The results are tabulated in Table V. Agreement is quite good by the three methods (within 4% absolute) with the exception of an inexplicably high NMR value for *cis*-methyl epoxystearate. From the NMR curves, it is also possible to determine the amount of OH formed per mole of compound. The following OH values/mole were obtained: *cis*-methyl epoxystearate 1.30; *trans*-methyl epoxystearate 1.07; methyl vernolate (epoxyoleate) 0.96; methyl diepoxystearate 1.50. Thus, approximately one OH is generated per mole of original oxirane. The relatively low OH, the disappearance of oxirane and incomplete reaction with picric acid, raise the question of the fate of the oxirane moiety. IR and NMR showed no appreciable carbonyl formation. The possibility of ethyl ether formation by reaction with solvent (15) was precluded by NMR examination. Dimerization was shown not to occur appreciably by cryoscopic molecular weight determinations which showed an increase of only about 15% above that accounted for by derivative formation. It is felt that, despite the foregoing unresolved questions, the method because of its high sensitivity has a distinct usefulness.

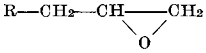
This method was shown to be appreciable to a number of different, commercially available, epoxides (see Table VI).

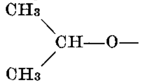
The extent of reaction appears to level off at about 45 hr in all cases, with the exception of styrene oxide which shows a steady decrease after 6 hr. The reaction proceeded to varying extents, depending on steric and electronic factors (see Table VII). Only one of all the compounds shown in Table VI failed to react to an appreciable extent, namely dipentene dioxide, which very likely undergoes rearrangment under the acidic conditions employed. All epoxides were examined in the standard ether/ethanol solvent with the exception of Epon 1031 which was insoluble. Reaction was attempted first in chloroform, then ether /chloroform and finally ethanol/chloroform to obtain a reasonably good reaction rate.

Nearly all of the epoxides tested (including the Epons) have terminal groups. A notable exception is the KP 90 (butyl epoxystearate) which has by far the largest optical density at all times. Thus, that epoxide which most resembles those derived from fats, reacts to the greatest extent.

TABLE VII

Variation of Reactivity of 3-Substituted Propylene Oxides with Polarity of Substituents



R	O.D. @ 490 mμ after 45 hr
CH_3—	0.870
	0.730
øO—	0.678
HO—	0.571
Cl—	0.167

The method has been found to be particularly well suited to the determination of epoxides in heated fats where the oxirane level is often less than 0.1% and where interfering substances such as α, β-unsaturated carbonyls, conjugated dienols and cyclopropenes make the standard HBr titration method (14) unsatisfactory.

ACKNOWLEDGMENTS

Gerhard Maerker, of the Eastern Regional Laboratories, USDA, provided helpful suggestions and supplied us with some samples of epoxides. R. McNaught assisted in running and interpreting NMR spectra.

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Water-Solubilizable Oxazoline Polyester Coating Resins[1]

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Abstract

Preparation of water-soluble coating resins was attempted by reaction of linseed acids with an aminopolyol, tris(hydroxymethyl)aminomethane, and then with itaconic acid. The amino alcohol reacts with linseed acids to form amides and then oxazolines. The oxazolines undergo ring-opening to increase their functionality to greater than two. The oxazoline-polyester resins are only partially water-soluble, but homogeneous aqueous solutions are formed by addition of isopropyl alcohol and neutralization with an amine. Film properties are described.

Introduction

The combination of air-drying ability and water solubility is a requirement hard to meet in a coating vehicle. Such a vehicle must be sifficiently hydrophilic in character to be soluble in aqueous systems yet retain enough unsaturation to form an air-dried water-insensitive film. Addition of such reagents as ethylene or propylene oxides of linseed acids can lead to water-soluble products deficient in drying power. This deficiency is caused by the failure of these reagents to increase the drying functionality of linseed acids. Alkyd-type resins can be prepared containing an excess of hydroxyl or acid groups to achieve water solubility. Salts of acids are particularly effective in solubilizing long carbon chains. A fugitive base, such as ammonia or a reasonably vol-

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[1] Presented at 148th ACS Meeting, Chicago 1964.

