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New genre of antioxidants from renewable natural resources: Synthesis and characterisation of rosemary plant-derived antioxidants and their performance in polyolefins

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ABSTRACT

Several ester derivatives of rosmarinic acid (rosmarinates) were synthesised, characterised (1D and 2D NMR, UV and FTIR spectroscopy) and tested for their potential use as antioxidants derived from a renewable natural resource. The intrinsic free radical scavenging activity of the rosmarinates was assessed, initially using a modified DPPH (2, 2-diphenyl-1-picrylhydrazyl radical) method, and found to be higher than that of commercial synthetic hindered phenol antioxidants Irganox 1076 and Irganox 1010. The thermal stabilising performance of the rosmarinates in polyethylene (PE) and polypropylene (PP) was subsequently examined and compared to that of samples prepared similarly but in the presence of Irganox 1076 (in PE) and Irganox 1010 (in PP) which are typically used for polyolefin stabilisation in industrial practice. The melt stability and the long-term thermo-oxidative stability (LTTS) of processed polymers containing the antioxidants were assessed by measuring the melt flow index (MFI), melt viscosity, oxidation induction time (OIT) and long-term (accelerated) thermal ageing performance. The results show that both the melt and the thermo-oxidative stabilisation afforded by the rosmarinates, and in particular the stearyl derivative, in both PE and PP, are superior to those of Irganox 1076 and Irganox 1010, hence their potential as effective sustainable bio-based antioxidants for polymers.

The rosmarinic acid used for the synthesis of the rosmarinates esters in this study was obtained from commercial rosemary extracts (AquaROX80). Furthermore, a large number of different strains of UK-grown rosemary plants (Rosmarinum officinalis) were also extracted and analysed in order to examine their antioxidant content. It was found that the carnosic and the rosmarinic acids, and to a much lesser extent the carnosol, constituted the main antioxidant components of the UK-plants, with the two acids being present at a ratio of 3:1, respectively.

1. Introduction

The potential replacement, partially or fully, of synthetic additives for polymers by bio-based alternatives derived from indigenous renewable non-food crop resources offers potentially a market opportunity for a green supply of raw materials for different industrial and health products. The main challenge for a bio-based sustainable development is primarily an economic one, hence the imperative of adopting an integrated approach to establish a profitable commercially viable utilisation strategy for harnessing the benefits of the entire biomass crop. To achieve this, much depends on a proactive involvement of the farming community in crop production while addressing the ever more stringent environmental and pollution laws.

Several plant extracts known to contain different polyphenols have been investigated as potential natural antioxidants for polymers. Extracts of green tea and black tea were examined as possible source of natural antioxidants for polypropylene (PP) and found to have good antioxidant activity, based on a DPPH (2,2-diphenyl-1-picrylhydrazyl radical) test [1]. By-products from industrial processing of crops containing polyphenols and tannins derived from red and white grape processing for wine production, and carotenoid-containing waste from processing of tomatoes, were used as antioxidants for PP [2,3]. The grape seed extracts were shown to be suitable as long-term antioxidants while the

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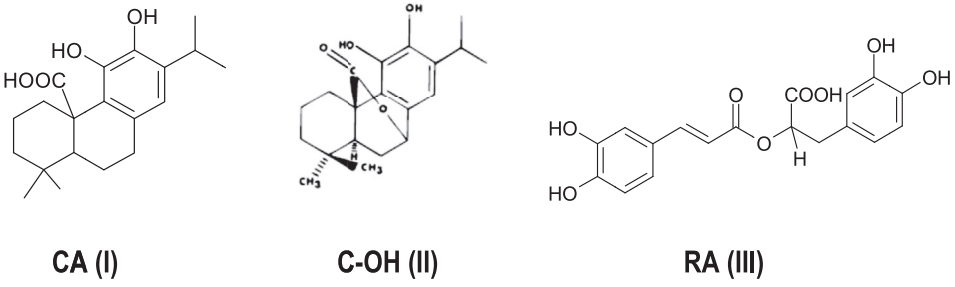
carotenoids and tocopherols present in the tomato extracts were effective processing stabilisers for the polymer [2]. Another by-product antioxidant obtained from olive processing, hydroxytyrosol (3,4-dihydroxy-phenylethanol), was found to offer good melt stability to PP [4]. Different flavonoids such as chrysin, hesperidin, naringin and quercetin were also considered as possible natural phenolic antioxidants and UV- stabilisers for PP [5]. Quercetin was found to be effective in stabilising PP against thermal oxidation and UV radiation, and against oxidation in PE melt [6]. Curcumin, the principal natural phenol curcuminoid of turmeric, was used also as a processing stabiliser in LLDPE and was shown to be more efficient than Irganox 1010 [7]. Further, the stabilising performance of vitamin E, both in its most bioactive form α-tocopherol [8–11] and as a mixture of the α, β, γ-tocopherols [12] were examined as natural antioxidants for protecting PE and PP against oxidation during high melt processing temperatures, and in-service, and was found to afford strong antioxidancy in both polymers, much higher than those obtained with the synthetic hindered phenols Irganox 1076 and Irganox 1010, and particularly, in the polymer melt.

