n-Alkylbenzenes and ω-Phenylcarboxylic Acids from the Thermal Treatment of Fatty Acids with Kraft Lignin

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ABSTRACT

A series of homologous *n*-alkylbenzenes and ω-phenylcarboxylic acids were detected and identified from the pyrolysis reaction of tall oil fatty acids and several pure fatty acids, respectively, with kraft lignin. Different reaction conditions (e.g., varying amounts of lignin) and different reaction times were applied. Temperatures were kept constant at 280 C. Products were distilled at 0.1 Pa and 150 C. After methylation, the distilled fractions were analyzed by gas chromatography-mass spectrometry (GC-MS). The method of detection and identification of the different substances by GC-MS is described. Pure singly and double unsaturated fatty acids (99.9% gas chromatographic purity) showed reactions to the title products (up to 4% total amount), whereas saturated fatty acids did not react at all. A possible reaction scheme taking quantitative parameters into account is suggested.

INTRODUCTION

Cyclizations and aromatizations of unsaturated fatty acids and long chain alkanes leading to cyclopentadienes and aromatic compounds have been reported (1,2). Reaction conditions (temperature, catalysts) were different from those applied in this work. In an earlier paper (3), the identification of *n*-alkylbenzenes as degradation products from the pyrolysis of tall oil fatty acids with kraft lignin was described. At the reaction conditions reported in that work—heating the mixture in a round bottom flask with a gas burner and keeping the reaction temperature constant at ca. 280 C—local overheating during the pyrolysis and the subsequent distillation could not be excluded. To avoid this, the pyrolysis mixture was now heated in a metal bath and distillation was carried out in a Kugelrohr (bulb-tube) apparatus at very low pressure (ca. 0.1 Pa).

In addition to *n*-alkylbenzenes, ω-phenylcarboxylic acids could be detected and identified by gas chromatography-mass spectrometry (GC-MS). To increase the yield of these 2 classes of products, reaction conditions were systematically modified. To improve the gas chromatographic separation, glass capillary columns of ca. 35 m length were prepared by the barium carbonate method (4).

EXPERIMENTAL

Pyrolysis

Pyrolysis reactions were carried out in 50-ml round-bottomed flasks equipped with a glass tube (30 cm length, 1.5 cm id) on top of which a glass T-shaped connector was mounted in a cork-stopper. This air condenser was sufficient to prevent low boiling substances from escaping during pyrolysis. The reaction temperature was kept constant (± 2 C) in a metal bath. The experimental conditions used for pyrolysis reactions are summarized in Table I.

Work-Up Procedures

The pyrolysis mixtures were cooled and stirred with 30 ml chloroform for ca. 10 min. Insoluble material (lignin) was filtered, dried at 80 C and weighed. The filtrate contained all products soluble in chloroform as fatty acids, products from the pyrolysis, modified soluble lignin and its degradation products.

The solvent was distilled and the residual mixture was then distilled in a Kugelrohr distillation unit (0.1 Pa, air bath temperature 150 C). The distillate was mixed with methanol (ca. 10%) and treated with a freshly prepared ethereal solution of diazomethane. The solvents were evaporated and the samples were dissolved in chloroform for gas chromatographic separation. Table II gives a summary of the amounts of products in the various experiments.

Gas Chromatographic Measurements

In all of the experiments described, the formations of *n*-alkylbenzenes (AB) and of low fatty acids (C) and ω-phenylcarboxylic acids (PC) were studied.

A 20-m SE-30 glass capillary column proved insufficient for the separation of AB and PC (the PC as methyl esters). A 35-M SE-30 WCOT column was consequently prepared (4). The film thickness was 0.3 μm and resolution (dodecane/tridecane) was 38.5. During column preparation the deactivation is performed with Carbowax, which is only stable up to ca. 230 C. After heating the column to 350 C, resolution decreased to 35 because of the loss of deactivation.

