Acknowledgment

The author is indebted to W. C. Ault, B. A. Brice, J. F. Couch, J. Naghski, D. Swern, and R. W. Riemenschneider, for their helpful suggestions and criticisms during this investigation, and to F. J. Cooper, C. S. Fenske Jr., H. B. Knight, F. Luddy, C. L. Ogg, M. L. Swain, and L. P. Witnauer for analytical data.

REFERENCES

1. A.O.A.C., "Official and Tentative Methods of Analysis," Ch. 31, Oils, Fats, and Waxes, 6th edition (1945).
2. Brice, B. A., and Swain, M. L., J. Optical Soc. Am., *35*, 532-544 (1945).
3. Brice, B. A., Swain, M. L., Schaeffer, B. B., and Ault, W. C., Oil and Soap, *22*, 219-224 (1945).
4. Fischer, H., and Gibian, H., Ann. 550, 208-251 (1942).
5. Krewson, C. F., and Couch, J. F., J. Am. Oil Chem. Soc., *28*, 382-385 (1951).
6. Krewson, C. F., J. Am. Chem. Soc., *73*, 1365 (1951).
7. Ogg, C. L., and Cooper, F. J., Anal. Chem., *21*, 1400-1402 (1949).
8. Podbielniak, W. J., Ind. Eng. Chem., Anal. Ed., *13*, 639-645 (1941).
9. Rimington, C., Biochemical Society Symposia No. 3. Partition Chromatography. Cambridge Univ. Press, 72-73 (1950).
10. Swain, M. L., and Brice, B. A., J. Am. Oil Chem. Soc., *26*, 272-277 (1949).
11. Witnauer, L. P., Nichols, P. L., and Senti, F. R., J. Am. Oil Chem. Soc., *26*, 653-655 (1949).

[Received May 25, 1951]

Polymerization of Styrene in the Presence of Fatty Acid Methyl Esters[1]

L. B. FALKENBURG, W. H. HILL, and HANS WOLFF, A. E. Staley Manufacturing Company, Decatur, Illinois

IN the preceding paper on the copolymerization of vegetable oils and styrene we were unable to draw any conclusions on whether the oils copolymerize with styrene or whether the reaction products are mixtures of oils and polystyrene (4). Satisfactory separation procedures for polystyrene and triglycerides were not available, and we studied therefore the copolymerization of styrene with methyl esters of fatty acids which can be separated from polystyrene by fractionation with methanol. This gave also an opportunity to investigate the effect of structural variations and of different functional groups of methyl esters on the polymerization with styrene. The object of this paper is to present our findings.

Experimental

Materials. Purified oleic acid was prepared from the Fischer U.S.P. product, using the crystallization procedure of Swern *et al.* (22). The material had an iodine value of 87.4 and contained less than 1.5% linoleic acid according to spectrophotometric analysis. The acid was used to prepare the methyl ester.

Elaidic acid was obtained from the purified oleic acid by isomerization with nitrous acid as described by Kass and Burr (10). The product had a melting point of 44°C. and an iodine value of 87.9. The acid was esterified with methanol.

Methyl ricinoleate was obtained from castor oil methyl esters by fractionation through a Vigreux column at 1 mm. Hg. (11).

Methyl 12-hydroxystearate was prepared from ricinoleate ester by hydrogenation, using Raney Nickel catalyst at 40 pounds' hydrogen pressure at 85-90°C. (6).

Methyl 12-ketostearate was obtained from the hydroxy analogue by oxidation with chromic acid in acetic acid solution (6).

Methyl 9,12-linoleate was prepared from tetrabromostearic acid by the usual debromination procedure followed by esterification of the linoleic acid with methanol.

The t,t-10,12,linoleic acid was prepared from dehydrated castor oil fatty acids according to the method of von Mikusch (13). The acid had a melting point of 56-57°C. and was employed for the preparation of the methyl ester.