[2] No. Utiliz. Res. and Dev. Div., ARS, USDA.

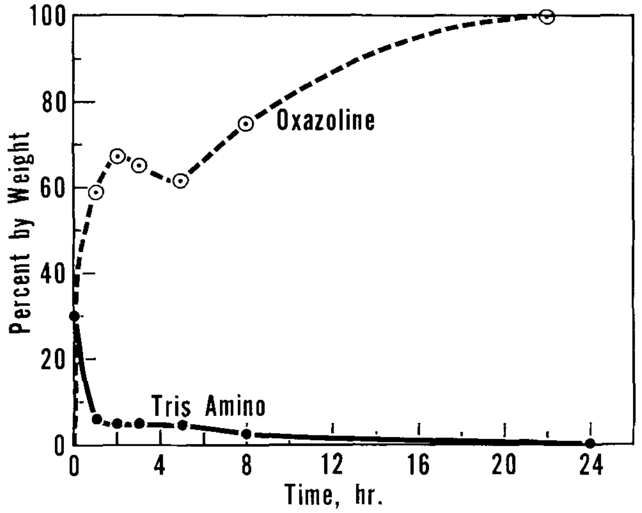


FIG. 1. Reaction of equal molar amounts of linseed acids and tris(hydroxymethyl)aminomethane (Tris Amino) at 180C with a nitrogen sparge.

atile amine, can be used to form the acid salt so that water sensitivity would not be indefinitely retained in films cast from the vehicle.

Polyols are not conveniently reacted with acids to yield uniformly partially acylated products. Some fully acylated polyols will be formed without hydrophilic character. To overcome this disadvantage of polyols, the use of an aminopolyol was tried such as tris(hydroxymethyl)aminomethane (referred to as Tris Amino). This report describes the preparation of water-solubilizable air-drying coating vehicles by reaction of linseed acids with appropriate polymer-forming and hydrophilic reagents. No consideration was given in this investigation to the problems of pigmenting and actually formulating coatings from such a vehicle.

Discussion

Tris Amino readily forms homogeneous systems when reacted with fatty acids. Furthermore, the reaction products tend to be uniform if equal molar amounts of acids and amine are reacted, since reaction will occur exclusively at the amine function. Upon reaction of equal molar amounts of linseed acids and Tris Amino, an amide is first formed:

$$RCO_2H + H_2NC(CH_2OH)_3 \longrightarrow RCONHC(CH_2OH)_3 + H_2O$$

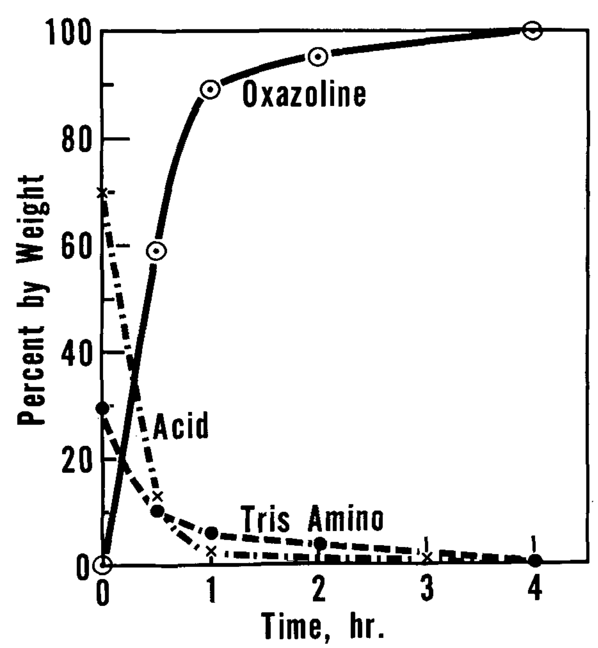
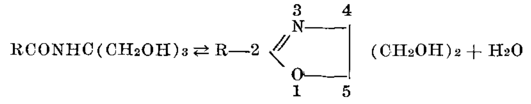


FIG. 2. Reaction of equal molar amounts of linseed acids and Tris Amino with water entrainment and xylene.