To determine the quantities of AB and PC the integration of the FID-chromatograms was necessary. This was performed on-line with an integrator (Minigrator, Spectra Physics) and compared to the TI-chromatograms (total ion) of the mass spectrometer. As the molar responses of different substances vary widely within any homologous series, the results of the FID integration had to be accordingly corrected (5,6). Application of an internal standard did not seem advantageous.

In order to compare individual chromatograms, standard conditions were adhered to which offered optimal separation for both FID and mass detection.

Hydrogen was used as carrier gas (FID) with a flow rate of 2.8 ml/min. The methylated samples were injected at 250 C with a split of 1:20 (Grob injector). The temperature program was: 80 C, 3 min isotherm, 5 C/min, upper limit 270 C.

GC-MS Analysis

For the combined GC-MS analysis the same column as that used for the FID-chromatograms was used. The injection temperature was also 250 C but helium was used as carrier gas. Loss of pressure in the ion source of the mass spectrometer (electron impact ionization) indicated the appearance of solvent after which the temperature program was started (50 C, 6 C/min, upper limit 270 C). The end of the column was heated to 300 C and was led directly into the ion source.

A Varian MAT 311-A mass spectrometer (double focusing, inverse Nier-Johnson geometry) was used for all MS measurements. Pressure in the ion source was kept constant below 10^{-3} Pa during the analysis with the aid of 2 turbomolecular pumps. The total scan rate from 25 to 300 was ca. 2 sec. Sometimes, 33 was used as lower mass limit in

TABLE I

Experimental Conditions of Several Pyrolysis Runs

Run no.	Substrate	Amount (g)	Kraft lignin (g)	Time (hr)
1	Tall oil FA[a]	8.8	2.5	0.5
2	Tall oil FA	8.8	2.5	3.0
3	Tall oil FA	8.8	7.5	0.5
4	Tall oil FA	8.8	7.5	3.0
5	Tall oil FA	8.8	2.5	15.0
6	Oleic acid	3.6	1.0	0.5
7	Linoleic acid	2.9	0.8	0.5
8	Palmitic acid	2.9	0.8	0.5
9	Linoleic acid	1.5	0.45	15.0

[a]Tall oil fatty acids.

TABLE II

Amounts of Solids, Filtrates, 150 C-Fraction and Distillation Residues from Pyrolysis Reactions

Run no.	Filtered lignin (g)	Remaining pyrolysis mixture (g)	150 C-fraction (g) (distillate)	Distillation residue (g)
1	2.11	6.11	1.06	4.98
2	2.37	5.08	0.58	3.45
3	7.51	5.96	1.20	4.46
4	9.42	2.28	0.31	1.86
5	–[a]	11.29	0.11	2.18
6	0.37	3.62	0.09	3.49
7	0.52	3.06	0.10	2.84
8	0.65	2.53	0.04	2.47
9	–[a]	1.90	0.02	1.88

[a]Filtration of lignin was impossible.

order to eliminate air peaks and to increase sensitivity. A resolution of 1000 ($m/\Delta m$) was satisfactory for every interpretation problem.

Recording of Spectra

For the recording of the spectra, a spectrosystem was used (SS 100 MS, Varian MAT). From every scan a spectrum was registered and stored and the single mass peaks were calibrated with the aid of perfluorokerosene.

Two different ways of recording were used and combined: (a) the sum of the intensities of all ions which were detected during one scan were written as a chromatogram. This "sum plot" (S) is similar to the total ion current at 20 eV; (b) detection of single ions was used during the whole analysis. Since some of the compounds showed characteristic prominent ions, it was possible to detect, using technique, substances which were barely seen in the sum plot, either because of low quantity or bad separation (Fig. 1).

Correlation of the FID-Chromatograms with Those of the Sum-plot

As some of the chromatographic peaks were not separated in the sum plot chromatogram but showed separation in the FID-chromatograms, correlation was only possible with the aid of single ion tracks. Additionally, correlation via the retention indices was possible, which showed a linear increase at increasing temperature and thus enabled easy extrapolation.

