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Phenolic Acids and Related Compounds as Antioxidants for Edible Oils

Stanley Z. Dziedzic & Bertram J. F. Hudson

Department of Food Science, University of Reading,
London Road, Reading RG1 5AQ, Great Britain

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ABSTRACT

A series of hydroxy aromatic acids, esters and lactones have been evaluated as antioxidants for lard at 120 °C at 0·025 %, 0·05 % and 0·1 % concentrations. Most of the compounds studied are direct biochemical precursors of chalcones and these, in turn, of various flavonoids commonly occurring in plant material.

Antioxidant efficiency has been shown to be very dependent on the number of phenolic hydroxyl groups in the molecule and also to be promoted by steric hindrance. Cinnamic acids are more effective than corresponding benzoic acids, and phenylacetic and phenylpropionic acids are even more effective. 3,4-Dihydroxy chalcone is more effective than the analogous caffeic acid. In general, the presence of a carbonyl group in the molecule appears to be necessary in this series for a high level of antioxidant activity.

INTRODUCTION

Studies with polyhydroxy-flavones, flavanones and flavonols (Hudson & Lewis, 1983), with *iso*-flavones (Dziedzic & Hudson, 1983*a*) and with chalcones (Dziedzic & Hudson, 1983*b*), have shown that many members of these groups of natural substances can display a high degree of antioxidant activity when incorporated into an edible oil or fat that does not already contain a primary antioxidant. Such compounds are

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widespread in plant material and their stabilising effects may well be relevant to the health of the tissues in which they occur.

A consideration of the biochemical pathways involved in the syntheses of these compounds indicates that 2-hydroxy chalcones are precursors of the corresponding flavanones and are themselves the result of condensations between C_6 and C_9 units. The question arises, therefore, do these smaller molecules, many of which are also of frequent natural occurrence, also exhibit antioxidant properties? Of course, many of them do. Catechol and pyrogallol, on the one hand, and hydroxy cinnamic acids such as caffeic and ferulic acids and their esters, on the other, are well known to display antioxidant properties. Such properties are not confined to C_6 and C_9 units. Gallic acid and its esters are also very active. The antioxidant properties of some of these phenolic acids have recently been studied very thoroughly by Thumann & Herrmann (1980).

Two further questions remain: are the antioxidant properties of these simpler molecules quantitatively comparable with those of the more complex flavonoids and chalcones, and can some molecular characteristics common to both groups be identified which are key features in promoting or inhibiting antioxidant activity? The studies reported in this paper were carried out with the object of answering these questions.

MATERIALS AND METHODS

As substrate for the oxidation studies, pure dried rendered lard, free from additives and not chemically processed, was used.

Compounds were purchased from Aldrich chemicals, Dorset, Great Britain. 3-(3,4,5-Trihydroxyphenyl) propionic acid, 3,4,5-trihydroxyphenylacetic acid and 3-(3,4-dihydroxyphenyl) propionic acid were prepared by demethylation of the commercially available methyl esters, by fusion with pyridinium hydrochloride.

Propyl esters of caffeic and dihydrocaffeic acid were prepared by refluxing the phenolic acid for 0·5 h in excess *n*-propanol with a trace of H_2SO_4 as catalyst.

Aesculetin was prepared by acid hydrolysis of aesculin and recrystallisation from aqueous methanol.

Chalcones were prepared by condensation of the methyl ethers of the appropriate phenolic acetophenones and benzaldehydes in 1·0M sodium methoxide, followed by demethylation with pyridinium chloride.

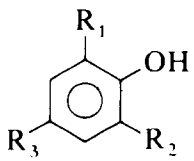
All potential antioxidants were repeatedly recrystallised to chromatographic standards of purity as judged by TLC on Merck silica F_{254} plates (elution with toluene/ethyl acetate/acetic acid, 50:30:1 v/v/v), or by dry pack column chromatography using the above solvent system. Chromatograms were visualised under UV, then re-inspected after spraying with 10 % H_2SO_4 in ethanol followed by brief heating at 110 °C, or after dipping plates in 1 % ethanolic $FeCl_3$.

Antioxidant activity was evaluated by measurement of induction periods after incorporation in lard using the Metrohm Rancimat (Hudson & Lewis, 1983).