The resulting amidopolyol will cyclize to yield an oxazoline with the loss of an additional molecule of water:

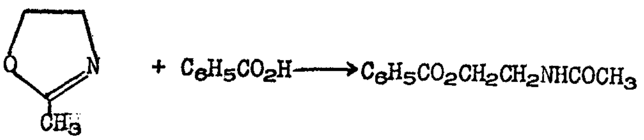


$$RCONHC(CH_2OH)_3 \rightleftarrows R{-}2\,\text{(oxazoline ring: N-3, C-4, C-5, O-1)}\,(CH_2OH)_2 + H_2O$$

The extent to which the second reaction occurs can be partially controlled by the conditions employed. The rate of oxazoline formation at 180C appears to be limited primarily by the rate at which water can be removed from the reaction mixture. This conclusion follows from examination of the data in Figures 1 and 2. In Figure 1 complete conversion to the oxazoline is reached in 24 hr of reaction time at 180C when a nitrogen sparge is used to remove the water of reaction. If xylene is used to entrain the water, complete conversion to the oxazoline can be effected in 4 hr (Fig. 2). The dip in the oxazoline curve in Figure 1 is probably caused by some hydrolysis of the oxazoline to amide caused by a slow rate of water removal from the reaction mixture coupled with increased miscibility of water with the reaction mixture. When more rapid methods are used to remove water, no reverse reaction is discernible.

If the unsaturated oxazoline diols with the structure 4,4-bis(hydroxymethyl)-2-alkenyl-2-oxazoline are reacted with dibasic acids to prepare linear polymers, gels are obtained if the reaction times are prolonged to secure a high-molecular weight. To eliminate unsaturated acids as a cause for gel formation, a saturated oxazoline diol, 4,4-bis(hydroxymethyl)-2-heptadecyl-2-oxazoline (I), was prepared from stearic acid and Tris Amino and then reacted with azelaic acid. In refluxing toluene only about 24% of the azelaic acid reacted in 16 hr. If the reactants are melted together at 150C for 6 hr, then at 200C for 2 hr, and finally at 180C and 80 mm Hg for 2 hr, a gel is obtained (Fig. 3). The oxazoline content drops rapidly at first to a minimum of about 82% and thereafter gradually rises to about 91% at the gel stage. At first, the reaction with azelaic acid forms water more rapidly than it can be removed by nitrogen sparging. Consequently, oxazoline is probably hydrolyzed during this period to amide, not the amino-ester, since the formation of amine is not detectable in the system. Approximately one-half of the amide recyclizes to the oxazoline. The remainder must exist then either in the hydroxyamide form or as branch points which may lead to crosslinks and gel formation.

Acidolysis as well as hydrolysis of oxazoline-diol could lead to potential crosslinks in the resins. Acidolysis of oxazolines with carboxylic acids has been reported (2). As to the direction of ring opening, we found that when 2-methyl-2-oxazoline was treated with benzoic acid, 2-acetamidoethyl benzoate was formed:



$$+\ C_6H_5CO_2H \longrightarrow C_6H_5CO_2CH_2CH_2NHCOCH_3$$

The entering acyl group takes a position on the oxygen atom rather than on the nitrogen atom. Our finding was in agreement with the observation of Frey (2) on the ring opening of 2-phenyl- and 2-*p*-nitrophenyl-2-oxazoline.