RESULTS AND DISCUSSION

Identification of ω-Phenylcarboxylic Acids (PC)

Detection was performed by GC-MS and the PC were separated and identified as their methyl esters. These compounds show mass fragmentation patterns of alkylbenzenes (Fig. 2) and fatty acid methyl esters. With the exception of methyl benzoate, methyl phenylethanoate and methyl phenylpropionate, all homologous acids have base peaks at m/e = 91 and rather intensive ions at m/e = 74 (ca. 30-80%). All of the PC were unbranched, which could be seen by the absence of fragmentation patterns characteristic for branched compounds. PC with side chain lengths of $C \geq 4$ have a prominent ion at m/e = 74 and (similar to saturated fatty acids) a peak at M-31 (OCH_3). In addition, M-32 (CH_3OH) fragmentation occurs; the aromatic ring obviously acts similar to double bonds in the chain (Fig. 3).

Quantitative Distribution of Fatty Acids (C), *n*-Alkylbenzenes (AB) and ω-Phenylcarboxylic Acids (PC)

The addition of increasing amounts of lignin does not drastically raise the yield of AB and PC, respectively

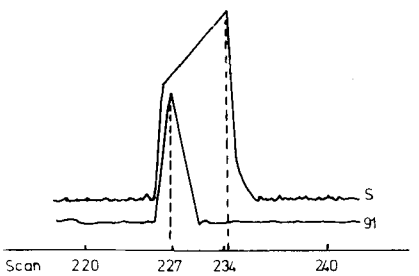


FIG. 1. Identification of different compounds by the single-ion method. S: track of sum plot; 91: track of m/e=91. Spectra 227 and 234 (scan numbers) represent 2 different substances; only spectrum 227 has an intensive ion at m/e=91.

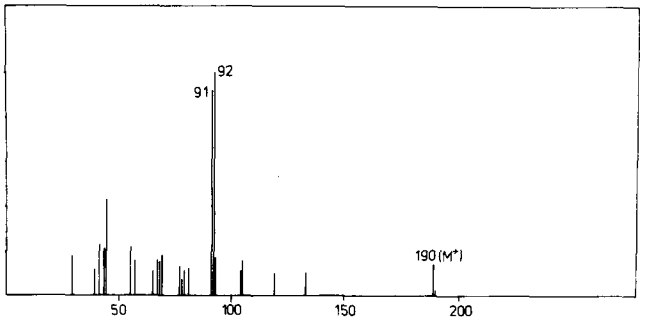


FIG. 2. Mass spectrum of *n*-octylbenzene.

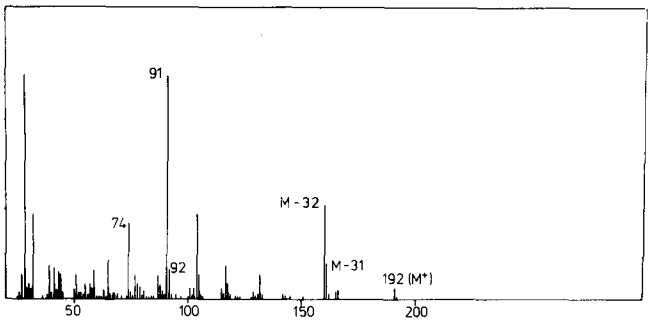


FIG. 3. Mass spectrum of methyl-ω-phenylpentanoate.

(Table III). In experiments 1 and 3 (reaction times 30 min) the quantitative distribution of all classes of substances is almost identical. This picture is palpably changed by an increase in reaction time. While in experiments 1 and 3 the total yield of AB and PC was ≤2% (based on the total volatile mixture), in the 3-hr run the yield of phenylheptanoic acid alone was 1.1%.

This shows clearly that AB can not be exclusively formed by the decarboxylation of PC: as the maximum of PC in all experiments was at phenylheptanoic acid the maximum of AB should be at *n*-hexylbenzene, but this is not the case. Also, the AB did not show a characteristic maximum as the PC; a reaction scheme thus had to be considered where AB and PC are formed by different mechanisms.