Blown methyl oleate was obtained by passing air through methyl oleate at a rate of 1 liter per minute at 80-85°C. until the desired peroxide value was obtained.

Methyl 9,10-epoxystearate was prepared from methyl oleate according to the method of Findley *et al.* (5).

Methyl 9,10-dihydroxystearate was obtained by hydrolysis of the epoxy ester.

Dimethyl dilinoleate was furnished by the Northern Regional Research Laboratory through the courtesy of Dr. J. C. Cowan. The ester was prepared from soybean oil and was distilled in a centrifugal molecular still.

Residual methyl dimeric ester was obtained by esterification of commercial "Dimer Acids" manufactured by Emery Industries Inc.

The styrene was a 99% commercial grade. It was distilled prior to use in an all-glass apparatus.

Eastman Kodak White Label benzoyl peroxide was used without purification.

Fischer's C. P. Xylene was shaken with fuming sulfuric acid, washed, dried over anhydrous sodium sulfate, and distilled prior to use.

Polymerization. In a typical experiment 10 g. of styrene and 10 g. of methyl ester were dissolved in 20 g. of xylene. The mixture was refluxed for 16 hours. Generally benzoyl peroxide, in amounts from 1 to 10% by weight based on the styrene, was added as a catalyst.

Separation Procedures. Unreacted styrene and solvent were removed from the reaction mixture in vacuo. The residue was then refluxed for 15 minutes with approximately 10 times its volume of methyl alcohol, and the alcohol was decanted from the insoluble residue. Extraction with methanol was repeated twice. From the combined methyl alcohol extracts a fatty ester fraction I was obtained by evaporation of the alcohol.

The methanol insoluble residue was dissolved in approximately twice its volume of benzene, and the precipitate formed by the addition of about 10 volumes of methanol for one volume of this benzene solution was separated. The benzene methanol solution was evaporated to dryness to recover fraction II. The insoluble residue, dried in vacuum, gave fraction III.

---

[1] Presented at 25th Fall Meeting, American Oil Chemists' Society, Chicago, Ill., Oct. 8-10, 1951.

TABLE I

Results Obtained When Treating Fatty Esters With Styrene

Physical Constants of Esters				Styrenation Data							
Ester	Iodine Value	Saponification Value	Other Constants	% Catalyst	% Styrene Reacted	Non-volatile Product	Fraction Number	% of Ester Recovered	Iodine Value	Saponification Number	Other
Methyl oleate	81.4	188.5		1	86.0	Heterogeneous	I II III	76.2 10.5	79.3	187.1 0	
Methyl oleate	81.4	188.5		5	97.5	Heterogeneous	I II III	84.4 12.9	77.1 62.5	185.1 172.0 8.2	
Methyl oleate	81.4	188.5		10	98.7	Clear	I II III	91.0	74.4 42.1	181.9 107.7 12.1	
Methyl elaidate	83.6	189.2		1	89.7	Heterogeneous	I II III	88.5 8.6	81.8	187.2 0	
Methyl ricinoleate	82.5[2]	181.2	Acetyl value = 155.7	5	99.3	Heterogeneous	I II III	92.5 6.1	77.3 63.4	170.3 150.4 2.7	
Methyl 12-hydroxystearate	......	......	m.p. = 56-7°C.	5	97.8	Heterogeneous	I III	99.8	....	...... 3.1	m.p. = 56-7°C.
Methyl 12-ketostearate	......	......	m.p. = 46-7°C.	5	89.0	Heterogeneous	I III	99.7	....	...... 3.0	m.p. = 46-7°C.
Methyl 9,10-dihydroxystearate	......	170.3	m.p. = 69-70°C.	5	93.2	Heterogeneous	I II III	81.9 13.2	....	168.1 145.4 8.7	
Methyl 9,12-linoleate	169.3	189.7		1	81.8	Heterogeneous	I III	96.2	137.4	187.1 4.5	10.6% diene conjugation
Methyl 9,12-linoleate	169.3	189.7		5	83.5	Heterogeneous	I III	91.0	132.7	189.0 7.7	11.5% diene conjugation
Methyl 9,12-linoleate	163.1	......		10	97.0	Clear	I II III	76.2 16.8	143.9 126.1	180.5 172.2 44.7	5.9% diene conjugation
Methyl t,t-10,12-linoleate	......	190.3	m.p. = 23-4°C.	1	61.8	Heterogeneous	I III	79.2	....	192.0 42.0	m.p. = 22-4°C.
Methyl t,t-10,12-linoleate	......	190.3	m.p. = 23-4°C.	5	88.0	Heterogeneous	I II III	80.9 7.7	....	193.5 120.0 21.0	m.p. = 23-4°C.
Blown methyl oleate	......	234.6	P.V. = 710	None	94.5	Clear	I III	99.0	53.1	182.1 3.2	
Blown methyl oleate	......	......	P.V. = 1556	None	95.0	Clear	I III	97.1	....	180.5 4.2	
Methyl 9,10-epoxystearate	......	180.1	Epoxy oxygen = 4.9	5	86.5	Clear	I IA II III	89.5 13.9	....	181.3 159.8 64.8 5.6	
Dimethyl dilinoleate	......	194.2		None	91.3	Clear	I IA II III	48.1 43.6	....	191.8 164.9 98.1 9.3	
Dimethyl dilinoleate	......	194.2		5	89.8	Clear	I IA II III	50.1 38.6	....	186.3 179.8 ...... 7.8	
Residual dimeric methyl esters	......	175.1		5	96.1	Clear	I IA II III	61.4 31.9	....	195.8 149.4 128.0 13.0	
Methyl Stearate	4.1	199.2		10	97.9	Clear	I III	96.4	....	190.3 15.4	

