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Review

Natural antioxidants from residual sources

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Abstract

The growing interest in the substitution of synthetic food antioxidants by natural ones has fostered research on vegetable sources and the screening of raw materials for identifying new antioxidants. Oxidation reactions are not an exclusive concern for the food industry, and antioxidants are widely needed to prevent deterioration of other oxidisable goods, such as cosmetics, pharmaceuticals and plastics. Polyphenols are the major plant compounds with antioxidant activity, although they are not the only ones. In addition, other biological properties such as anticarcinogenicity, antimutagenicity, antiallergenicity and antiaging activity have been reported for natural and synthetic antioxidants. Special attention is focussed on their extraction from inexpensive or residual sources from agricultural industries. The aim of this review, after presenting general aspects about natural antioxidants, is to focus on the extraction of antioxidant compounds (mainly polyphenols) from agricultural and industrial wastes, as well as to summarize available data on the factors affecting their antioxidant activity and stability, and, in some cases, the reported major active compounds identified. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Natural antioxidants; Polyphenols; Agricultural and industrial residues; Review

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1. Introduction

The oxidative deterioration of fats and oils in foods is responsible for rancid odours and flavours, with a consequent decrease in nutritional quality and safety caused by the formation of secondary, potentially toxic, compounds. The addition of antioxidants is required to preserve flavour and colour and to avoid vitamin destruction. Among the synthetic types, the most frequently used to preserve food are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and tert-butyl hydroquinone (TBHQ). Tocopherols are also used as antioxidants for food, the order of antioxidant effectiveness being $\delta > \gamma > \beta > \alpha$. Reports revealing that BHA and BHT could be toxic, and the higher manufacturing costs and lower efficiency of natural antioxidants such as tocopherols, together with the increasing consciousness of consumers with regard to food additive safety, created a need for identifying alternative natural and probably safer sources of food antioxidants (Sherwin, 1990; Wanasundara & Shahidi, 1998).

The replacement of synthetic antioxidants by natural ones may have benefits due to health implications and functionality such as solubility in both oil and water, of interest for emulsions, in food systems. However, some of them such as those from spices and herbs (oregano, thyme, dittany, marjoram, lavender, rosemary) have limited applications in spite of their high antioxidant activity, as they impart a characteristic herb flavour to the food, and deodorization steps are required (Reglero et al., 1999). Naturally occurring antioxidant substances also need safety testing. Caution regarding an assumption of safety of natural antioxidants has been repeatedly advised, since the fact than an antioxidant comes from a natural source does not prove its assumed safety. Hattori, Yamaji-Tsukamoto, Kimagai, Feng and Takahashi (1998) summarises the requirements that antioxidants must satisfy for use as food additives.

Vegetable materials contain many compounds with antioxidant activity. Several plants have been studied as sources of potentially safe natural antioxidants for the food industry; various compounds have been isolated, many of them being polyphenols. A large range of low and high molecular weight plant polyphenolics presenting antioxidant properties has been studied and proposed for protection against lipid oxidation (Hagerman et al., 1998).

Polyphenolic compounds affect the functional and nutritional values of vegetable proteins, reducing the nutritional values of foodstuffs, and contributing to the sensory and organoleptic properties of fruits and vegetables (colour, taste, astringency) (Serra & Ventura, 1997). Polyphenols have other undesirable effects in food systems such as the formation of strong complexes with dietary proteins (Naczk, Amarovicz, Sullivan & Shahidi, 1998; Naczk, Oickle, Pink & Shahidi, 1996) and with salivary proteins (Naurato, Wong, Lu, Wroblewski & Bennick, 1999; Sarni-Machado, Cheynier & Montounet, 1999), with digestive enzymes (Tebib, Rouanet & Besançon, 1994), and protein-polyphenol haze in beverages (Siebert, Carrasco & Lynn, 1996; Siebert, Troukhanova & Lynn, 1996; Siebert, 1999). Their identification has been extensively reported in seeds that are sources of both food or feed-grade protein (Hurrell & Finot, 1985; Leung, Fenton & Clandinin, 1981; Sabir, Sosulski & Finlayson, 1974; Shamanthaka & Sastry, 1990; Sosulski, 1979). Polyphenol polymerization, due to autoxidation, is responsible for colour loss in processed vegetables (Talcott & Howard, 1999); tannins also affect the yields of protein extraction (Barbeau & Kinsella, 1983; Youssef, 1998). The presence of phenolic compounds, associated with the soluble-pectin fraction, can contribute to changes in cell adherence leading to textural defects such as hard-to-cook beans (García, Filisetti, Udaeta & Lajolo, 1998). Therefore, the potential of tannins to diminish nutrient availability should be considered when using them as biological antioxidants.

1.1. Biological activity of antioxidants

Oxidative stress is involved in the pathology of cancer, arteriosclerosis, malaria and rheumatoid arthritis, and could play a role in neurodegenerative diseases and ageing processes (Aruoma, 1997; Aruoma, Spencer, Warren, Jenner, Butler & Halliwell, 1997; Hollman, Hertog & Katan, 1996; Meyer, Heinonen & Frankel, 1998; Meyer, Jepsen & Sørensen, 1998; Nakagami, Nanaumi-Tamura, Toyomura, Nakamura & Shigehisa, 1995). The protection that fruits and vegetables provide against several diseases has been attributed to the various antioxidants, vitamin C, vitamin E, α-tocopherol, βcarotene and polyphenolic compounds (Abushita, Hebshi, Daood & Biacs, 1997; Aruoma, 1998). Biological antioxidants, especially vitamin E, were the first studied (Tappel, 1997). In living systems, dietary antioxidants (α-tocopherol, β-carotene, ascorbic acid) and endogenous enzymes (superoxide dismutase, glutathione peroxidase, catalase) protect against oxidative damage. Several studies have shown that phenolic compounds reduce in vitro oxidation of low density lipoprotein; particularly those phenolics with multiple hydroxyl groups which are generally the most efficient for preventing lipid and low density lipoproteins (LDL) oxidation and therefore, by inference, atherogenesis (Meyer, Heinonen & Frankel, 1998; Meyer, Jepsen & Sørensen, 1988; Moon & Terao, 1998; Nakagawa et al., 1999). Regeneration of α-tocopherol in human LDL was observed in the presence of tea catechins in a dose-dependent manner (Zhu, Huang, Tsang & Chen, 1999), although inhibition of LDL oxidation did not reduce arteriosclerotic lesions (Wakabayashi, 1999). Recent scientific studies have proved that antioxidants are capable of protecting cells from free radical damage (Saint-Cricq de Gaulejac, Provost & Vivas, 1999). Furthermore, other physiological activities of natural antioxidants have been described, such as antibacterial, antiviral, antimutagenic (Ikken, Morales, Martínez, Marín, Haza & Cambero, 1999), antiallergic (Noguchi et al., 1999), anticarcinogenic effects (Carrol, Kurowska & Guthrie, 1999; Kawaii, Tomono, Katase, Ogawa & Yano, 1999), antimetastasis activity (Maeda-Yamamoto, Kawahara, Tahara, Tsuji, Hara & Isemura, 1999), platelet agregation inhibition, blood-pressure increase inhibition (Ito et al., 1998), antiulcer activity (Saito, Hosoyama, Ariga, Kataoka & Yamaji, 1998; Vilegas, Sanomimiya, Rastrelli & Pizza, 1999) and anticariogenicity (Tanabe, Kanda & Yanagida, 1995). Their use as chemopreventive agents by inhibiting radical generation has been suggested (Miyake, Murakami, Sugiyama, Isobe, Koshimizu & Ohigashi, 1999) since free radicals are responsible for DNA damage and radical scavengers are probably important in cancer prevention (Carrol et al., 1999; Chung et al., 1999; Sawa, Nakao, Akaike, Ono & Maeda, 1999). Other studies have reported antimicrobial and antifungal properties of the polyphenolic extracts from *Sempervivum tectorum*. (Abram & Donko, 1999), potato peel (Rodríguez de Sotillo, Hadley & Wolf-Hall, 1998), vanillin (Cerrutti, Alzamora & Vidales, 1997) and liquid smoke (Estrada-Muñoz, Boyle & Marsden, 1998). Carbonneau, Léger, Descomps, Michel and Monnier (1998) during in vivo antioxidant assays with red wine polyphenols, observed that these compounds could play a co-antioxidant role, similar to that described for vitamin C and a sparing role toward vitamin E, which increases due to supplementation with phenols. However, a prooxidant effect of phenolics has also been reported (Yen, Chen & Peng, 1997). More research is needed in order to establish the activity, bioavailability and other in vivo effects of natural antioxidants.

2. Natural sources of antioxidant compounds

Many of the antioxidants other than vitamin C, vitamin E and carotenoids, occur as dietary constituents. Wang, Cao and Prior (1996) and Kalt, Forney, Martin and Prior (1999) published works about strong antioxidant compounds found in fruits. For example, antioxidants with important activity have been found in berries (Abuja, Murkovic & Pfannhauser, 1998; Heinonen, Lehtonen & Hopia, 1998; Heinonen, Meyer & Frankel, 1998; Prior et al., 1998), cherries (Wang, Nair, Strasburg, Booren & Gray, 1999; Wang, Nair, Strasburg, Chang, Booren & Gray, 1999; Wang, Nair, Strasburg, Chang, Booren, Gray & DeWitt, 1999), citrus (Saleh, Hashem & Glombitza, 1998) and in kiwi fruit (Dawes & Keene, 1999) prunes (Donovan, Meyer & Waterhouse, 1998) and olives (Romani, Mulinacci, Pinelli, Vincieri & Cimato, 1999). High activity antioxidants were found in olive oil (Blekas & Boskou, 1998; Papadopoulus & Boskou, 1991) and also in fruit juices (Chambers, Lambert, Plumb & Williamson, 1996; Spanos & Wrolstad, 1990, 1992; van Buren, de Vos & Pilnik, 1976; Wen, Wrolstad & Hsu, 1999). Recently a comprehensive review summarised the role of phenolic compounds in the oxidative process of fruits (Robards, Prenzler, Tucker, Swaitsitang & Glover, 1999). The effects of processing and storage were evaluated on the changes and content of polyphenols in strawberry (Gil, Holcroft & Kader, 1997), plum (Raynal, Moutounet & Souquet, 1989), olive oil (Angerosa & di Giovacchino, 1996; Caponio, Allogio & Gomes, 1999), grape juice (Spanos & Wrostad, 1990, 1992), onions, beans and peas (Ewald, Fjelkner-Modig, Johansson, Sjöholm & Åkesson, 1999).

Several studies have analysed the antioxidant potential of a wide variety of vegetables (Furuta, Nishiba & Suda, 1997; Gazzani, Papetti, Massolini & Daglia, 1998; Hertog, Hollman & Katan, 1992; Vinson, Hao, Su & Zubik, 1998), and particularly, of cacao beans (Sanbongi, Osakabe, Natsume, Takizawa, Gomi & Osawa, 1998), potato (Al-Saikhan, Howard & Miller, 1995; Friedman, 1997; Ramamurthy, Maiti, Thomas & Nair, 1992), tomato (Abushita et al., 1997), spinach (Gil, Ferreres & Tomás-Barberán, 1999), legumes such as *Phaseolus vulgaris* (Ganthavorn & Hughes, 1997; Tsuda, Ohshima, Kawakishi & Osawa, 1994) or vegetables such as paprika (Markus, Daood, Kapitány & Biacs, 1999; Matsufuji, Nakamura, Chino & Takeda, 1998). Both natural extracts and commercial products from garlic and ginger (Aruoma et al., 1997), from rosemary (Che Man & Tan, 1999; Güntensperger, Hämmerli-Meier & Escher, 1998; Jaswir & Che Man, 1999; Özcan, 1999), from dietary supplements (Chambers et al., 1996), from smoke flavourings containing lignin dimers (Guillén & Ibargoitia, 1998), or from drinks (Cano, Acosta & Bañón, 1998) were evaluated for antioxidant activity. Also antioxidants from seashore plants (Masuda et al., 1999) and seaweeds (Nakayama, Tamura, Kikuzaki & Nakatani, 1999) were studied.