The oxazoline-diols formed by reaction of Tris Amino with carboxylic acids may be reacted with dibasic acids to form highly crosslinked resins since ring opening of the oxazolines occurs. High-acid-level resins may be formed by reaction with excess dibasic acid. By alcoholysis of dibasic acid esters with diols, linear oxazoline-containing polyesters may be formed. For the purpose of preparing water-soluble coating vehicles, high-acid-level, partially crosslinked resins are more desirable. Two types of these resins were prepared differing in molar ratios of linseed acids to Tris Amino to dibasic acid. Both types of resin were made with itaconic acid as the dibasic acid. One type (1-2-2) was made by first reacting 2 moles of linseed acids per mole of Tris Amino followed by reaction with 2 moles of itaconic acid per mole of Tris Amino employed. The other type (1-1-2) was similarly made except Tris Amino was first reacted with an equimolar amount of linseed acids followed by reaction with 2 moles of itaconic acid per mole of Tris Amino. Reaction of 2 moles of linseed acids per mole of Tris Amino produces a mixture of the oxazoline-diol and mono- and di-acylated diol presumably in the statistical ratio of 1:2:1, respectively. The mixture then consists of mono-, di-, and tri-functional reactants since even the diacylated diol must be considered monofunctional due to ring opening by either water or carboxylic acid. Gels will form in the reaction with itaconic acid much more readily with the 1-1-2 resins (about 2 hr) than with the 1-2-2 resins (about 17 hr) at 180C because of the greater reactivity of the former.

The resulting polymers might be expected to consist of ester and amide linkages with some oxazoline ring structures tied into the whole. The data in Figure 4 show the molecular weight and viscosity of water-washed samples vs. time of reaction for the preparation of a 1-2-2 resins. It is seen that no pronounced increase in number average molecular weight occurred up to 1 hr short of gel; however, viscosity increased greatly. The acid value declined quite slowly, dropping only from 85 to about 75. The acid value showed a slight, steady decline from 132 to 121 probably due to dilution caused by continued addition of itaconic acid to the water-insoluble portion. Kienle et al. (4) observed only modest number average molecular weights in samples of glyceryl phthalate taken just before gelation.

The oxazoline component in the 1-2-2 composition studied here should have not greater functionality than two in the absence of acidolysis reactions. Hence, gelation may have its origins in some itaconate-vinyl type polymerizations. There is some evidence to suggest that this may be true. The resins washed with water do not wet steel, glass, or aluminum surfaces when cast from aqueous alcoholic solutions, whereas unwashed resins do. Additions of detergent will correct this deficiency. Perhaps some itaconate-derived homopolymers are involved in this phenomenon. Itaconate esters seem to have differing tendencies to undergo polymerization with heat. Diethyl itaconate heated for 17 hr under nitrogen did partially polymerize. However, a low molecular-weight polyester prepared by alcoholysis of diethyl itaconate with I underwent little further polymerization in 18½ hr under the same conditions.

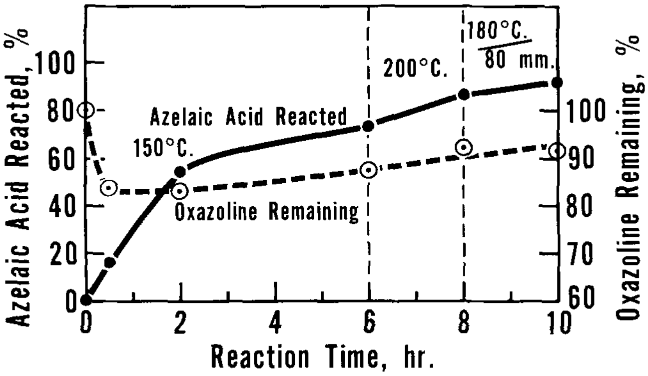


FIG. 3. Reaction of 4,4-bis(hydroxymethyl)-2-heptadecyl-2-oxazoline (I) with azelaic acid in the melt.

The resins were insoluble in water even with the addition of sufficient dimethylaminoethanol to neutralize all the acid. However, with the addition of isopropyl alcohol, homogeneous compositions were obtained. A typical 1-2-2 resin formed solutions ranging from 23% to more than 50% resin (including weight of amine). In general the homogeneous solutions required more isopropyl alcohol than water, but as the resin concentration was increased, the water tolerance of the system increased.

