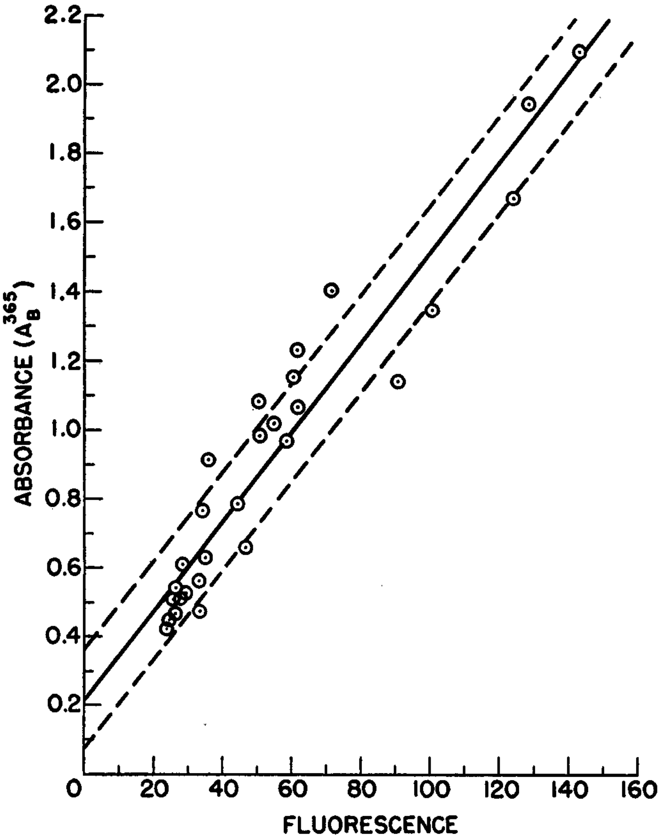

FIG. 1. Relation between fluorescence and absorbance due to brown substances in soybean lecithin.

brown color, A_B^{365}, calculated from measurements of the 5% solutions of lecithin in carbon tetrachloride in 1-cm. cells, is plotted against the fluorescence of 0.1% solutions measured as described above. A correlation coefficient is calculated at 0.95. The regression equation for the correlation line is:

$$A_B^{365} = 0.216 + 0.01313\,F \qquad (5)$$

where F (fluorescence) is the unit of scale reading. The standard error of estimate is 0.140. Lines indicating this standard error are shown in Figure 1 together with the line of the regression equation. This linear relation indicates that the fluorescence is mainly due to brown substances and that under the conditions used the fluorescence is little affected by such factors as self-absorption, absorption by carotenoids or chlorophyll and its degradation products, and fluorescence by constituents other than the brown substances.

Of the samples tested 9 were plastic lecithin and 19 were fluidized. Eleven were considered to be unbleached, 9 were single bleached, and 8 were double bleached. Inspection of the points on the curve indicated that neither source nor treatment had an effect on the behavior of the different types of samples. Two methods for measuring the extent of browning of soybean phosphatides are indicated by this work; one a spectrophotometric method requiring the measurement of absorbance at two wave-lengths and a calculation as prescribed by equation 4; the second a fluorophotometric method depending on the fluorescent property of browning reaction products. While the spectrophotometric method has been used successfully in the case of the data of Figure 1 in order to verify the expected linear relations between absorbance and fluorescence, it is believed that its use will be limited to research purposes. The instability, variability, and uncertainties of the absorption ratio for the carotenoid mixture introduces relatively large errors into corrections for carotenoid absorptions.

The determination of fluorescence is simple and rapid and appears to be uncomplicated by the presence of pigments and major components. In view of the linear relation between fluorescence and the calculated spectral absorbance, a measurement of fluorescence should prove a useful index of browning.

Summary

The fluorescence of soybean lecithin increases in a linear fashion with an increase in brown substances. Since the measurement of fluorescence is simple and rapid, this measurement should prove a useful index of browning.

Acknowledgment

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Direct Esterification of Phenols with Higher Fatty Acids[1,2]

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THE GENERALIZATION that phenols may not be directly esterified with fatty acids has long been incorporated in textbooks of organic chemistry. Thus Conant and Blatt (1) state that "the acyl derivatives (the esters) of phenols cannot be made by direct esterification. They are prepared by the use of acid anhydrides or acid chlorides." Similarly Hill and Kelly (2) have pointed out the following: "phenol reacts with an acid chloride or anhydride, but not with an acid, forming an ester." Ralston (3) in his exhaustive treatise on fatty acids does not mention a single instance where these compounds are used to esterify phenols directly.

The discovery of the direct esterification of phenols with fatty acids evolved from the attempt to devise

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[2] Paper No. 155, Journal Series, Research Laboratories, General Mills Inc.

