estly priced commercial instrument.

The Trebor GT-90 whole grain analyzer was used for the measurement of protein and moisture in whole kernels of HRS wheat and barley. Calibrations were based on a very large number of samples. Protein identification and segregation of HRS wheat into protein sublevels are achieved in Canada by tests carried out at terminal grain elevators by near-infrared reflectance instruments such as the Pacific Scientific GQA31EL or the Dickey-john GAC III. A sample is tested by NIR for protein and moisture during the first minute of unloading a car. The protein figure corrected to 13.5% moisture is used for segregation and is compared statistically with a second NIR test carried out in Winnipeg by the ADA (Williams et al., 1978) subsequently on the official sample that represents the total carload. The standard deviation of differences between the "early" and official series of results is normally between 0.35 and 0.40 with essentially no bias. Table XV illustrates data taken from Tables VI and VII of Williams et al. (1983), which described a comparative study of commercial NIR reflectance instruments. On the basis of the current experiments, the Trebor GT-90 appeared to be satisfactory for the testing of HRS wheat for protein identification and segregation purposes. The NIR reflectance instruments routinely used for these operations are the InfraAlyzer 300 and 200, the GAC III, and the GQA 31EL and 101. These gave statistics of the same order of magnitude as the GT-90. The InfraAlyzer 400 is more sophisticated and is not normally employed in such routine situations as testing carlots of wheat. The standard deviation of differences between GT-90 and standard results was slightly higher than with reflectance instruments and powdered samples, but the elimination of grinding and cell-loading errors and the large sample size, with consequent reduction in sampling error, tend to compensate for the difference in the test accuracy. The overall error of the testing process was maintained at, or slightly improved over, customary levels of system accuracy. Temperature compensation was satisfactory, and errors introduced by season, location, kernel size, grade, and grain type could be compensated for by comprehensive calibration. Samples containing above 5% foreign material should be cleaned before testing, and this is of particular importance if excessive quantities of small seeds are present. The GT-90 can be used for testing of wheat for moisture within 1 h of addition of tempering water. The accuracy of moisture testing by the GT-90 was superior to that of protein testing and on the basis of comparison with the AACC 2-stage air oven method was equivalent to the Model 919 (Motomco) meter.

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Polyhydroxydihydrochalcones as Antioxidants for Lard

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Six polyhydroxydihydrochalcones have been evaluated at 120 °C as antioxidants for lard. Eight of the chemically corresponding chalcones and flavanones have been evaluated under the same conditions. The dihydrochalcones show more antioxidant activity than the corresponding chalcones, just as the polyhydroxydihydrocinnamic acids are more active than the corresponding cinnamic acids. Flavanones are significantly less active than the corresponding chalcones.

In recent studies on polyhydroxy aromatic compounds as antioxidants for edible oils, we have reported on flavones and flavanones (Hudson and Lewis, 1983), isoflavones (Dziedzic and Hudson, 1983a), chalcones and flavanones (Dziedzic and Hudson, 1983b), and phenolic acids and esters (Dziedzic and Hudson, 1984a). With favorably located phenolic hydroxy groups, all these chemical classes exhibit marked antioxidant activity.

Particularly marked activity was noted with certain chalcones and phenolic acids or their propyl esters. Perhaps surprisingly, dihydrocinnamic acids were more active than cinnamic acids, which, in turn, were more active than the corresponding substituted benzoic acids. It therefore became pertinent to enquire whether dihydrochalcones were also more active than the corresponding chalcones. The studies reported here were undertaken mainly to settle this question.

A few dihydrochalcones have been reported to be present in plant material as natural products. The best known is the glucoside phloridzin, which occurs in the bark and leaves of the apple. They are largely confined to the Rosaceae and Ericaceae families (Williams, 1966) and can be regarded as precursors of the polyhydroxyflavones (e.g., phloretin, the aglycon of phloridzin, is the precursor of apigenin).

Certain dihydrochalcones also have interesting organoleptic properties. Neohesperidin dihydrochalcone is potentially important as an artificial sweetener (Horowitz and Gentili, 1963).

