

Effect of the Position of Linoleic Acid in Triacylglycerols on its Hydrogenation Rate

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ABSTRACT

Cottonseed, sesame, soybean and safflower oils were partially hydrogenated under selective conditions using Rufert nickel catalyst. Samples drawn at intervals were subjected to pancreatic lipase hydrolysis, and the positional distribution of fatty acids was determined. Results indicate preferential hydrogenation of linoleic acid present in the 1,3-position over that present in the 2-position of the triacylglycerols.

INTRODUCTION

Earlier workers (1-4) observed that the position of an unsaturated fatty acid in triacylglycerols does not exert any effect on its hydrogenation rate. Our preliminary studies (5) with cottonseed oil indicated that unsaturated fatty acids located in the 1,3-position of triacylglycerols are hydrogenated faster than those present in the 2-position. Further studies on cottonseed as well as sesame, soybean and safflower oils are reported here.

EXPERIMENTAL PROCEDURES

Materials

Cottonseed and soybean oils were extracted, refined and bleached in the laboratory. Raw commercial sesame oil was refined and bleached in the laboratory. Safflower oil was a commercially refined and bleached sample. The cottonseed, sesame, soybean and safflower oils had iodine values 95.2, 106.6, 128.1, and 146.8, respectively. The low iodine value for cottonseed oil is not unusual for Indian oils (6). All the oils had acid values of less than 0.5 and did not contain peroxides. Commercial Rufert nickel catalyst containing 25.2% Ni was used.

Methods

Hydrogenation of 500 g-samples was carried out in a Parr hydrogenator of one litre capacity (180 C, 5-10 psig, 0.1% Ni). Samples were drawn at intervals. Iodine values, melting points and isolated *trans* acid contents were determined according to Official and Tentative Methods of the AOCS (7). Pancreatic lipase hydrolysis was carried out according to Luddy et al. (8). The monoacylglycerols were isolated by preparative TLC on silica gel G using light petroleum (40-60 C)-diethyl ether-formic acid (60:40:1, v/v) and transmethylated using 1% sodium methoxide in methanol. The methyl esters, prepared from monoacylglycerols as well as from the total triacylglycerols, were analyzed by GLC using an F&M Model 720 dual column programmed temperature unit equipped with a thermal conductivity detector. A stainless steel column (8' x 1/8") packed with 15% DEGS on Chromosorb W (60-80 mesh) was used with hydrogen as carrier gas (60 ml/min). The column temperature was 200 C and the injection port and detector were maintained at 300 C.

RESULTS AND DISCUSSION

The percentage reduction in iodine value at any stage of hydrogenation is calculated and given in Table I (column

1), as this is more meaningful than either the duration of hydrogenation or the iodine value itself for a comparison of the extent of hydrogenation for different oils. From the fatty acid compositions of triacylglycerols (columns 2-5) and monoacylglycerols obtained by lipolysis (columns 6-9), the composition of fatty acids in the 1,3-positions was calculated (columns 10-13). From these compositions the percentage proportionate loss of linoleic acid (18:2) in the 1,3- and 2-positions at any stage during hydrogenation relative to its concentration in the respective positions in the unhydrogenated sample was calculated (columns 14 and 15). The relative loss of 18:2 in the 1,3- and 2-positions (columns 14, 15) is shown in column 16. The loss of 18:2 only was taken into consideration since it is difficult to draw definite conclusions with oleic and elaidic acids due to simultaneous formation and hydrogenation or isomerization of these acids. Further, no acid more unsaturated than 18:2 occurs in the oils studied except in soybean oil which contains ca. 5% of linolenic acid (18:3). Indian-grown soybeans have a lower content of 18:3 than American soybean oils and a fairly typical oil sample has ca. 4% of 18:3 (9). It is assumed that 18:3 is hydrogenated selectively to 18:2 only, and hence 18:3 lost (footnotes a and g in Table I) at any particular stage is deducted from the apparent content of 18:2 at that stage to calculate the actual loss of 18:2. Since the amount of 18:3 is small, any error arising from this assumption will not adversely affect the conclusions.

