GC/MS Analysis of Some Long Chain Esters, Ketones and Propanediol Diesters

M. VAJDI, W.W. NAWAR, Department of Food Sciences and Nutrition, University of Mass., Amherst, MA 01003, and C. MERRITT, Jr., Food Sciences Laboratory, U.S. Army Natick Research and Development Command, Natick, MA 01760

ABSTRACT

Identification of radiolysis products which are formed in lipids in the range of molecular weights from 400-600 has been established on the basis of gas chromatography/mass spectrometry (GC/MS) studies of long chain authentic samples of alkyl esters, ketones and propanediol diesters. This paper describes the GC/MS behavior of these compounds. Double hydrogen rearrangement was found to be the predominant ion in the spectrum of long chain saturated esters whereas in the unsaturated esters, a peak corresponding to the loss of alcohol from the molecular ion was more pronounced. On the contrary to short chain ketones, McLafferty rearrangement did not appear to be the major fragmentation in the spectrum of saturated and unsaturated long chain ketones. α-Cleavage was found to be the predominant fragmentation in the spectrum of these ketones. The "McLafferty + 1" rearrangement peak was more pronounced for the long chain ketones than those found in the spectrum of smaller ketones. Fragmentation patterns of propanediol diesters were shown to be similar to those in triglycerides, giving rise to predominant peaks corresponding to acylium ion $[RCO]^+$ and parent minus acyloxy ion $[R\text{-}COO]^+$.

INTRODUCTION

The presence of long chain esters and diol diesters have been indicated in nature from various sources (1,2). In our studies of irradiated triglycerides and natural fats (3,4), certain long chain esters, ketones and propanediol diesters have been identified. The spectra of these compounds have not been studied or reported previously. This paper describes the gas chromatographic and mass spectrometric (GC/MS) behavior of these compounds.

MATERIALS AND METHODS

The reagents used for the preparation of compounds in this study were purchased from ICN, Pharmaceutical Inc., Plainview, NY. The purity of each product was established by GC.

Long chain esters (pentadecyl palmitate, pentadecyl oleate and hexadecenyl oleate) were synthesized by the reaction of the alcohol and the corresponding acid chloride in a solution of chloroform and pyridine.

The symmetrical ketone (16-hentriacontanone) and the monounsaturated ketone (18-tritriaconta-9-enone) were prepared according to the Gilman and Nelson method (5).

Propanediol diesters were prepared using 1,2-propanediol, and 1,3-propanediol with the appropriate acid chloride by the Baumann et al. method (1).

GC/MS data for all the compounds were obtained on a Dexil-400 column (operating conditions are given in Fig. 1) and a system composed of a PE Model 3920 gas chromatograph coupled to a Dupont Model 21-491 double focusing mass spectrometer via a glass jet molecular separator. Mass spectral data were acquired and analyzed by means of a data system employing HP Model 2116 and DEC PDP 15/76 computers.

RESULTS

The mass spectra of the long chain esters and ketones are shown in Table I. Some typical mass spectra are represented as histograms in Figures 2-5.

Gas chromatograms of the authentic isomers of propanediol diesters were obtained individually and as a mixture to obtain resolution and retention time data for comparison with those of the unknown mixtures analyzed in the radiolysis studies (3,4).

The gas chromatograms of the propanediol diesters demonstrated an adequate resolution between the synthesized isomers. 1,2-Propanediol diesters appeared before 1,3-propanediol diesters when separated on Dexil-400 column (Fig. 1).

The mass spectra of 1,2-propanediols were similar to those of 1,3-propanediols with respect to the fragmentation pattern. Table II presents the relative abundance of the major fragmentation ions obtained from propanediol diesters. The parent ions were not observed.

DISCUSSION

Because of the similarity of mass spectra within each group, only a few examples were chosen to be discussed here in detail.

Saturated Esters

In the spectra of short chain methyl esters, β-cleavage with a transfer of γ-hydrogen (McLafferty rearrangement) results in the formation of a characteristic base peak at m/e 74 (6). Although double hydrogen rearrangement occurs to a small

