protein isolates (6), and the flavor of the isolates was compared. The results are also shown in Table IV and indicate that the overall scores are the same and that the flavor intensity values for the four different flavors are not significantly different.

This study indicates only minor differences between BM_2 and TS-280 soybeans. The proximate analysis, protein, amino acid, and fatty acid composition and flavor evaluation show that the mature seeds from soybeans grown in Mexico and soybeans grown in Central Illinois are very similar.

ACKNOWLEDGMENTS

J. F. Cavins made the near infrared reflectance, amino acid and methyl ester analyses.

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Maleyl Esters of Monoglycerides of Saturated Fatty Acids

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ABSTRACT

Esterification between maleic anhydride and monoglycerides of saturated fatty acid has been studied. The nature of reaction vessels, temperature and reaction time have been evaluated in view of the product distribution in the final product. Concentration of monoesters (half-esters) diesters and dimers has been calculated and related to the reactants' ratio, time and temperature of the esterification.

INTRODUCTION

Esterification of maleic anhydride with almost any straight chain alcohol has been carried out yielding mono- and dialkylmaleates (1). Addition of sodium bisulfite to the above esters forms sodium sulfosuccinic alkyl esters, known as important detergents and wetting agents (1).

Caryl (2) in his review, claims that he was able to form, from 50 alcohols, over 50 diesters, 50 half-esters, and 1,225 mixed esters (all sodium salts). All these esters can be further esterified with methyl or some other alkyl or aryl substitute to prepare, theoretically, over 1,125,000 different possible compounds. The majority of the sulfosuccinic esters that have been made have surface-active properties.

Esterification of succinic anhydride and monoglycerides of fatty acids has been the subject of a US patent in 1966 (3). The half-esters of succinylated monoglycerides (SMG) were mentioned as possible food emulsifiers mainly in the bread baking industry (4).

The esterification of monoglycerides with maleic anhydride yields maleyl esters, which can be further sulfonated with sodium bisulfite to form sodium sulfosuccinic monoglyceryl esters. In order to obtain valuable wetting and detergent agents, it is very important in the first stage to prepare mainly the half-esters (or monoesters) and to minimize as much as possible the formation of diesters, other byproducts, or polymerization reactions. Such unwanted products would give, on further sulfonation, poor surfactants. To the best of our knowledge, direct esterification between maleic anhydride and commercial distilled monoglycerides of fatty acids has not yet been fully studied (1,3), and no reaction parameterization has been done.

The present report reinvestigates the esterification reaction between maleic anhydride and distilled monoglycerides under controlled conditions. The type of reaction vessels, reactant ratios, temperatures and time were evaluated. Efforts have been made to obtain full product distribution and to determine the amount of dimers and diesters formed in this reaction.

EXPERIMENTAL

Reagents

Distilled monoglycerides, containing 90–92 wt % monoglycerides, 6–8 wt % diglycerides and 1–2 wt % glycerol from tallow (Dimodan TH, Grindsted, Denmark), from palm (Dimodan PVP, Grindsted), from vegetable oil (Myvaplex 600, Eastman Kodak and Empilan GMS 90 from

Albright & Wilson, England) were used. Myvaplex 600 was used throughout most of the experiments and the optimum results were checked with the others. The monoglyceride content was evaluated by the periodate method and gas liquid chromatography (GLC). As traces of water were found in the monoglyceride, a pretreatment before each test was necessary and the monoglyceride was heated to 130–140 C, until the bubbling stopped and an additional heating of 10–15 min was employed to ensure the complete elimination of water. The monoglyceride content was checked to ensure that no chemical change had occurred. Maleic anhydride from Ftalital, Italy (commercial sample) and from Riedel de Haehn (analytical grade) was used. Prior to each experiment, the maleic anhydride was tested for free maleic acid by dissolving the maleic anhydride in xylene (1 mL in 25 mL xylene). A clear solution indicates the absence of any free maleic acid. Throughout most of the experiments, the Ftalital anhydride was used and the Riedel de Haehn maleic anhydride was used for comparison at the optimum reaction conditions.

Experimental Procedure

Prior to any esterification reaction the monoglyceride was preheated to 130–140 C to eliminate water, the temperature was then adjusted to the chosen reaction temperature and the maleic anhydride was introduced. The reaction time was measured from the moment the maleic was added. Normally, with the introduction of maleic anhydride, the temperature drops and, 5–10 min later with the beginning of the reaction, the temperature rises. In order to find the optimum conditions for maximum monoester and minimum diester content in the final product, several types of vessels were examined.

