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(54) **Edible fats.**

(57) Edible fats particularly for confectionery are prepared by rearrangement, in the presence of more highly saturated fatty acids or their esters and lipase enzyme catalyst, of fats and glyceride oils having a high oleic acid content, especially sunflower oil.

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Description

EDIBLE FATS PREPARATION

This invention relates to edible fats and their preparation for use in particular in confectionery including chocolate, shortenings, margarine and other plastic emulsion food spreads.

The modification of edible oils and fats by rearrangement of the fatty acid residues on the glycerides of which they are composed, has been practised in the food industry for a considerable time. According to US patent 2928745 assigned to Lever Brothers Co., hydrogenated palm kernel oil was randomised using sodium methoxide as rearrangement catalyst and subsequently fractionated to provide a confectioners' hard butter.

Proposals have also been made to synthesise triglycerides. According to US patent 3012890, mono- and di-glycerides of fatty acid are reacted with acid chlorides to produce synthetic triglycerides. More recently, catalysts both for rearrangement and synthesis processes have been proposed comprising lipase enzymes. A particularly interesting proposal is the use of selectively active enzymes which are effective in the 1-and 3-positions of glycerides, while leaving the 2-position unaffected. US patent number 4275081 describes rearrangement processes under the influence as rearrangement catalyst of lipase enzymes activated with a small amount of water. By the use of this development, unsaturated vegetable oils for example sunflower oil, may be converted in the presence of saturated fatty acids themselves or alkyl esters thereof, to symmetrical disaturated triglycerides, particularly of palmitic and stearic acids, the presence of which in cocoa butter and other vegetable butters accounts for the sharp - melting and other physical attributes for which these expensive and often scarce products are so highly prized. The most beneficial of these glycerides are the 2-oleoyl homologues. The corresponding 2-linoleoyl and linoleneoyl disaturated triglycerides exhibit somewhat less satisfactory characteristics; being more highly unsaturated they are significantly softer and materially more susceptible to deterioration by oxidation. Their conversion to mono-olefinic unsaturation by selective hydrogenation is not a satisfactory solution, owing to the high simultaneous incidence of conversion by isomerisation to elaidic acid i.e. the trans-form of oleic acid, thereby introducing a higher melting glyceride to the glyceride composition than the corresponding 2-oleoyl isomer, which is the naturally occurring form. The higher-melting 2-elaidoyl disaturated triglycerides additionally confer a degree of incompatibility with the triglycerides already present and this is reflected in anomalous and undesirable melting behaviour. Moreover, the by-products of all rearrangement processes of highly unsaturated glyceride oils which are separated from more saturated products, are themselves highly unsaturated and similarly unstable, being susceptible to atmospheric oxidation. While they may be hydrogenated to saturated fatty acids or their derivatives, for recycle to the rearrangement process, they consume considerable quantities of hydrogen in the process.

The presence of substantial amounts of 2-linoleoyl and 2-linoleneoyl triglycerides in many vegetable oils including sunflower oil has therefore limited their value in 1, 3 regiospecific rearrangement processes for the preparation of fats suitable for use in chocolate and confectionery. The present invention provides a rearrangement process in which this disadvantage is overcome in an expedient and economic manner.

The present invention provides a process for the preparation of edible fats suitable for use in confectionery and like edible compositions by rearrangement of unsaturated glyceride oils and fats to more highly saturated fats by contact as rearrangement catalyst with lipase enzyme and in the presence of saturated fatty acids or esters thereof, wherein the oil or fat exhibits a high oleate content and preferably consists substantially of 2-unsaturated triglycerides at least 90% of which are 2-oleoyl triglycerides. The present invention also provides novel fats comprising symmetrical disaturated triglycerides of C_{16} and C_{18} fatty acids in which the saturated fatty acid residues are in random distribution between the 1 and 3-positions and the unsaturated fatty acid residues comprise at least 80% oleic acid residues, preferably at least 90% and more particularly at least 95% of such residues. Such fats are obtained by the rearrangement processes of the present invention using as rearrangement catalyst a 1, 3-regiospecific lipase, as described in US patent 4275081.