MATERIALS AND METHODS

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

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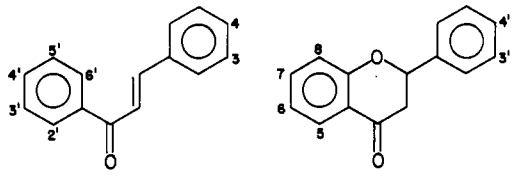
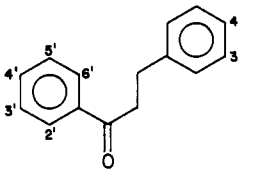
Table I. Test Antioxidants

code	structure (trival name)	source
I	4′,5,7-trihydroxyflavanone (naringenin)	*a*
II	2′,4′,6′,4-tetrahydroxydihydrochalcone (phloretin)	*a*
III	4′-methoxy-3′,5,7-trihydroxyflavanone (hesperetin)	*a*
IV	4-methoxy-2′,4′,6′,3-tetrahydroxydihydrochalcone (dihydrohesperetin)	*b*
V	2′,3′,4′,3,4-pentahydroxychalcone (okanin)	*c*
VI	3′,4′,7,8-tetrahydroxyflavanone	*c*
VII	2′,3′,4′,3,4-pentahydroxydihydrochalcone (dihydrookanin)	*b*
VIII	2′,4′,6′,3,4-pentahydroxychalcone	*d*
IX	3′,4′,5,7-tetrahydroxyflavanone (eriodictyol)	*e*
X	2′,4′,6′,3,4-pentahydroxydihydrochalcone	*b*
XI	3,4-dihydroxychalcone	*c*
XII	3,4-dihydroxydihydrochalcone	*b*
XIII	4′,3,4-trihydroxychalcone	*c*
XIV	4′,3,4-trihydroxydihydrochalcone	*b*

[a] Purchased from Sigma (London), Ltd., England. [b] These five dihydrochalcones were prepared from the corresponding chalcones by hydrogenation of solutions of the chalcones in ethanol at atmospheric pressure in the presence of a catalytic amount of 10% Pd/C for 30 min. Identities were confirmed by MS and NMR spectra. [c] See Dziedzic and Hudson (1983b). [d] Prepared by the method of Russell and Todd (1934). [e] By the acid-catalyzed isomerization of VIII and crystallization from aqueous alcohol.

The antioxidants evaluated are listed in Table I. They all fall into one or other of three chemical classes:





In Table I, and later in Table II, the 14 test antioxidants are divided into groups of two or three to facilitate comparison between corresponding compounds on the basis of the above classification.

The compounds that were not commercially available were prepared as indicated and recrystallized to chromatographic standards of purity.

Tests were carried out at 120 °C both because induction periods at this temperature were of a convenient length and because this is a realistic temperature for the simulation of many food processing and culinary operations. Of course, induction periods at lower or higher temperatures cannot be precisely predicted from such data [see, for example, Dziedzic and Hudson (1984b)] though it is generally true that induction periods at lower temperatures are longer and at higher temperatures shorter.

Induction periods can be determined by the AOM stability test, by the measurement of oxygen absorption in the FIRA-Astell equipment, or, as in the present case, by monitoring changes in conductivity when oxidation products are dissolved in water in the automated Metrohm Rancimat. In general, similar values are obtained in all three methods.

RESULTS AND DISCUSSION

Table II lists induction periods for the 14 antioxidants at each of three concentrations in lard. Induction periods throughout increased progressively with concentration.

Compounds I–IV display a low order of activity compared with the remaining 10. This is a reflection of the presence of the vicinal 3,4-dihydroxy group structure in compounds V–XIV, which is absent in I–IV.

Dihydrochalcones are clearly significantly more effective as antioxidants than the corresponding chalcones, which, in turn, are better than the corresponding flavanones. The inferiority of the flavanones is not surprising since they carry one less phenolic hydroxyl group than the other two classes of compound.

Under the conditions of the test, chalcones with hydroxyl substituents in the 2′-position could possibly be converted to flavanones owing to the presence of protons derived from the acids (mainly formic acid) generated during the early stages of oxidation. This applies to compounds I and VIII, which could be converted to the less active flavanones VI and IX. However, the chalcones XI and XIII cannot undergo this isomerization yet they are inferior as antioxidants to the corresponding dihydrochalcones XII and XIV. It therefore appears that all di-

Table II. Induction Periods of Hydroxychalcones and Analogous Flavanones and Dihydrochalcones in Lard[a] at 120 °C (Rancimat)

added antioxidant			induction periods, h, at concn of		
chalcones	flavanones	dihydrochalcones	0.025%	0.05%	0.1%
	4′,5,7-trihydroxy		0.35	0.4	0.4
		2′,4′,6′,4-tetrahydroxy	1.0	1.3	1.7
	4′-methoxy-3′,5,7-trihydroxy		0.5	0.6	0.7
		4-methoxy-2′,4′,6′,3-tetrahydroxy	1.5	2.2	4.4
2′,3′,4′,3,4-pentahydroxy			9.9	18.2	21.8
	3′,4′,7,8-tetrahydroxy		7.8	15.4	19.7
		2′,3′,4′,3,4-pentahydroxy	12.5	22.3	31.6
2′,4′,6′,3,4-pentahydroxy			4.5	11.0	15.6
	3′,4′,5,7-tetrahydroxy		3.9	7.0	9.5
		2′,4′,6′,3,4-pentahydroxy	12.8	24.1	44.2
3,4-dihydroxy			10.3	17.9	26.6
		3,4-dihydroxy	12.0	20.1	29.1
4′,3,4-trihydroxy			12.3	22.8	27.2
		4′,3,4-trihydroxy	15.1	24.0	29.9

[a] The induction period for lard without additives is 0.35 h.

hydrochalcones are at least slightly better antioxidants than the corresponding chalcones.