A closed vessel comprised a one-necked Erlenmayer flask, equipped with a thermometer and an arrangement for the possible escape of vapors during the experiment. Upon heating, some of the maleic anhydride crystallizes on the unheated flask-neck which also serves as a cooling tower. A reflux type of vessel comparised a three-necked flask with a reflux column. The flask was heated with a paraffinic oil bath in which it was completely immersed. The open type of vessel, though similar to the closed one, was completely open, and as the reaction mass occupied by volume one third to one half of the vessel, the unheated neck had the role of a reflux column. The maleic anhydride, which normally sublimes and evaporates during the experiments, crystallized on the neck and was periodically reintroduced into the flask. In some experiments, an open type of vessel heated by complete immersion in a paraffinic bath was used. Under such conditions, the maleic anhydride evaporated to a large extent.

Samples were withdrawn from the esterification vessel at a given time and were analyzed for their monoglyceride content, acid value, maleic acid content, (FMA/BMA–free and bound maleic acid), and diester content. The product composition was determined by calculation.

METHODS OF ANALYSIS

Analysis of reactants and products was done by conventional wet chemistry extraction techniques (especially developed for this study) and in part by GLC methods.

Monoglyceride Content

Normally the monoglyceride (MG) and glycerol (G) content of the reactant was evaluated using the periodate method (5). The analysis was quite tedious since the monoglyceride maleate, being an emulsifier, disturbs the chloroform/water phase separation in the original method.

For most experiments, the monglyceride content was obtained using the standard method with small modifications. The samples were dissolved in chloroform and without further separation, or removing the glycerol titrated with reagents. The result is represented in terms of monoglyceride content:

$$\% \text{ MG + G (as MG)} = \frac{(V_{blank} - V_{sample}) \times 1.7927}{W_{sample}}$$

The reagents and some products were examined by GLC for monoglyceride content and the results were compatible with those of the periodate method. The samples containing ca. 20 mg of monoglyceride, were diluted in 1 mL of reagent composed of 9 mL dry and fresh pyridine, 3 mL HMDS (hexamethyldisilazane, Fluka) and 1 mL TCS (trimethylchlorosilane, Fluka). An internal standard made from 20 mg cholesteryl acetate in 25 mL pyridine was generally used (6).

A Packard model 420 gas chromatograph, equipped with 3'x 1/8" glass column packed with 3% OV-17 on Gaschrom-Q with a flame ionization detector was used. A temperature program was used from 110 to 320 C at 10 C/min.

Maleic Acid Content

Free and bound maleic acid (FMA/BMA) have been determined by the FMA in water and the BMA in benzene, according to the method described in the literature (7) for succinylated monoglycerides. Some difficulties were encountered during the separation, due to the presence of the emulsifier. The addition of sodium chloride solved the separation problem.

Diester Content

The diester content was calculated by extraction of the alkaline water solution of the product with diethyl ether. Usually 0.5 g of maleic ester was dissolved in 100 mL of water by addition of NaOH to a pH of 9.5–10. A portion of 100 mL diethyl ether was added in a separating funnel and the diethyl ether phase was separated. The extraction was continued with two portions of 50 mL of fresh diethyl ether. The diethyl ether phases were subsequently washed with three portions of water. The ether phase was evaporated, 10 mL of acetone were added and the product was dried in the oven at 70 C to constant weight.

Product Composition Calculation

In the alkaline medium the monoester of the sodium salt is water soluble and the diester will be diethyl ether soluble. The unreacted monoglyceride is also diethyl ether soluble, therefore the ether portion (DES) was also checked for monoglyceride content (MG_{DES}). Both results were represented as percentages from the product: diesters (%) = DES (%) – MG_{DES} (%). The monoester content was determined from bound maleic acid, calculating first the bound maleic acid as diester:

$$\% \text{ BMA (as diester)} = (\% \text{ diester}) \times \frac{116}{780}$$

and finally:

$$\% \text{ BMA (as monoester)} = \text{BMA} - \text{BMA (as diester)}$$

In the experiments in which the acid value decreased significantly, it was assumed that some polymerization had occurred (8, 9). This assumption was sustained by material balance calculations. As no direct method for calculating

dimer content was found, an estimation was made and re-examined by the BMA balance. For instance, if 7.5% dimer should be formed, it would account for 1% BMA. Taking the MW of dimer as 860, the BMA (as monoester) should be:

$$\% \text{ BMA (as monoester)} = \text{BMA}_{\text{total}} - \text{BMA (as dimer)} - \text{BMA (as diester)}$$

This is obviously a rough approximation from many points of view and particularly when a trimer or a longer polymer forms.

