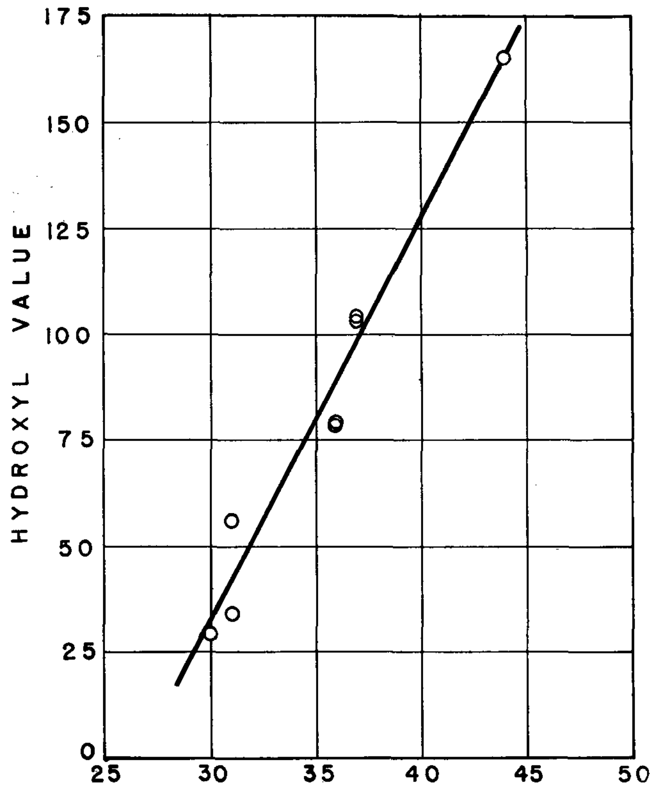

FIG. 3. Relationship between melting point and hydroxyl value of acetostearin made by acetylating monostearin B.

is a relationship between the melting point and hydroxyl value.

A number of acetostearins other than those given in Table III and Figure 3 were found to have melting points higher and lower than those shown. Some products were liquid at room temperature and others melted as high as 60°C. It is evident that, within limits, acetostearins can be prepared with any desired melting range by the proper choice of monostearin and proportion of acetic anhydride.

Summary

1. Acetostearins were prepared by reacting various proportions of acetic anhydride with a monostearin of 99.2% purity, a commercially available monostearin containing 91.5% monoglycerides, and a technical grade monostearin containing 61% monoglycerides. The last mentioned product was prepared from a completely hydrogenated cottonseed oil. After the removal of unreacted acetic anhydride and acetic acid from the reaction products, the flexibility and melting characteristics were determined.

2. All of the acetostearins tested were non-greasy solids at room temperature yet were highly flexible. At a temperature of 22°C. most of them could be stretched more than 800% under the test conditions. Bending tests revealed that some of the products possessed good flexibility even at 4°C.

3. The melting characteristics of the products were dependent on the purity of the monostearin used and the degree of acetylation. Some products melted completely below body temperature (37°C.), and others melted at temperatures up to 60°C. The temperature interval over which melting occurred was usually very short (1-3°); however products made from technical grade monostearin melted over a temperature range of 10-20°C.

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Effect of Winterization on the Composition and Stability of Cottonseed Oil

C. H. MACK, R. N. MOORE,[1] and W. G. BICKFORD, Southern Regional Research Laboratory,[2] New Orleans, Louisiana

DESPITE the fact that winterization of cottonseed oil has been practiced on an industrial scale for nearly half a century, no information could be found in the literature with respect to the effect of this process on the composition and autoxidative stability of the products. The two most important factors affecting the autoxidative stability of cottonseed oil are its content of unsaturation and tocopherols. It is known that the saturated components of the glycerides are decreased when cottonseed oil is winterized (1), but no data are available regarding the effect of this practice on the tocopherols. Consequently no correlation of tocopherol content and composition of the glycerides with autoxidative stability has been made.

In order to investigate the relationship of the three factors mentioned above, a series of oils consisting of refined and bleached cottonseed oil, the same oil after winterization, and the stearine press cake remaining after winterization was analyzed with respect to the compositions of the glycerides, total tocopherol contents, autoxidative stability, and color. The samples were obtained from three refineries located in different cotton-producing states, namely, Tennessee, Louisiana, and South Texas. Before being analyzed, the samples were freed of soaps, when necessary, and deodorized in a laboratory deodorizer (2).