RESULTS AND DISCUSSION

Induction periods (IP's) were determined in all cases at 120 °C and at three concentrations (0·025 %, 0·05 % and 0·1 %) in lard. Induction periods, as has always proved to be the case with primary antioxidants in previous investigations, increased with concentration of primary antioxidant, but not in proportion to increase in concentration. This suggests that, at a concentration somewhat above 0·1 %, a maximum stabilising effect is obtainable for each test antioxidant.

Table 1 lists IP's for antioxidants of the general structure (I), where



(I)

R_1 and/or R_2 are H, OH or OCH_3 and R_3 is CO_2H or an alkyl or alkenyl radical carrying CO_2H, or propyl esters of such carboxylic acids. It is possible in some cases to compare activities with those of the analogous chalcones by reference to Table 2. Molar IP's (MIP's), also listed in Tables 1 and 2 (at 0·1 % concentrations only), are calculated by multiplying IP's by molecular mass and provide a more realistic comparison of activities between analogous molecular species.

From the results listed in Table 1 a number of conclusions can be drawn, some of which are in confirmation of those of previous workers,

TABLE 1
Observed (IP) and Molar (MIP) Induction Periods at 120 °C in Lard of Phenolic Acids and Propyl Esters

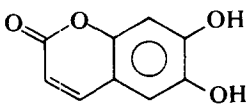
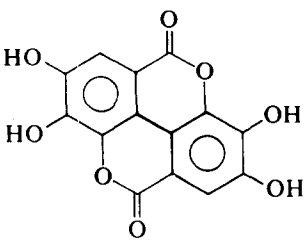
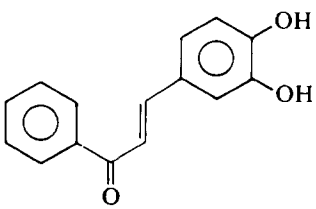
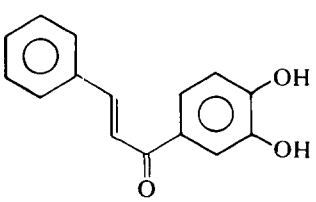
Ring substituents in (I)	$-R_3$	*IP(h) at*			*MIP at*
		0·025%	*0·05%*	*0·1%*	*0·1%*
4-OH *p*-Coumaric acid	—CH=CHCOOH	0·3	0·8	1·0	164
3,4-Di-OH Protocatechuic acid	—COOH	3·0	4·8	7·6	1 170
3,4-Di-OH	$-CH_2COOH$	11·2	24·0	41·2	6 922
3,4-Di-OH	$-CH_2CH_2COOH$	20·4	31·4	44·0	8 008
3,4-Di-OH	$-CH_2CH_2COOPr$	13·5	20·3	25·9	5 802
3,4-Di-OH Caffeic acid	—CH=CHCOOH	14·0	23·3	30·7	5 526
3,4-Di-OH	—CH=CHCOOPr	8·3	14·6	23·2	5 150
4-OH, 3-OCH_3 Ferulic acid	—CH=CHCOOH	1·1	2·0	3·5	679
3,4,5-Tri-OH Pyrogallol	—H	8·5	13·0	14·6	1 840
3,4,5-Tri-OH Gallic acid	—COOH	16·3	28·6	38·2	6 494
3,4,5-Tri-OH Propyl gallate	—COOPr	12·7	21·8	31·6	6 699
3,4,5-Tri-OH	$-CH_2COOH$	20·1	40·1	59·2	10 983
3,4,5-Tri-OH	$-CH_2CH_2COOH$	22·6	30·5	35·6	7 049
4-OH 3,5-Di-OCH_3 Sinapic acid	—CH=CHCOOH	3·6	8·0	15·0	3 360

The induction period for lard without additives is 0·35 h.

especially Thumann and Herrmann. These are as follows:

(1) The introduction of a carboxyl function into the pyrogallol molecule brings about a great increase in antioxidant activity (cf. pyrogallol versus gallic acid).
(2) Activity increases still further if the carboxyl group is separated from the aromatic ring (cf. 3,4,5-trihydroxyphenylacetic acid and 3-(3,4,5-trihydroxyphenyl) propionic acid versus gallic acid; also 3,4-dihydroxyphenylacetic acid and 3-(3,4-dihydroxyphenyl) propionic acid versus protocatechuic acid).