Wines contain a variety of polyphenolic compounds, the most abundant being anthocyanins (Fogliano, Verde, Randazzo & Ritiene, 1999; Ghiselli, Nardini, Baldi & Scaccini, 1998; Heinonen, Lehtonen & Hopia, 1998; Hurtado, Caldú, Gonzalo, Ramon, Mínguez & Fiol, 1997; Lapidot, Harel, Akiri, Granit & Kranner, 1999; Larrauri, Sánchez-Moreno, Rupérez & Saura-Calixto, 1999; Saint-Cricq de Gaulejac et al., 1999; Sato, Ramarathnam, Suzuki, Ohkubo, Takeuchi & Ochi, 1996; Simonetti, Pietta & Testolin, 1997); antioxidant activity was also reported in whiskeys (McPhail, Gardner, Duthie, Steele & Reid, 1999), sake (Kitagaki & Tsugawa, 1999), Jerez-Sherries (Monedero, Olalla, Martín-Lagos, López & López, 1999) and cavas (Satué-Gracia, Andrés-Lacueva, Lamuela-Raventós & Frankel, 1999).

Green and black teas have been extensively studied for antioxidant properties since they can contain up to 30% of the dry weight as phenolic compounds (Lin, Lin, Liang, Lin-Shiau & Juan, 1998). Among studies of the antioxidant activity and identification of polyphenols in green and in fermented teas are those of Cao, Sofic and Prior (1996), Chambers, Jimbin and McDonald (1988), Chen, Wang, Chan, Zhang, Chung and Liang (1998), Frankel, Huang and Aeschbach (1997), Lin, Juan, Liang and Lin (1996), Singh et al. (1999), Yen, Chen and Peng (1997), Wanasundara and Shahidi (1998), Yokozawa et al. (1998). Rooibos tea has also been investigated (von Gadow, Joubert & Hansmann, 1997a, b; Yen & Hsieh, 1998). Benzie and Szeto (1999) correlated the antioxidant activity with total phenolics content of the tea and found higher activity for green tea than for oolong or black tea. Among the major components (−)epigallocatechin 3-gallate, which was thoroughly studied by Copeland, Clifford and Williams (1998), (−)epigallocatechin, (−)epicatechin 3-gallate, (−)epicatechin, (+)gallocatechin and (+)cate-chin were also identified.

Some of the active principles of some medicinal products are polyphenolic compounds. Thus, flavones that possess antimutagenic activity (Nakasugi & Komai, 1998), flavanones and xanthones, that exhibit antiviral, antimicrobial and antiinflamatory activities, and isoflavones and coumestans that present important physiological effects in humans, have antioxidant action. A number of studies deal with the antioxidant activity of extracts from herbs, medicinal plants and spices (De la Torre Boronat & López Tamames, 1997; Duh & Yen, 1997b; Jung, Kim & Kim, 1999; Kim, Kim, Kim, Oh & Jung, 1994; Madsen, Sørensen, Skibsted & Bertelsen, 1998; Nieto et al., 1993; Pietta, Simonetti & Mauri, 1998). The antioxidant activity of sage components has been widely studied (Abdalla & Roozen, 1999; Aruoma, 1999; Guillén & Manzanos, 1999; Marinova & Yanishlieva, 1997; Wang, Li, Rangarajan, Shao, LaVoie, Huang & Ho, 1998; Wang, Shao, Li, Zhu, Rangarajan, LaVoie & Ho, 1999; Wang, Yieh & Shih, 1999; Weinberg, Akiri, Potoyevski & Kanner, 1999; Yanishlieva, Marinova, Gordon & Raneva, 1999). Also ginger (Kikuzaki & Nakatani, 1993), Ganoderma species (Yen & Wu, 1999), dittany (Møller, Madsen, Aaltonen & Skibsted, 1999), green pepper (Bandyopadhyay, Narayan & Variyar, 1990), *Visnea mocanera* L.F. (Hernández-Pérez, Hernández, Gómez-Cordovés, Estrella & Rabanal, 1996), *Chrysanthemum* (Chuda, Ono, Ohnishi-Kameyama, Nagata & Tsushida, 1996; Duh, 1999), Honeybush (Ferreira et al., 1998) or drugs (Ogata, Hoshi, Shimotohno, Urano & Endo, 1997) are antioxidants. Selection of clonal lines with high polyphenol content was studied for lavender (Al-Amier, Mansour, Toaima, Korus & Shetty, 1999). A number of studies focused on the composition of rosemary due to its potent antioxidant action applied either to the retarded oxidation in oil (Cuvelier, Richard & Berset, 1996; Houlihan, Ho & Chang, 1984; Madsen et al.; Wu, Lee, Ho & Chang, 1982) or to the reduction of the loss of colour of carotenoids (Osuna-García, Wall & Waddell, 1997, 1998). The elucidation of the antioxidant mechanisms of its components has also been addressed (Hall, Cupett & Dussault, 1998).

Other potential vegetable sources, such as trees, have been evaluated for antioxidant compounds (Chung et al., 1999; Hernández-Pérez et al., 1996; Venkatamuru, Patel & Rao, 1983; Yen & Hsieh, 1998). Among the different parts of the plants, leaves deserve especial attention, e.g. those from green barley (Osawa, Katsuzaki, Hagiwara, Hagiwara & Shibamoto, 1992), *Pelargonium sp.*, *Thalictrum flavum*, *Nerium oleander L.* (Mallet, Cerrati, Ucciani, Gamisans & Gruber, 1994), several willow species (Julkunen-Tiito, 1985), mulberry (Zhishen, Mengcheng & Jianming, 1999) or avocado (Torres, Mau-Lastovicka & Rezaaiyan, 1987). Roots (Yan, Suzuki, Ohnishi-Kameyama, Sada, Nakanishi & Nagata, 1999), buckwheat groats (Watanabe, 1998), cork from *Quercus suber* (Cadahía, Conde, Fernández de Simón, García-Vallejo, 1998; Conde, Cadahía, García-Vallejo & Fernández de Simón, 1998), bark from

Fraxinus ornus (Marinova, Yanishlieva & Kostova, 1994), and sprouts from mung beans (Sawa et al., 1999) were also reported to contain antioxidants.

Seeds are another source of antioxidants as reported for tamarind (Tsuda, Watanabe, Ohshima, Yamamoto, Kawakishi & Osawa, 1994), canola (Krygier, Sosulski & Hogge, 1982; Naczk, Amarovicz, Sullivan & Shahidi, 1998; Wanasundara, Amarovicz & Shahidi, 1994), sesame (Shahidi, Amarovicz, Abou-Gharbia & Shehata, 1997), evening primrose (Balasinska & Troszynska, 1998; Wettasinghe & Shahidi, 1999), flaxseeds (Oomah, Kenaschuk & Mazza, 1995), lupinus seed (Tsaliki, Lagouri & Doxastakis, 1999), buckwheat (Pryzbylski et al., 1998), sunflower (Kubicka, Jędrychowski & Amarowicz, 1999) and *Rosa rubiginosa* and *Gevuina avellana* (Moure, Franco, Sineiro, Domínguez, Núñez & Lema, 2000). Also in cereals (Baublis, Decker & Clydesdale, 2000; Lehtinen & Laakso, 1998), as in a recent study on corn kernel (Kurilich & Juvik, 1999), antioxidant activity was detected.

Hulls contain compounds with antioxidant activity (Shahidi & Naczk, 1995). Active compounds were detected in hulls from peanut (Yen, Duh & Tsai, 1993; Yen & Duh, 1994; Yen & Duh, 1995; Duh & Yen, 1995 and 1997a; Xing & White, 1997), mung bean (Duh, Yen, Du & Yen, 1997) and buckwheat (Watanabe, Ohshita & Tsushida, 1997). During the extraction of oil from oilseeds, the antioxidant compounds present in the hulls could be incorporated in the oil, as reported for peanut oil extracted from the coated seeds, which contained higher oxidative stability than the oil from dehulled seeds (Shahidi, Amarovicz, Abou-Gharbia & Shehata, 1997). The bran fraction has been reported to have more antioxidant activity than other fractions, as observed for durum wheat by Onyeneho and Hettiarachchy (1992), or in the coat of tamarind seeds, with strong oxidation-inhibiting activity, whereas no activity was detected in the germ (Tsuda, Ohshima, Kawakishi & Osawa, 1994). Also, in red and black bean seed coat of *Phaseolus vulgaris*, pro-oxidant species were found in the germ and not in the hulls (Muanza, Robert & Sparks, 1998). Baublis et al. (2000) found higher inhibition of iron-accelerated oxidation of phosphatidylcholine liposomes for the water-solubles from high-bran wheat than for refined wheat. The outer layers usually contain a greater amount of polyphenolic compounds, as expected from their protective function in the plants.

Agricultural and industrial residues are attractive sources of natural antioxidants. Potato peel waste (Rodríguez de Sotillo, Hadley & Holm, 1994a, b), rape of olive (Sheabar & Neeman, 1988), olive mill waste waters (Visioli et al., 1999), grape seeds (Gabrielska, Oszmianski & Lamer-Zarawska, 1997; Karakaya & Nehir, 1999; Pekić, Kovač, Alonso & Revilla, 1998; Pietta et al., 1998; Saint-Cricq de Gaulejac et al., 1999; Saura-Calixto, 1998; Wulff, 1997; Yamaguchi, Yoshimura, Nakazawa & Ariga, 1999) and grape pomace peels (Bonilla, Mayen, Merida & Medina, 1999; Larrauri, Sánchez-Moreno & Saura-Calixto, 1998; Lu & Foo, 1999; Meyer, Jepson & Sørensen, 1998) have been studied as cheap sources of antioxidants and recently increased antioxidant activity in rat plasma after oral administration of grape seed extracts was reported (Koga et al., 1999). Identification of polyphenolic compounds from apple pomace (Lu & Foo, 1997), grape pomace (Lu & Foo, 1999, 2000), citrus seeds and peels (Bocco, Cuvelier, Richard & Berset, 1998), carrot pulp waste (Chen & Tang, 1998), old tea leaves (Zandi & Gordon, 1999), cocoa by-products (Azizah, Nik Ruslawati & Swee Tee, 1999), non-volatile residue from orange essential oil (Vargas-Arispuro, Sanz, Martínez-Téllez & Primo-Yúfera, 1998), and soybean molasses (Hosny & Rosazza, 1999) has also been reported. Spent ground coffee oil from the residue from the production of instant coffee was used to obtain an antioxidant product useful for food preservation and for aroma stabilisation, the antioxidant activity being due to the 5-hydroxytryptamide carboxylic acids (10–75% dry wt. of the product) (Bertholet, Kusy, Rivier & Colarow, 1998).

Scarce literature exists on studies with by-products other than those of plant origin, e.g. shrimp shell waste (Li, Seymour, King & Morrissey, 1998; Seymour, Li & Morrissey, 1996; Wang, Yieh & Shih, 1999). Other compounds such as the dipeptide carnosine (beta-alanyl L-histidine) (Kansci, Genot, Meynier & Gandemer, 1997; Lee & Hendricks, 1997; Lee, Hendricks & Cornforth, 1998) showed antioxidant potential. Protein (Roch, Dreyer, Lacan, Baccou & Ginoux, 1998), protein hydrolysates (Amarovicz & Shahidi, 1997), soluble elastin peptides (Hattori et al., 1998), water-soluble proteins (Okada & Okada, 1998) and pressure treated β-lactoglobulin (Møller, Stapelfeldt & Skibsted, 1998) were also reported as antioxidant agents. Essential oils (Zygadlo, Lamarque, Maestri & Grosso, 1995), conjugated linoleic acids (Chen, Chan, Kwan & Zhang, 1997) and phospholipids (Bandarra, Campos, Batista, Nunes & Empis, 1999; Chu & Hsu, 1999; Saito & Ishihara, 1997) present antioxidant activity. Palm oil β-carotene (Farombi & Britton, 1999) and capsaicin, responsible for the pungent effect of hot chilli peppers (Henderson, Slickman & Henderson, 1999) are antioxidants, although this latter study evaluates the purified compound. Maillard reaction products were also reported as antioxidant agents (Alfawaz, Smith & Jeon, 1994; Bersuder, Hole & Smith, 1998; Lingnert & Waller, 1983; Nakamura, Ogawa, Nakai, Kato & Kitts, 1998; Pischetsrieder, Rinaldi, Gross & Severin, 1998; Tubaro, Micossi & Ursini, 1996; Wijewickreme & Kitts, 1998; Wijewickreme, Krejpcio & Kitts, 1999). The derivation of natural products with antioxidant activity from brewing seeds, grains and/or germs has been claimed by

Niwa and Motoyama (1991) and Watanabe (1999). Also some microorganisms can produce antioxidants (Lin & Yen, 1999; Shimoni, Ampel, Zähner & Neeman, 1998).

