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[Received October 19, 1982]

Investigation of 1-Decyne Formation in Cottonseed Oil Fried Foods[1]

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ABSTRACT

1-Decyne identified in oxidized cottonseed oil was previously thought to originate from oleic acid. However, we have demonstrated that 1-decyne is a degradative product from the photooxidation of cyclopropenoid fatty acids (CPFA) naturally present in cottonseed oil. Products containing photooxidized cottonseed oil have the distinct off-flavor of 1-decyne. Experiments were conducted to identify the factors involved in 1-decyne formation. Reactions were done under the following conditions: (a) in the dark or under light, (b) with or without removal of CPFA from cottonseed oil, (c) in the presence or absence of singlet oxygen quenchers, (d) in the presence or absence of a hydroperoxide-reducing agent (triphenylphosphine), and (e) with or without photosensitizers. Methyl sterculate was used as a substrate for studying 1-decyne formation under photosensitized oxidation conditions in a model system. We have concluded that 1-decyne is formed by the photooxidation of CPFA utilizing chlorophyll as a photosensitizer. A reaction mechanism for 1-decyne formation is proposed.

INTRODUCTION

Potato chips prepared with cottonseed oil and subsequently exposed to light develop a distinct off-flavor which is defined as "light-struck". Although this off-flavor is easily detected by sensory evaluation, the nature of this light-struck phenomena was unknown. Experiments were thus designed to investigate this problem with respect to the following questions. (a) What is the major compound responsible for "light-struck" off-flavor? (b) Is cottonseed oil the only chipping oil that exhibits "light-struck" aroma upon exposure to light? (c) Were there precursors? (d) Could we develop methods to destroy or remove the undesirable reactants from cottonseed oil? (e) What was the possible reaction mechanism?

EXPERIMENTAL PROCEDURES

Materials

Commercial cottonseed oil was purchased from Levelland Vegetable Oil Company (Lubbock, TX). *Sterculia foetida* seed oil was a gift from Dr. Randall Wood of Texas A & M University, College Station, TX. Methyl sterculate was obtained from Supelco, Inc. (Bellefonte, PA). Chlorophyll, oleic acid, and linoleic acid, were received from Sigma Chemical Company (St. Louis, MO). Aluminum silicate and absorption alumina were purchased from Fisher Chemical Company (Fairlawn, NJ). Triphenylphosphine was obtained from Alfa Division, and 1,4-diazabicyclo[2.2.2] octane (DABCO) was received from Aldrich Chemical Company (Milwaukee, WI).

Methods

The concentration of cyclopropenoid fatty acids (CPFA) was determined according to a modified Halphen procedure (1), using a standard curve of methyl sterculate under the same conditions. Chlorophyll was measured spectrophotometrically according to the AOAC method (2). Peroxide value was determined based on the AOAC method (3).

Headspace volatiles of oil or chip samples were collected by nitrogen purging into a trap containing Tenax-GC absorbent. The Tenax-trapped volatiles were then desorbed onto gas chromatographs of 10% SP-2100 column for analysis by gas chromatography-mass spectrometry (GC-MS) using the Hewlett-Packard model 5985B.

RESULTS AND DISCUSSION

1-Decyne is the Major Light-Struck Flavor

1-Decyne was identified by GC-MS and sensory evaluation as the major photodegradative off-flavor in cottonseed oil or cottonseed oil fried potato chips (Fig. 1).

Cottonseed Oil is Unique for 1-Decyne Formation

Among the common chipping oils (cottonseed, peanut, and soybean), cottonseed oil is the only oil which possessed the distinct off-flavor of 1-decyne after photooxidation (Table I). There were no detectable amounts of 1-decyne produced from peanut oil or soybean oil. Since 1-decyne was formed

[1]Presented at the 73rd AOCS annual meeting, Toronto, 1982.