TABLE I

PREPARATION OF PHENOLIC ESTERS

Preparation of Phenolic Esters

Ester	Amt. of Phenol g.	Amt. of Acid g.	Catalyst	Amount of Catalyst g.	Temp.	Time of Reaction hrs.	Yield of Purified Product based on phenol used %	n_D^{30}	Density D_{25}^{25}	m.p. °C.	b.p. °C.	Acid No.	OH No.	% C Found	% C Calcd.	% H Found	% H Calcd.	Remarks
Phenyl butyrate	94	94	H_2SO_4	2	115-30°	71	80	1.4880	1.0156	....	110-11°/17mm.	8.29	....	73.81	73.17	7.07	7.32	Benzene was used as azeotrope.
Phenyl caprylate	75	75	H_2SO_4	2	125-40°	12	70	......	......	....	150°/10mm.	1.6	....	75.92	76.32	8.87	9.09	Eastman Caprylic acid was used. Benzene was used as azeotrope.
Phenyl laurate	58	58	H_2SO_4	2	150°	5	77.5	1.4772	D_{30}^{30} 0.9356	....	145-6°/160μ	0.35	....	78.04	78.98	10.05	10.14	Eastman Lauric acid was used.
Phenyl[4] stearate	94	280	H_2SO_4	1	155°	24	47	......	......	50-1°	200-5°/30μ	12.6	32.0	.....	.....	.....	.....	Commercial 90% stearic acid was used. Benzene was used as azeotrope.
Phenyl oleate	120	282	H_2SO_4	2	180°	16	33	n_D^{24} 1.4830	......	....	200-10°/600μ	0.33	....	.....	.....	.....	.....	Emery 98.5% oleic acid was used. Iodine value — 66.75.
p-chlorophenyl caprylate	64	72	H_2SO_4	2	160°	12	82	1.4938	D_{25}^{25} 1.0564	....	135°/440μ	1.2	....	66.74	66.01	7.53	7.46	Percent Cl found 13.89 (calculated 13.95).
p-chlorophenyl laurate	64	100	H_2SO_4	2	170°	12	73.5	......	......	40-2°	175°/450μ	2.0	....	69.92	69.56	8.70	8.69	Percent Cl found 11.26 (calculated 11.43).
p-chlorophenyl stearate	21.5	47.5	H_2SO_4	2	143-5°	8	58	......	......	59-63°	195°/75μ	6.8	....	73.08	73.00	9.84	9.88	Eastman stearic acid was used. Percent Cl found 8.85 (calculated 8.99).
p-*t*-butylphenyl caprylate	37.5	36.0	H_2SO_4	2	145°	6	73	1.4830	D_{25}^{25} 0.9381	....	108-10°/20μ	0.82	....	78.30	78.26	10.14	10.14	. . . .
p-*t*-butylphenyl laurate	30	40	H_2SO_4	2	150°	6	65	1.4817	D_{25}^{25} 0.9247	....	145-55°/30-50μ	0.93	....	79.65	79.52	10.77	10.52	. . . .
p-*t*-butylphenyl stearate	25	47.5	H_2SO_4	2	150°	6	50	......	......	46-7°	200°/40μ	0.59	....	80.65	80.76	11.31	11.54	Eastman stearic acid was used.
Cardanol ester of soya bean oil fatty acids	150	150	lead stearate	3	235°	72	97	1.4940	......	....	....	1.52	4.9	.....	.....	.....	.....	Distilled Cardanol was used.
p-phenylphenyl stearate	85	141	H_2SO_4	2	170°	6	62	......	......	74-6°	245°/50μ	....	....	83.15	82.57	10.54	10.09	Commercial 90% stearic acid was used. Product was recrystallized from Solax.
β-naphthyl stearate	72	141	H_2SO_4	2	153°	21	70	......	......	70.5-73.5°	230°/20μ	1.3	37.6	.....	.....	.....	.....	Commercial 90% stearic acid was used.
Resorcinol Monolaurate	110	200	H_2SO_4	2	145-55°	2	53	......	......	82-3°	....	....	....	74.04	73.97	9.45	9.56	Commercial 90% lauric acid was used. Product was recrystallized several times from alcohol.
Resorcinol distearate	55	281	zinc stearate	4	240°	8	14	......	......	64.5-6.5°	....	2.9	0	.....	.....	.....	.....	Commercial 90% stearic acid was used.
m-Phenylene dioleate	88	451	Triphenyl phosphite	3	216-21°	10	88.5	......	......	....	....	5.3	0	.....	.....	.....	.....	Emery's 98.5 oleic acid was used. Product heated to 275° at 50μ.
2,5-di-*t*-butyl hydroquinone dicaprylate	111	144	H_2SO_4	2	155°	22	71	1.4815	......	....	165-200°/20-50μ	1.8	30.0	.....	.....	.....	.....	. . . .
2,5-di-*t*-butyl hydroquinone distearate	111	282	zinc stearate	4	235°	94	99	......	......	78-80°	....	1.1	35.5	.....	.....	.....	.....	Commercial 90% stearic acid was used. Product heated to 250° at 10μ and recrystallized from Solax.
p,*p*′-dihydroxy biphenyl distearate	52	158	H_2SO_4	2	153-62°	24	57	......	......	109-115.5°	....	1.1	13.3	.....	.....	.....	.....	Commercial 90% stearic acid was used. Product recrystallized from butanol.
2,2-bis-*p*-hydroxyphenyl propane dicaprylate	114	144	H_2SO_4	2	157-63°	37	40	1.5144	......	....	210-45°/30-100μ	3.8	11.1	.....	.....	.....	.....	. . . .
2,2-bis-*p*-hydroxyphenyl propane dilaurate	114	200	lead stearate	2	236-90°	48	95	1.5020	......	....	....	0.5	1.5	.....	.....	.....	.....	Product heated to 280° at 0.8mm.
2,2-bis-*p*-hydroxyphenyl propane distearate	57	141	no catalyst	..	210-29°	117	98	......	......	55-3°	....	1.8	21.2	.....	.....	.....	.....	Commercial 90% stearic acid was used. Product heated to 280° at 50μ.