The maleic anhydride balance was checked by calculating the maleic anhydride content as:

$$\%\ \text{MA}_{\text{found}} = \frac{(\text{BMA} + \text{FMA}) \times 98}{116}$$

As a check of the approximation made on the product composition, the monoglyceride balance was calculated, and in this way, using independent results, a satisfactory fit of experimental data was obtained.

For instance, in a closed vessel at 100 C after 300 min at 1.05 reactant ratio (see expt 1, Table I), MG + G = 13.3%, meaning $\text{MG}_{\text{out}} \sim 9\%$.

As

$$\text{MG}_{\text{in}} = \frac{W_{\text{Myvaplex}} \times (\%\ \text{MG})}{W_{\text{total}}} \times 100$$

$$= \frac{39 \times 0.91}{50} \times 100 = 71\%$$

then

$$\text{MG}_{\text{reacted}} = \text{MG}_{\text{in}} - \text{MG}_{\text{out}} = 62\%$$

If diester = 13.3%, then BMA (as diester) = $13.3 \times \frac{116}{780} = 2\%$.

If the amount of the dimer is zero, then

$$\text{BMA (as monoester)} = (19.2 - 2) \times \frac{448}{116} = 66.4\%$$

And in monoglyceride terms:

$$\text{MG (bound as diester)} = 13.3 \times \frac{350}{780} \times 2 = 11.9\%$$

$$\text{MG (bound as monoester)} = 66.4 \times \frac{350}{448} = 51.8\%$$

The sum of the bound MG is 63.7% and this figure approximates the value of $\text{MG}_{\text{reacted}}$ (62%). The two values have been found by independent methods.

As a further check, a similar exercise was done, calculating the acid value of the approximate composition found, and comparing it with the experimentally measured value.

$$\text{AV}_{\text{calculated}} = \text{AV}_{\text{monoester}} \times (\text{monoester content}) + \frac{(\text{FMA}) \times \text{AV}_{\text{maleic acid}}}{100}$$

Satisfactory results have been obtained, as can be seen from two typical examples (Table II) at different reaction conditions:

(a) At 300 min, 1.05 reaction ratio, 100 C:

$$\text{AV}_{\text{calc}} = 123 \times 0.66 + \frac{4.3 \times 1145}{100} = 130.4$$

$$\text{AV}_{\text{found}} = 127$$

(b) At 180 min, 1.72 reaction ration, 100 C:

$$\text{AV}_{\text{calc}} = 123 \times 0.87 + \frac{8.5 \times 1145}{100} = 204.3$$

$$\text{AV}_{\text{found}} = 212$$

Glycerol Esters

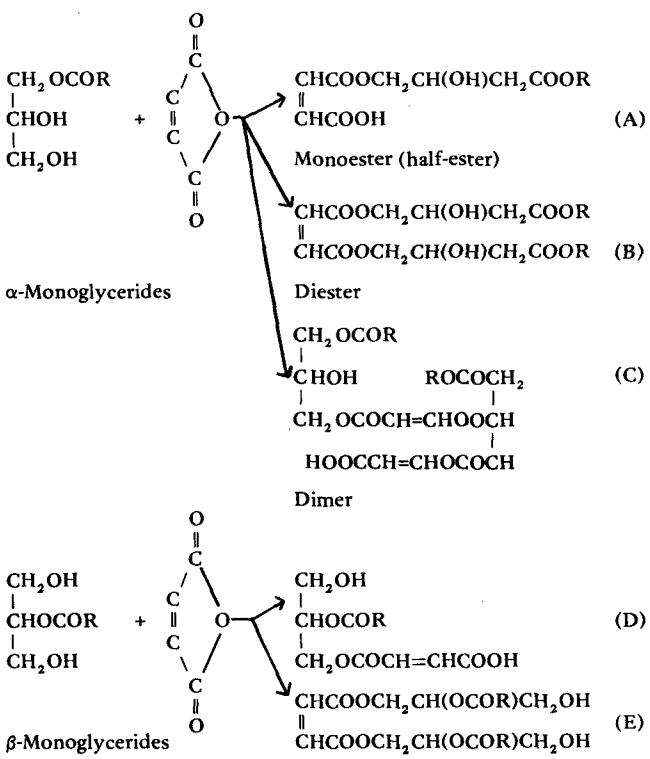
In the commercially available distilled MG there is 1–2% free glycerol which reacts with maleic anhydride to form glycerol esters. Such a reaction causes the consumption of the glycerol and, as a result, the glycerol content of the product compared to the reactant is significantly reduced. Usually, more than 50% of the available glycerol, present as an impurity in the reactants, was found in the final product. In order to check the extent of esterification, glycerol was reacted alone with maleic anhydride in equimolar ratio at 100 C.