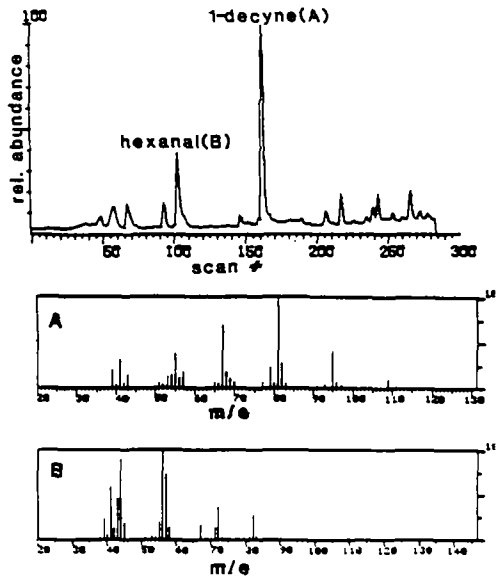

FIG. 1. Identification of light-struck flavor by GC-MS. Cottonseed oil fried potato chips packaged in opaque bags are stored at room temperature under 700 foot candles of fluorescent light for 6 days.

only in the presence of light, it was thought that a photosensitizer might be involved. The endogeneous chlorophyll pigment in the oil, a well known photosensitizer, was the most probable candidate. Indeed, exogenous chlorophyll did enhance the formation of 1-decyne in cottonseed oil. Chlorophyll was also added to peanut oil and no 1-decyne was formed (Table I). Experiments were performed to determine whether peanut oil lacked a precursor for 1-decyne formation or if an inhibitor was present. Since cottonseed oil produced the same amount of 1-decyne even in the presence of peanut oil (Table I), we concluded that there was no inhibitor in peanut oil. Furthermore, the results indicated that there was a unique precursor in cottonseed oil.

TABLE I

Cottonseed Oil is the Only Common Chipping Oil Producing 1-Decyne

Oil Sample[a]	Chlorophyll added (ppm)	1-Decyne[b]
Cottonseed oil	0	4.8
Cottonseed oil	10	7.8
Peanut oil	0	ND[c]
Peanut oil	10	ND
Soybean oil	0	ND
Cottonseed oil + peanut oil	0	4.8
Oleic acid	0	ND
Oleic acid	10	ND
Linoleic acid	0	ND
Linoleic acid	10	ND

[a]Five g of oil or fatty acid sample in a sealed half-pint, clear glass jar was stored under 500 foot candles of fluorescent light at room temperature for five days.
[b]ng/10 cm^3 headspace volatiles.
[c]Not detectable.

CPFA is the Precursor and Chlorophyll is the Photosensitizer

A reaction mechanism for 1-decyne formation through oxidation of oleic acid was proposed by Chang et al. in 1965 (4). Since cottonseed oil was the only common chipping oil which produced 1-decyne upon photooxidation in our experiments, and all these oils contain oleic acid, it seemed unlikely that oleic acid was the precursor. However, we prepared pure samples of oleic acid and linoleic acid and exposed them to light to test Chang's hypothesis. Our results clearly demonstrated that neither oleic acid nor linoleic acid produce 1-decyne after photooxidation, even in the presence of a photosensitizer (Table I).

Since CPFA is unique to cottonseed oil among the common chipping oils, we thought it should be investigated

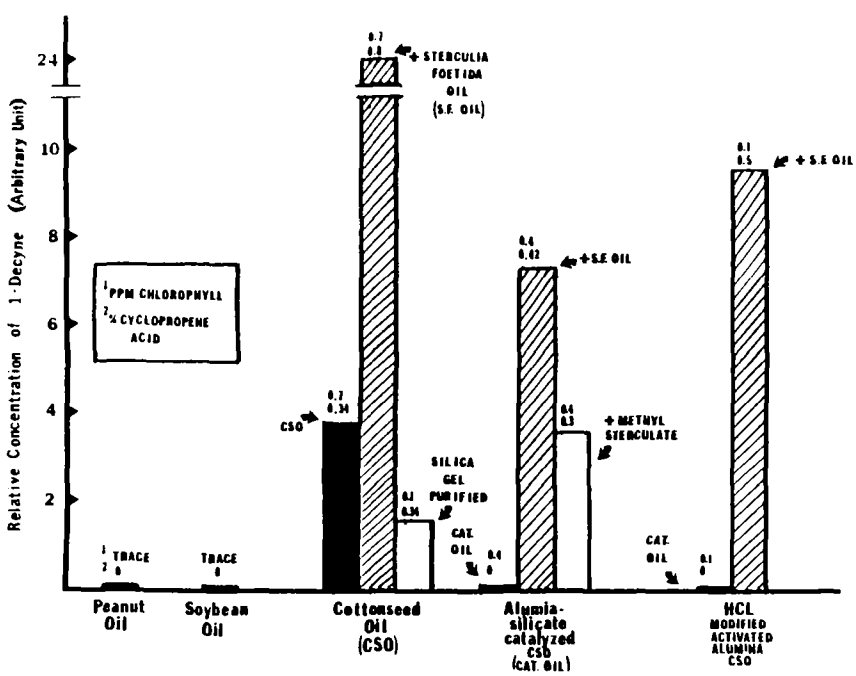

FIG. 2. CPFA is the precursor and chlorophyll is the photosensitizer for 1-decyne formation.