Comparisons of the drying properties of the two types of resin are given in Table I. Comparison was also made with the drying properties of a commercial sample of water-soluble linseed oil and a bodied linseed acid-derived Tris Oil [linseed acids treated with Tris Amino and then with formaldehyde (1)]. Films cast from the solutions of the 1-2-2-type resin were quite satisfactory in regard to their air-drying properties. They also generally had higher pencil hardnesses than did the films prepared from the 1-1-2 resins. The 1-2-2 resins did not appear to be at all water sensitive, whereas the films cast from the 1-1-2 resins were. The latter films were removed from the substrate or noticeably softened within 5 min by 60–70C water. Films cast from the isopropyl alcohol-water solutions of the 1-1-2 resins remained tacky even after 70 hr of air-drying. Even the films cast from toluene solutions of this resin were quite soft and water sensitive.

Further studies of these types of resins are in progress.

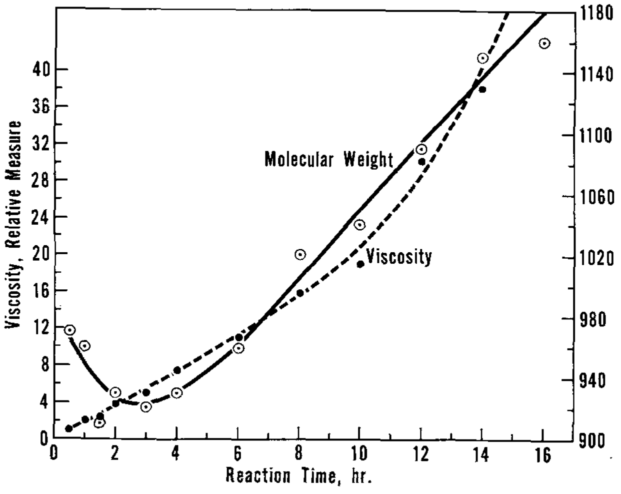


FIG. 4. Viscosity and molecular weight changes during preparation of Tris Amino-linseed acids-itaconic acid resin with molar ratio of 1:2:2 of the respective reactants.

TABLE I

Comparison of Drying Properties of Resins with a Sanderson Drying-Time Meter[a]

Resin	Solvent	Drier	Dry-to-touch, hr	Tack-free, hr	Pencil hardness
Tris Amino (1)—LFA (2)—IA (2)[b]	45% i-PrOH 55% H_2O	None	>19	>19	2
Tris Amino (1)—LFA (2)—IA (2)	45% i-PrOH 55% H_2O	0.1% Co 0.1% Pb	2	>19	4
Tris Amino (1)—LFA (2)—IA (2)	Toluene	0.1% Co 0.1% Pb	4	16	4
Commercial sample; boiled linseed Tris Oil	Toluene	0.1% Co 0.1% Pb	6	>19	3
Commercial sample; water-soluble linseed oil (contains 13% coupler)	H_2O	0.1% Co 0.1% Pb	>19	>19	....
Tris Amino (1)—LFA (1)—IA (2)[b]	Toluene	None	<1	....	1
Tris Amino (1)—LFA (1)—IA (2)	Toluene	0.1% Co 0.1% Pb	<1	....	1
Tris Amino (1)—LFA (1)—IA (2) (warmed to effect solution)	40% i-PrOH 60% H_2O	0.1% Co 0.1% Pb	>19	>19[c]	....
Tris Amino (1)—LFA (1)—IA (2) (warmed to effect solution)	40% i-PrOH 60% H_2O	None	>19	>19[c]	....

[a] All films at 1 mil thickness.
[b] LFA = Linseed fatty acids. IA = Itaconic acid. Numbers in parentheses indicate moles.
[c] Not dry after 2 days.

Experimental

All melting points are corected. All boiling points are uncorrected. Oxazolines were determined by potentiometric titration (1). Molecular weights were determined on a Mechrolab vapor pressure osmometer, Model 301. Viscosities were measured with a Haake Rotovisco viscometer at 40C.

Pure stearic acid was prepared from stearic acid (mp 69–70C, Matheson, Coleman and Bell and mp 68–69.5C, Fisher Scientific). Samples of both the commercial stearic acids were converted to the methyl esters. Both methyl esters appeared to contain, from their GLC curves, approximately 88% stearate with the principal impurities being methyl palmitate and lesser amounts of methyl linoleate, methyl linolenate, and possibly methyl palmitoleate. The impurities more volatile than methyl stearate were separated by distillation through a Podbielniak 2-ft HeliPak column operating at 2 mm Hg pressure and a high reflux ratio. The residue then contained methyl stearate of 99% purity. The methyl stearate was then distilled through a short column and saponified.