It was found that 43% of the glycerol is in the product mass and an acid value of 230-250 was measured.

If our assumptions are correct, then glycerol esters and dimers, with a molecular weight of ca. 3–4 times that of the glycerol, are obtained. In this way we can estimate the glycerol ester content, which has to be added as an additional product to the total percentage composition of the final product (see Tables I and II).

RESULTS AND DISCUSSION

Esterification of maleic anhydride with 90% commercial distilled monoglycerides will yield several possible esters. The main products are listed below:



Since the α-form is the main isomer existing in the

TABLE I

Type of Vessel and Effect of Conditions on Product Composition

Exp. no.	Type of vessel	Reactant ratio MA/ (MG+G)	Tempera- ture (C)	Time (min)	Acid value	Unreacted MG+G as MG (wt %)	FMA (wt %)	BMA (wt %)	Diester (wt %)	Monoester (wt %)	Dimer (wt %)	Unreacted MG (wt %)	Unreacted glycerol (wt %)
1	Closed	1.05	100	60	158	23.1	6.6	16.8	10.0	59–61	0–3	16.2	2
				180	135	15.1	4.9	18.5	12.0	62–65	0–5	10.6	1.8
				300	127	13.3	4.3	19.2	13.3	62–66	0–7	9.3	1.5
2	Reflux	1.05	100	90	152	24.5	5.6	16.5	11.2	52	0–3	17.0	1.9
				180	136								
				300	126	18.2	4.3	17.5	12.4	56–60	0–7	12.7	1.4
3	Open	1.05	100	60	140	19.7	–	–	–	–	–	13.9	–
				180	121	17.0	–	–	–	–	–	11.2	–
				300	109	15.2	3.4	15.0	13.7	46–50	0–7	10.3	1.3
4	Closed	1.05	120	60	138	16.0	5.2	17.9	12.0	58–62	0–7	11.0	1.3
				180	115	14.4	–	–	–	–	–	–	
				300	107	12.6	4.5	17.9	14.2	53–61	0–15	9.0	1.0
5	Reflux	1.05	120	60	138	19.1	4.5	17.5	14.0	56–60	0–7	13.3	1.5
				180	124	15.6	–	–	–	–	–	–	-
				300	114	14.7	3.6	12.4	19.2	25–37	0–23	10.3	1.1
6	Open	1.05	120	60	133.5	16.6	4.2	17.0	13.8	–	–	–	–
				180	112.5	14.3	–	–	–	–	–	–	–
				300	92.1	11.2	2.9	11.4	17.0	0–20	30–50	5.8	1.4
7	Open immersion bath	1.05	120	60	87.5	31.9	–	–	–	–	–	–	–
				90	76.8	31.7	2.1	11.1	–	–	–	–	–
				240	50.1	27.5	1.1	4.8	–	–	–	–	–