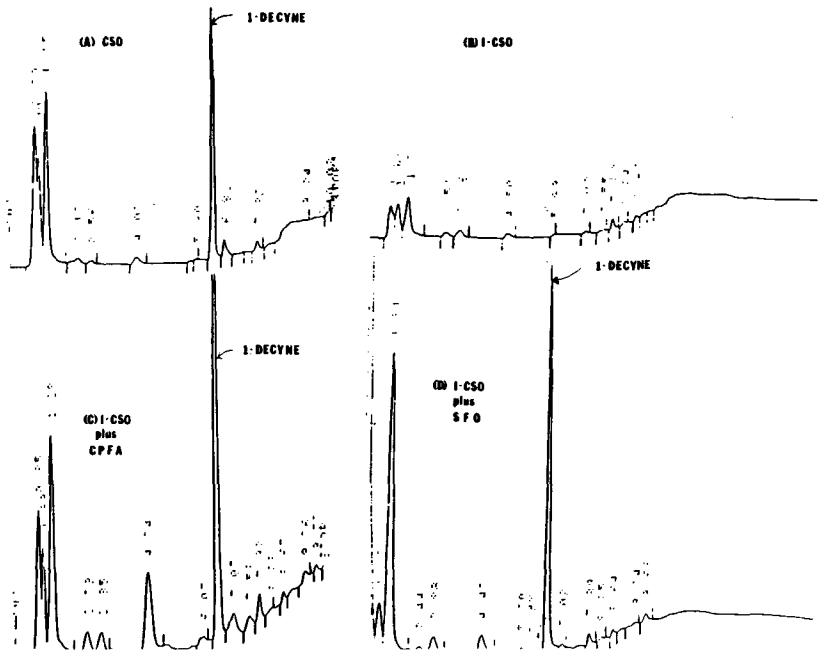

FIG. 3. GLC volatile profile of precursor identification. CSO is cottonseed oil and I-CSO is an improved cottonseed oil. SFO is *Sterculia foetida* seed oil.

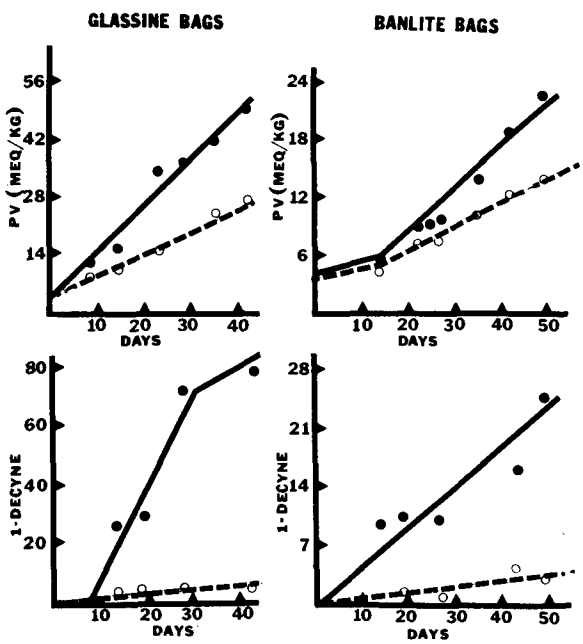

FIG. 4. Potato chips comparative stability: normal process vs double deodorized cottonseed oil. Potato chips were packed in glassine and opaque bags, respectively, and then stored at room temperature under 200 foot candles of fluorescent light to monitor peroxide value, 1-decyne, and sensory scores. The dotted line represents the double deodorized oil.

as a precursor for 1-decyne formation. These cyclic fatty acids have the following general structure:

$$CH_3 - (CH_2)_x - \underset{\diagdown}{\overset{\diagup}{C}}{=}\underset{\diagup}{\overset{\diagdown}{C}} - (CH_2)_y\ COOH$$