Few studies deal with the antioxidant activity of the bound phenolic compounds, linked to lignin or arabinoxylans (Cruz, Domínguez, Domínguez & Parajó, 1999; Lehtinen & Laakso, 1998; Ohta, Yamasaki, Egashira & Sanada, 1994), even though their antioxidant activity in barley and malt is reported to be two-fold higher than that of free phenolic compounds (Maillard & Berset, 1995; Maillard, Soum, Boivin & Berset, 1996). However, other authors have found that the antioxidant activity of citrus peels and seed extracts is not directly related to the free or bound phenolic compounds (Bocco et al., 1998).

3. Antioxidant activity of phenolic compounds

3.1. *Methods for determining antioxidant activity*

During lipid oxidation, antioxidants act in various ways, binding metal ions, scavenging radicals and decomposing peroxides. Often, more than one mechanism is involved, therefore causing synergism. In food related systems, antioxidant activity means chain-breaking inhibition of lipid peroxidation, whereas in in vivo systems, free radicals can damage proteins, DNA and other small molecules. To use antioxidants in food systems efficiently, the mechanism of in vivo antioxidation as well as the potential health benefits of these compounds should be known (Aruoma, 1997, 1998, 1999). Bioavailability, absorption, metabolism and pharmacokinetics must all be considered before attempting to extrapolate from in vitro procedures to the human in vivo situation. At present, no data on the metabolism of natural extracts are available, and only recently have studies on the human metabolism of chlorogenic been published (Plumb, García, Kroon, Rhodes, Ridley & Williamson, 1999). Depending on their action, De la Torre Boronat and Löpez Tamames (1997) classified the antioxidants into three types (1) antioxygen radical ($^1O_2$ and $^3O_2$), reducing substances (ascorbic acid), and antioxidants such as carotenes, (2) antiradicals and primary antioxidants, (3) metal chelators. Another widely used classification considers primary or chain-breaking antioxidants and secondary antioxidants, that reduce the rate of chain initiation; but some compounds possess both primary and secondary antioxidant activity. The most frequently measured products are conjugated diene hydroperoxides for primary oxidation and volatile compounds (TBARS) for secondary.

Therefore, the antioxidant activity can and must be evaluated with different tests for different mechanisms. The most frequently used methods for measuring the levels of oxidative damage in humans assess (1) total oxidative DNA damage, (2) levels of antioxidant enzymes, levels of low molecular weight antioxidants (catalase, superoxide dismutase, glutathione peroxidases, uric acid, glutathione, flavonoids, catechins, anthocyanins) and vitamins (E, C and β-carotene), (3) oxidative damage to lipids (isoprostanes, TBARS) and (4) protein damage (numbers of protein carbonyl and modified tyrosine residues) (Aruoma, 1997). Most of the chemical methods are based on the ability to scavenge different free radicals, but also UV-absorption and chelation ability are responsible for the antioxidant activity in oily systems (Chen & Ahn, 1998). Tests measuring the scavenging activity with different challengers, such as superoxide radical ($O_2^{\cdot -}$), hydroxyl (·OH), nitric oxide (·NO), alkylperoxyl radicals, $ABTS^{\cdot +}$ (radical cation of 2,2′-azinobis(3-ethylbenzothiozoline-6-sulphonate), (α,α-diphenil-β- picrylhydrazyl radical) (DPPH) have been developed (Table 1). Methods for determining reactive oxygen species, relevant for examining food antioxidants, were reviewed by Aruoma et al. (1997).

Measurement of the protective action toward lipid oxidation has been frequently used, with pure triacylglycerols, vegetable oils (sunflower, soybean, olive, palm), fish oils or lard as oxidation substrates. Other oxidation substrates, such as phospholipids or lipoproteins have also been employed. Marine oils are rich in polyunsaturated fatty acids (PUFA), with interest due to their ability to lower serum triacylglycerols and cholesterol, reducing thrombosis, and coronary heart disease, hypertension, and other inflammatory and autoimmune disorders. PUFA are highly sensitive to oxidative deterioration and have also been used to test natural antioxidants (Nieto et al., 1993; Wanasundara & Shahidi, 1998; Yi, Han & Shin, 1991). Different peroxidation-inducing systems have also been used: organic solvents or reverse and aqueous micelles (Foti, Piattelli, Baratta & Ruberto, 1996; Han, Yi & Shin, 1990; Roedig-Penman & Gordon, 1998). Since many food systems are emulsions, the study of lipid oxidation in emulsified systems is basic to the study of stability, and the water-soluble substances present in the aqueous phase influence the antioxidant activity (Ponginebbi, Nawar & Chinachoti, 1999). Liposomes and microsomes have also been used to study oxidation, in a system resembling practical in vivo conditions, due to the similarity between lipid membrane composition and that of biological membranes (Chambers et al., 1996; Gabrielska et al., 1997). Inhibition of LDL oxidation in vitro has been extensively studied to evaluate the antioxidant capacity of a compound in the blood plasma of rats or humans after oral administration of polyphenolic compounds, since it simulates the oxidation of low-density lipoproteins that contribute to the pathogenesis of arteriosclerosis (Carbonneau et al., 1998; Koga et al., 1999; Meyer, Heinonen et al., 1998; Meyer, Jepsen et al., 1998; Vinson, Dabbagh, Serry & Jang, 1995; Vinson et al., 1999; Vinson, Hao, Su & Zubik, 1998; Visioli et al., 1999).

Table 1
Assays for determining antioxidant activity[a]

Assay	References
Oxidation in hydrophobic, hydrophilic and emulsions of	
Vegetable and marine oils	Frankel et al. (1996); Han et al. (1990); Nieto et al. (1993).
Fatty acids, fatty acid methyl esthers, triacylglycerols	Foti et al. (1996); Heinonen et al. (1997); Ponginebbi, (1999)
Phospholipids	Farombi and Britton, (1999); Kuo et al. (1999); Marinova and Yanishlieva (1996)
Citronellal	Bocco et al. (1998),
β-Carotene oxidation in linoleic acid emulsion	Al-Saikhan et al. (1995); Mallet et al. (1994); Marco (1968); von Gadow et al. (1997a)
Lard	Kim et al. (1994); von Gadow et al. (1997c)
Scavenging of radicals	
ABTS^{+} (metmyoglobin assay)	Hagerman et al. (1998); Rapisarda, Tomaino, Lo Cascio, Bonina, De Pasquale & Saija (1999)
Alkyl peroxyl radical	Milič et al. (1998); Sawa et al. (1999)
α,α-diphenyl-β-picrylhydrazil radical scavenging activity	Brand-Williams et al. (1995); Duh (1998); Larrauri et al. (1998); Okada and Okada (1998); von Gadow et al. (1997 b,c),
Hydroxyl radical scavenging activity	Duh (1998); Watanabe et al. (1997)
Oxygen radical absorbance capacity	Cao et al. (1996); Kalt et al. (1999); Lin et al. (1996); Pior et al. (1998)
Superoxide scavenging activity	Aruoma et al. (1993); Nakamura et al. (1998), Yen and Duh (1994); Okada and Okada; Yamaguchi et al. (1999)
Others	
Redox potential	Hagerman et al. (1998)
Reducing power (reducing potassium ferricyanide)	Duh et al. (1997); Duh (1998)
Degradation rate of phenolic compounds as a consequence of their antioxidant activity	Chimi et al. (1991)
Chelating activity of Fe^{+2} or Cu^{+2}	Arora and Strasburg (1997); Chen and Ahn (1998); Hudson and Lewis (1983); Lin and Yen (1999); Okada and Okada (1998); Yen and Duh (1994); Yen and Wu (1999)
Oxidation in biological membrane models, cell assays and in vivo assays	
Liposome membranes (UV induced lipid peroxidation)	Gabrielska et al. (1997)
Oxidation of rat liver mitochondria	Yen and Hsieh (1998)
Lipid oxidation in egg lecithin microsomes	Yen and Hsieh (1998)
NADPH/iron-induced peroxidation in liver microsomes	Chambers et al. (1996); Yen and Hsieh, (1998)
Phosphatidylcholine liposome oxidation	Aruoma, (1997); Baublis et al. (2000)
Human plasma radical scavenging capacity	Carbonneau et al. (1998)
Cu-induced or **AAPH**-induced human LDL oxidation	Abuja et al. (1998); Carbonneau et al. (1998); Meyer, Heinonen et al. (1998); Meyer, Jepsen et al. (1998); Visioli et al. (1999); Zhu et al. (1999)
DNA oxidation and fragmentation assays, bleomycin-dependent DNA damage	Aruoma (1999); Aruoma et al. (1997); Aruoma et al. (1993); Hagerman et al. (1998); Saint-Criq de Gaulejac et al. (1999); Yen et al. (1997); Yokozawa et al. (1998)
Rat plasma antioxidant capacity, with Cu-induced or AAPH-induced formation of cholesteryl ester hydroperoxides	Koga et al. (1999)
Oxidation of blood plasma	Miyake and Shibamoto (1998); Nakagawa et al. (1999)
Oxidative susceptibility of **ILDL** in animals	Wakabayashi (1999)
Animal experiments, reduction of uremic toxins in the blood of rats	Yokozawa et al. (1998)
Inhibition of oxidation induced apoptosis in healthy human cells	Muanza et al. (1998)
Antiulcer activity	Saito et al. (1998)
Guinea pig complement serum hemolysis	Nakagami et al. (1995)
Leukotriene production by human neutrophiles	Visioli et al. (1999)
Food stability	
Storage of meat	Kanatt, Paul, D' Souza and Thomas, (1998)
Lipid stability in extruded corn	Camire and Dougherty (1998)
Lipid stability in precooked meat	Alfawaz et al. (1994); Güntersperger et al. (1998); Ramezanzadeh et al. (1999)
Lipid oxidation in flour-lipid mixtures	Lehtinen and Laakso (1997); Wijewickreme and Kitts (1998)
Stability of oils during frying	Che-Man and Tan, (1999); Jaswir and Che-Man (1994); Zandi and Gordon (1999)
Colour stability and lipid oxidation of Rockfish	Li et al. (1998); Seymour et al. (1998)
Storage of ground beef	Lee and Hendricks (1997), Lee et al. (1998)
Colour stability of carotenoids containing materials (paprika, carrot, etc.)	Han et al. (1998); Osuna-García et al. (1997); Talcott and Howard (1999)
Oxidative stability of turkey thigh meat homogenate	Møller et al. (1999)

[a] Abbreviations: AAPH, 2,2′-azobis (2-aminopropane)dihydrochloride; ILDL, intermediate and low density lipoproteins; NADPH, nicotinamide adenin dinucleotide phosphate in hydrogenated form.

Optionally, metallic cations can be used as catalysts during the oxidation assays (Chen & Ahn, 1998; Ganthavorn & Hughes, 1997; Hudson & Lewis, 1983; Yen & Duh, 1994), and also organic molecules with a complexed metal, such as haemoglobin (Kuo, Yeh & Pan, 1999). Fe and Cu ions have been widely used as inducers in different systems (Chambers et al., 1996; Møller et al., 1999; Ponginebi et al., 1999). The antioxidant activity depends on the metallic catalyst employed for generating the reactive species (Lapidot et al., 1999), and it determines whether the supposed antioxidant could act as prooxidant (Roedig-Penman & Gordon, 1998). Common metal ions, such as Fe^{3+}, can be reduced by the antioxidants to a catalytically-active ion Fe^{2+} that provokes the antioxidant to behave as prooxidant. The same effect is common to other transition metals. Therefore, the chelating activity determination on metal ions (usually Fe^{2+}, Cu^{2+}) was used as a measure of the ability to prevent this effect, as an indirect antioxidant activity measurement (Chen & Ahn; Hudson & Lewis; Okada & Okada, 1998). Non-food uses of tannins and tannin-containing materials related to the ability to complex metal ions have been reported (McDonald, Mila & Scalbert, 1996).

The redox potential (Hagerman et al., 1998), the reducing power (Duh et al., 1997; Duh, 1998) and the degradation rate of the antioxidant substance have also been positively correlated with antioxidant activity (Chimi, Cillard, Cillard & Rahmani, 1991).