TABLE II

Effect of Time and Temperature on Product Composition

Exp. no.	Type of vessel	Reactant ratio MA/ (MG+G)	Tempera- ture (C)	Time (min)	Acid value	Unreacted MG+G as MG (wt %)	FMA (wt %)	BMA (wt %)	Diester (wt %)	Monoester (wt %)	Dimer (wt %)	Unreacted MG (wt %)	Unreacted glycerol (wt %)
1	Closed	1.05	100	0	252	77.0	–	–	–	–	–	–	–
				15	243	40.8	9.5	16.9	4.5	–	–	–	–
				30	221	39.3	8.2	16.3	8.0	–	–	–	–
				60	158	23.1	6.6	16.8	10.0	59–61	0–3	16.2	2.0
				180	135	15.1	4.9	18.5	12.0	62–65	0–5	10.6	–
				300	127	13.3	4.3	19.2	13.3	63–66	0–7	9.3	1.5
				1380	101	12.5	4.1	11.7	25.3	4–15	30–50	–	–
2	Closed	1.05	120	60	138	16.0	5.2	17.9	12.0	58–62	0–7	11.0	1.3
				180	115	14.4	–	–	–	–	–	–	–
				300	107	12.6	4.5	17.9	14.2	53–61	0–15	9.0	1.0
				1380	62	7.1	3.5	8.9	50.0	0–1	30–50	5.0	0.5
3	Closed	1.05	160	60	112	13.3	3.9	13.6	15.5	–	–	–	–
				180	84	7.0	1.0	10.2	–	–	–	–	–
				300	64	4.4	0.5	10.1	48.0	–	–	–	–
4	Closed	1.72	100	0	361	63.2	–	–	–	–	–	–	–
				15	349	29.5	22.6	15.7	0	–	–	–	–
				30	314	19.8	19.2	17.7	–	–	–	–	–
				60	255	10.5	10.2	21.0	1.5	80	0–1	7.3	0.7
				180	212	3.0	8.5	23.0	3.2	86	0–1	2.1	0.2
				300	201	2.0	7.2	23.0	8.0	84	0–1	1.4	0.1
5	Closed	1.72	120	60	223	3.5	10.8	18.6	4.0	65–69	0–7	2.4	0.3
				180	206	2.6	7.9	18.5	5.4	65–69	0–7	1.8	0.2
				300	183	1.4	7.7	20.5	10.1	69–73	0–7	1.0	0.1
6	Open	1.72	100	60	250	10.8	11.2	20.0	9.1	72	0–1	7.6	0.8
				180	214	5.2	8.4	22.0	12.4	78	0–1	3.6	0.4
				300	201	3.9	7.0	22.1	15.3	76	0–1	2.7	0.3
7	Open	1.72	120	60	230	6.0	10.3	21.0	12.2	74	0–1	4.2	0.5
				120	211	–	–	–	–	–	–	–	–
				180	203	3.4	6.0	22.5	13.6	79	0–1	2.4	0.2
8	Open	1.72	160	60	193	2.7	9.5	19.3	10.3	61–69	0–15	1.9	0.2
				180	143	0.9	6.2	12.5	15.0	15–24	30–50	0.6	0.1
				240	114	0.9	6.3	8.3	19.3	0–6	30–50	0.6	0.1

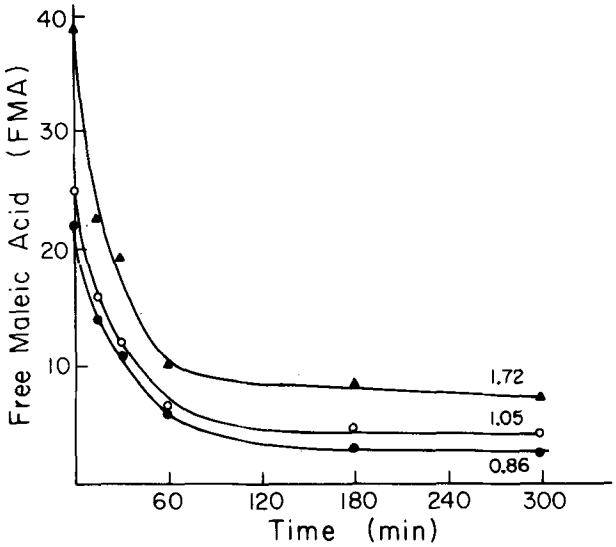


FIG. 1. Reaction profile of esterification of monoglycerides of fatty acids with maleic anhydride. Carried out in closed vessels at 100 C. (▲) Maleic anhydride:monoglyceride molar ratio 1.72; (○) molar ratio of 1.05; (●) molar ratio of 0.86.

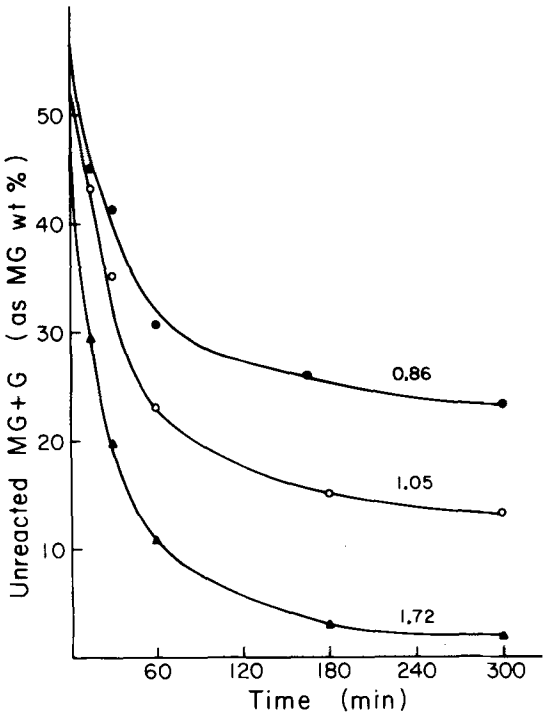


FIG. 2. Monoglyceride conversion in the esterification between maleic anhydride and monoglyceride. Carried out at 100 C in closed vessels. (▲) MA/MG molar ratio of 1.72; (○) 1.05; (●) 0.86.

monoglyceride, one should expect mainly the formation of product A, B and C and only minor percentages of products D and E could be visualized.