CH_2

x = 7; y = 7; sterculic acid

x = 7; y = 6; malvalic acid

Halphen (5) introduced a color reaction to detect cottonseed oil in oil mixtures in 1897 which is based on the endogenous CPFA. Experiments were conducted to determine if CPFA was the precursor and chlorophyll was the photosensitizer; the results are presented in Figure 2. Again, peanut oil and soybean oil contain no CPFA and produce no 1-decyne. The addition of *Sterculia foetida* seed oil (SFO), which was extracted from a tropical plant and contained 50% CPFA, into the cottonseed oil sample did produce more 1-decyne. Partial removal of chlorophyll was accomplished by silica gel column chromatography of cottonseed oil. The silica gel-purified cottonseed oil containing the same amount of CPFA produced less 1-decyne because it consists of 0.1 ppm chlorophyll pigment instead of 0.7 ppm (Fig. 2). Recently, we demonstrated that there are no detrimental effects of consuming the small amounts of CPFA occurring naturally in cottonseed oil (6). The improved cottonseed oil prepared either by aluminum-silicate catalysis (7) or by HCl modified activated alumina treatment (8) contains no CPFA, and thus produces no 1-decyne. This improved cottonseed oil can then produce 1-decyne if CPFA either from SFO or pure methyl sterculate is added back (Fig. 2). The GLC volatile profile further identifies CPFA as the precursor of 1-decyne (Fig. 3).

Steam Deodorization is the Major Step in the Removal of CPFA During Oil Refining

Since unrefined cottonseed oil contains a much higher concentration of CPFA than that of refined oil (9,10), it was of interest to determine the major process in the destruction of CPFA during oil refining. Based on the analysis of three samples of oil, it is concluded that steam deodorization is the major step in the removal of CPFA (data not shown). It is thus postulated that longer steam deodorization time may remove more CPFA from cottonseed oil. The double time deodorization decreases CPFA from 0.55% to 0.06%. Potato chips prepared in this double time deodorized cottonseed oil have less oxidation, as determined from peroxide value and 1-decyne formation (Fig. 4). Banlite bags are opaque bags which offer a better light barrier than glassine bags. More 1-decyne is produced

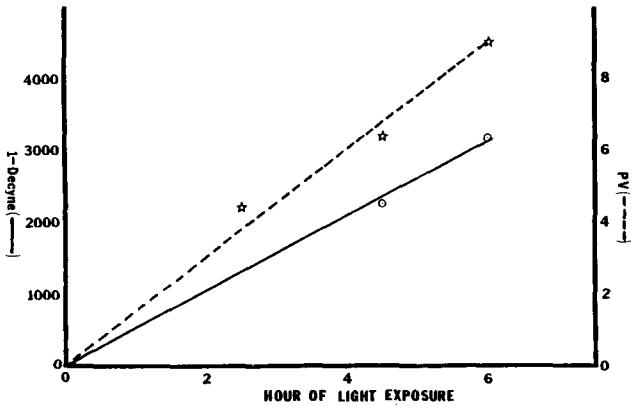

FIG. 5. 1-Decyne and peroxides are being formed simultaneously during the photooxidation of methyl sterculate.

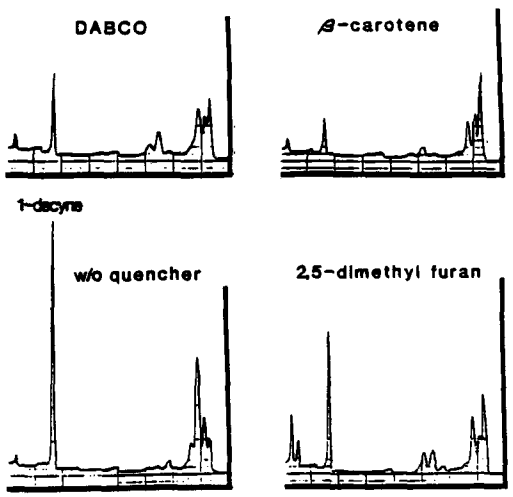

FIG. 6. The effect of singlet oxygen quenchers on the photooxidation of cottonseed oil. Two hundred ppm quenchers are added into the oil sample and then subject to 600 foot candles of fluorescent light for 17 hr at 28 C.