A long-time experiment (15 hr) indicated that the quantity of lignin is not the decisive factor: although in this run all lignin was consumed (no solid residue could be filtered), the composition of the reaction mixture was quite similar to the other runs. In this experiment, 1-butyltetralin and 1-pentylindane could be identified. The manner of their formation was not immediately obvious. The proposed reaction scheme offers an explanation for the formation of these compounds (see following). Figures 4 and 5 show the quantitative distribution of AB and PC.

Formation of ω-Phenylcarboxylic Acids and *n*-Alkylbenzenes

The main components of tall oil fatty acids, hexadecanoic acid, 9-octadecenoic acid and 9,12-octadecadienoic acid were originally assumed to be the precursors of AB and PC. Consequently each of these acids (99.9% gas chromatographic purity) were submitted to pyrolysis with kraft lignin under the same conditions as already described. Since no AB or PC could be found in run no. 8 (hexadecanoic acid), the conclusion must be drawn that saturated fatty acids do not cyclize and aromatize under these conditions. In run no. 6 (9-octadecenoic acid), AB and PC could be detected in very small amounts, but none of the 2 substance classes showed pronounced maxima; this means the reaction does not proceed in a specific manner. Only run no. 7 (9,12-octadecadienoic acid) showed the

TABLE III

Quantitative Distribution of *n*-Alkylbenzenes (AB), ω-Phenylcarboxylic Acids (PC) and Fatty Acids (C)

Compound	Run no. 1	2	3	4	6	7	9
C 6:0	<1.0[a]	2.9	1.4	1.1	1.4	11.1	12.3
C 7:0	4.1	16.2	5.4	5.4	17.6	51.5	62.5
C 8:0	14.5	39.6	15.7	17.3	27.7	276.5	298.3
AB 5	<1.0	–	–	<1.0	–	<1.0	1.8
C 9:0	3.8	11.4	3.8	4.7	2.9	20.9	48.7
AB 6	<1.0	<1.0	<1.0	1.7	<1.0	<1.0	1.6
PC 3	<1.0	<1.0	–	<1.0	<1.0	–	–
C 10:1	6.4	9.8	4.4	6.3	1.9	180.0	2.4
C 10:0	1.9	6.6	1.8	3.1	20.4	61.0	15.2
AB 7	1.1	3.0	1.3	2.3	2.6	4.1	1.6
PC 4	<1.0	1.9	<1.0	<1.0	<1.0	<1.0	1.3
C 11:0	<1.0	3.6	<1.0	1.8	3.1	3.9	2.4
AB 8	<1.0	2.8	<1.0	1.6	<1.0	4.4	1.8
PC 5	1.3	2.7	<1.0	<1.0	<1.0	<1.0	1.4
C 12:0	<1.0	<1.0	<1.0	<1.0	<1.0	5.9	1.7
AB 9	<1.0	1.5	1.8	1.3	<1.0	3.5	1.5
PC 6	<1.0	3.5	1.0	2.2	1.4	1.0	1.7
C 13:0	<1.0	<1.0	<1.0	<1.0	<1.0	–	–
AB 10	<1.0	1.4	<1.0	<1.0	<1.0	<1.0	1.2
PC 7	2.9	11.2	2.9	6.2	1.7	10.1	9.3
C 14:0	1.3	1.8	1.3	1.2	<1.0	–	–
AB 11	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
PC 8	2.4	7.2	1.8	5.5	1.7	3.2	<1.0
C 15:0	1.3	2.0	1.7	1.6	<1.0	–	–
PC 9	1.6	1.3	1.3	<1.0	3.4	–	<1.0
C 16:0	96.8	119.2	104.5	107.0	1.3	3.6	12.4

[a]Quantities are given in parts per thousand and are based on the total amount of distillate (including lignin degradation products and unreacted C18 acids).

expected results. The maximal amount of PC was identical to that in tall oil runs but the maximum of AB was shifted to *n*-octylbenzene.