(2) The 2-minute Wijs method employed—Skell & Radlove,, Ind. Eng. Chem., Anal. Ed., *18*, 67 (1946).

TABLE II

Comparison of the Separation of Copolymerized Styrene and Methyl Esters With the Separation of Mixtures of Polystyrene and Esters

Ester	Type	Fraction	% of Ester Recovered	Saponification Number	Remarks
Blown methyl oleate P.V. = 710	Copolymerization conditions	I	94.8	194.9	97.7% styrene polymerized. Non-volatile—clear resin.
		II	......	63.8	
		III	......	22.0	
Blown methyl oleate P.V. = 710	Mixture	I	77.3	224.6	Styrene polymerized with 5% catalyst in xylene solution. 92.4% styrene polymerized. Ester added to polystyrene solution. Mixture a clear resin.
		II	24.2	129.4	
		III	......	9.7	
Residual methyl dimeric esters	Copolymerization conditions	I	61.4	195.8	97.1% styrene polymerized. Non-volatile—clear resin.
		IA	39.1	149.4	
		II	......	128.0	
		III	......	13.0	
Residual methyl dimeric esters	Mixture	I	54.5	191.2	97.8% styrene polymerized (in xylene solution with 5% catalyst). Dimer ester refluxed in xylene with 5% benzyl peroxide. Solutions mixed. Residue—clear resin.
		IA	50.1	149.5	
		II	......	99.7	
		III	......	8.0	
Residual methyl dimeric esters	Copolymerization conditions	A*	114.5	155.2	91.1% styrene polymerized. Non-volatile—clear resin.
		B	......	162.4	
		C	......	113.2	
		D	......	7.7	
Residual methyl dimeric esters	Mixture	A*	109.1	158.7	Styrene polymerized with 5% benzyl peroxide in xylene. Ester added to polystyrene solution. Non-volatile—clear resin.
		B	......	164.0	
		C	......	127.3	
		D	......	7.3	
Methyl 9,10-epoxystearate	Copolymerization conditions	I	57.4	181.3	93.5% styrene polymerized. Non-volatile—clear resin.
		II	33.8	125.6	
		III	......	7.7	
Methyl 9,10-epoxystearate	Mixture	I	85.1	177.4	Styrene polymerized with 5% catalyst in xylene. 96% styrene polymerized. Ester refluxed in xylene with 5% catalyst. Solutions mixed. Non-volatile—clear resin.
		II	......	109.9	
		III	......	7.9	
Methyl 9,10-epoxystearate	Mixture	I	86.8	172.8	Styrene polymerized in xylene with 5% catalyst. 94% styrene polymerized. Ester added to polystyrene solution. Non-volatile—clear resin.
		II	......	90.5	
		III	......	6.0	