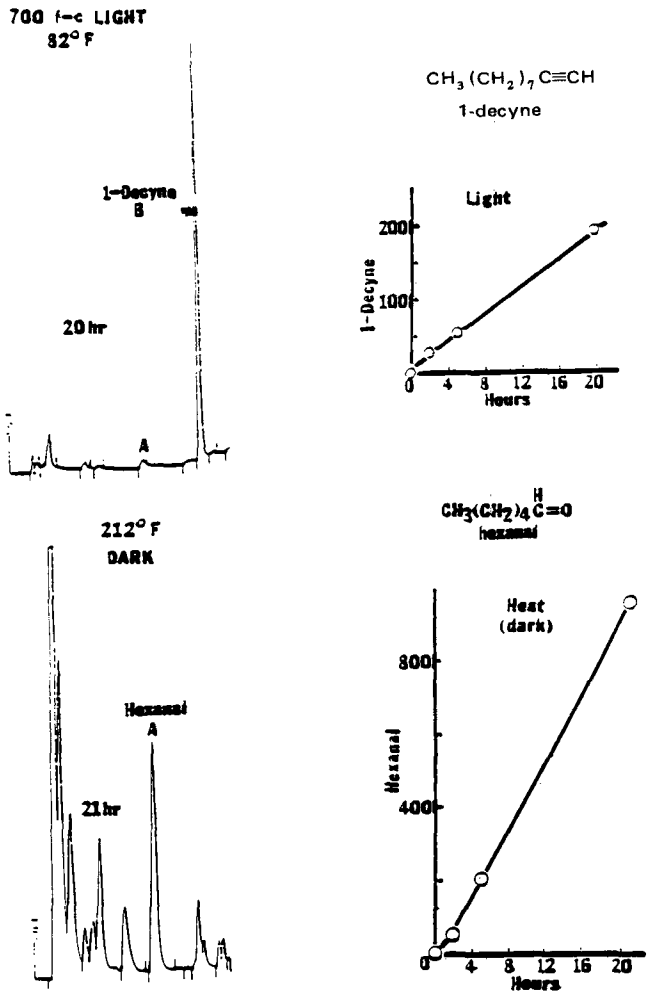

FIG. 7. Cottonseed oil thermo- and photooxidation.

in glassine-packaged chips due to more light transmission. Potato chips fried in double deodorized cottonseed oil also have a longer shelf-life, as confirmed by sensory evaluation (11).

Reaction Mechanism Study

Cottonseed oil was subjected to thermo- and photooxidation to investigate the mechanism of 1-decyne formation. 1-Decyne is the predominant volatile byproduct from photooxidation, and hexanal is the major byproduct from thermooxidation (Fig. 5). In the absence of light or oxygen, there are no detectable amounts of 1-decyne produced in cottonseed oil. Utilizing methyl sterculate as a substrate and chlorophyll as a photosensitizer in a model study demonstrated that 1-decyne and peroxide are being formed simultaneously (Fig. 6). In the presence of a hydroperoxide reducing agent, triphenylphosphine (12), methyl sterculate does not produce detectable amounts of 1-decyne upon light exposure.

These data clearly revealed that hydroperoxide is an intermediate during 1-decyne formation. Since the reaction requires oxygen and a photosensitizer, it is suggested that singlet oxygen may participate in the reaction. Indeed, some of the well known singlet oxygen quenchers such as β-carotene and DABCO reduce 1-decyne formation (Fig. 7).

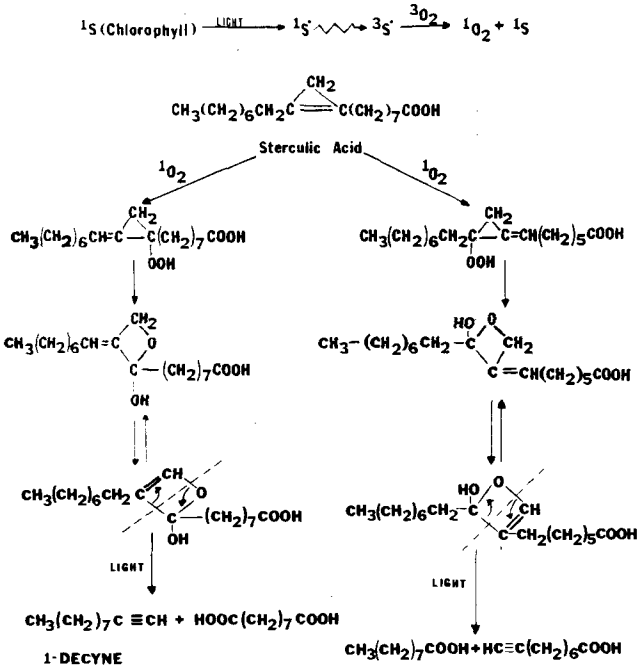

FIG. 8. A proposed mechanism for the formation of 1-decyne from sterulic acid.