Possible Reaction Mechanism

Under the conditions applied the reactions are likely to proceed via a radical mechanism. The broad spectrum of reaction products requires an explanation which assumes the shift of double bonds of 9,12-octadecadienoic acid in either direction. The double unsaturated carboxylic acids thus formed can then react in various ways which are discussed for the 9,12-double bond positions as a typical example. With this acid, the allylic positions at C-8, C-11 and C-14 are favored:

$$CH_3\text{-}(CH_2)_3\overset{14}{\text{-}}CH_2\text{-}CH{=}CH\text{-}\overset{11}{CH_2}\text{-}CH{=}CH\text{-}\overset{8}{CH_2}\text{-}(CH_2)_6\text{-}COOH$$

Pathway 1

If radical formation takes place at C-8, ring closure with C-13 can occur; the radical will be located at C-12. This system is stabilized by elimination of an alkyl rest and by the formation of a double bond. The cyclohexadiene ring is then aromatized with the aid of lignin, which serves as hydrogen acceptor. ω-Phenylheptanoic acid is formed and may decarboxylate to *n*-hexylbenzene. This seems to be the predominant reaction sequence.

Pathway 2

With radical formation at C-14, the product of ring closure is stabilized by elimination of a carboxylic acid (in this case octanoic acid); this explains the formation of low-molecular-weight fatty acids. The other product is an alkylbenzene (here *n*-butylbenzene). The 2 competing pathways 1 and 2 cause the lack of a clearly defined maximum for the formation of AB (Fig. 4).

Pathway 3

Position 11 is sterically hindered toward cyclization. Formation of a radical can, however, result in cleavage of the acid, which explains the prominent occurrence of decenoic acid (ca. 18% in run no. 7).

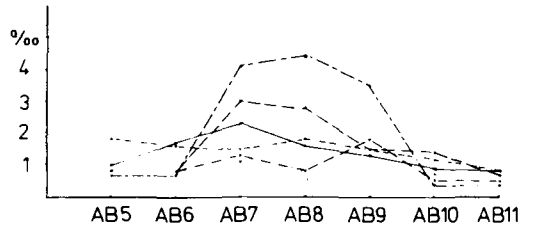


FIG. 4. Quantitative distribution of *n*-alkylbenzenes (AB). Run no.: 1 ···; 2 — — —; 3 — · — · —; 4 ———; 7 — · — · —; 9 — — · · — — · ·. (AB 5=*n*-pentylbenzene, e.g.)