Methods of Analysis and Calculations

Iodine values were determined by the American Oil Chemists' Society modification of the Wijs method

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[1] Present address, Naval Stores Station, Bureau of Agricultural and Industrial Chemistry, Olustee, Fla.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE 1

Characteristics and Composition of Original and Winterized Cottonseed Oils and Stearine Press Cake

Characteristic or constituent	Processor A Louisiana			Processor B Texas			Processor C Tennessee		
	Original	Winter-ized	Press cake	Original	Winter-ized	Press cake	Original	Winter-ized	Press cake
Peroxide value[a]	0.0	0.0	1.0	0.0	1.0	0.0	1.0	1.0	0.0
Iodine value	105.9	109.7	83.8	104.2	108.4	87.2	114.6	116.8	99.4
Thiocyanogen value	64.4	67.4	50.6	66.1	68.0	54.9	69.6	71.0	59.9
Color (yellow/red)	35/3.92	35/3.86	20/2.27	70/6.05	70/4.05	70/3.96	35/3.22	35/3.22	35/2.27
Unsaturated acids expressed as									
Linolein, %	51.4	52.4	41.2	47.0	49.8	39.7	55.6	56.6	48.8
Olein, %	19.6	22.0	14.6	26.3	25.5	21.0	21.2	21.9	17.2
Saturated acids expressed as glycerides									
Determined, %[b]	27.4	25.0	42.3	27.2	23.4	38.0	23.1	21.6	34.0
Tocopherols, %	0.079	0.098	0.049	0.079	0.084	0.059	0.087	0.097	0.068
Stability, AOM hrs.[c]	8.8	9.3	9.8	9.9	8.8	8.6	7.0	9.2	9.5

[a] Milliequivalents peroxide per kilogram of oil.
[b] Determined by the modified Bertram oxidation method.
[c] Time required by substrate to attain a peroxide value of 100 milliequivalents during aeration at 97.7°C. with an air flow of 2.33 ml./sec.

(11), using a 100% excess of reagent and a 30-minute reaction time. Thiocyanogen values were determined with a 0.2 *N* solution of thiocyanogen, prepared by bromination of dry lead thiocyanate (9) suspended in a mixture of purified and dried glacial acetic acid and carbon tetrachloride. A 200% excess of reagent was used with a reaction time of 24 hours at 19°C. (8). Total tocopherols were determined by the Parker and McFarlane modification (12) of the Emmerie and Engel method (4). Autoxidative stability was determined by the active oxygen method (3, 6, 7, 10). Color was determined and expressed according to the official method of the American Oil Chemists' Society (11).

The percentages of saturated constituents, expressed as glycerides, were determined by the Pellikan and von Mikusch (13) modification of the Bertram oxidation method, using sintered glass filter sticks for the filtrations (5). The percentages of olein and linolein were calculated as prescribed in the Official Methods of the American Oil Chemists' Society (Cd 2-38) by substituting the iodine and thiocyanogen values in the following equations:

$$\%\ \text{Olein} = 2.525\ \text{T} - 1.348\ \text{I}$$
$$\%\ \text{Linolein} = 1.246\ \text{I} - 1.253\ \text{T}$$

where T and I represent thiocyanogen and iodine values respectively (11).

The peroxide values were determined by the method described by Moore and Bickford (10) and are reported as milliequivalents of peroxide oxygen per kilogram of oil.

Results and Discussion

Data for the characteristics, glyceride composition, tocopherol content, and autoxidative stability, determined by the methods described above are given in Table 1. The total unsaturation, expressed as iodine values, of the winterized oil increased approximately 3% and that of the stearine press cake decreased approximately 20% compared to the original oil. A slight increase in the content of oleoyl and linoleoyl portions of the glycerides occurred in the winterized oil, and a marked decrease occurred in the stearine press cake compared to the original oil whereas the reverse was true in the case of saturated constituents.

The tocopherol content increased in the winterized oil and decreased in the stearine press cake compared to the original oil. At the temperature used for winterization the tocopherols are apparently more soluble in the unsaturated than in the saturated glycerides. These results might have been expected on the basis of the work reported by Singleton and Bailey (14), who found it impossible to prepare high concentrations of tocopherols by low temperature crystallizations of unhydrogenated cottonseed oil owing to the fact that the tocopherols remained in solution with the more highly unsaturated portion of the glycerides.

The stabilities of the original cottonseed oil, winterized oil, and stearine press cake are essentially the same. In two cases reported the stability was slightly increased in both the winterized oil and the stearine press cake, and in the other case there was a slight decrease. It is apparent therefore that the two factors affecting the autoxidative stability of the oils tend to counterbalance one another. When the unsaturation increases, there is a corresponding increase in the tocopherol content and vice versa. Moore and Bickford (10) observed that the stability of cottonseed oil is decreased when alpha and gamma tocopherols are added to cottonseed oil. However the increase in the concentration of total tocopherols in the winterized oil was accompanied by a change in fatty acid composition.

The color of the original and winterized oils and stearine press cake remained unchanged, indicating that the pigment bodies were not disproportionally distributed between the winterized oil and press cake by this process.

Summary

The relationship between tocopherol content, fatty acid composition, and autoxidative stability has been investigated for a series of three cottonseed oils representing a commercially refined and bleached oil, the same oil after winterization, and the corresponding stearine press cake. The results indicate that an increase occurs in unsaturation of the glycerides, which is accompanied by an increase in the tocopherol content of the winterized, compared to the unwinterized oil. The reverse is true of the stearine press cake fraction. The changes in fatty acid composition and tocopherol content are such that they tend to counterbalance one another and lead to the same final autoxidative stability in each product. The red and yellow color components of the products are unaffected by the winterization process.