* Special fractionation procedure employed. Non-volatile dissolved in twice its volume of benzene. By adding 10 volumes of petroleum ether a precipitate (1) was formed. The benzene-petroleum ether solution was evaporated to dryness to yield fraction A. This fraction was extracted with petroleum ether by refluxing with 3 times its volume. The residue was labeled fraction B. Precipitate (1) was redissolved in twice its volume of benzene and reprecipitated by adding 10 volumes of petroleum ether. The soluble fraction was C; the precipitate D.

In several experiments the precipitation procedure was omitted.

In the case of methyl epoxystearate the methanol extraction of the non-volatile residue was followed by a similar extraction, using petroleum ether to give a fraction IA. The residue obtained was dissolved in benzene, and petroleum ether was employed as the precipitant.

The dimethyl dilinoleate and residual dimeric ester products were also submitted to both the methanol and petroleum ether extractions. However the residues were dissolved in approximately twice their volume of an ethyl ether acetone (50-50 by volume) mixture and precipitated with petroleum ether. Several sets of experiments were performed in which mixtures of polystyrene (prepared by refluxing styrene in xylene for 16 hours with 5% benzoyl peroxide) and the ester were prepared and submitted to the separation procedure and the fractions compared with those obtained from the copolymerized products.

Methods of Analysis

Iodine Value. The Wijs 3-minute procedure was used except where noted (9).

Peroxide Value. The Wheeler method was employed for determining the amount of peroxide in the esters (23).

Acetyl Value. The method of Helrich and Rieman was used (7).

Epoxy Oxygen. The procedure of Swern *et al.* was employed (21).

Saponification Values. The standard A.O.C.S. method was employed. In the case of polystyrene fractions the sample was dissolved in toluene before addition of the alcoholic KOH.

Conjugation. The degree of conjugation was measured with a Beckman Quartz Spectrophotometer, Model DU, using the A.O.C.S. Tentative Method Cd: 7-48 (12).

Percentage of Styrene Reacted. The amount of styrene which polymerized was calculated by means of the following equation:

% styrene reacted $= 100\,(R - E)/S$; where
$R =$ percentage of non-volatile in reaction product,
$E =$ percentage of ester in reaction mixture, and
$S =$ percentage of styrene in reaction mixture.

The methyl esters used in this study are listed in Table I along with their analytical constants, the percentage of catalyst employed, and the percentage of the styrene which polymerized. In addition, the results of the separation of the products are given.

In Table II comparative data are presented on separations of reaction mixtures of styrene and fatty esters heated in the presence of catalyst with separations of polystyrene and fatty ester mixtures.

Results and Discussion

There are two schools of thought concerning the polymerization of styrene and vegetable oils as outlined in the preceding paper (4), and also references (8), (14), and (17). Homogeneity of the reaction products of oils and styrene was often given as evidence for copolymerization (1, 8, 18). Inability to separate the reaction products of styrene and fatty acids or esters was also presented as evidence for interpolymerization of these reactants (3, 16).

Another group of investigators considers "styrenated" oils as mixtures of oils and polystyrene (2, 15). Our findings lend support to the idea that no reaction takes place between styrene and fatty acid radicals. After the removal of solvent we obtained for the most part heterogeneous, opaque mixtures which could be readily separated into relatively pure fatty esters and polystyrene as evidenced from the results presented in Table I.