The content of 18:2 in the oils studied varied from 39.7 to 76.4% and in the 2-position of the respective triacylglycerols from 48.3 to 84.6%. The 18:2 content was decreased by hydrogenation to 4.5-23.9% in triacylglycerols and 9.2-27.5% in the 2-position of the respective triacylglycerols. Hence, the triacylglycerols that are likely to be present at various stages of hydrogenation are mainly LLL, LLX, LXL, XLX and LXX, where L stands for 18:2 and X for oleic, elaidic, or saturated acid. The relative loss of 18:2 calculated theoretically for these glycerides varies from 0.0 to infinity depending on whether hydrogenation takes place exclusively at the 2-position or 1,3-position or at equal rates. For example, if hydrogenation takes place at equal rates in all positions, the relative loss will be 0.5 for LLL, 0.33 for a mixture of LLX and LXL and 1.0 for a mixture of XLX and LXX. A comparison of the actual relative losses (column 16) for the various oils at different stages of hydrogenation with the theoretical relative losses for probable triacylglycerols or triacylglycerol mixtures does indicate that the 18:2 in the 1,3-position is preferentially hydrogenated over that present in the 2-position. This observation becomes more significant when it is considered that all the oils studied had higher concentrations of 18:2 in the 2-position than in the 1,3-position. For this reason the differences between the theoretical and actual relative losses of 18:2 narrowed down as the hydrogenation proceeded.

Another way of examining the effect of position of an unsaturated fatty acid on its hydrogenation rate is to follow the relative formation of *trans* acids in the 1,3- and 2-positions, since hydrogenation is accompanied by isomerization. The percentage proportionate formation of *trans* acids in the respective positions at any stage during hydrogenation was calculated relative to the content of total unsatu-

TABLE I
Effect of the Position of Linoleic Acid in Triacylglycerols on Its Hydrogenation Rate