a procedure for estimating the phenolic hydroxyl groups present in a partially hydrogenated *p-tert*-butylphenol-formaldehyde resin. The projected procedure involved the determination of the aliphatic secondary hydroxyl groups by esterification with higher fatty acids. This value subtracted from the total hydroxyl content, determined by the acetic anhydride method, should have provided an indication of the quantity of phenolic hydroxyl groups present. It was indeed surprising to discover that both the aliphatic and the phenolic hydroxyl groups of the partially hydrogenated polymer were esterified by higher fatty acids with relative ease at 220-250°C.

To test the general applicability of this reaction, fatty acid esters of many monohydric and dihydric phenols were prepared by direct esterification. Since in this investigation the reaction was of greater interest than the actual products obtained, much of the work was carried out with commercially available fatty acids and mixtures thereof. The phenols used included: phenol, *p-tert*-butylphenol, *p*-chlorophenol, *p*-phenylphenol, *o*-phenylphenol, cardanol, β-naphthol, 2,2-bis-*p*-hydroxyphenylpropane, *p,p'*-dihydroxydiphenyl, and 2,5-di-*tert*-butyl hydroquinone. Among the fatty acids used were: stearic acid, lauric acid, caprylic acid, oleic acid, and soya bean oil fatty acids. The methods of preparation yields and properties are given in Table I.

The esterification was accelerated by catalysts such as sulfuric acid, phosphoric acid, zinc stearate, lead stearate, and triphenyl phosphite. Of these, sulfuric acid was the most effective although its use was limited to distillable products since it caused the reaction mixture to darken. Zinc and lead stearate were equal to each other in activity but exerted less catalytic effect than sulfuric acid.

The esters were prepared azeotropically, using xylene or benzene to remove the water of esterification. The reaction temperature was controlled by the quantity of xylene or benzene present in the reaction mixture as well as by the amount of heat applied externally. Reaction times varied from 6 to 117 hrs. whereas temperatures varied from 115-290°C. The volatile esters were fractionally distilled whereas the unreacted fatty acids were removed from the nonvolatile esters by heating the products at 250°C. below 0.1 mm. No attempt was made to obtain maximum yields.

Experimental

o-Phenylphenyl Stearate. A mixture of *o*-phenylphenol (85 g.), stearic acid (141 g.), xylene (110 cc.), and conc. sulfuric acid (2 g.) was heated at 173-8° with agitation for 22 hrs. The reaction vessel was equipped with a water-trap of the Dean-Stark type, which allows the removal of the water formed during esterification azeotropically. After six hours of reaction 90% of the theoretical quantity of water had collected. The theoretical amount of water was not obtained until the reaction mixture was heated for 22 hrs. The product was diluted with xylene, washed with water, and dried over anhydrous sodium sulfate. The solution was filtered and concentrated, and the residue was fractionally distilled through a 1-ft. Vigreux column. A fraction (14 g.) was collected, which distilled below 215°/0.05 mm. The main fraction, 177 g., $b_{50\mu}$ 230°, was a low-melting solid. The yield was 81%. The product was recrystallized from Solax and acetone. Melting point 42-3°; % carbon found 82.86, 82.61 (th 82.57); % hydrogen found 10.18, 10.24 (th 10.55).

This is a general procedure. Preparations, yields, physical properties, and analyses of esters are given in Table I.

Acknowledgment

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Solubility of 1-Monostearin in Various Solvents[1]

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IN THE COURSE of research on acetostearins and other synthetic fats, large quantities of 1-monostearin were needed. These were prepared satisfactorily from technical grade products by fractional crystallization from solvents according to conditions described in earlier publications (4, 10). To prepare products of high purity however, repeated crystallization from solvents was necessary; and it became desirable to know more exactly the solubility of 1-monostearin in a number of common solvents. The solubility determinations which were made are described in the present paper.

Materials

Monostearin. The 1-monostearin used in the solubility determinations was prepared as described by Singleton and Vicknair (10). Purified stearic acid and 36.2% of U.S.P. glycerol were reacted at 200°C. for 3 hrs., using 0.1% of sodium hydroxide as catalyst. The reaction product was acidified to destroy the soap and then washed repeatedly with hot water, followed by fractional crystallization from an isopropanol-water solution (70% isopropanol). Final purification consisted of repeated crystallization from commercial hexane.

Purity of the product was 99.2%, according to the periodic acid method of analysis (5), and the melting point was 81.8°C. by the capillary tube method, which

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