Commercially useful high oleic sunflower varieties suitable for use on the present invention may be obtained by conventional plant breeding techniques, for example by crossing the naturally occurring high oleic varieties such as that reported by Horowitz and Winter (Nature 179:582 (1975)). High oleic mutants produced by artificial means, such as the mutagen treatment of seed, can also be used and the Pervenets variety (reported by Kharachenk in Fisiologiya Rastenii 26:1226 (1979)) is an example. Progenies derived from such mutants are known, eg. those reported by Fick. Preferably sunflower seed is used from plant varieties giving oils with 10% or less eg. 3% of linoleic acid, particularly those having AOM values (Active Oxygen Method) of at least 100 hours measured by the AOCS method Cd12-57. Other oils suitable for use in the present invention include selected olive oil, shea olein, sal olein and cottonseed olein, including winterised cottonseed oil.

Enzyme rearrangement processes in accordance with the present invention are carried out in substantially non-aqueous and essentially water-immiscible liquid phase. A small amount of water is nevertheless necessary to activate the catalyst initially. This may be achieved either by contacting the catalyst first with water or by including a little water in the feedstock in batchwiese operations. A balance is required between the faster reaction rates provided by more water increasing the activity of the catalyst and correspondingly increased tendency to hydrolysis of the reactants and products, since the rearrangement process is reversible. Preferably therefore the water activity of the system is maintained at between 0.2 and 0.6. In continuous processes in accordance with the invention in which the reactants are passed over a fixed bed of supported lipase enzyme catalyst, the water activity of the system is maintained, preferably within these limits,

by including a small amount of water in the feedstock supplied to the catalyst in a fixed bed. By this means the water activity is preferably maintained at a level of which the rearrangement reaction is substantially completed with a contact time less than 2 hours, to minimise the effect by isomerisation of partial glyceride by-products leading to the appearance in the product of 2-saturated triglycerides, where 1, 3-regiospecific catalysts are used to produce symmetrical disaturated 2-oleoyl triglycerides.

The rearrangement reaction may be carried out in the presence of a water-immiscible non-polar solvent eg. hexane or other hydrocarbon to maintain the reactants in liquid phase. Where a solvent used, the concentration of reactants in the solvent is preferably from 20-50% by weight.

The reaction may be operated at moderately elevated temperatures for example 40 to 80°C, at which the catalyst selected remains active and the reactants are wholly in liquid phase.

The catalyst is preferably supported on an inert support for example Celite or other particulate siliceous, inert inorganic support or ion exchange medium, either organic for example a resin, or inorganic for example zeolitic. The amount of lipase is preferably 0.01-0.1% by weight of the support. Lipase is present in commercially available products in an amount of approximately 1% and sufficient commercial product is used to achieve this concentration of lipase on the support.

Suitable 1, 3 regiospecific enzymes include Mucor miehei, Rhizopus, A. niger or other Aspergillus species.

The acidolysis reactant used with the sunflower or other oil or fat in accordance with the invention, may be in the form of a free saturated fatty acid , preferably palmitic or stearic acid, or a mixture of both. Alternatively, they may be present as esters, preferably of short chain saturated mono hydric alcohols, for example methyl and ethyl palmitate and stearate. Preferably from 1 to 5 moles of acidolysis reactant per mole of oil is used, more preferably 3-5 moles per mole.

The rearranged triglyceride product of the invention is preferably recovered from the reactant mixture after first separating any free fatty acid and any reactant solvent this has been used, by fractional crystallisation at a temperature, preferably from 10-40°C, at which the unsaturated acid or ester by-products are liquid and can be separated from the crystallised product. The fractionation may be effected from suitable solvent for example acetone. Alternatively, these by-products may be distilled off, preferably at reduced pressure using conventional acid refining methods. The by-products may be hydrogenated to the corresponding stearic acid or ester thereof and recycled for use as the acidolysis reactant.

