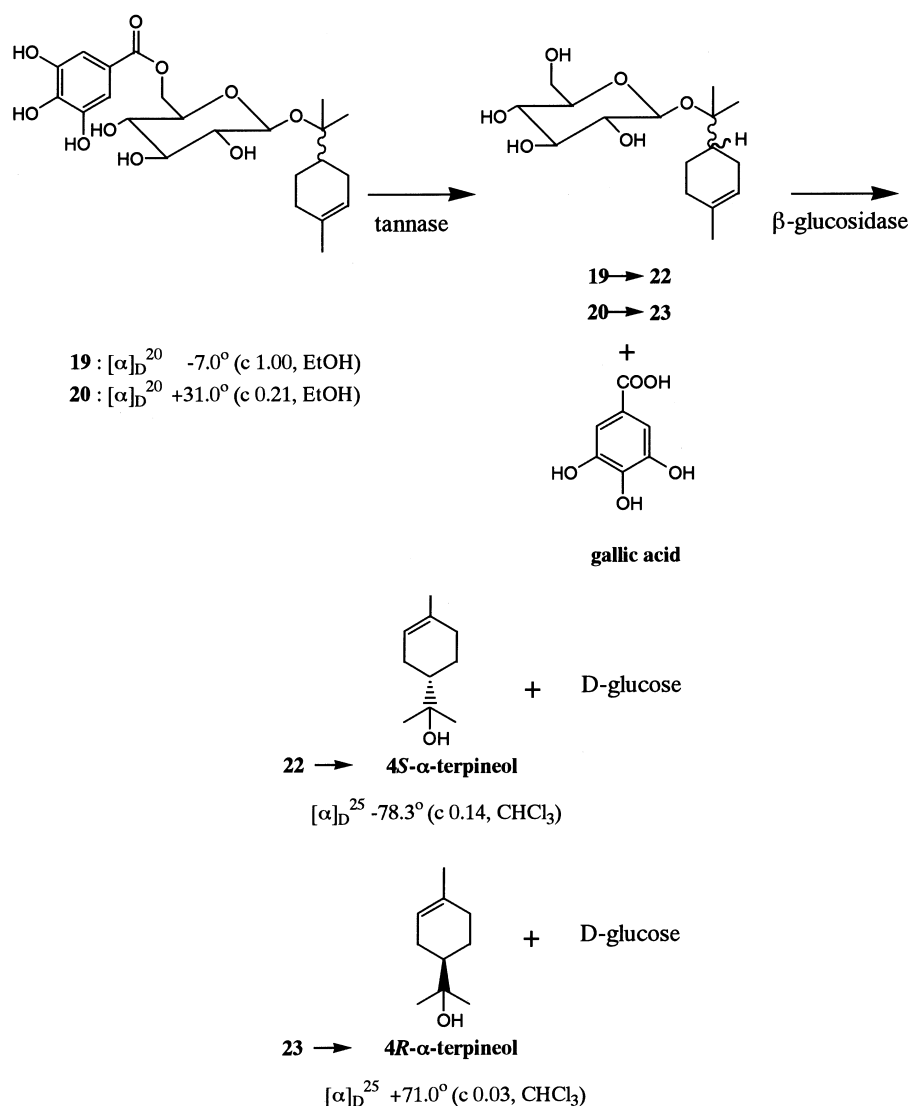


Fig. 4. Enzymatic hydrolysis of compounds 19 and 20.

## 5. Conclusion

Over production of active oxygen radicals in human body causes oxygen stress in DNA and cell membrane, and consequently induces toxic effects and diseases. Self defense system against these oxidative damages is supported by antioxidants such as  $\alpha$ -tocopherol and ascorbic acid. It is well known that catechins, antioxidant from green tea, have a wide range of biological activities that contribute to chemopreventive effects on tumor initiation and promotion. It has been reported that the methanol extract of leaves of rosemary inhibited skin tumor initiation caused by 12-*O*-tetradecanoylphorbol-13-acetate (TPA) in mouse epidermis [19]. Carnosol (4), one of the major antioxidants of rosemary, inhibited TPA-induced inflammation and tumoral promotion. The anti-inflammatory activity of curcumin (14) from turmeric was evaluated by topical application on chemical-induced edema of mouse ears [20].

Many new antioxidants have been isolated and determined from herbs and spices. The daily intake of these foods might be one of the most promising sources against major disease leading to a healthier life. It is strongly expected that biochemical results on antioxidants in edible plants may lead to chemoprevention of lipid peroxidation, inflammation, cancer and aging in human organs.

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