Based on the results from the aforementioned experiments, a reaction mechanism is thus proposed using sterculic acid as a substrate (Fig. 8). The endogeneous trace amount of chlorophyll acts as a photosensitizer to produce singlet oxygen (13). The singlet oxygen then attacks the cyclopropenoid fatty acid, such as sterculic acid, followed by degradative cleavage and molecular rearrangement as commonly seen in an organic reaction (14) and leads to 1-decyne formation. Other compounds were also formed and are identified as shown in Figure 8.

ACKNOWLEDGMENTS

Ken Hartman and Bob Longan provided information on 1-decyne and CPFA, respectively. Lynn Warren, Gail Womack, Michael Ma and David Duval provided technical assistance. John Fulcher helped to elucidate the mechanism, and George Pucak reviewed this manuscript.

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[Received November 4, 1982]

Phenolic Acids in Rapeseed and Mustard

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ABSTRACT

The compositions of free phenolic acids in rapeseed flours of diverse origin and white mustard were highly variable but represented less than 10% of the total phenolic acids. Phenolic acids released from hydrolysis of soluble esters constituted the major fraction, with Polish varieties having higher levels than a Canadian variety or white mustard. Yellow Sarson contained low levels of phenolic acids. Sinapic acid isomers constituted over 94% of the 13 phenolic acids found in the rapeseed varieties. Only traces of several phenolic acids appeared to be structurally bound to rapeseed and mustard proteins and carbohydrates.

INTRODUCTION

Phenolic acids and their derivatives are commonly occurring compounds in the plant world. Their presence in seeds causes a deterioration in the taste, odor and color of protein concentrates and prepared food products. Besides unfavorable organoleptic changes, oxidized phenolic compounds can bind with essential amino acids such as lysine or methionine, forming complexes which are unassimilable in the digestive tract of animals and man (1-3).

Preliminary investigations have demonstrated that rapeseed contained a wide range of phenolic acids (4-8). While sinapic acid, as a component of sinapine, was the major phenolic acid, the quantities and presence of other phenolic acids differed among these studies, depending on the method of analysis. Sosulski et al. (9) fractionated the phenolic constituents in canola flour into free phenolic acids, soluble esters and glycosides of phenolic acids, and insoluble-bound phenolic compounds. Phenolic acids in bound forms were released by acidic, alkaline and enzymatic hydrolysis prior to quantitation by gas liquid chromatography (GLC). Krygier et al. (10) refined these procedures by removing fatty acids and other contaminants from the hydrolysates and used thin layer chromatography (TLC), GLC and GLC-MS (mass spectrometry) to identify the major and minor phenolic constituents in each fraction. The flours of three cultivars were found to contain 6-98 mg/100 g of free phenolic acids, 768-1196 mg/100 g of phenolic acids from hydrolyzed esters and no phenolic acids in the residues (11). Sinapic acid represented 99% of the esterified phenolic compounds, minor components being *p*-hydroxybenzoic, vanillic, gentisic, protocatechuic, syringic, *p*-coumaric and ferulic acids. The *trans* isomers predominated but the *cis* forms of sinapic and ferulic acids occurred in most fractions.

The objective of the present investigation was to determine the phenolic composition of a wide range of rapeseed varieties as well as white mustard. The extraction procedure was modified to remove the residual lipids from the flours, and extracts were further purified by extraction with diethyl ether and monosodium carbonate.

MATERIALS AND METHODS

The varieties used in the present study were selected to represent a range in growth habit, seed color, erucic acid and glucosinolate levels (Table 1). The Polish varieties were grown at the Institute of Plant Breeding and Acclimatization, Pozen, Poland, and the remaining samples were supplied by the Department of Crop Science, Saskatoon, Canada. The intact glucosinolate content was determined by glucose release after enzymatic hydrolysis.

Flours for investigation of phenolic acids were prepared