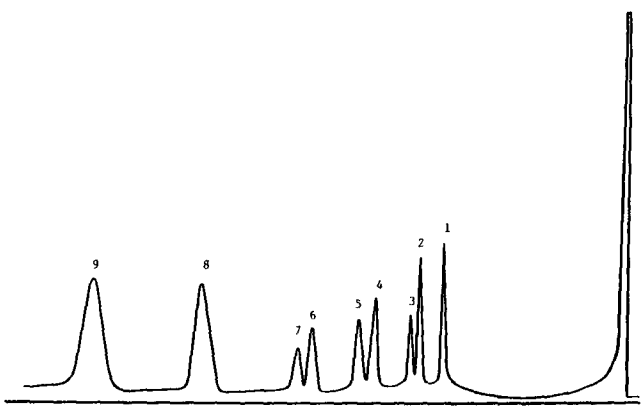


FIG. 1. Gas chromatogram of propanediol diesters. Column: 3% Dexil 400 (5' X 1/8"); temp.: 250 C-340 C (10C/min); flow rate: 30 ml/min. Peak No. 1 = 1,2-tetradecanoyl propanediol diesters; 2 = 1,3-tetradecanoyl propanediol diesters; 3 = 1,2-tetradecanoyl propanediol diesters; 4 = 1,3-tetradecanoyl propanediol diesters; 5 = 1,2-hexadecanoyl propanediol diesters; 6 = 1,3-hexadecanoyl propanediol diesters; 7 = 1,2-hexadecanoyl pntadecenoyl propanediol diesters; 8 = 1,2-octadecenoyl propanediol diesters; 9 = 1,3-octadecenoyl propanediol diesters.

TABLE I

Relative Abundance of Ions in the Mass Spectra of Some Long Chain Esters and Ketones

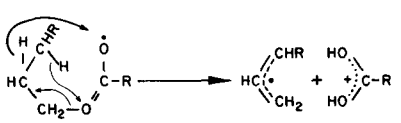
	Esters				Ketones				
Compound[a]	1	2	3	4	5	6	7	8	9
m/e	Intensity								
41				60					
43	80	100	98		92	97	100	55	100
55			100	100					
57	82	85			90	98	90	48	80
58					58	70	80	30	22
69			82	96					55
71	55	70			100	100	98	40	
83	60	62	80	85					38
85					55	58	68	20	
96					45	47	50	18	
97	48	64	65	80					40
100									
111	30	18	41	15					
124				48					
125	22		24						
138				38					
182	13	4							
183					10	5			
210	40								
211					90α	56α		7	
222			20	50					
224		16							
225							80		
226					25M	15M			
227					40H	30H			
237									10
239	20	55			12γ	50α	94α	100α	35α
240							45		
241							38H		
253					5				
254						15M	28M	35M	
255	10	22				17H	35H	62H	18H
257	100r	52r							
264			90	32					
265				38					30α
267						10r	15γ	18γ	12γ
268							25		
283			25r	15r					5H
293									5γ
307									15
321									32
394					2P				
422						4P			
436							5P		
449									12
450								10P	
466	52P								
476									2P
480		18P							
492			12P						
504				8P					

[a]1 = Pentadecyl palmitate (MW 466); 2 = Hexadecyl palmitate (MW 480); 3 = Pentadecyl oleate (MW 492); 4 = Hexadecenyl oleate (MW 504); 5 = 14-Heptacosanone (MW 394); 6 = 14-Nonacosanone (MW 422); 7 = 15-Triacontanone (MW 436); 8 = 16-Hentriacontanone (MW 450); 9 = 18-Tritriaconta-9-enone (MW 476); H = McLafferty + 1 rearrangement; r = double hydrogen rearrangement; α = alpha cleavage; γ = gamma cleavage; P = Parent ion; M = McLafferty rearrangement ion.

extent in the short chain compounds, it becomes predominant with an increase in the aliphatic alkyl chain beyond the propyl group (7), and replaces the McLafferty rearrangement ion as the most abundant ion.

The predominant double hydrogen rearrangement peak in the mass spectrum of the esters of long chain alcohols and long chain fatty acids may be depicted as a decomposition of the odd electron parent ion with rearrangement of two hydrogen atoms (Scheme I).

SCHEME I



The process accounts for the base peak of m/e 257 in the spectrum of pentadecyl palmitate and an abundant peak in the spectrum of hexadecyl palmitate (Fig. 2). The hydrogen-type peaks at m/e 210 and 224 [M-256] in each of the saturated palmitate esters correspond to a loss of the acid moiety. Similar peaks were observed by Ryhage and Stenhagen (6) in the spectra of other long chain saturated esters. Other peaks may be expected at M-(RCOOH + 28). A distinct molecular ion is present as well as a peak at m/e = [M-211], indicating cleavage at the acyloxy site.