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Cottonseed and Peanut Meal Glues. Resistance of Plywood Bonds to Chemical Reagents[1]

JOSEPH T. HOGAN and JETT C. ARTHUR JR., Southern Regional Research Laboratory,[2] New Orleans, Louisiana

THE preparation and strength properties (4, 6), viscosity (1, 2, 5, 8), and resistance to accelerated service tests (7) of cottonseed and peanut meal glues have been described in previous reports from this laboratory. It was indicated that cottonseed and peanut meal glues prepared from solvent-extracted meals compare favorably with commercial casein glues in static strength properties and that cottonseed meal glue is superior to peanut meal glue and compares favorably with commercial casein glue on an interior test basis for 5 cycles, the strength of the casein bond changing from 384 to 283 pounds per square inch and of the cottonseed meal bond changing from 375 to 264 pounds per square inch.

The purpose of this report is to present data on the resistance of cottonseed and peanut meal plywood glue bonds to chemical reagents and to suggest fundamental interpretations of these data relative to the chemical factors affecting adhesion of cottonseed and peanut protein to wood.

Experimental

Glue formulation. Cottonseed meal glue, consisting of 100 parts of hexane-extracted meal, 4 parts of sodium hydroxide, 15 parts of sodium silicate, 15 parts of calcium hydroxide, and 3 parts of carbon disulfide-carbon tetrachloride, was prepared as previously described (6). Peanut meal glue was prepared from solvent-extracted peanut meal in a similar manner (4). The casein glue was a commercially available glue mix which required only the addition of water.

Plywood preparation. The method used was similar to that described in other reports (4, 6). Each glue mix was prepared and applied to birch veneer to form 3-ply panels as recommended to give maximum shear strengths. These recommended conditions were selected in order that each glue could be compared under its optimum utilization. The cottonseed meal glue was applied at a rate of 21 pounds of glue (dry basis) per 1,000 square feet of glue line, cold pressed at 80°F. and 200 p.s.i. for 1,440 minutes, and followed by hot pressing at 237°F. and 200 p.s.i. for 10 minutes. The peanut meal glue was applied at a rate of 28 pounds of glue (dry basis) per 1,000 square feet of glue line and cold pressed at 80°F. and 200 p.s.i. for 1,440 minutes. The commercial casein glue was applied at a rate of 26 pounds of glue (dry basis) per 1,000 square feet of glue line, cold pressed at 80°F. and 200 p.s.i. for 10 minutes. The press opening during these operations was five $\frac{3}{16}$-inch panels. Test pieces, $\frac{3}{16}$ inch, $3\frac{1}{4}$ inches by 1 inch, cross-slotted to give a center section of 1 square inch, were cut from the plywood panels; then they were conditioned at 77°F. and 32% relative humidity for 6 days (3).

Method of testing. The method of testing the chemical resistance of cottonseed and peanut meal glue

TABLE I

Effects of Organic Reagents on Tensile Shear Strengths of Birch Veneer Bonded with Cottonseed Meal, Peanut Meal, and Casein Glues

Reagent	Number of Days Immersed	Tensile Shear Strengths – Wood Failure (lbs./in.^{2} – %)		
		Cottonseed Meal Glue	Peanut Meal Glue	Casein Glue
Carbon Tetrachloride	0	343 – 55	321 – 65	368 – 90
	1	152 – 30	175 – 60	182 – 30
	2	180 – 25	....	188 – 25
	4	168 – 30	202 – 40	195 – 35
	8	176 – 35	....	206 – 40
	10	....	206 – 35	....
	12	178 – 25	....	210 – 40
	14	183 – 30	225 – 40	231 – 40
Benzene	1	184 – 35	165 – 50	224 – 45
	2	189 – 25	171 – 55	214 – 40
	4	201 – 20	180 – 35	....
	8	194 – 35	....	217 – 30
	10	....	205 – 25	....
	12	185 – 40	....	215 – 30
	14	195 – 30	183 – 45	221 – 35
Acetone	1	141 – 30	126 – 40	194 – 30
	2	153 – 25	131 – 40	197 – 40
	4	160 – 20	141 – 35	206 – 45
	8	169 – 20	148 – 30	212 – 25
	10	....	157 – 35	....
	12	175 – 30	....	224 – 40
	14	174 – 25	166 – 30	241 – 35
Ethanol 95%	1	159 – 25	146 – 40	205 – 30
	2	172 – 30	157 – 45	203 – 30
	4	171 – 25	154 – 35	201 – 35
	8	163 – 35	160 – 30	204 – 30
	10	....	173 – 15	....
	12	174 – 30	....	197 – 25
	14	155 – 20	159 – 50	209 – 30
Ethanol 50%	1	143 – 25	114 – 15	192 – 40
	2	139 – 5	113 – 10	174 – 20
	4	114 – 0	101 – 0	155 – 15
	8	81 – 0	68 – 0	101 – 0
(Water)	1	144 – 25	129 – 10	181 – 30
	2	131 – 20	105 – 0	153 – 30
	4	75 – 0	50 – 0	124 – 20
Methanol	1	126 – 30	117 – 25	137 – 40
	4	134 – 35	126 – 30	145 – 35
	10	142 – 30	136 – 30	140 – 30
	14	135 – 25	142 – 25	151 – 30

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[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.