What remains to be established is whether these compounds, potent antioxidants in in vitro tests, can be absorbed and, if possible, whether they are still active after absorption and metabolism. Binding to certain enzymes has been suggested as a possible mechanism for inhibiting their activity (Saint Cricq de Gaulejac et al., 1999). In vivo studies are required to assess that the "potential" antioxidant found by in vitro assays really acts in the same way in biological systems. Animal cells offer an excellent biological model for studying in vitro lipid oxidation (Balasinska & Troszynska, 1998).

3.2. *Comparison of antioxidant activity of model phenolic compounds*

The antioxidant activity of phenolic compounds is affected by their chemical structure. Structure–activity relationships have been used as a theoretical method for predicting antioxidant activity and are studied by Das and Pereira (1990), Hudson and Lewis (1983), Ogata et al. (1997), Saint-Cricq de Gaulejac et al. (1999) and Zhang (1999) among others. Polymeric polyphenols are more potent antioxidants than simple monomeric phenolics: Hagerman et al. (1998) demonstrated the higher antioxidant ability of condensed and hydrolyzable tannins at quenching peroxyl radicals over simple phenols; Yamaguchi et al. (1999) observed that the higher the polymerization degree of flavanols, the stronger the superoxide-scavenging activity. A similar effect was reported for the capacity to inhibit the O_2^- radical, which increased with the degree of procyanidin polymerization (Saint-Cricq de Gaulejac et al.), or for the stronger inhibition of lipid peroxidation by dimers of ferulic than by ferulic acid (García-Conesa, Wilson, Plumb, Ralph & Williamson, 1999). As a general trend, improved stabilization of the phenoxyl radical is desirable, but the lipophilic nature of the molecules and the affinity of the antioxidant for the lipids could be determinant (von Gadow, Joubert & Hansmann, 1997c). Also the antilipoperoxidant effect depends on the number and position of hydroxyl and methoxyl groups in the benzene ring and on the possibility of electron delocalization in the double bonds (Milič, Djilas & Čanadanović-Brunet, 1998). The presence of sugar substituents of flavonols from different vegetables has been demonstrated to significantly affect antioxidant activity of flavonols (Plumb, Price & Williamson, 1999a,b).

The antioxidant activity also depends on the type and polarity of the extracting solvent, the isolation procedures, purity of active compounds, as well as the test system and substrate to be protected by the antioxidant (Meyer, Heinonen et al., 1998). It has been suggested that the determining factor for the antioxidant activity is the lipophilic nature of the molecules and the affinity of the antioxidant for the lipid (Brand-Williams, Cuvelier & Berset, 1995; von Gadow et al., 1997c). A close dependency on the antioxidant activity of phenolic acids (Pekkarinen et al., 1999; von Gadow et al., 1997c) has been reported for phenolic compounds, and even the recommended concentration of synthetic antioxidants has been indicated for some tests (Karamac & Amarovicz, 1997). The antioxidant potential of a compound is different according to different antioxidant assays or, for the same assay when the polarity of the medium differs, since the interaction of the antioxidant with other compounds plays an important role in the activity (Pekkarinen et al.). Dramatic differences in the relative antioxidant potential of model compounds were observed when one model compound is strongly antioxidant with one method and prooxidant with another (von Gadow et al.). A phenomenon known as 'Polar paradox' has been repeatedly reported; hydrophilic antioxidants are more effective than lipophilic antioxidants in bulk oil, whereas lipophilic antioxidants present greater activity in emulsions.

Table 2 summarizes the order of antioxidant activity of phenolic compounds, measured with different methods. Antioxidants of natural origin or synthetics and from crude extracts or their fractions have frequently been compared.

3.3. *Prooxidant action of antioxidants*

Potent antioxidants can autoxidize and generate reactive substances and thus also act as prooxidants,

Table 2
Comparison of the antioxidant activity of polyphenols found in vegetable materials[a]

	Decreasing order	**Reference**
Inhibition of		
Lard oxidation	Fs > Tx > Bu > Fis > Q > Qr > C	Hudson and Lewis (1983)
Lipid peroxidation (palm oil)	Mo > K > My > Q > vit A > α-toc > Ap > Chr > D > Lul > Na > Tx > Ru > BHT > Nan	Das and Pereira (1990)
Lipid oxidation (AOM)	PA > CA > CaA > pBA > GeA > FA > VA > SA > pCA	Onyeneho and Hettiarachchy (1992)
Methyl linolenate oxidation	GA > CCA > PA > BHA > CA	Cuvelier et al. (1992)
Sunflower oil oxidation	L-ascorbic acid 6-palmitate > BHA > GA > CA	Rodríguez de Sotillo et al. (1994b)
Peroxidation of linoleic acid	α-toc ≈ 2-H-3′,4′-DHAP≈ m3,4-DHB ≈ 3,4-DHPA > EC	Tsuda et al. (1994a)
Oxidation of ethyl linoleate	GA, Ca A, RA > BHA > GeA,PA > BHT > iEu > FA > E > VA	Brand-Williams et al. (1995)
Lipoprotein-bound antioxidant activity	EGCG > Toc > Res > Q > CA,Ru > CyC > Hes,Ge	Vinson et al. (1995)
in vitro antioxidant effectiveness	EGCG > EC > CyC > Q > CA > Res > Ru > Toc > Hes > Ge	Vinson (1995)
Sunflower oil oxidation	CaA > SpA > 3,4-DBA > FA	Yanishlieva and Marinova (1995)
Lipid peroxidation	Q > Cy > CA	Furuta et al. (1997)
β-carotene-linoleic oxidation	BHT > Lul > BHA > α-toc > Q > As > VA > FA > V > iQr > SA > pBA > pCA > Ru > C > PA	von Gadow et al. (1997c)
Rancimat	C > Q > CaA > pCA > iQr > BHT > Ru > As > pBA > FA > pCA	von Gadow et al.
Formation of methyl linoleate hydroperoxides	α-toc > Ca > β-car ≈ Zex > Lu	Matsufuji et al. (1998)
Bulfrog oil oxidation	Bol > Q > BHT > Mo > Nan	Méndez et al. (1998)
UV-induced lipid oxidation	Q > Ru,CaA,FA ,Se > C	Chen and Ahn (1998)
Refined olive oil	GA > BHA ≈ C > BHT ≈ EC > Q > PA > Q3Gl > VA,Q3 Ga,K	Bonilla et al. (1999)
LDL oxidation	ECG > Tx > Q ≈ Res > > QR ≈ ChA > Cy	Vinson et al. (1999)
LDL oxidation (in vivo human Cu catalyzed)	C > Cyd ≈ CaA > Q > EA	Meyer, Heinonen et al. (1998)
Linoleic acid oxidation (hemoglobin catalyzed)	BHA > PG > DL-αtoc > EC > BHT > My > Q	Kuo et al. (1999)
Methyl linoleate (in bulk oil) oxidation	CaA ≈ SpA > α-toc > FA > 2,3-dhBA > 3HBA,VA	Pekkarinen et al. (1999)
Methyl linoleate (emulsion) oxidation	α-toc > SpA > FA > VA	Pekkarinen et al.
Methyl linoleate (in bulk oil)	My > α-toc > Q > Qr > iQr > Ru	Hopia and Heinonen (1999)
Scavenging of		
DPPH radical	CaA > Q > C > IQ > As > Ru > Lul > PA > SA > BHA > FA > BHT > VA > pCA > V	von Gadow et al. (1997c)
ABTS$^{\otimes +}$ (metmyoglobin method)	PC > PGG > C > MG	Hagerman et al. (1998)
Lipid alkoxyl radical	GA > CCA > > Ch A > VA > SA	Milič et al. (1998)
Alkyl peroxyl radical	Ru≈ChA > V≈VA≈NH≈GA≈α-Toc > Q > IS	Sawa et al. (1999)
Peroxyl radical	EGCG > EGC > ECG > GA > EC > C	Lin et al. (1996)
Superoxide anion	sPC5 > sPC3 > sPC4 > SPC2 > C	Yamaguchi et al. (1999)
Superoxide radical	EC3 > EC4 > EC2 > Q > EC > ChA > QGl	Lu and Foo (2000)
Hydroxyl radical	CaA > Ole > hT > T	Chimi et al. (1991)
DPPH radical	GA > Ge A > CaA > RA ,PA > BHA,BHT > GeA ≈ pCA > iEu > FA	Brand-Williams et al. (1995)
DPPH radical	2,3-DBA > SpA > Ca A > α-toc > FA > VA > 3-HBA	Pekkarinen et al. (1999)
DPPH radical	QGl > PC > > ChA ≈ 3-hPhlz > vit E > Vit C > Phlz	Lu and Foo (2000)

[a] α-toc, α-tocopherol; β-car, β-carotene; As, aspalathin; Ap, apigenin; Bol, boldine; Bu, butein; Ca, capsanthin; C, catechin; Chr, chrysin; Cy, cyanin; Cyd, Cyanidin; CyC, cyanidin chloride; EC, epicatechin, ECG, epigallocatechin; EGCG, epigallocatechin gallate; K, kaempferol; D; datiscenin; 2-H-3′,4′-DHAP,2-hydroxy-3′,4′-dihydroxyacetophenone; m3,4-DHB,methyl 3,4-dihydroxybenzoate; 3,4-DHPA,3,4-dihydroxyphenyl acetate; iEu, isoeugenol; Hes, Hesperetin; Ge, genistein; Fis,Fisetin; Fs, Fustin; 3-hPhlz, 3-Hydroxyphloridzin, Lu, Lutein; Lul, Luteolin; NH,Neohesperidin; MG, Methylgallate; Mo, Morin; My, Myricetin; Na, Naringin; Nan, Naringenin; Ole, Oleuropein; PC, Procyanindin; Phlz, Phloridzin; sPC, synthetic procianidin; PGG, β-1,2,3,4,6-Penta-O-galloyl-D-glucose; Q, Quercetin; QGl, Quercetin Glycosides; Q3Gl, Quercetin 3-Glucoside; Q3Ga, Quercetin galactoside; QR, quercetin rutinoside; Qr, Quercitrin; iQr, iQuercitrin; Res, resveratrol; Ru, rutin; Se, Sesamol; T, tyrosol; hT, Hydroxytyrosol; Tx, Taxifolin; V, vitexin; Zex, Zeaxanthin; DPPH, α,α-diphenyl-β-picrylhydrazil. Phenolic acids: CA, chlorogenic; CaA, caffeic; CnA, cinnamic; EA, ellagic; FA, ferulic; GA, gallic; GeA, gentisic; QA, quinic; SA, syringic; VA, vanillic; pCA, protocatechuic; pBA, p-hydroxybenzoic; pCA, p-coumaric; RA, rosmarinic; SA, Salicylic; SpA, sinapic; 2,3-DBA, 2,3-dihidroybenzoic; 3,4-DBA, 3,4-dihydroxybenzoic; 3-HBA, 3-hydroxybenzoic.

depending on the systems, as observed for gallic acid and derivatives (Aruoma, Murcia, Butler & Halliwell, 1993), green tea extracts (Wanasundara & Shahidi, 1998) and flavonols in the presence of metal salts (Roedig-Penman & Gordon, 1998). von Gadow et al. (1997c) observed a prooxidant action of caffeic acid in emulsion during β-carotene bleaching, whereas this compound showed a strong DPPH radical-scavenging activity and inhibition of lard oxidation in aqueous and oil systems, respectively. It is important to characterize them in biological systems, since antioxidant activity can enhance free radical damage of other compounds and these compounds could be prooxidants in biological systems. Differences in activity due to differences in the relative partition between phases in different lipid systems can explain why green teas were active antioxidants in corn oil and soybean lecithin liposomes, and prooxidant in oil-in-water emulsions due to greater affinity for the polar surface of the lecithin bilayers (Frankel et al., 1997).