Fraction I in the separation of the reaction products consists essentially of pure fatty esters. The second fraction is also a fatty ester fraction although of lesser purity. The sum of these two fractions is close to the total amount of starting esters, showing that very little if any copolymerization with styrene occurred.

On the other hand, blown methyl oleate and polymeric fatty acid esters without catalyst, and methyl epoxystearate with 5% and methyl oleate and linoleate with 10% catalyst yielded clear transparent reaction products.

These homogeneous reaction products could not be easily separated into fatty esters and polystyrene by the fractionation procedure; we used in some cases an additional fractionation step. However we experienced the same difficulties in separating mixtures of polystyrene with these esters as shown in Table II. The fractions obtained on extracting and precipitating mixtures of polystyrene and these fatty esters and the ones obtained from the esters and styrene submitted to copolymerizing conditions are so similar that neither clarity of the reaction products nor inability of separation in starting ester and polystyrene can be considered as evidence for copolymerization of epoxystearate, blown methyloleate, and residual dimeric esters with styrene. From these findings it would appear that homogeneity depends on the mutual solubilities of polystyrene and fatty esters; the same conditions may apply for homogeneity of "styrenated" oils. In the case of oils however the conditions necessary to obtain mutual solubility are much more exacting. For example, the viscosity, the degree and type of unsaturation, and the amount of oxidation of the oil are important factors (1, 4, 8, 14, 19). The polystyrene itself, its molecular weight, and structural features would also be expected to influence mutual solubility.

The effect of viscosity of an oil on the homogeneity of the styrenated product has been described previously, increased viscosity promoting greater compatibility (4, 8). We observed the same phenomenon. Polymeric fatty esters, being more viscous than unpolymerized esters, gave a clear product whether reacted with styrene or mixed with polystyrene.

The role of unsaturation in oils in promoting homogeneity is not apparent from our results with such esters. The unsaturated esters we investigated appear to exert little if any influence for they are almost totally immiscible with polystyrene and are recovered practically quantitatively. The unsaturation in the methyl linoleate was noticed to have partially shifted to a conjugated form. This finding is different from the results observed with triglycerides where it has been noted that increased unsaturation of the fatty acid components promotes homogeneity on styrenation (8, 14). Diene conjugation per se does not appear to increase homogeneity in the reaction of fatty esters with styrene. For example, neither 9,12-methyl linoleate nor t,t-10,12-methyl linoleate give homogeneous products.

We have not examined trienoic esters, but, working with linseed oil and linseed fatty acids which are rich in trienoic constituents, Petit and Fournier found no evidence for copolymerization (15). However these authors found evidence for some reaction of one mole of styrene with one mole of unsaturated fatty acid by the Diels-Alder addition. A small amount of reaction of this type could lead to homogeneity in triglycerides while it would not necessarily be sufficient to give homogeneity with monoesters. Conjugated triene unsaturation as with tung oil has been examined by Brunner and Tucker (2), who found evidence for copolymerization. It is quite possible however that in this case too a Diels-Alder reaction between styrene and fatty acid radicals contributed to homogeneity.

The influence of the concentration of catalyst on the homogeneity of "styrenated" oils has been previously demonstrated (4). We obtained similar results with the linoleate and oleate esters. Using 5% catalyst, no homogeneous product was obtained, but, by increasing the amount of benzoyl peroxide to 10%, a compatible mixture could be obtained. We have also found that a homogeneous mixture is obtained with methyl stearate if 10% benzoyl peroxide is present. Schulz showed that increasing the concentration of benzoyl peroxide in styrene will decrease the average molecular weight of the polystyrene (20). It can be expected that fatty esters and oils are more miscible with polystyrene of low average molecular weight than with polystyrene of high average molecular weight.