Tris Amino as received had mp 170–171C and equivalent weight 122. It was purified by dissolving in aqueous ethanol, treating with Darco G-60, filtering and crystallizing. The crystals after drying had mp 171.5–172C and equivalent weight 121.5.

Itaconic acid was recrystallized from hot water after treatment with Darco G-60. The acid had equivalent weight 64.1 before and 65.3 after purification.

Azelaic acid, mp 104.5–105C, was dissolved in water, treated with Darco G-60, and crystallized. The dried crystals melted at 105.5–106.5 [reported 106.5C (3)].

The linseed acids used had bp 185–190C at 0.5 mm Hg, iodine value 185, and equivalent weight 276.

2-Methyl-2-oxazoline was prepared by the method of Wenker (7).

Diethyl itaconate was prepared by the sulfuric acid-catalyzed esterification of itaconic acid and with benzene azeotropic removal of the water. The distilled ester was obtained in 35% yield and had bp 123C, n_D^{20} 1.4372, n_D^{30} 1.4332 [reported n_D^{20} 1.4387 (5)].

4,4-Bis (hydroxymethyl)-2-heptadecyl-2-oxazoline (I) (6) was prepared by reaction of equimolar amounts of stearic acid and Tris Amino while removing the water azeotropically with toluene. Crude I was purified by repeated crystallization from methanol-chloroform to yield a colorless crystalline I of mp 107.5–108.5C with the theoretical oxazoline equivalent weight. Thin-layer chromatography showed no impurities.

Poly(4,4-bis(hydroxymethyl)-2-heptadecyl-2-oxazoline) itaconate was prepared by reaction of 7.39 g (20 mmoles) I with 4.32 g (20 mmoles) diethyl itaconate in the presence of an added 0.5 ml of 1.5*N* sodium methoxide in methanol at 120C for 3 hr at atmospheric pressure followed by a like period of heating at 80 mm Hg. The product was taken up in chloroform and washed with water containing a little acetic acid. The isolated polymer had a molecular weight of 900. Previous experiments had shown no loss of oxazoline content under these conditions. This polymer failed to undergo significant further polymerization when heated at 180C for 18½ hr under nitrogen. The molecular weight increased to 1,100.

Diethyl itaconate (5.0 g) was heated at 180C under nitrogen for 17 hr. From this material 2.6 g diethyl itaconate was recovered by distillation. The residue was a viscous colorless liquid having only 31% of the unsaturation level of diethyl itaconate.

Azelaic acid (7.52 g; 40 mmoles) and I (14.76 g; 40 mmoles) were heated at 150C by an oil bath for 6 hr. The temperature was then raised to 200C for 2 hr, and then lowered to 180C while the pressure was reduced to 80 mm Hg for 2 hr. Samples were removed periodically for determination of oxazoline and azelaic acid. The final product was a brown gel swollen by benzene-methanol. Titration showed only a trace of non-oxazoline amine.

The resins were prepared in similar fashion. The procedure is illustrated by the following description of the preparation of a 1-2-2 type.

In a 1-liter resin flask were placed 552 g (2 moles) linseed acids and 121.5 g (1 mole) Tris Amino. The flask was equipped with nitrogen sparge, mechanical stirrer, reflux condenser, and water trap. The contents were heated to 180C, about 2 hr being required. The mixture became homogeneous at about 130C and after 15 min of heating. The contents were held at 180C. Samples in some tests were periodically removed and titrated to determine the amount of linseed acids remaining. In other tests, additional samples were taken to determine the Tris Amino and oxazoline contents. After about 10–12 hr, the titratable acid is essentially nil. The time to reach this point depends upon how rapidly the temperature is raised, and upon the stirring and nitrogen sparging rates. Then 260.8 g (2 moles) itaconic acid were added, and the temperature was raised again to 180C and held at this point for 16 hr. During one run, samples were periodically removed, dissolved in chloroform, and water-washed to remove soluble materials. The samples were dried and the chloroform was stripped. Portions were titrated for acid. Other portions of the samples were treated with diazomethane to zero acid value and molecular weights measured by using the Mechrolab vapor pressure osmometer. Previous experience had shown that gelation would occur in 17 hr. The resin produced was characterized by: molecular weight 1,420, equivalent weight 645, iodine value 112.3, and lack of alcohol absorption in the infrared. The resin was soluble in toluene. When the resin was treated with dimethylaminoethanol equivalent to the acid present, the resin was soluble in isopropyl alcohol-water from 23–55% resin plus amine (wt/wt). Dilution of these samples with water to the point of phase separation showed that the higher the resin content the greater the resin tolerance for water.