Aruoma et al. (1993 and 1997) reported the ability of ginger and garlic to scavenge hydroxyl radicals, but the interaction with iron chelates facilitated OH· generation, and ginger exerted prooxidant action, accelerating damage to DNA in the presence of iron. The prooxidant activity is a result of the ability to reduce metals, such as Fe^{3+} to forms that react with O_2 or H_2O_2 to form initiators of oxidation. Wanasundara and Shahidi (1998) confirmed that the presence of chlorophyll was responsible for the prooxidant effect of tea extracts on the oxidation of marine oils. The transition metals have prooxidant action on tea, ascorbic acid and α-tocopherol, but may possibly not be important in vivo, where transition metals can be sequestered (Cao et al., 1996), except in pathological conditions. As a general rule, the antioxidants extracted from plants can show prooxidant activity at low concentration and antioxidant activity over certain critical values (Yen et al., 1997; Wanasundara & Shahidi). However, the opposite effect, i.e. antioxidant effect at low concentration and behaved as prooxidant at high concentration (Przybylsky et al., 1998) is known. Environmental factors, such as climatic growth conditions, growth, ripening stage, temperature and duration of storage and thermal treatment have been related with antioxidant activity due to inactivation of peroxidases (responsible for prooxidant action) (Gazzani et al., 1998).

4. Crude extracts from materials of residual origin

4.1. Composition of the crude extracts

Table 3 summarizes the main polyphenolic compounds detected in extracts from residual sources. When available, the total extractable polyphenol (T.E.P.) content is also indicated. Due to the wide nature of the agricultural and industrial wastes, a wide variety in the phenolic components exists. Robards et al. (1999) reviewed the main phenolic compounds of some studied fruits.

4.2. Factors affecting antioxidant activity (of extracts from materials of residual origin)

The quality of natural extracts and their antioxidative performances depends not only on the quality of the original plant, the geographic origin, climatic condition, harvesting date and storage (Cuvelier, Richard & Berset, 1996; Hagerman et al., 1998), but also environmental and technological factors affect the activities of antioxidants from residual sources.

4.2.1. Relation between phenolic content and antioxidant activity

Different results were reported on this aspect; whereas some authors found correlation between the polyphenol content and the antioxidant activity, others found no such relationship. Andarwulan, Fardiaz, Wattimena and Shetty (1999) found a parallel increase between phenol content and antioxidant activity during germination of *Pangium edule* and Tsaliki et al. (1999) observed an increase in the antioxidant activity of lupin seed flour with the different compounds responsible for this activity such as phenolic compounds, peptides/amino acids and phospholipids. No correlation between antioxidant activity and phenolic content was found in malts, since other compounds are responsible for the antioxidant activity (Maillard & Berset, 1995), nor was this relationship between antioxidant activity and phenolic composition found in citrus residues (Bocco et al., 1998), fruit berry, fruit wines (Heinonen, Lehtohen et al., 1998) or in plant extracts (Kähkönen et al., 1999).

4.2.2. Variety, plant and maturation stage

Total polyphenol content and antoxidant activity was found to be different for different parts (leaf, phloem, bark, cork, needle) of trees (pine, birch, spruce, aspen) (Kähkönen et al., 1999). The superoxide radical-scavenging activities of flavonoids extracted from different parts (leaves, tender leaves, branches and bark) of mulberry trees were also different (Zhishen, Mengcheng & Jianming, 1999). The extraction yield and the antioxidant activity differs among fractions of the milled durum wheat bran (bran, head shorts, tail shorts, low-quality flour and low-grade flour), but slight and non-significant differences were observed for different varieties (Onyeneho & Hettiarachchy, 1992). Torres, Mau-Lastovicka and Rezaaiyan (1987) found a slight reduction in the amounts of the total polyphenol (as gallic acid equivalents) content from young and mature leaves of different varieties of Avocado, but no differences in the mesocarp content. Andarwulan et al. (1999) and

Table 3
Extraction yields of soluble material, total extractable polyphenols and composition of crude extracts from agro-industrial wastes[a]

Residue	Solvent	Solubles yield (% dry weight) or T.E.P. (as equivalents)	Identified compounds	Reference
Durum wheat bran	Ethanol	12.1 (% dry weight) 2.769 (HPLC)	PA, pBA, GA, CaA, VA, CA, SA, pCA, FA	Onyeneho and Hettiarachchy (1992)
Fraxinus ornus bark	Ethanol	14.5 (dry weight)	Hydroxycoumarin (Es, Est, Fx, Fxt)	Marinova et al. (1994)
Corn bran hemicellulose	NaOH	3.259 (FA)	FA; pCA; dFA	Ohta et al. (1994)
Potato peel extract	Water (100°C)	0.048 (HPLC)	CA, GA, PA, CCA	Rodríguez de Sotillo et al. (1994a)
	Methanol (4°C)	0.041 (HPLC)	CA, GA, PA, CCA	
Shrimp shell waste	95% Ethanol	–	1,2 diamino-1(o-hydroxyphenyl)propene	Seymour et al. (1996)
Red grape pomace peels	Methanol water (1,1)	4.3 (tannic acid)		Larrauri et al. (1997)
	Acetone,water (7,3)	c. t., 27.0 (")		
Apple pomace	70% acetone		EC, CA, 3- hPhlz, Phl-2-x, Phlz, Q-3-gal, Q-3-glu, Q-3-xyl, Q-3-ara, Q-3-rha	Lu and Foo (1997)
Buckwheat hulls	Ethanol	23.8 (HPLC)	PA, 3,4-dihydroxybcenzaldehyde, Hy, Ru, Q, Vi, iVi	Watanabe et al. (1997)
Oat hulls	Methanol	0.035 (GC-MS)	FA, pCA, VA, pBA, V, 4-PhA, catechol, o-coumaric acid, SA, SaA	Xing and White (1997)
Lemon seeds	Methanol	0.2333 [(1)]	CaA, pCA (*cis* and *trans*), FA, SA, Eri, Nar, Neh	Bocco et al. (1998)
Sweetorange seed		0.0544	CaA, pCA (*cis* and *trans*), FA, SA, Nat, Nar, Hes	
Sour orange peel		2.526	CaA, pCA (*cis* and *trans*), FA, SA, Ner, Nat, Nar, Hes	
Bergamot peel		1.359	CaA, pCA (*cis* and *trans*), FA, SA, Ner, Nar, Neh	
Lentil seed coat (brown)	Water	22.3 (% dry weight)	L, Q, K, PC, PD, FA, PA, CaA	Muanza et al. (1998)
(green)		8.7 (% dry weight)		
Grape marc	Ethyl acetate	0.224 (HPLC)	K, Q, iRh3glu; K-3-glu; Q-3-glu; Q-3-gal; EC; C; VA; PA; GA	Bonilla et al. (1999)
	Water	0.021 (HPLC)	M-3(6-a)glu; Po-3(6-a)glu; M-3-glu; Po-3-glu; Pt-3-glu; Cy-3-glu; D-3-glu; PC	
Grape pomace	80% Ethanol	42% (dry weight)	GA; GA 3-βglup; GA 4-βglup; *trans*-CfA; *cis* and *trans* CtA; 2-h-5(2he)pβ-D-glp; C; EC; PCB1; Q-3glup; Q-3-glurcp; K-3-glup; K.3-galp; Ey; At; En	Lu and Foo (1999)
Lemon peel	Methanol-Water	0.02% (dry weight)	coumarins (8-geranyloxypsolaren, 5-geranyloxypsolaren, 5 geranyloxy-7 methoxycoumarin)	Miyake et al. (1999)
Grape seeds	95% Ethanol	–	pCA; GA; CAA; C,-EC, procyanidins (B1-B8)	Saint-Cricq de Gaulejac et al. (1999)
Non-volatile residue from orange essential oil	–	–	α-toc; 3,3′,4′,5,6,7 hexamethoxyflavone; 3,3′,4′,5,6,7,8,-heptamethoxyflavone; 4′,5,6,7,8 pentamethoxyflavone	Vargas-Arispuro et al. (1998)
Olive mill waste waters	Water:Ethanol	8.11 (% dry weight)	hT, T, EA, oleuropein derivatives, Lu-7-glu, Q, CnA derivatives, hT derivatives	Visioli et al. (1999)
	Ethyl acetate	22.78 (% dry weight)		
Grape seed extract	20% Ethanol	–	proanthocianidins, monomeric flavonols	Yamaguchi et al. (1999)

[a] e.p., extractable polyphenols; n.e., non extractable; UP; unidentified polyphenols; c.t., condensed tannins; [(1)]glycosylated flavanone + phenolic acids content; GC–MS, gas chromatography–mass spectroscopy. Phenolic acids; CA, chlorogenic; CaA, caffeic; Cf A, caftaric; CnA, cinamic; Ct A, Coutaric; EA, elenoic; FA, ferulic; dFA, diferulic; GA, gallic; KA, kiwic; QA, quinic; VA, vanillic; SA, syringic; CnA, cinnamic; PA, protocatechuic; pBA, p-hydroxybenzoic; GeA, gentisic; pCA, p-coumaric; VA, vanillic; At, Astilbin; Ct, catechol; EC, Epicatechin; C, Catechin; Cy-3-glu, Cyanidin-3-glucoside; D-3-glu, Delphinidin-3-glucoside, En, Engeletin; Eri, eriocitrin; Es, Esculin; Est, Esculetin; Ey, Eucryphin: Fx, Fraxin; Fxt, Fraxetin; GA 3-βglup, Gallic acid 3-β-glucopyranoside; GA 4-βglup, Gallic acid 4-β-glucopyranoside; 2-h-5(2he)pβ-D-glp, 2-hydroxy-5-(2-hydroxyethyl(phenyl-β-D-glucopyranoside; Hes, hesperidin; Hy, Hyperin; K, Kaempferol; K-3-glu, Kaempferol-3-glucoside; K-3-glup: Kaempferol 3-β-D-glucopyranoside; K-3-galp: Kaempferol 3-β-D-galactopiranoside; Lu-7-glu, Lu-7-glucoside M-3(6-a)glu,Malvidin-3-(6-acetyl)-glucoside; M-3-glu,Malvidin-3-glucoside; Nar, naringin; Nat, narirutin; Neh, neohesperidin; Ner, neoeriocitrin; PC, Procyanidin; PD,Prodelphinidin; 4-PhA, 4-hydroxyphenilacetic acid; 3,4-PhE, 3,4-hydroxyphenilethanol; 3,4-dB, 3,4-dihydroxybenzaldehyde; 3-hPhlz, 3-Hydroxyphloridzin; Phl-2-x,Phloretin-2′- xyloglucoside; Phlz,Phloridzin; Po-3(6-a)glu,Peonidin-3-(6-acetyl)-glucoside; Pt-3-glu,Petunidin-3-glucoside; Q,Quercetin; Q-3-gal, Quercetin-3-galactoside; Q-3-glu, Quercetin-3-glucoside; Q-3-glucr, Quercetin-3-glucuronide; Q-3-glurcp: Quercetin 3-β-D glucuropyranoside; Q-3-glup: Quercetin 3-β-D glucopyranoside; Q-3-xyl, Quercetin-3-xyloside; Q-3-ara, Quercetin-3-arabinoside; Q-3-rha, Quercetin-3-rhamnoside; iRh3Glu, isoRhamnetin-3-glucoside; Ru, Rutin; SaA, Salicilyc acid; T, tyrosol; hT, hydroxytyrosol; V,Vanillin Vi, Vitexin; iVi, isovitexin

Sawa et al. (1999) reported phenol mobilization during seed germination and increased content and antioxidant activity during the production of precursors for the synthesis of lignin. Yen and Duh (1994) studied the effect of the maturity of peanuts on both the polyphenol content of the hulls and the antioxidant activity of their methanolic extracts. Luteolin and total phenols increased with maturity, but a maximum antioxidant activity (92.9–94.8% inhibition of linoleic acid peroxidation) was detected at a total polyphenol content of 1.67 mg/g hulls, the luteolin content being more dependent on the maturity than on the variety. However, Yen and Duh (1995) found that the total phenol content differed significantly among peanut cultivars, although the specific antilipoperoxidant activity was similar. In paprika, harvesting at different ripening stages affected the content of ascorbic acid and tocopherols (Markus et al., 1999). Other factors, such as insect infestation, were reported to increase polyphenol content in maize, wheat and sorghum and, in the latter two, phytic acid content also (Jood, Kapoor & Singh, 1995).