TABLE 2
Observed (IP) and Molar (MIP) Induction Periods at 120 °C in Lard of Phenolic Lactones and Chalcones

Structure	*IP(h) at*		*MIP at*	
	0·025%	*0·05%*	*0·1%*	*0·1%*
 Aesculetin	10·6	15·5	17·4	3097
 Ellagic acid	0·35	0·35	0·4	
 3,4-Dihydroxy chalcone	10·0	18·2	26·1	6264
 3′,4′-Dihydroxy chalcone	3·4	6·2	11·0	2640

(3) Activity also increases if the carboxyl group is in the form of substituted cinnamic acids rather than benzoic acids (cf. caffeic acid versus protocatechuic acid) although less so than in the case of the corresponding saturated acids (see (2) above).
(4) Propyl esters (e.g. the well known commercial antioxidant, propyl gallate) have similar activities, on a molar basis, to those of their parent acids.
(5) Steric hindrance of phenolic hydroxyls by neighbouring inert groups (e.g. methoxyl) enhances antioxidant activity (cf. ferulic acid and, even more, sinapic acid, versus *p*-coumaric acid). This factor must be considered in relation to the many natural phenolic compounds that also embody methoxyl groups or glycosidic substituents. It is also exploited in the very well known antioxidants BHA and BHT and is a major feature of the tocopherols.

Two other related types of compound, lactones and chalcones, were also studied in the course of this work, with the results reported in Table 2.

Aesculetin can be compared with propyl caffeate. Both are esters, one with a closed ring and the other involving an open chain structure. As an antioxidant, propyl caffeate is somewhat the better. The other, more complex, lactone, ellagic acid, is also a natural product and has structural relationships with both protocatechuic acid and gallic acid. It has recently been reported to be among the oxidation products formed during the process of UV irradiation of propyl gallate in ethanol solution (Kurechi & Kunugi, 1983). Surprisingly, it exhibited no antioxidant activity in our tests, although it possesses structural parameters associated with good antioxidant properties. Kurechi & Kunugi (1983) have, however, found ellagic acid to be active, but less so than propyl gallate.

Of the two chalcones, the more effective one is 3,4-dihydroxy chalcone, which is somewhat more active as an antioxidant on a molar basis than caffeic acid or propyl caffeate and has the same order of activity as these analogous compounds on a weight basis. The natural product butein, 2′,4′,3,4-tetrahydroxy chalcone, is even more active (Dziedzic & Hudson, 1983*b*), but the synthetic 3′,4′-dihydroxy chalcone, as shown here, is less active. The comparative activities of the two chalcones correspond with those of the analogous phenolic acids, caffeic acid being much more active than protocatechuic acid.

GENERAL CONCLUSIONS

Polyphenols generally, whether simple compounds such as phenolic acids or their esters, or more complex, though chemically related, compounds such as lactones and chalcones, or flavonoids, display marked antioxidant activity towards fat oxidation. Essential molecular features, if a high level of activity is to be achieved, are, however:

(1) At least two, and, even better, three, neighbouring phenolic hydroxyl groups (catechol or pyrogallol structures).
(2) A carbonyl group, in the form of an aromatic acid, ester or lactone, or a chalcone, flavanone or flavone.

Unless these features are present, it appears that steric hindrance of phenolic groups is necessary, as in the tocopherols, the synthetics (BHA, BHT and TBHQ) and (as shown here) sinapic acid.

The very pronounced antioxidant activity of the polyphenols is exploited in the commercially important propyl gallate. However, hitherto their use in edible oils and fats has been limited by their poor oil-solubility, their sensitivity to oxidative conditions and the discoloration that attends their use in systems containing Fe^{+++} and in alkaline media.

REFERENCES

Dziedzic, S. Z. & Hudson, B. J. F. (1983*a*). Hydroxy isoflavones as antioxidants for edible oils. *Food Chem.*, **11**, 161–6.

Dziedzic, S. Z. & Hudson, B. J. F. (1983*b*). Polyhydroxy chalcones and flavanones as antioxidants for edible oils. *Food Chem.* (In press.)

Hudson, B. J. F. & Lewis, J. I. (1983). Polyhydroxy flavonoid antioxidants for edible oils. Structural criteria for activity. *Food Chem.*, **10**, 47–55.

Kurechi, T. & Kunugi, A. (1983). Studies on the antioxidants. Part XVII. Photo-oxidation products of concomitantly used butylated hydroxyanisole and propyl gallate. *J. Am. Oil Chem. Soc.*, **60**, 109–13.

Thumann, I. & Herrmann, K. (1980). Uber die antioxidative Wirkung von hydroxizimtsauren und benzoesauren. *Deutsche Lebensm.-Rundschau*, **76**, 344–8.