Selection of Reaction Vessel and Reaction Conditions

The esterification between maleic anhydride and monoglyceride does not liberate water, therefore the selection of the proper reaction vessel is influenced by the fact that maleic anhydride tends to sublime easily and to evaporate from an open reaction vessel. On the other hand, the second esterification between the MA-monoglyceride monoester and additional monoglyceride releases water that has to be removed. Closed tubes and open reaction vessels equipped with air condensers were tested. Table I shows that closed systems had an advantage over open vessels, if all reactants were preheated and dried thoroughly to eliminate any presence of water in the MA or the monoglycerides. It can be seen that the acid value (AV) drops to 126–127 when a closed system or reflux conditions were chosen (reactants' ratio 1.05, 100 C, 300 min). Keeping the reaction vessel "open" caused a more drastic decrease in the acid value (109 after 300 min), indicating a possible loss of sublimed maleic anhydride. The acid value of the product is a complex composition of the free maleic acid, half-ester (A) and dimer (C). However, the main contribution to the acid value comes from the maleic acid (free maleic acid has an acid value of 1,145).

A similar phenomenon can be observed when the free maleic acid (FMA) is examined. In closed and refluxed systems there is a gradual increase in these values. At higher temperatures (120 C) the FMA concentration drops faster in refluxed systems in comparison to closed vessels. The FMA values are significantly lower in open tubes (reactant ratio 1.05, 300 min and 120 C) in comparison to the closed vessels (2.9, 3.6 and 4.5% for open, refluxed, and closed systems, respectively).

The bound maleic anhydride values (BMA) reach a value of 16.8% after 60 min and a value of 19.2% after 30 min in closed systems, at 100 C. Under reflux, only 17.5% BMA were detected. In open vessels the values are smaller and reach only 15%. This is to say that less MA is bound to the monoglycerides to form MGE in an open vessel than in closed tubes. This effect becomes more pronounced at more elevated temperatures (17.9, 12.4 and 11.4 for closed, reflux, and open tubes, respectively, at 120 C after 30 min).

The amount of diester was calculated directly from the ether soluble fraction. At low temperatures there is no significant difference between the three reaction vessels. However, at 120 C, only 14.2% of the product was diester in closed vessels, whereas 17.0% and 19.2% were found in open and refluxed flasks. It should therefore be noted that whereas most MA sublimes out of the open vessel, the MA in the closed systems tends to react further with the half-ester to form diester. In closed systems, the released water from the second esterification reaction tends to depress the esterification and the amount of diester formed is controlled. In open vessels, the second esterification equilibrium reaction is shifted towards the formation of the diester, when the water is removed from the reaction.

The percentage of the dimer in the product is estimated from more complex calculations, as explained in the experimental part. According to our estimation, at temperatures of ca. 100 C, the dimers formed are not more than 7% of the final product in all types of vessels. But by raising the temperature to 120 C, even 30–50% dimers (or other possible polymers) are formed in open vessels, and maybe as many as 20% are formed in refluxed vessels after 300 min. At the same conditions, in closed vessels, not more than 7% dimers are formed.

The required monoester (half-ester) is 59–66% of the final product composition (after 60–300 min at 100 C) in closed systems. Only 52–60% of the product is obtained in refluxed vessels. At more elevated temperatures (120 C), only 25–37% of the product is monoester in refluxed vessels, and it seems that not more than 20% monoester exists in open vessels after 300 min. In closed vessels, under the same conditions almost 53–61% of monoester is obtained after 300 min.

One has to understand the limitations of our calculations sometimes where polymerization occurred and the acid

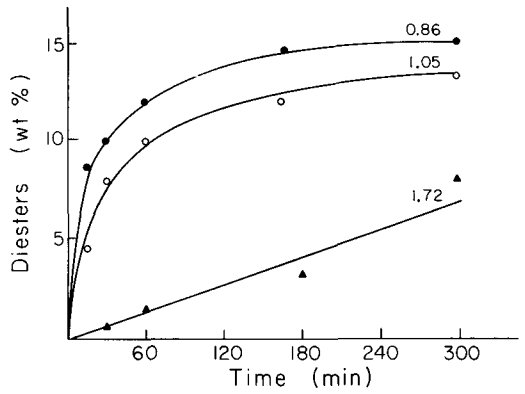


FIG. 3. Diester yield in similar esterification reaction. (▲) MA/MG molar ratio of 1.72; (○) 1.05; (●) 0.86.

value decreased drastically; the above figures must be considered as rough approximations.