4.3. Processing conditions

4.3.1. Effect of the extracting solvent

Solvent extraction is more frequently used for isolation of antioxidants and both extraction yield and antioxidant activity of extracts are strongly dependent on the solvent, due to the different antioxidant potential of compounds with different polarity (Julkunen-Tiito, 1985; Marinova & Yanishlieva, 1997). Apolar solvents are among the most employed solvents for removing polyphenols from water. Ethyl acetate and diethyl ether have been used for extraction of low molecular weight phenols from oak wood (Fernández de Simón, Cadahía, Conde & García-Vallejo, 1996) and the polyphenols extracted with ethyl acetate from natural materials were reported to have strong antioxidant activity (Marinova & Yanishlieva). Ethanol and water are the most widely employed solvents for hygienic and abundance reasons, respectively. Since the activity depends on the polyphenol compounds and the antioxidant assay, comparative studies for selecting the optimal solvent providing maximum antioxidant activity are required for each substrate. Less polar solvents such as ethyl acetate, provided slightly more active extracts than mixtures with ethanol or methanol, or methanol alone for tamarind seed coats (Tsuda, Watanabe et al., 1994) although ethanol and methanol extracts also presented high lipid peroxidation-inhibiting activity, comparable to α-tocopherol. Selective extraction of more apolar compounds was reported to enhance the antioxidant activity of lentil husk extracts (Muanza et al., 1998). Lower IC_{50} values for the DPPH radical (amount of antioxidant required for causing a 50% reduction in the absorbance of DPPH) were observed for butanol extracts, followed by those in ethyl acetate. Those obtained with methanol-water were less efficient.

Julkunen-Tiito (1985) found a different behaviour in the extraction of different compounds and total extractable polyphenols (TEP). Maximum total phenolics extraction yields were attained with methanol, whereas 50% acetone extracted more selectively leucoanthocyanins and no significant effects were observed in the extraction of glycosides. Also, for extracts from burdock roots, water (regardless of the temperature used) yielded the greatests amount of extract and exhibited the strongest antioxidant activity (Duh, 1998). Azizah et al. (1999) reported maximum antioxidant activity from cocoa by-products (cocoa powder, cocoa nib, cocoa shell) in the methanol, followed by mixtures of chloroform, ether and dichloroethane or chloroform, methanol and dichloroethane. The polyphenol extraction yield was higher for the more polar solvents for extracts from *Gevuina avellana* hulls (Moure, Franco, Sineiro, Domínguez, Núñez & Lema, 1999). Also Przybylski et al. (1998) reported that the antioxidant activity of buckwheat extracts varied with the polarity of the solvent, those extracted with methanol being the most active.

The effect of the extraction pH has also been reported. Sheabar and Neeman (1988) reported maximum solubility of polyphenols from olive rape at pH4 in the organic phase. Baublis et al. (2000) reported increased antioxidant activity of aqueous fractions from wheat bran after treatment at acidic conditions, probably due to altered phenol composition. The pH has also been considered by Lehtinen and Laakso (1998) for the aqueous extraction of antioxidants from oat fibre, the highest yield being attained at pH6 and the highest antioxidant activity at pH10. At alkaline pH, the fractions with high protein and fatty acid contents are solubilized; and due to contradictory data on the higher antioxidant activity of carbohydrate or proteins, the antioxidant activity was probably carried by the protein-rich fraction. The physical state of the fibre rather than the total concentration of some specific fibre compound were suggested as responsible for the higher antioxidant activity. Bonilla et al. (1999) reported selective extraction of flavan-3ol monomers, catechin and flavonols from grape marc, preferentially in the organic phase, whereas procyanidins were extracted in the aqueous phase.

Reduction in particle size favours solvent extraction of polyphenols and both mechanical crushing (Bonilla et al., 1999) and enzyme demolition were reported on grape marc. Enzyme-aided extraction of antioxidants from grape pomace has been reported by Meyer, Jepsen et al. (1998). The yield of extracted phenols was correlated with the plant cell wall breakdown caused by pectinases and cellulases, although these latter did not cause the degradation of grape pomace polysaccharides. Particle size reduction significantly increased the antioxidant activity as a result of both increased extractability and enhanced enzymatic degradation of polysaccharides. Increased polyphenol recovery from rosemary and sage, during enzyme-assisted ensiling with cellulases, hemicelulases and pectinases, was reported by Weinberg et al. (1999).

4.3.1.1. Temperature. The temperature, during drying and extraction, affects the compound stability due to chemical and enzymatic degradation, losses by volatilization or thermal decomposition (Ibáñez, Oca, de Murga, López-Sebastián, Tabera & Reglero, 1999); these latter have been suggested to be the main mechanism causing the reduction in polyphenol content (Larrauri et al., 1997). Also, for synthetic antioxidants, evaporation and decomposition were the main mechanisms for the loss of activity (Hamama & Nawar, 1991). In addition to thermal decomposition, phenols can react with other plant components, impeding their extraction. Decomposition to more active compounds has also been described; Guillot, Malnoë & Stadler (1996) observed that mild pyrolysis of some polyphenolic acids increased the antioxidant activity over that of the original compounds, especially in the case of caffeic acid. Degradation, caused by other agents, has been observed; Cilliers and Singleton (1990) demonstrated ring-opening during alkaline oxidative conditions, as in non-enzymatic reactions involving polyphenolic compounds in food systems, and identified the resulting products as compounds analogous to natural lignans and neolignans (Cilliers & Singleton, 1991). Prolonged exposure at moderate temperatures can also cause phenolic degradation during their enzyme-assisted extraction from grape pomace for 48 h hydrolysis (40°C and pH 5), whereas at 1–8 h, no degradation was observed. Maillard and Berset (1995) observed 20% reduction in antioxidant activity during kilning at 90°C for bound and free polyphenols. The temperature during extraction can affect the extractable compounds differently: boiling and resting increases the total phenol content in *Quercus suber* cork (Conde et al., 1998); however, proanthocyanidin content decreased (Cadahía et al., 1998). Milder extraction temperatures are desirable in those cases where some compound can be degraded, e.g. carnosic acid, and, for these reasons, supercritical fluid extraction was reported to provide extracts with higher antioxidant activity (Ibáñez et al., 1999).

The effect of temperature has been studied in spray-drying of carrot pulp waste (Chen & Tang, 1998), but the drying method also affects the retention and preservation of β-carotene, drum drying being the best preservation method due to the particle size and surface carotenoid content (Desobry, Netto & Labuza, 1997). Larrauri et al. (1997) found a significant reduction in extractable polyphenols and condensed tannins when red grape pomace peels were dried with air at 100°C or higher. The antioxidant activity of samples dried with air at 100°C was reduced by 28% and, at 140°C by half, with respect to drying at 60°C, that did not significantly affect either the extractable polyphenols or condensed tannins, with respect to freeze-drying. Drying at 100°C caused a reduction of 18.6% and at 140°C of 32.6% in the TEPs, which in this material are a complex group of different substances (phenolic acids, anthocyanins, flavonols, flavan-3-ols, and flavanonols). Anthocyanins were also probably degraded since the visible spectrum showed both a reduction in the peak at 400–500 nm and reduction in red colour. The reduction in antioxidant activity was higher than that expected from the reduction in polyphenols content, probably due to the synergistic effect of natural phenols. The amount of flavonoids in fresh Mulberry leaves was higher for air-dried than for oven-dried, probably due to decomposition after storage or to lowered extractability due to modification of the matrix (Zhishen et al., 1999). Both thermal decomposition and losses by volatilizing have been suggested as the main causes for lowered yields. Also, Julkunen-Tiito (1985) reported a maximum yield of total willow leaf polyphenols when the drying temperature was below 50°C; increasing the temperature above 60°C significantly lowered the phenols, the leucoanthocyanins content being the most affected by temperature.

4.4. Factors affecting stability of extracts from materials of residual origin

Temperature and light are the major factors influencing antioxidant activity during storage. These factors affect different compounds to different extents. The reduction in the free radical-scavenging activity, caused by exposure at high temperature, was more marked for red grape pomace peel (28.5) than white grape pomace peel (22.9) and these latter more than BHA (15.3), but all of them were lower than for α-tocopherol (Larrauri et al., 1998). The stability of different extracts from the same material was dependent on the extracting solvent used for the solubilization and removal of the polyphenolic compounds; methanol extracts from cocoa by-products were stable up to 50°C and in a wide range of pH (3–11), whereas other extracts (chloroform, methanol, dichloroethane) were less stable (Azizah et al., 1999).

Rodríguez de Sotillo et al. (1994a) found that neither autoclaving nor storage at 25°C caused changes in potato peel polyphenol concentrations, whereas those exposed to light suffered complete degradation of chlorogenic acid after 7 days, and an increase in caffeic acid slightly higher than the 60% of the disappeared chlorogenic acid, the remaining portion probably being degraded into another compound or compounds. The caffeic acid disappeared completely in 20 days. No stability loss was noticed in freeze-dried samples during storage (Rodríguez de Sotillo et al., 1994b), but degradation of caffeic acid and increase of gallic acid during freeze-drying were observed as a result of the freeze-drying process. This extract was found to be stable for 3 years when stored, tightly capped, in plastic vials at room temperature (23°C), since non-significant changes in both total phenols and antioxidant activity were found when measured as inhibition of sunflower oil oxidation (Rodríguez de Sotillo et al., 1994b, 1998). Moure et al. (1999) found that, in the darkness at 4°C after 6 months, the ethanolic and aqueous extracts from *G. avellana* hulls were stable, but those extracted with acetone showed a 97% reduction in the β-carotene bleaching activity and 43% in DPPH radical-scavenging activity with respect to the freshly prepared ones. Azizah et al. (1999) reported increased stability of the antioxidant activity from cocoa by-products with increasing pH from 3 to 11.

4.5. Effect of extract concentration

The antioxidant activity depends on the extract concentration. As a general trend, increased antioxidant activity was found with increasing extract concentration, but the concentration leading to maximum antioxidant activity is closely dependent on the extracts and, for the same extract, is dependent on the antioxidant activity test (Yen & Wu, 1999). Dose-response curves are different for different antioxidants. Yamaguchi et al. (1999) compared grape seed extract with natural antioxidants, such as tocopherol and ascorbic acid and observed different effectiveness, depending on the assay. The superoxide anion-scavenging activity was found to be dependent on the flavanol concentration. Marinova and Yanishlieva (1997) observed absence of linearity in the dependence of stabilization factor on esculetin concentration, probably due to the participation of the antioxidant in reactions other than in chain termination. Fig. 1 shows the concentration-activity curves for the antioxidant activity measured with different tests. As a general trend, the antioxidant activity increases with the antioxidant concentration, but only up to a certain level, which depends on both the antioxidant and the test. In liposomes, the optimal concentration of grape seed and rose hip extracts was 0.1 mM, whereas for BHT it was 0.02mM and for catechin a steady state was observed in the range 0.05–0.2 mM (Gabrielska et al., 1997). For most tests and natural extracts, maximum antioxidant activity was achieved using a 0.05% concentration. Acetone extracts from *G. avellana* hulls when used at concentrations under 1000 mg/l (Moure, Franco, Sineiro, Domínguez, Núñez & Lema, 1999), showed prooxidant activity, but increased antioxidant activity was observed with increased concentration.