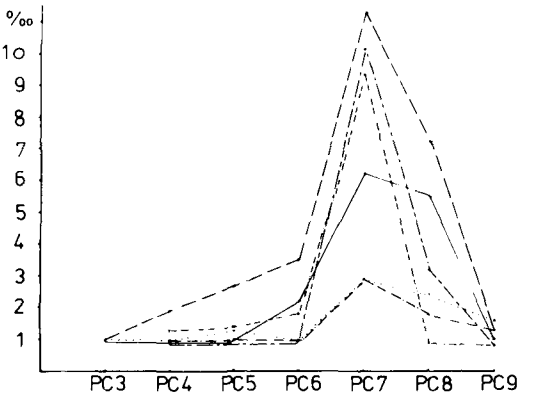
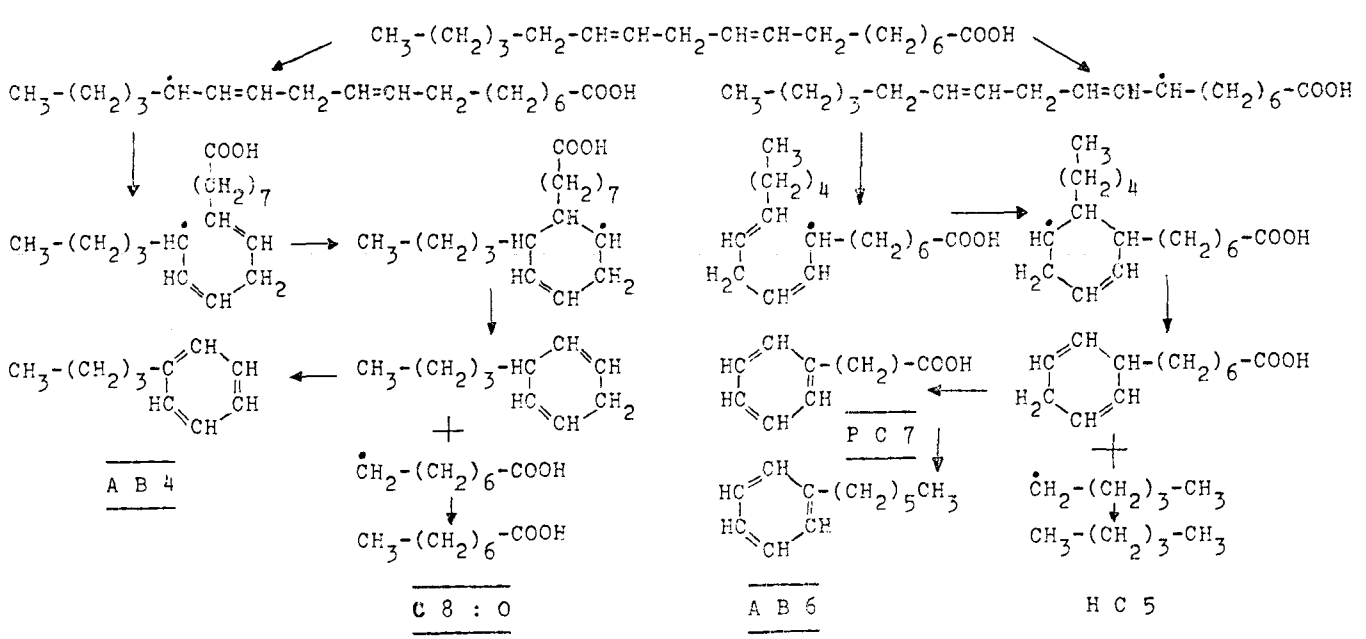
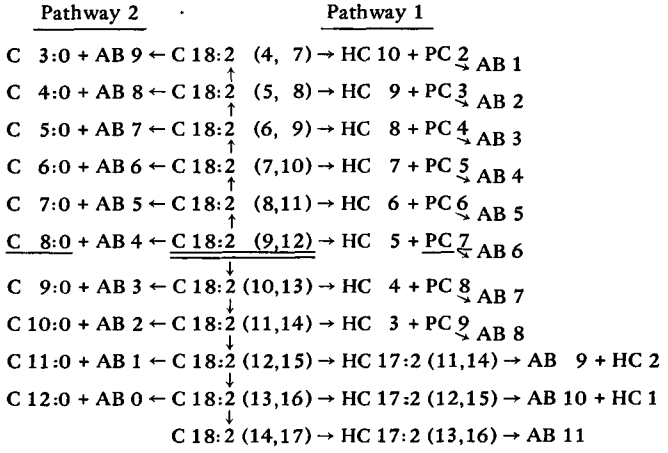


FIG. 5. Quantitative distribution of ω-phenylcarboxylic acids. Run no.: 1 ···; 2 — — —; 3 — . — · —; 4 ———; 7 — · — · —; 9 — — · · — — · ·. (PC 7=ω-phenylheptanoic acid, e.g.)

These possible reaction pathways are summarized in Scheme I. They still fail to explain the broad spectra of AB and PC, which were also found in the pyrolysis of tall oil fatty acids. Shift of the double bonds after radical formation at one of the allylic positions (7) seems to offer a reasonable explanation: starting with 9,12-octadecadienoic acid the position of unsaturation can shift to (10,13), to (11,14) and so on up to (14,17), or alternatively, to (8,11), (7,10) down to (5,8). The resulting



SCHEME I. Possible reaction scheme of the pyrolysis of 9,12-octadecadienoic acid with lignin. Substances which could be detected and identified are underlined. AB=*n*-alkylbenzenes; PC=ω-phenylcarboxylic acids; C=fatty acids; HC-hydrocarbons.