Example 1

A mixture of equal parts of high oleic sunflower oil and stearic acid was dissolved in twice its weight of hexane. Half the feedstock obtained was saturated with water by passage through a column containing a bed of wet silica gel and was then recombined with the remainder of the feedstock.

The combined feedstock was pumped at a flow rate of 6 Kg per hour at 50°C, through a reactor column containing 1 Kg of interesterification catalyst consisting of Mucor miehei lipase supported on Celite, prepared as described in British patent 1577933 and pre-activated with 10% water prior to use. Residence time was approximately 15 minutes.

After removing solvent by evaporation, the free fatty acids were separated using a falling film evaporator and the reaction product fractionated at -5°C in acetone using a solvent to oil ratio 5:1, in a scraped-surface heat exchanger to recover a stearin fraction rich in StOSt.

In Table 1 analytical data is given both for the product and stearin and olein fractions obtained, compared with the composition of a commercial shea stearin.

TABLE 1

EXAMPLE WT%		TRIGLYCERIDE WT%					DIGLYCERIDE WT%	FFA
		S_3	SOS	SSO	SLns	SOO	Others	
1)	FEED	-	1.6	-	-	25.7	72.7	2.4	1.5
2)		-	3.3	1.7	1.7	60.5	33.2	8.5	1.3
1)	PRODUCT	1.2	36.3	1.5	3.0	41.0	17.0	7.2	5.6
2)		6.4	43.4	5.2	4.0	31.1	9.9	12.7	7.3
1)	STEARINE	3	88	3	3	2	1	2.5	0.2
2)	(TOP)	60.1	31.6	6.9	1.1	0.3	0	18.7	0.5
	SHEA STEARINE	2	75	1	8	9	5	-	-
1)		-	4	1	3	63	29	9.0	8.8
2)	OLEINE	-	3.9	2.1	2.7	66.2	25.1	15.8	-
2	MID-FRACTION	1.1	79.9	9.5	6.4	2.3	0.8	4.5	1.1

The substantially greater SOS content of the stearine fraction and lower content of SLnS is apparent from Table 1. The enzyme and shea stearines were evaluated for confectionery fats, both alone and in blends of

equal parts of mid-fraction, by Jensen Cooling Curve determination in Table 2.

TABLE 2

Example Stearine	%PMF	Tmax °C	Tmin °C	AT °C	Tmax Secs	Tmin Secs
1	0	36.8	29.6	7.2	47	12
	50	29.1	24.3	4.2	52	24
Shea	0	36.4	27.9	8.5	51	14
	50	31.3	25.9	5.4	55	22
2 (mid)		33.8	28.7	5.1	34	13

The enzymatically produced stearine exhibited excellent confectionery fat characteristics and was similar to shea stearine.

Example 2

Example I was repeated using as feedstock the olein by-product recovered from Example I, the catalyst in this case being supported on a phenol-formaldehyde weak anion exchange resin.

In this example the deacidified product was first fractionated in acetone with a solvent:oil ratio of 5:1 at a temperature of 0°C, to remove an olein fraction in 56% yield. The stearine fraction remaining was then redispersed in acetone at a 3:1 ratio and a second stearine fraction separated in 10% yield overall at a temperature of 25°C, consisting substantially of saturated glycerides and leaving a mid-fraction recovered in 34% overall yield from the solvent. The saturated glycerides of the upper stearine fraction result from the presence of partial glycerides in the recycled olein undergoing isomerisation followed by interesterification in the reactor.

The characteristics of the products obtained appear in the accompanying Table 1 and 2 and are compared with a commercial shea stearine.

Example 3

A reactant mixture of high oleate sunflower oil (2.5 parts by wt) and myristic acid (1.0 parts by wt) dissolved in 100-120° petroleum ether (8 parts by wt) was saturated with water at 40° C by passage through a bed of acid washed celite (4.0g) containing 80% by wt of water. The water saturated reaction mixture was pumped at 40° C using a flow rate of 15m/hr^{-1} through a bed of catalyst (2.0g) consisting of Rhizopus japonicus lipase suppored on celite. The catalyst, prepared as described in our patent GB 1577933, contained 1700 lipase units per gm, and was activated with 10% water prior to use. The mean residence time of the reactant mixture in the catalyst bed was approximately 15 mins.