Dihydrookanin (VII) and its isomer (X) are particularly good antioxidants, the latter being the better of the two.

CONCLUSIONS

The present study establishes that polyhydroxydihydrochalcones are more effective than the corresponding chalcones as antioxidants for lard at 120 °C. In this respect, therefore, they are analogous to the polyhydroxydihydrocinnamic acids, which are superior to the corresponding cinnamic acids. This is presumably due to the fact that the dihydro derivatives form more stable free radicals than the unsaturated compounds. Why this should be so, however, is not at this stage obvious.

Registry No. I, 480-41-1; II, 60-82-2; III, 520-33-2; IV, 35400-60-3; V, 484-76-4; VI, 489-73-6; VII, 72666-14-9; VIII, 73692-51-0; IX, 552-58-9; X, 57765-66-9; XI, 72704-76-8; XII, 94324-67-1; XIII, 88191-22-4; XIV, 94324-68-2.

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Mass Spectral Identification of a Metabolite of Chlorpropham in Potatoes

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Chlorpropham (CIPC), isopropyl *N*-(3-chlorophenyl)carbamate, is a selective herbicide that also is used as a sprout suppressant on stored potatoes. Residues of CIPC have been encountered in table-ready potatoes examined under the Total Diet Program conducted by the Food and Drug Administration. A second compound, detected by GC, was found to be associated with many of these residues. This suspected metabolite of chlorpropham was identified by GC–MS, with comparison to synthesized reference standards, as isopropyl *N*-(3-chloro-4-methoxyphenyl)carbamate. Home-grown potatoes, previously free of all detectable residues, were found to contain isopropyl *N*-(3-chloro-4-methoxyphenyl)carbamate 21 days after chlorpropham postharvest application, thus confirming this methoxy derivative as a formerly unreported metabolite of CIPC. Levels of this metabolite as high as 0.063 ppm (French fries) have been encountered in various table-ready potatoes.

The Food and Drug Administration (FDA) monitors residues of pesticides, industrial chemicals, metals and nutrients in the nations food supply, through several programs. One of these, the Total Diet Program, is one of FDA's oldest residue surveillance studies, having been in operation since 1964. Results of this study are published periodically (Johnson et al., 1984a,b; Podrebarac, 1984a,b).

Each sample (market basket) consists of 232 retail grocery items from each of three cities in one of four geographic region of the country. Samples reflect dietary preferences for eight age–sex groups represented in the United States and are based on data obtianed from the Nationwide Food Consumption Survey (U.S. Department of Agriculture) and the Second National Health and Nutrition Examination Survey (National Center for Health Statistics) (Pennington, 1982, 1983).

Each food is prepared for consumption (table ready), just as it might be in the average home. For example, oranges are peeled, meats are roasted, baked, or fried, and potatoes are baked, boiled, scalloped, etc. Foods requiring this processing are prepared by dieticians in institutional kitchens. After preparation, the items are examined individually or as recipe items (e.g., meatloaf, lasagna, soups, etc.). Thus, 234 table-ready foods (including 13 recipe items) are screened for pesticides, herbicides, industrial chemicals, toxic metals, and selected nutrients.

Extraction and cleanup procedures used routinely for pesticides and industrial chemicals are described elsewhere (AOAC, 1980; FDA, 1981; Storrherr et al., 1971; Carson, 1981; Krause, 1980; Hopper, 1982).

With the exception of *N*-methylcarbamates, which are determined by liquid chromatography, organic chemical contaminants are determined by gas chromatography (GC). Routinely, sample eluates are initially examined by GC with a relatively nonpolar stationary phase and electron-capture (EC) or element-specific detectors (halogen, P, S, N). Confirmation of residues detected is attempted by using one or more stationary phases of different polarity.

Retention data, element-specific detector responses, cleanup column elution patterns, and expert interpretation by the residue chemist combine to identify all but the most unusual chemical contaminants. Those residues that defy identification are classified as unidentified analytical responses (UAR's) and become candidates for mass spectrometric (MS) analysis.

One such UAR has occasionally been detected in some of the several potato items (i.e., mashed, boiled, baked, scalloped, French fries, and potato chips). The occurrence of this compound has always been associated with residue

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