4.6. Combined action (synergistic, additive or antagonist)

Synergistic actions between synthetic only, natural and synthetic, and natural antioxidants have been observed (Bandarra et al., 1999; Duh et al., 1997; Frankel, 1996; Heinonen, Haila, Lampi & Pironen, 1997; Hattori et al., 1998; Hudson & Lewis, 1983; Meyer et al., 1998a,b; Saucier & Waterhouse, 1999; Wijewickreme & Kitts, 1998; Yi et al., 1991). This effect is defined as the combined action which results in increased antioxidant potential more than that expected from a mere additive effect. Yi et al. observed that α-tocopherol and ascorbic acid acted highly synergistically with each other in a fish oil/lecithin/water system, requiring a minimum of 0.01–0.02% ascorbic acid. Maillard and Berset (1995) observed this effect between p-coumaric and ferulic acids with ratios between 0.14–0.22 for the expected/observed antioxidant activity measured as percentage increase (respect to a control) in the half-life during accelerated oxidation of methyl linoleate. Protective effects against caffeic acid autoxidation in the presence of ascorbic acid were also observed by Cilliers and Singleton (1990). Synergistic effects of phenols from grape seeds and pomace polyphenols have been reported. Mixtures of tocopherol and carotene (Yamaguchi et al., 1999), as well as mixtures with other substances (ascorbic acid, lecithin), which have been reported to enhance the antioxidant activity (Chambers et al., 1988). Meyer, Heinonen et al. (1998) found interactive effects between flavonoids and phenolic acids. However, the simultaneous presence of some compounds may present lower antioxidant activity than expected; in this way antagonist effects were observed between ellagic acid and catechin. The authors suggested the possible existence of hydrogen-bonding between carbonyls in ellagic acid and o-dihydroxyl groups in catechin. Synergistic antioxidant effects between the compounds found in natural extracts are probably responsible for the higher antioxidant activities observed for the crude extracts than that measured in simulated extracts (Table 4). Synergistic antioxidant effects were observed for mixtures of crude extracts of burdock and tocopherol (Blekas & Boskou, 1998; Duh, 1998) and of grape seed extracts and ascorbic acid. Other substances could also act synergistically with the phenols; therefore, these compounds could not be the only ones responsible for the antioxidant activity (Onyeneho & Hettiarachchy, 1992). These authors reported a PV value of 37 meq/kg for soy oil after 9 h active oxygen method (AOM) treated with durum wheat bran extract, but a significantly higher value of 46.0 meq/kg for the simulated extract with the authentic standards in the proportions found in the extracts. The PV for the oil, subjected to oxidation in the presence of added pure polyphenols, ranged from 84 meq/kg when

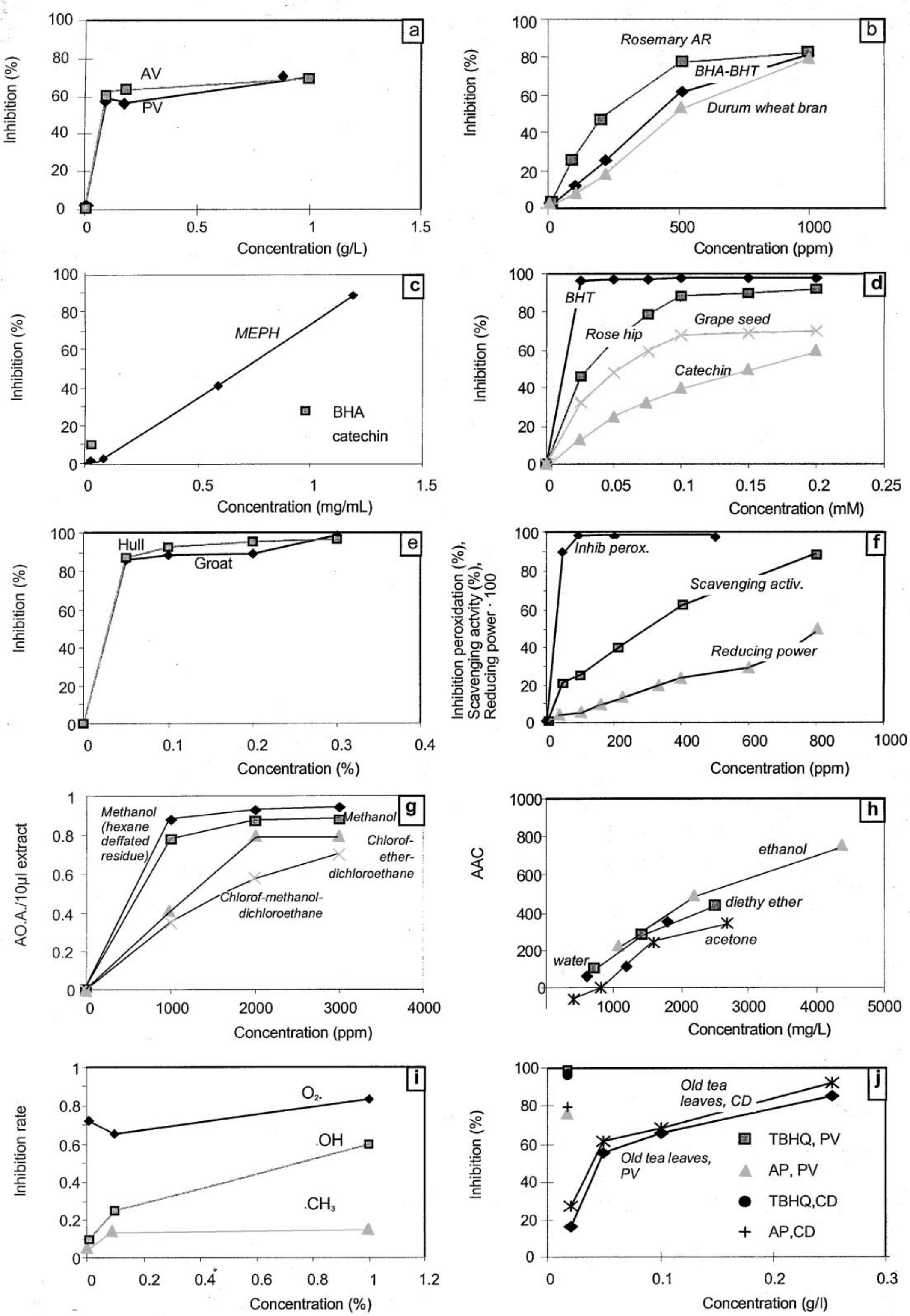

Fig. 1. Effect of the extract concentration on the antioxidant activity measured as, (a) inhibition of refined olive oil (Sheabar & Neeman, 1988), (b) inhibition of soy oil oxidation (Onyeneho & Hettiarachchy, 1992), (c) scavenging activity on free-radical and active-oxygen species (Yen & Duh, 1994), (d) inhibition of lecithin liposome oxidation (Gabrielska et al., 1997), (e) inhibition of soy oil oxidation (Xing & White, 1997), (f) inhibition of the oxidation of linoleic acid (Duh et al., 1997), (g) inhibition of oxidation of linoleic acid (Azizah et al., 1999), inhibition of β-carotene bleaching (Moure, Franco, Sineiro, Domínguez, Núñez & Lema, 1999), (h) β-carotene bleaching inhibition by *Gevuina avellana* hulls extracts (Moure et al., 1999) (i) free radical-scavenging activity (Yamaguchi et al., 1999), (j) inhibition of the oxidation of rapeseed oil (Zandi & Gordon, 1999). AV, Anisidine Value; PV, Peroxide value; CD, conjugated diene; TBHQ, tertiary butyl hydroquinone; AP, Ascorbyl palmitate.

Table 4
Antioxidant action of the crude extracts, fractions and synthetic mixtures[a]

Extract	Antioxidant assay	Antioxidant activity		Reference
		Crude	Synthetic mixture or fractions	
Durum wheat bran	Soy oil oxidation (PV)	71.08	64.09	Onyeneho and Hettiarachchy (1992)
Potato peel waste	Sunflower oil oxidation (I.P) (I.P.)	26.3	22.1 (mixture) GA, 15.8% CA, 12.6%	Rodríguez de Sotillo et al. (1994b)
Tamarind seed coat	Linoleic acid oxidation (%)	10% (200 μg)	5% (20 μg A0) 8% (20 μg A1) 12% (20 μg) 28% (20 μg A3)	Tsuda, Watanabe et al. (1994)

[a] PV, peroxide value; I.P., inhibition percentage respect to control; GA, gallic acid; CA, chlorogenic acid; A0-A3, chromatographic fractions.

p-coumaric acid was added to 39 meq/kg when protocatechuic acid was used. Other plausible reasons could be the synergistic effects of the different phenolic compounds. Rodríguez de Sotillo et al. (1994b) reported higher antioxidant activity for freeze-dried potato peel extract during sunflower oil oxidation than for the synthetic mixture of individual compounds. Similarly, Watanabe et al. (1997) and Watanabe (1998) reported significantly higher peroxyl-radical scavenging activity of some of the purified fractions of buckwheat hull extracts over the crude extracts. Synergy among the different classes of polyphenols was observed and reported as hypothetically existing in red wine (Ghiselli et al., 1998). However, an antagonist effect of the methanolic extract with peanut hulls and tocopherol and with BHA, both at 48 and 120 ratios (Duh & Yen, 1997a) was reported.

Since there is no single antioxidant that can scavenge all kinds of radicals or that performs optimally for all lipid products, mixtures of antioxidants resulting in a synergistic effect are preferred for preventing free radical-induced diseases. Combined use of antioxidants will probably be desirable, as observed for model compounds (Bruun-Jensen, Skovgaard, Madsen & Skibsted, 1996; Bruun-Jensen, Skovgaard, Madsen, Skibsted & Bertelsen, 1996; Yi et al., 1991). The use of synergistic mixtures of antioxidants allows a reduction in the concentration of each and also increases the antioxidant effectiveness with respect to the activity of the separate components although, even in widely used and commercialized extracts, such as rosemary, the antioxidative behaviour and synergistic actions of most of the compounds remain unknown (Cuvelier et al., 1996). Chu and Hsu (1999) observed a two or three times higher oxidative stability index for peanut oil when mixtures of antioxidants were used. The beneficial effects of using mixtures of antioxidants were summarized by Sherwin (1990) as: (1) advantages of their different effectiveness; (2) minimalisation of solubility or colour problems presented by individual compounds; (3) better control and accuracy of application; (4) complete distribution or solution of antioxidants and chelating agents.

5. Potential antioxidant activity from residual wastes

Table 5 summarizes the antioxidant activity of extracts from residual sources and, when reported, the antioxidant activity of natural or synthetic antioxidants is given for comparative purposes. The concentrations tested, for both the natural extracts and for the standard compounds used for comparative purposes, are also indicated. As a general rule the extracts from vegetable materials of residual origin showed antioxidant activity, in some cases comparable to that of synthetic antioxidants, and their extraction and use could be an alternative for obtaining natural antioxidants. Even when the natural extracts are less efficient, the use of some of them as food antioxidants can be advantageous. Maximum levels established for synthetic food additives need not be applicable to naturally occurring compounds, e.g. those from grape marc (Bonilla et al., 1999).

6. Practical applications

The natural antioxidants from residual sources may be used for increasing the shelf life of food by preventing lipid peroxidation and protecting from oxidative damage. Increasing the oxidation stability of vegetable oils is important for industrial practice, and many antioxidant tests are based on this ability to retard or inhibit the oil rancidity. Many tests of antioxidant activity use pure triacylglycerols or fatty acid methyl esters and many others use either crude, refined or commercial vegetable oils. These assays are carried out under extreme conditions; however, more practical assays

Table 5
Antioxidant activities of extracts from residual materials from agro-industrial origin[a]