The interesterification reaction product contained 58% triglyceride, 6% diglyceride and 36% free fatty aic. The triglyceride fraction was isolated and analysed. The results given in Table 3 show that myristate was incorporated into the sunflower oil triglycerides and valuable SOS triglycerides were generated.

Example 4

A mixture of high oleate sunflower oil (2.5 parts by wt) and methyl palmitate (2.4 parts by wt) dissolved in 100-120° petroleum ether (8 parts by wt) was reacted as described in Example 3 using a catalyst ved of Rhixopus niveus lipase supported on celite and a flow rate of 4ml hr $^{-1}$. The catalyst contained 1500 lipase units per gm. The mean residence time of the reactant mixture in the catalyst bed was approximately 1 hour.

The reaction product contained 50% triglyceride, 4% diglyceride, 43% methyl esters and 3% free fatty acid. Analysis of the triglyceride fraction showed that extensive interesterification occurred. Palmitate was incorporated into the sunflower oil triglycerides and valuable SOS triglycerides were produced (Table 1).

TABLE 3

Fatty acyl group	Feed Sunflower oil (%)	Product Example 3 (%)	Product Example 4 (%)
14:0	0.0	24.8	0.3
16:0	4.2	2.5	35.4
18:0	4.0	2.5	2.9
18:1	80.1	62.0	54.3
18:2	9.5	6.6	5.7
Others	1.5	1.6	1.4
TG Species			
SSS	0.0	0.0	0.0
SOS	1.9	23.3	35.6
SSO	0.0	0.0	0.0
SLnS	0.2	2.1	3.5
SOO	20.1	43.2	41.8
Others	77.8	31.4	19.1

The results show that the enzymically prepared mid-fraction is similar to shea stearine.

Claims

1. Process for the preparation of edible fats suitable for use in confectionery and like edible compositions by rearrangement of unsaturated glyceride oils and fats under the influence as rearrangement catalyst of lipase enzyme in the presence of saturated fatty acids or esters thereof, wherein the oil or fat exhibits a high oleate content and preferably consists substantially of 2-unsaturated triglycerides at least 80% of which are 2-oleoyl triglycerides.

2. Process according to claim 1 wherein the oil or fat contains at most 10 per cent combined linoleic acid.

3. Process according to claim 2 wherein the oil is sunflower oil having an AOM value of at least 100 hours.

4. Process according to claim 1 or 2 wherein the oil comprises olive oil.

5. Process according to claim 1 or 2 wherein the oil comprises an olein fraction of shea, cottonseed or sal oil.

6. Process according to any of the preceding claims wherein the said lipase enzyme is 1, 3-regiospecific.

7. Process according to any of the preceding claims wherein the saturated fatty acid or ester comprises

palmitic or stearic acid or alkyl esters thereof.

8. Process according to any of the preceding claims wherein from 1 to 5 moles of fatty acid per mole of oil or fat are used.

9. Process according to any of the preceding claims wherein water activity of the reaction mixture is maintained from 0.2 to 0.6.

10. Continuous process according to any of the preceding claims wherein the reaction mixture is brought into contact with a fixed bed of supported lipase enzyme as rearrangement catalyst with a contact time less than 2 hours.

11. Process according to any of the preceding claims wherein the product is recovered by fractional crystallisation from the reaction mixture at a temperature from 10-40° C.

12. Process according to any of the preceding claims wherein unsaturated by-products recovered from the reaction mixture are recycled.

13. Confectionery fat comprising symmetrical disaturated triglycerides of palmitic and/or stearic acid in which the saturated fatty acids are arranged in random distribution between the 1 and 3-postions and at least 90% of which are 2-oleoyl triglycerides.

14. Confectionery fat according to claim 13 in which at least 90% of the said triglycerides are 2-oleoyl triglycerides.