Similar and usually, even more pronounced effects were observed when the reactants' ratios were 1.72, as can be seen in Table II. By examining the results of expt 4–7, one can find that in using closed vessels at 100 C not more than 1.5–3.2% diesters and 80–86% monoesters are formed after 60–180 min, while, under the same conditions in open vessels, 9.1–12.4% diesters and 72–78% monoester are found.

The above results clearly demonstrate the advantage of using closed vessels for this reaction, since the product is richer in monoesters, that are probably better intermediates for further sulfonation.

Reaction Profile

The esterification between maleic anhydride and monoglyceride is a rather fast reaction even at relatively low temperatures and without catalyst. The reaction profile has been examined using three reactant molar ratios of MA/(MG + G) = 0.86, 1.05 and 1.72 at 100 C. The reatants' conversion has been determined by measuring the MA and MG + G consumption with time. Figures 1 and 2 present these results. Fast consumption of MA is observed in the first 30–60 min, typical of simple esterification reactions. After more prolonged exposure of the MA to the MG + G, or to the product obtained in the first step, secondary reactions take place forming the diester and the dimers. Therefore the MA consumption slows down and approaches a plateau. Similar behavior is observed even when MA is in significant excess (reactants' ratio 1.72), but the trend is less pronounced emphasizing slower consumption of the MA.

Seventy wt % of MG + G was consumed after 60 min of reaction when the reactants' ratio is 1.05, and after 300 min, 82 wt % of the total MG + G were esterified. Higher conversions of MG + G were detected when the molar ratio of the reactants was 1.72. Practically all MG + G were esterified (97%) after 300 min of reaction.

Figure 3 demonstrates, in part, the reaction yields. Since measurements of the diester formation are easier and more accurate, it has been decided to plot diester formation vs time for the three reactants' ratios. As expected the diester formation is increased with increasing temperature, reaction time and the decrease in reactants' ratio. 10–15% diesters were formed within 60–300 min at 100 C at molar ratio of 1.05, whereas only 1.5–8% diester were detected at 1.72 molar ratio.

Effect of Reactants' Ratio, Temperature and Time

Most esterification reactions between maleic anhydride and monoglycerides are summarized in Tables I and II. A close examination of these results will reveal that it is difficult to recommend best reaction conditions for such reactions since the product composition varies significantly when type of vessel, reaction temperature, reaction time and reactants are varied. It will be the choice of the operator to decide on reaction conditions and reactants' ratio, according to the nature of product composition that is required and the type of byproducts tolerated in the final product. Often FMA is not allowed, while frequently minimum amounts of diester and dimers are required. For example, using closed systems with a reactant ratio of 1.05, by increasing the temperature from 120 to 160 C, most maleic anhydride will be consumed, but the amount of diesters will increase very significantly (see Table II). On the other hand, an excess of maleic anhydride (1.72) will form a product rich in monoesters and poor in dimers and diesters, but almost 7% of FMA are present in the final product. A similar situation is observed when analysis of the glycerol and monoglyceride content is examined.

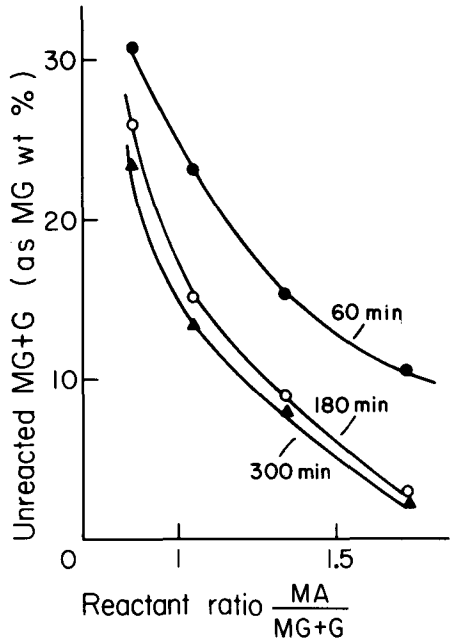


FIG. 4. Effect of reactants' ratio on MG conversion. (●) 100 C and 60 min reaction; (○) 100 C and 180 min; (▲) 100 C and 300 min.