Residue (solvent)	Antioxidant activity assay	Activity (conc. antioxidant)	Reference
Rape of olives (A + E)	Refined olive oil oxidation	PV (Control), 52 meq/kg	Sheabar and Neeman (1988)
		PV (1000 ppm), 18 meq/kg	
	Refined olive oil oxidation	AV (Control), 175	
		AV (1000 ppm), 60	
Durum wheat bran (E)	Soy oil oxidation	PV (0.05%),37.6–42.0 meq/kg	Onyeneho and Hettiarachchy (1992)
		PV (0.05% BHA–BHT),22.0 meq/kg	
		PV (control),129.0 meq/kg	
Fraxinus oxinus bark (E)	Triacylglycerols of lard and sunflower oil oxidation	F(0.05%), 3.6–4.8	Marinova et al. (1994)
		F(0.1%), 4–6.1	
		ORR (0.05%), 0.6–0.28	
		ORR (0.1%), 0.5–0.28	
Corn bran hemicellulose fragments (FA sugar esters)	Lipid peroxidation of rat liver microsomes	ABS_{510nm} (control), 0.23	Ohta et al. (1994)
		ABS_{510nm} (Toc 0.5 mM), 0.03	
		ABS_{510nm} (0.5 mM), 0.065	
Potato peel waste (W)	Sunflower crude oil oxidation	PV (200 ppm) ,37.47	Rodríguez de Sotillo et al. (1994b)
		PV (200 ppm BHA), 37.47	
		PV (Control), 49.15	
Tamarind seeds coats (E) (EA)	Linoleic acid oxidation	ILP (α-tocopherol 0.2 mg), 90%	Tsuda, Watanabe et al. (1994)
		ILP (0.2 mg), 90%	
		ILP (0.2 mg), 98%	
Wild rice hulls (M)	–	TBARS (0.1%), 2.4	Wu et al. (1994)
		TBARS (0.2%), 0.9	
		TBARS (Control), 3.8	
		TBARS (0.02%), 0.3	
Peanut hulls (M)	DPPH radical scavenging	IP (extract 1.5 mg/mL), 89.3%	Yen and Duh (1994)
		IP (BHA 240μM), 92.6%	
		IP (catechin 8μM), 89.3%	
Peanut hulls (M)	Linoleic acid oxidation	AA (9.6 mg), 96.1-96.8%	Yen and Duh (1995)
Mung bean hulls (M)	Linoleic acid peroxidation	ABS_{500nm} (100 ppm), 0.20	Duh et al. (1997)
		ABS_{500nm} (BHA, 100ppm), 0.23	
		ABS_{500nm} (control), 0.95	
	Soybean oil oxidation	PV (100 ppm),70	
		PV (BHA, 100 ppm),55	
		PV (control),105	
	Soybean oil oxidation	ABS_{535nm} (100 ppm), 0.7	
		ABS_{535nm} (BHA, 100ppm), 0.75	
		ABS_{535nm} (control), 1.4	
Peanut hulls (M)	Soybean and peanut oil oxidation	O.S. (0.48%), 194	Duh and Yen (1997b)
		O.S. (1.20%), 292	
		O.S. (0.01% BHA), 143	
		O.S. (Control), 107	
Grape seeds (EA – C pptn)	Lecithin liposome oxidation	ILLO (0.1 mM),86%	Gabrielska et al. (1997)
		ILLO (0.1 mM BHT), 88.5%	
		ILLO (+)catechin,40%	
Rose hips (EA–C pptn)	Lecithin liposome oxidation	ILLO (0.1 mM),68%	Gabrielska et al.
		ILLO (0.1 mM BHT), 88.5%	
		ILLO (+)catechin,40%	
Buckwheat hulls/(E-separation by cromatography)	Methyl linoleate oxidation	PV (Control),3.5 mM	Watanabe et al. (1997)
		PV (0.042 g/l),1.75-2.5 mM	
		PV (BHA),0.75 mM	
Oat groats (M)	Soybean oil oxidation	IO (0.3%),98.4%	Xing and White (1997)
Oat hulls (M)	Soybean oil oxidation	IO (0.3%),96.4%	Xing and White
Lemon peel (M)	Citronellal oxidation	AOP, 0.16 L/g	Bocco et al. (1998)
Mandarin seeds (M)		AOP, 0.5 L/g	
Sour orange peel (M)		AOP, 0.27 L/g	
Sweet orange (M)		AOP, 0.20 L/g	
Eucalyptus wood acid hydrolysates (EA)	Linoleic acid and β-carotene oxidation	AAC (400 mg),588	Cruz et al. (1999)

(continued on next page)

Table 5 (*continued*)

Residue (solvent)	Antioxidant activity assay	Activity (conc. antioxidant)	Reference
		AAC (BHT 400 mg),916	
Grape pomace (enzyme treatment, A)	Cu-induced human LDL oxidation	NPIT (catechin 3μM GAeq), 110.4 min	Meyer, Jepsen et al. (1998b)
		NPIT (catechin 3μM GAeq), 62.2 min	
Grape seed extract (E)	Antiulcer activity (200 mg/kg)	Lesion length (control), 111mm	Saito et al. (1998)
		Lesion length (catechin), 88 mm	
		Lesion length (extract), 4–20 mm	
Grape pomace (M,W-A,W)	DPPH radical scavenging	IC_{50},0.2 g (4 mg extractable polyph)	Saura-Calixto (1998)
		IC_{50} (D,L, α-tocopherol), 0.02 g	
	Linoleic acid oxidation	IC_{50} ,0.7 g (14 mg extractable polyph)	
		IC_{50} (D,L, α-tocopherol), 0.3 g	
Olive mill waste water (W-E)	Cu-induced human LDL oxidation	LOOH (control) ,0.35 nm	Visioli et al (1999)
Olive mill waste water (EA)		LOOH (20 ppm), 0.1–0.2 nm	
Shrimp shell waste (95% E)	β-carotene bleaching	34.09%	Li et al. (1998)
		BHA/BHT/citric acid, 11.36%	
Lentil seed coat (MW)	50% inhibiton in the reduction of the nitro blue tetrazolium (NBT)	IC_{50},4.52 μg/ml	Muanza et al. (1998)
		IC_{50} (ascorbic acid), 5.5 μg/ml	
		IC_{50} (catechin), 1.9 μg/ml	
Brown lentil husk (M-W)	DPPH radical scavenging	IC_{50},12.58-14.83 μg/ml	Muanza et al.
(EA)		IC_{50},6.62 μg/ml	
(B)		IC_{50},4.04 μg/ml	
		IC_{50} (catechin), 5.46 μg/ml	
		IC_{50} (quercetin), 1.73 μg/ml	
		IC_{50} (gallic acid), 0.63 μg/ml	
		IC_{50} (ascorbic acid), 2.58 μg/ml	
Non-volatile residue from orange essential oil	Olive oil	Oxidation (%)(3000 ppm),52-64%	Vargas-Arispuro et al. (1998)
	70°C, 48 h	Oxidation (%)(BHA, 200 ppm),72%	
Red grape marc (EA)	Refined olive oil oxidation	IP (100 mg/kg),22 h	Bonilla et al. (1999)
		IP (100 mg/kg BHA),26 h	
		IP (100 mg/kg BHT),24 h	
Grape seed (W)	Cu-mediated oxidation of rat plasma	Lag phase, 95 min (control)	Koga et al. (1999)
		Lag phase 175 min (proanthocyanidin, incubation 30 min)	
Lemon peel (M)	Hemoglobin catalysed peroxidation of linoleic acid	IC_{50},122.0 ppm	Kuo et al. (1999)
Orange peel (M)		IC_{50},68.8 ppm	
Peanut hull		IC_{50},111 ppm	
		IC_{50} (BHA),0.65 ppm	
Gevuina avellana hulls (E)	β-carotene bleaching	AAC (4000 mg/l),767	Moure et al. (1999)
		AAC (230mg BHA/l),901	
		IO (1 g/l),73.1%	
G. avellana hulls (M)	crude soybean oil oxidation	IO (0.01 g BHA/l),12.8%	
		IO (0.01 g BHT/l),34.8%	
Old tea leaves/(M)	Rapeseed oil	(control); AV,80.7; PV, 290 meq/kg	Zandi and Gordon (1999)
	60°C, 20 days	(OTL 0.25%); AV ,9.5; PV, 30 meq/kg	
		(TBHQ 0.02%); AV,2.7; PV, 5 meq/kg	
		(Rosemary 0.1%); AV,4.8; PV, 25 meq/kg	

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[a] A, Acetone / C, Chloroform / B, Butanol / E, Ethanol / EA, Ethylacetate / M, methanol / W, Water; IO, Inhibition of soybean oil oxidation, after 20 days at 60°C in the dark, $((PV_{control}-PV_{treatment})/PV_{control})*100$; AA, Antioxidant activity (thiocyanate method), calculated as percentage of inhibition of peroxidation of linoleic acid; AAC, Antioxidant Activity Coefficient (Miller, 1971), (Absorbance of $extract_{120h}$-Absorbance of $control_{120h}$)/(Absorbance of $control_{0h}$-Absorbance of $control_{120\ h}$); A.O.P., Reciprocal of the concentration required to double the half-life time of citronellal (l/g dry matter peel or seed); ABS_{500nm}, Measure of linoleic acid oxidation by the thiocyanate method after 12 days; ABS_{510nm}, Measure of lipid peroxidation in rat liver microsome; ABS_{535nm}, Formation of TBARS (Thiobarbituric acid reactive sustances) on soybean oil after accelerated oxidation; BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; DPPH, α α-diphenyl-β-picrylhydrazil; F (protection factor),IP_{inh}/IP_0, IP_{inh} is the induction period in the presence of an inhibitor and IP_0 is the induction period of the non inhibited system; ILLO, Inhibition of lecithin liposome oxidation as increase in ABS_{535nm}; ILP, Inhibition of linoleic acid peroxidation respect to a control (thiocyanate method); I.P., Induction Period, the time required for the fluorescence spots on a silica gel TLC plate sprayed with a 3% solution of linoleic acid in hexane, which was considered the induction period for lipid oxidation; IC_{50}, Inhibitory concentration for 50% inhibiton in the reduction of oxidation; Lag phase of CE-OOH accumulation in $CuSO_4$-induced oxidation of rat plasma (min); LOOH, lipid peroxide production; NPIT, Net Prolongation of Induction Time (min) for conjugated diene hydroperoxide formation; O.R.R. (Oxidative Rate Ratio), W_{inh}/W_o, W_{inh} is the initial oxidation rate in the presence of an inhibitor, W_o is the initial oxidation rate of the non inhibited system; OS,Oxidative stability (h); AV, Anisidine value; PV, Peroxide value; TBHQ, tertiary butyl hydroquinone.

have been used for food during storage or processing (Table 1).

The stability of processed foods has also been assessed after addition of antioxidants. Both synthetic and natural phenols enhanced the oxidative stability of freeze-dried, ground extruded corn starch–soybean oil mixtures (Camire & Dougherty, 1998). Zandi and Gordon (1999) evaluated the methanolic extracts of old tea leaves (OTL) during deep-fat frying of potato crisps at 180°. The authors found that OTL extracts are slightly more active antioxidants than rosemary extract (both at 0.1%) during the frying stages. In this kind of assay, rosemary was more active than BHA or BHT (Che Man & Tan, 1999).

The antioxidant compounds from residual sources could be used for increasing the stability of foods by preventing lipid peroxidation and also for protecting oxidative damage in living systems by scavenging oxygen radicals. Studies to incorporate the crude extracts or the whole vegetable material in foods (meats) as 'antioxidant ingredients' are scarce. Wu, Zhang, Addis, Epley, Salih and Lehrfeld, (1994) reported the beneficial effects of using wild rice as an antioxidant, particularly after particle size reduction and cooking. Water extracts are advantageous in relation to certification for food (Møller et al., 1999). Maillard reaction products were evaluated as antioxidants in cooked ground beef during storage at 4°C (Alfawaz et al., 1994) or natural antioxidants in cooked, minced turkey (Bruun-Jensen, Skovgaard, Madsen & Skibsted, 1996; Bruun-Jensen, Skovgaard, Madsen, Skibsted & Bertelsen, 1996). Improvement in colour stability for different species of rock fish was observed in the presence of antioxidant extracts from shrimp shell waste. Carotenoid degradation was decreased by inhibiting autooxidation and/or lipoxygenase activity, this activity being increased with increasing concentrations of shrimp shell waste (Li et al., 1998). Antioxidants have also been proposed for preventing loss or improving the stability of pigments from red beet juice in the food industry (Han, Kim, Kim & Kim, 1998), as well as for aroma protection and stabilization (Bertholet et al., 1998) and for use in oral and topical pharmaceutical and cosmetic compositions (Wulff, 1997). Chambers et al. (1988) reported the use of antioxidant extracts for inhibiting the warmed-over flavour commonly associated with cooked roast beef which has been reheated. Probably the dietary supplementation of antioxidants in feed improves the antioxidative stability of processed meat, as recently reported for supplementation of vitamin E and β-carotene (Ruiz, Pérez-Vendrell & Esteve-García, 1999).

The organoleptic characteristics of the extracts must be suitable for incorporation into food products without conferring the intense herb flavour that may limit some applications, as occurs for natural rosemary extract which has excellent antioxidant properties. In addition to colour and flavour, aspects such as production cost, antioxidant activity and toxic or pathogenic activity should be considered.

The search for cheap, renewable and abundant sources of antioxidant compounds is attracting worldwide interest. Much research is needed in order to select raw materials; those of residual origin are especially promising due to their lower costs. However, extensive research on potential sources, optimisation of extraction processes, knowledge of the mechanisms of the in vivo action and assimilation, are still required.

7. Conclusions

In this review it has been emphasized that many residues are antioxidant sources; perhaps by-products of grape processing, such as seeds and peels are the most promising, together with vegetable residues such as tea leaves. Extract production is a key step for obtaining antioxidants with an acceptable yield. To select a solvent, comparative studies are required for each substrate. Besides conventional extraction with solvents as ethanol, methanol, ethylacetate, other methods such as supercritical extraction must be assayed, because they offer a good yield and preserve the properties of the antioxidants: Natural antioxidants often shown antioxidant powers lower than those of synthetic ones, but they are not law-limited in quantity. In any case, a detailed economic study, with reliable consideration of their potential toxicity must be done before any possible application on a practical scale.

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