AB = *n*-alkylbenzenes; PC = ω-phenylcarboxylic acids; C = fatty acids; HC = hydrocarbons.

SCHEME II. Summary of possible reactions taking shift of double bonds into consideration.

radicals can cyclize in a manner entirely analogous to the one just discussed. The products formed this way then represent the complete spectrum of all AB, PC and fatty acids found.

Branched or more unsaturated fatty acids with at least 3 double bonds must be considered as precursors for the formation of 1-butyltetralin and 1-pentylindane (ca. 0.2% each) in experiments 1 and 4, respectively; for a summary of possible reactions see Scheme II. In this reaction scheme the main products of the pyrolysis of 9,12-octadecadienoic acid without shift of double bonds are underlined.

With the double bond shifted into the direction of the carboxylic group, the isomerized acid reacts to C7:0 and AB5. A further shift of the double bonds apparently takes place only to a very small extent. If the double bonds are shifted in the opposite direction, decarboxylation can take place before or after cyclization.

ACKNOWLEDGMENTS

We express our thanks to "Österreichische Nationalbank" for the financial support as well as to Westvaco Corp., Charleston, SC, and G. Billek for providing a large number of samples. A. Nikiforov helped in operating the mass spectroscopical equipment.

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[Received December 26, 1979]

The Effect of Soybean Moisture during Storage on the Lipid Composition of Extracted Crude Oil

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ABSTRACT

The quality of soybean oil extracted from seed stored under constant temperature and relative humidity for 42 days was evaluated over a wide range of moisture levels. Storage of soybeans at 9, 13 and 18% moisture had little affect on the major lipid components (neutral lipids), even though seed stored at 18% moisture became infected with mold. The level of phospholipid in the extracted crude oil decreased during the last 3 weeks of storage in seeds stored at 13 and 18% moisture from 4 to 2.5% of the total oil. During the same period, the level of free fatty acids, (FFA) (primarily 16:0 and 18:2) in these samples increased. This study indicated that the increase in FFA during seed storage at high moisture levels was the result of soybean lipase and possibly phospholipase activity. These findings suggested that soybeans should be kept at less than 13% moisture for long-term on-farm storage to preserve oil quality.

INTRODUCTION

The recommended soybean moisture for harvest is 13% (1); however, in actual practice, soybeans are harvested between 13-18% (2). Soybeans harvested at the higher moisture levels should be dried to 13% or less for storage (1,3). When soybeans are stored for very long periods (2 yr), a moisture of 12.0% is recommended to maintain a good seed grade (4). At present, no scientific reason has been given for the selection of this particular moisture level. However, high levels of phospholipids have been found in extracted crude oil from soybeans stored for very short storage periods under high moisture and temperature conditions (5).

Unusually wet weather during soybean harvest is sometimes a problem in southeastern United States. High-moisture soybeans may become damaged in the field or during storage. Because of the high temperatures (35-45 C) of silos and storage bins in this geographical area, soybeans not dried to proper moisture levels can be severely damaged. Soybeans damaged in such a manner are characterized by high levels of free fatty acids, (FFA) high peroxide values and Lovibond color in extracted crude oil, which greatly reduces the commercial grade of an oil (6-8). A penalty is imposed on crude oil for export markets with FFA levels exceeding 0.75% of the total oil (8). These undesirable oil qualities are attributed to mold growth on oilseeds harvested at or stored under high moisture (9,10).

The purpose of this study was to determine the effects of several constant soybean moisture levels on the lipid composition of extracted crude oil during short-term storage and to establish the involvement of soybean enzymatic reactions on extracted oil quality.

MATERIALS AND METHODS

Locally produced soybeans (mixed var.) that had been