Reduction in iodine value, %	Triacylglycerols										Fatty acid, mole % ^a				Proportionate loss of 18:2 ^d , %				Relative loss of 18:2		Proportionate formation of <i>trans</i> ^e , %		Relative formation of <i>trans</i>	
	18:0		18:1		18:2		<i>Trans</i> ^c		2-position		1,3-position ^b		1,3-pos.		2-pos.		1,3-pos.		2-pos.		1,3-pos.		2-pos.	
	18:0	18:1	18:2	<i>Trans</i> ^c	18:0	18:1	18:2	<i>Trans</i> ^c	18:0	18:1	18:2	12	13	14	15	16	17	18	19					
0.0	2.7	26.5	39.8	0.0	0.0	36.4	61.1	0.0	4.0	21.5	29.1	0.0	44.5	28.6	1.6	9.3	10.9	0.8	0.0	0.0	0.0	0.0	0.0	
14.7	3.5	39.8	25.3	6.7	2.1	50.8	43.6	10.6	4.2	34.3	16.1	4.7	54.8	65.6	0.8	28.7	19.7	1.5	0.0	0.0	0.0	0.0	0.0	
24.5	7.5	45.5	15.8	16.1	5.0	69.9	21.0	19.2	8.7	33.3	13.2	14.5	62.3	71.7	0.9	33.8	21.4	1.6	0.0	0.0	0.0	0.0	0.0	
27.4	8.9	46.3	13.1	18.4	7.3	70.4	17.3	20.9	9.7	34.2	11.0	17.1	71.9	71.7	1.0	47.8	17.4	1.7	0.0	0.0	0.0	0.0	0.0	
31.6	9.2	47.8	11.2	21.8	7.1	70.3	17.3	17.0	10.2	36.5	8.1	24.2	71.9	71.7	1.0	47.8	17.4	1.7	0.0	0.0	0.0	0.0	0.0	
Cottonseed oil (I.V. 95.2)																								
0.0	7.4	41.6	39.7	0.0	0.9	49.2	48.3	0.0	10.6	37.8	35.4	0.0	28.4	11.4	2.5	N.D.	N.D.	N.D.	0.0	0.0	0.0	0.0	0.0	
5.0	8.3	49.0	31.2	N.D. ^f	0.8	54.1	42.8	N.D.	12.0	46.4	25.4	N.D.	71.3	52.4	1.4	25.3	34.1	0.7	0.0	0.0	0.0	0.0	0.0	
20.1	8.5	66.2	14.4	23.2	2.3	73.3	23.0	32.6	11.6	62.6	10.1	18.5	75.8	64.0	1.2	36.1	28.8	1.3	0.0	0.0	0.0	0.0	0.0	
22.4	7.8	69.3	11.5	26.8	1.5	79.9	17.4	27.6	10.9	64.0	8.5	26.4	94.0	80.9	1.2	57.0	31.0	1.9	0.0	0.0	0.0	0.0	0.0	
28.3	8.6	75.2	4.5	37.7	1.8	87.9	9.2	29.7	12.0	68.8	2.1	41.7	94.0	80.9	1.2	57.0	31.0	1.9	0.0	0.0	0.0	0.0	0.0	
Sesame oil (I.V. 106.6)																								
0.0	3.5	22.5	55.8	0.0	0.0	23.7	71.6	0.0	5.2	21.9	47.9	0.0	42.0	21.9	1.9	31.3	21.0	1.5	0.0	0.0	0.0	0.0	0.0	
13.8	4.4	40.0	37.8	22.6	0.5	39.1	57.0	20.7	6.2	40.4	28.2	23.5	51.3	52.9	1.0	37.6	26.9	1.4	0.0	0.0	0.0	0.0	0.0	
22.6	5.4	50.3	29.8	27.7	1.6	60.2	36.3	26.6	7.3	45.4	26.5	28.2	61.0	82.5	0.7	59.6	36.7	1.6	0.0	0.0	0.0	0.0	0.0	
29.0	5.3	62.1	20.6	41.9	1.0	82.5	15.9	36.2	7.4	51.9	22.9	44.7	61.0	82.5	0.7	59.6	36.7	1.6	0.0	0.0	0.0	0.0	0.0	
Safflower oil (I.V. 146.8)																								
0.0	2.2	14.3	76.4	0.0	0.0	15.4	84.6	0.0	3.3	13.7	72.3	0.0	22.4	24.5	0.9	15.9	14.8	1.1	0.0	0.0	0.0	0.0	0.0	
12.7	2.6	31.6	58.7	14.1	0.0	36.1	63.9	14.8	3.9	29.3	56.1	13.7	34.7	37.2	0.9	30.8	16.9	1.8	0.0	0.0	0.0	0.0	0.0	
18.0	2.3	42.0	49.2	23.3	0.0	46.9	53.1	16.9	3.4	39.5	47.2	26.5	69.4	67.5	1.0	58.4	30.0	1.9	0.0	0.0	0.0	0.0	0.0	
31.5	2.3	67.4	23.9	43.5	0.0	72.5	27.5	30.0	3.4	64.8	22.1	50.2	69.4	67.5	1.0	58.4	30.0	1.9	0.0	0.0	0.0	0.0	0.0	

^aRemainder constitutes mainly 16:0 and traces of other saturated acids in sesame and cottonseed oils and 18:3 in soybean oil. The percentages of 18:3 in total triacylglycerols, 2-position and 1,3-position are 4.6, 4.0, 1.6 and 0.7; 3.4, 2.3, 0.8 and 0.0; and 5.2, 4.8, 2.0 and 1.0, respectively, in the successive samples.

^b(Triacylglycerols x 3)-2-pos.

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^cIncluded in unsaturated acids.

^dLoss of 18:2 in 1,3-(or 2-) position in hydrogenated sample compared to that in the original sample X 100

^eContent of 18:2 in 1,3-(or 2-) position in the original sample

Content of *trans* acids in 1,3-(or 2-) position X 100

Content of total unsaturated acids in 1,3-(or 2-) position in the original sample

^fNot determined.

It is assumed that 18:3 is hydrogenated selectively to 18:2 only, and hence 18:3 lost (footnote a) by any particular stage is deducted from the apparent content of 18:2 at that stage to calculate the actual loss of 18:2.

rated acids in the unhydrogenated sample. These values are also given in Table I (columns 17 & 18). Column 19 gives the relative formation of *trans* acids in these positions (columns 17 and 18). These values increase steadily as the hydrogenation proceeds showing preferential formation of *trans* acids in the 1,3-positions.

Recent studies by Drozdowski (10) on the hydrogenation of linseed and cod liver oils as well as rearranged soybean and rapeseed oils using nickel or platinum catalyst also show that unsaturated fatty acids in the 1,3-position of triacylglycerols are hydrogenated faster than those present in the 2-position.

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