Film Properties

Films were cast from 20% solutions of the polymers and from two commercial samples at 5 mil wet-film thicknesses by using a doctor blade on 6-in. diameter steel discs. The drying data in Table I were determined with a Sanderson drying time meter.

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The Lipid Composition of Wheat Flours Varying Widely in Bread-Making Potentialities[1,2]

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Abstract

Lipids were extracted with petroleum ether (average 0.93%) and with water-saturated n-butanol (average 1.20%) from flours milled from composite 8 hard red winter, 5 hard red spring, and each from red soft, durum, and club wheat varieties. The butanol-extracted lipids were fractionated into nonpolar and polar lipids by silicic acid column chromatography, and the two major fractions were subfractionated by thin-layer chromatography. The extracted, washed, lipids contained about 52% nonpolar, and 48% polar lipids. Flours milled from durum wheat contained substantially less polar lipids, than flours milled from hard red winter or hard red spring wheats. The triglycerides constituted about 50% of the nonpolar lipids. Among the polar lipids, digalactosyl glyceride was the major component (about 40%); an unidentified compound, and a mixture of monogalactosyl glyceride with phosphatidic acid were about 20% each; and phosphatidyl ethanol amine, phosphatidyl choline and phosphatidyl serine comprised about 4, 7, and 4.5% of the polar lipids, respectively.

Introduction

LIPIDS COMPRISE only a small portion of most cereals. They form about 2% of the barley, rice, rye and wheat kernel, about 3.5% of millet, and around 5% of corn. Nevertheless, lipids have engaged the attention of cereal chemists because research over many years has suggested that lipids are involved in processing and storage, as a source of fat soluble vitamins and essential fatty acids, and in complex transformations during plant development and germination. A number of workers (1–4) have reviewed the role of wheat flour lipids in bread-making and nutrition. Reviews of the complex cereal lipids, and methods of their isolation and fractionation, were presented by Fisher (5) and Mecham (6). A number of reports dealing with the neutral lipids and fatty acids of wheat flour have been published, but publications on cereal polar lipids are of a rather limited scope (7–13). This report presents data on fractionation of wheat flour lipids from 16 wheat varieties (from a number of locations and varying widely in bread-making potentialities) by silicic acid column and quantitative thin-layer chromatography (TLC).

Materials and Methods

Flours

Untreated flour, used for extraction of lipids and preparation of standards for quantitative TLC, was milled on an Allis experimental mill from a composite grist of several hard-red winter-wheat varieties grown at a number of locations throughout the Great Plains in 1963 (14). In addition 16 flour samples from the 1963 crop were milled on a Miag "Multimat." The flours were milled from wheat composites of single varieties grown at an average of 8 locations. The chemical composition and baking quality of these flours, summarized in Table I, were determined as described elsewhere (14).

Lipid Extraction

Lipids were extracted exhaustively with Skellysolve B in a Goldfish extractor. In addition, lipids were extracted from 15 g flour with water-saturated n-butanol by the following procedure. The lipids were extracted in a Stein Mill with 100, 50, and 50

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[1] Contribution No. 514. Kansas Agricultural Experiment Station, Manhattan.

[2] A report of work done in part under contract with the US Department of Agriculture and authorized by the Research and Marketing Act 1946. This contract was supervised by the W. Res. and Dev. Div., ARS, USDA.