Blown oils (4, 14, 19) and our results on blown methyl oleate show that oxidation leads to homogeneous products with styrene. Although our results cannot rule out small amounts of these esters in the polystyrene, the fact that the saponification values in extracted residues from mixtures are as high as the ones from copolymerizing condition products would indicate that no fatty esters interpolymerized with the styrene. The effect of the hydroperoxide, one of the principal constituents of blown esters and oils, may be similar to the effect of increasing the concentration of peroxide catalyst. Since blown methyl oleate is miscible with polystyrene and the unblown ester is not, our findings do not allow any conclusions as to the presence and possible importance of such a catalytical effect of hydroperoxide groups on the styrene polymerization.

Blowing of unsaturated fatty esters gives not only hydroperoxides but also other oxygenated groups such as keto, hydroxy, and possible epoxy groups. Of these functional groups only the epoxy leads to homogeneity. This group might therefore be an additional factor in giving homogeneous products with blown oils.

Our results would indicate that little if any copolymerization takes place when styrene is polymerized in the presence of the fatty acid esters under the conditions outlined in this paper. The "styrenated" oils are possibly complex mixtures of the fatty components and polystyrene but not necessarily copolymers in the true sense. The fact that some of the homogeneous products may not be true copolymers does not necessarily detract from their utility as surface coating agents.

It would be of interest to study the effect of other catalysts, of modifiers, and of the mass and emulsion reaction techniques when polymerizing styrene in the presence of fatty acid methyl esters and to investigate the resulting products.

Summary

Data on the products obtained on polymerizing styrene in the presence of various methyl esters of fatty acid have been presented. These data show that no copolymerization between the esters and styrene occurs and that homogeneity of some of the reaction products cannot be considered as proof for interpolymerization.

REFERENCES

1. Armitage, F., Hewitt, D. H., and Sleightholme, J. J., J. Oil and Colour Chem. Asso., *31*, 437-450 (1949).
2. Brunner, H., and Tucker, D. R., Research, *2*, 42-46 (1949).
3. Dyer, E., and Maxwell, J. L., J. Am. Oil Chem. Soc., *26*, 649-51 (1949).
4. Falkenburg, L. B., Hill, W. H., and Wolff, Hans, J. Am. Oil Chem. Soc. (in press).
5. Findley, T. W., Swern, D., and Scanlan, J. T., J. Am. Chem. Soc., *67*, 412-414 (1945).
6. Grummitt, O., and Siedschlag, K. G., J. Am. Oil Chem. Soc., *26*, 690-1 (1949).
7. Helrich, K., and Rieman III, W., Anal. Chem., *19*, 691 (1947).
8. Hewitt, D. H., and Armitage, F., J. Oil and Colour Chem. Asso., *29*, 109-128 (1946).
9. Hoffmann, H. D., and Green, C. E., Oil and Soap, *16*, 236-238 (1939).
10. Kass, J. P., and Burr, G. O., J. Am. Chem. Soc., *61*, 1062-1066 (1939).
11. Kass, J. P., and Radlove, S. B., *ibid.*, *64*, 2253-2257 (1942).
12. Mehlenbacher, V. C., editor, "Official and Tentative Methods of the American Oil Chemists' Society," Chicago, Ill., 1948.
13. Mikusch, J. D. von, J. Am. Chem. Soc., *64*, 1580-1582 (1942).
14. Peterson, N. R., Am. Paint J., *32*, No. 4, 32, 34, 37-8, 40 (1948).
15. Petit, J., and Fournier, P., Official Digest Fed. Paint and Varnish Prod. Clubs, pp. 609-614, August 1950.
16. Powers, P. O., Ind. Eng. Chem., *42*, 2096-2099 (1950).
17. Rinse, J., Chem. Weekblad, *22*, 373-377 (1950); C.A. *44*, 8675 (1950).
18. Rinse, J., and Korf, C., J. Oil and Colour Chem. Asso., *32*, 593-597 (1949).
19. Schroeder, H. M., and Terrill, R. L., J. Am. Oil Chem. Soc., *26*, 153-157 (1949).
20. Schulz, G. V., and Staudinger, H., Z. Physik. Chem., *39B*, 246-274 (1938).
21. Swern, D., Findley, T. W., Billen, G. N., and Scanlan, J. T., Anal. Chem., *19*, 414-415 (1947).
22. Swern, D., Knight, H. B., and Findley, T. W., Oil and Soap, *21*, 133-139 (1944).
23. Wheeler, D. H., *ibid.*, *9*, 89-97 (1932).