Herbs and spices from the Labiatae family, particularly rosemary (Rosmarinum officinalis), a plant that is native to the Mediterranean basin but is now successfully grown in the UK and worldwide, contain also a variety of bioactive polyphenolic antioxidant compounds, most abundant of which are the carnosic acid (**CA, I**), the carnosol (**C-OH, II**) and the rosmarinic acid (**RA, III**) [13,14].



CA (I) C-OH (II) RA (III)

In spite of the large volume of literature available on the assessment of the antioxidant activity of rosemary extracts in a variety of unsaturated food lipids and food model compounds [15–17], to our knowledge, there is scant information in the open literature on the stabilising performance of the main rosemary-antioxidants in polyolefins [18–20], and the antioxidant role of the ester derivatives of rosmarinic acid in polyolefins under melt processing and long-term thermo-oxidative conditions. The aim of this work was, therefore, to first synthesise (and characterise) a number of new ester derivatives (rosmarinates) of rosmarinic acid, RA, (the RA used for the synthesis was obtained from a commercial rosemary extract), and then to investigate the antioxidant efficacy of the synthesised rosmarinates in polyethylene (PE) and polypropylene (PP) and to compare their overall performance with that of the commercial hindered phenol antioxidants used normally for the stabilisation of polyolefins, i.e. Irganox 1076 and Irganox 1010 (synthetic), and vitamin E (bio-based).

2. Experimental

2.1. Materials

Unstabilised Ziegler–catalysed linear low density polyethylene (LLDPE), ex. ExxonMobil Chemical Company, used has a density of 0.92 g/cm^3, peak melting temperature of 120 °C and a melt flow rate (MFR) of 1 g/10 min (at 190 °C/2.16 kg). Isotactic polypropylene homopolymer (PP), Moplen HF500 N (Lyondell Basell) used has a melt flow rate of 12 g/10 min (at 230 °C/2.16 kg). Low density polyethylene (LDPE), Lupolen 2420H (Lyondell Basell) used has a density of 0.92 g/cm^3 and MFR of 1.9 g/10 min (at 190 °C/2.16 kg). The commercial hindered phenol antioxidants Irganox 1076, Irganox 1010 and vitamin E (alpha-tocopherol) were kindly donated by Ciba Specialty Chemicals (now BASF). Low odour, low taste rosemary aqueous extract (AquaROX 80) which contain mainly rosmarinic acid (minimum 93.4%) was purchased from Vitiva d.d., Slovenia, and used for the synthesis of all the ester derivatives reported here. The active ingredients (CA and RA) extracted from UK-grown rosemary leaves during the course of this collaborative project were used only for the quantification of the amount of these active ingredients in UK-grown rosemary plants. DMAP (4-dimethylaminopyridine) and DCC (N, N′-dicyclohexylcarbodiimide), ex. Aldrich, were used as catalysts. All solvents, either deuterated for the NMR measurements (ex. Goss Scientific) or of HPLC grade (Fisher), were used without further purification.

2.2. Synthesis of rosmarinic acid esters (rosmarinates)

Aliphatic alcohols (1.5 mol) and rosmarinic acid, AquaRox 80, (216 g, 0.6 mol) were dissolved in (THF) tetrahydrofuran (1.6 L). A solution of (DMPA) 4-Dimethylaminopyridine (1.46 g, 12 mmol) in THF (50 ml) was added dropwise. A solution of (DCC) *N*,*N*′-Dicyclohexylcarbodiimide (148.5 g, 0.72 mol) in THF (300 ml) was then added dropwise over 1 h at 20–25 °C. The reaction mixture was stirred over 4 days at room temperature. Acetic acid (9 ml, 0.15 mol) was added and after 2 h, the precipitate formed was filtered through a 5 mm layer of Celite and washed with THF (200 ml). The solvent was evaporated and the crude product was purified on silica gel eluting with petroleum ether. Brown material was decolourised with charcoal in methanol to obtain rosmarinates produced from different aliphatic alcohols: methyl (**RA-Me**), *n*-butyl (**RA-But**), ethyl-hexyl (**RA-EH**), n-octyl (**RA-Oct**) and stearyl (**RA-Str**). All the esters were highly viscous yellowish products which solidified in the fridge with melting points at around room temperature; yields were 70% (except for the octyl rosmarinates which gave a yield of 68%).

2.3. Characterisation of rosmarinates

The synthesised rosmarinate derivatives, and the commercial **r**osemary extract containing rosmarinic (**AquaROX 80**) acid were characterised by spectroscopic techniques. NMR experiments were performed on a Bruker Avance-300 spectrometer at ambient temperature using tetramethylsilane (TMS) as internal standard. 1D