Table II and Figure 4 demonstrate the effect of reactants' ratio on the conversion of MG + G in typical reactions carried out at 100 C. It can be seen that an excess of MA will cause a more drastic decrease in the MG + G content in the final product. After 60 min, 10.5% of MG + G will remain in the product (at reactant ratio of 1.72), while only 2% will be left over in the product unreacted after 300 min. On the other hand, as explained above, the diester and dimer contents will increase significantly.

The present study tried to examine the esterification reaction between maleic anhydride and monoglycerides of saturated fatty acids in view of the product composition. It was seen that closed vessels have advantages over open reaction flasks. The reactants' ratio, as well as the temperature and reaction time, should be chosen in view of the product composition formed.

A complex mixture of free maleic anhydride, free glycerol, free monoglycerides together with monoesters, diesters and dimers is usually formed. Careful analysis allowed estimation of these ingredients in the final product and emphasizes the importance of selecting the right reac-

tion conditions to achieve best results and the proper product according to its use.

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Preparation of Colorless Sunflower Protein Products: Effect of Processing on Physicochemical and Nutritional Properties

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ABSTRACT

A comparison was made of the different technological treatments for the preparation of colorless sunflower protein products from the viewpoint of the effect of processing conditions on the extraction yield of nitrogen and lipid, chemical, physicochemical and nutritional properties of the processed products. The technological treatments comprised soaking dehulled seeds in dilute citric acid or sodium bisulfite solution and washing the defatted meal with the respective solution. The defatting process was carried out with hexane or azeotrope (hexane/ethanol). Nitrogen and lipid recovery was slightly greater for hexane defatted products than for azeotrope defatted products. About 21.4% of the phenolic compounds of the sunflower seeds were bound to the proteins of the seeds before processing and therefore could not be eliminated by the aqueous extraction. Aqueous extraction of phenolic compounds was limited for full fat seed. The free phenolic compounds were very stable in acid medium but sensitive to oxidation in alkaline medium and had no significant effect on in vitro enzymatic proteolysis and growth inhibition of rats. Lysine and the bound phenolic compounds were the critical factors responsible for inhibition of enzymatic proteolysis and reduced growth of rats. The diet containing whole seed meal presented a low protein efficiency ratio (PER) value. Citric acid, a chelating agent, proved to be an antioxidant as effective as sodium bisulfite; the products obtained by citric acid treatment had a visually whiter color than those processed by sodium bisulfite.

INTRODUCTION

The potential uses of sunflower proteins are limited by the presence of phenolic substances, particularly chlorogenic acid (1). The isolation of protein and removal of chlorogenic acid from sunflower meal have been investigated by numerous scientists. Various methods have been devised. These include extraction of the meal with aqueous ethanol (2, 3), aqueous methanol (4), acidic butanol (5) and NaCl solution (6). Gheyasunddin et al. (7) produced a colorless sunflower protein isolate by treating the soluble protein with sodium sulfite and washing the precipitated protein with 50% isopropanol, and Sosulski et al. (8) produced stable white concentrate by hot aqueous diffusion of cracked sunflower kernels.

However, these processes were hardly feasible for industrial use. The high volumes of extract liquor from aqueous solvent processes would create a serious problem of water disposal or solvent recovery for commercial application. The diffusion process was very temperature-dependent. Due to the long extraction periods, the large volumes of water and high temperature, the operational costs of the batch diffusion methods would be prohibitive. In addition, these processes caused a greater loss of proteins and lipids, and alcohol may denature a protein by destroying its native configuration (9, 10). An excessive protein denaturation is not desirable for some food applications (11). In view of extending the utilization of sunflower proteins in human foods, a simple economical process has to be developed; the operational costs and the feasibility for industrial use and commercial application should be taken into account.

Colors and flavors of sunflower protein products are associated with the presence of hulls, polyphenolic compounds and low molecular weight carbohydrates. The hydrogen bonding between the hydroxyl groups of phenolic compounds and the peptide bonds in proteins is known to be unusually strong and the equilibrium in aqueous solution strongly favored the formation of complexes (12). Therefore, the complete extraction of chlorogenic acids from sunflower flour with polar organic, aqueous, or aqueous/organic solvents would be difficult to achieve. The extraction with NaCl solution could induce discoloration of the proteins, since minerals can accelerate oxidation of phenolic compounds. Chlorogenic acid is readily oxidized to quinone, both nonenzymatically by oxygen at alkaline pH and enzymatically in the vicinity of neutral pH by polyphenol oxidase (13), therefore during the extraction procedure of chlorogenic acid, the use of a reducing agent is necessary.

A systematic and comprehensive study of conditions af-