[Received June 14, 1951]

Modification of Vegetable Oils. XII. Plasticity of Some Aceto Derivatives of Monostearin[1,2]

R. O. FEUGE, E. J. VICKNAIR, and N. V. LOVEGREN, Southern Regional Research Laboratory,[3] New Orleans, Louisiana

A RELATIVELY stable fat which solidifies to a non-greasy yet flexible solid should have many potential uses. So far as the authors are aware, a fat which is non-greasy and highly flexible at the same temperature has never been prepared heretofore. Normally non-greasiness and flexibility in fats are mutually exclusive properties. The authors have found that fats composed of certain mixtures of acetostearins are extremely flexible solids at and below room temperature. The preparation and some of the properties of these acetostearins are described here.

Preparation of Acetostearins

Acetostearins were prepared by reacting acetic anhydride with monostearin. A temperature of 110°C. and a reaction time of one hour were used in most instances. The reactants were stirred and kept under dry hydrogen to prevent reaction of the acetic anhydride with atmospheric moisture. The reaction was interrupted as desired by adding hot water to the reaction mixture and stirring for 10 minutes to hydrolyze the unreacted acetic anhydride. After washing the reaction product with distilled water it was dried by warming it under reduced pressure and stripping with hydrogen.

Three monostearins, referred to as A, B, and C, were used to prepare the acetostearins. Monostearin A, prepared from pure stearic acid, contained 99.2% monostearin by analysis (1) and had a hydroxyl value of 306.5 according to the acetylation method of West *et al.* (2), modified by using one part of acetic anhydride to three parts of pyridine. Monostearin B was a commercial, molecularly distilled product. It had a hydroxyl value of 335.5 and a monoglyceride content of 91.5%. The average molecular weight of the combined fatty acids in this product was 270.5, which corresponds to a 1:1 ratio of stearic and palmitic acids. Of the three monostearins only monostearin B contained free glycerol, about 2%. Monostearin C was a technical grade product made from completely hydrogenated cottonseed oil. Its hydroxyl value was 236.9, and it contained 61.0% monoglycerides of fatty acids, having an average molecular weight of 280.0.

Physical properties of the acetostearins formed by reaction of monostearin with acetic anhydride could be controlled to a considerable extent by manipulating the reaction time, temperature, and proportion of acetic anhydride employed. None of the reactions was carried to 100% completion, as evidenced by the hydroxyl value of the finished products. A plot of the hydroxyl value *vs.* reaction time at 110°C. between one hydroxyl-equivalent of monostearin B and one mole of acetic anhydride is reproduced in Figure 1. A similar curve was obtained when different proportions of acetic anhydride were reacted for one hour at 110°C.

The ratios of monostearin to acetic anhydride used in making the products subjected to elongation and bending tests were such that one equivalent of hydroxyl in the monostearin was mixed with 0.5, 1.0, and 2.0 moles of acetic anhydride, respectively. The reactions were stopped after one hour at 110°C.

Since the acetostearins were used solely for making physical measurements, no precautions were taken to assure that they were entirely free of odor and taste.

Composition of the Products

The free fatty acid content of the acetostearins was nearly always between 1.0 and 1.5%, which is quite low in view of the fact that two of the monostearins used to prepare the products contained several tenths of a per cent of free fatty acids. Therefore it must

---

[1] Report of study made under the Research and Marketing Act of 1946.

[2] Presented at the 42nd Annual Meeting of the American Oil Chemists' Society, New Orleans, La., May 1-3, 1951.

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