Unsaturated Esters

In the mass spectra of pentadecyl oleate, the predominant major fragmentation typical of unsaturated esters is found

TABLE II

Relative Abundance of Principle Ions in the Mass Spectra of Propanediol Diesters

Compound[a]:	1	2	3	4	5	6	7	8	9	10	11
m/e	Intensity										
41								10			18
43	98	90	60	45	70	35	27		78	55	
55								15	76		48
57	82	55	64	34	68	25	28			58	
69									60	38	44
71	63	20	45	20	45	20	17	12			
84	50	38	45	15	50	18	4	5	38	35	12
98	50	25	58	18	55	19	5	15	56	38	22
100	55	40	68	26	70	18	10	12	62	35	12
113	52	42	60	25	65	30	25	30	65	50	28
169	25	15	25	10	25	12	18	10	25	15	12
211	98	85	50			30					
229	22	8	4			4					
239		60	45	70	55		25	15	50		
257		12	2	10	3		3	2	5		
264						35		20	75	25	15
265						20		18	44	15	30
267							15			32	
269	100	100	100			100					
283						2		5	2	1	
285							2			2	
287	45	15	25			12					
297		95	98	100	100		100	100	85		
315		12	10	12	20		8	2	25		
322						45			98	35	42
323						50		38	100	50	100
325							25			100	
341						3		2	1	2	4
343							5			2	

[a]1 = 1,2-Tetradecanoyl propanediol diesters (MW 496); 2 = Tetradecanoyl hexadecanoyl 1,2-propanediol diesters (MW 524); 3 = Tetradecanoyl hexadecanoyl 1,2-propanediol diesters (MW 524); 4 = 1,2-hexadecanoyl propanediol diesters (MW 552); 5 = 1,3-Hexadecanoyl propanediol diesters (MW 552); 6 = Tetradecanoyl octadecenoyl 1,3-propanediol diesters (MW 550); 7 = Hexadecanoyl octadecanoyl 1,2-propanediol diesters (MW 580); 8 = Hexadecanoyl octadecenoyl 1,2-propanediol diesters (MW 578); 9 = Hexadecanoyl octadecenoyl 1,3-propanediol diesters (MW 578); 10 = Octadecanoyl octadecenoyl 1,3-propanediol diesters (MW 606); 11 = 1,20Octadecenoyl propanediol diesters (MW 604).

at m/e 264 due to the apparent loss of a fragment corresponding to the alcohol group [M-288]. This behavior is similar to the apparent loss of methanol from methyl oleate when M-32 becomes the base peak in that spectrum (6). Another characteristic peak is seen at m/e 222 [M-270] corresponding to a similar peak found in methyl oleate [M-74]. The lost species may be postulated to be a rearrangement fragmentation of the McLafferty type, with cleavage β to the carboxyl and a transfer of hydrogen to the carboxyl, where the charge remains on the alkenyl residue rather than the carboxyl moiety. Double hydrogen rearrangement also occurs, but to a lesser degree (25%) than with saturated esters yielding a peak at m/e 283 (Table I).

The apparent loss of alcohol is similarly evident in the mass spectrum of hexadecenyl oleate (Fig. 3), producing a peak at m/e 264. Cleavage at the acyl site produces a large peak at m/e 265, whereas the peak at m/e 222 corresponds as in pentadecyl oleate to β-cleavage [M-282] with hydrogen transfer to the carboxyl.

Ketones

α-Cleavage is a predominant fragmentation in the spectra of long chain ketones (Table I), yielding the acyl ion (RCO or, i.e., M-R). It produces the base peak in a symmetrical ketone such as palmitone (16-hentriacontanone). In an unsymmetrical ketone such as 15-triacontanone, the cleavage,

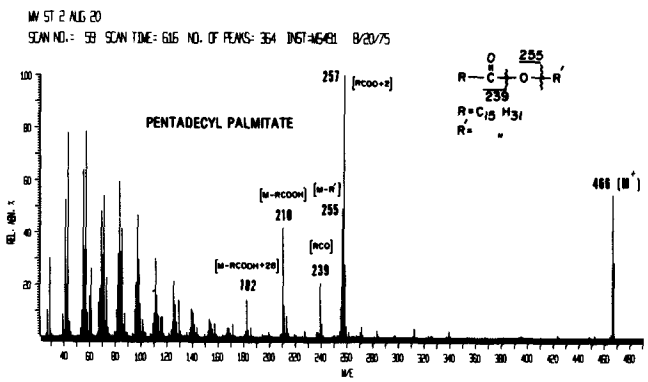


FIG. 2. Mass spectrum of pentadecyl palmitate.

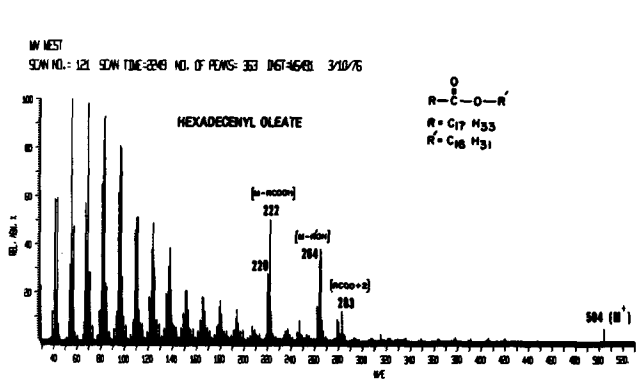


FIG. 3. Mass spectrum of hexadecenyl oleate.

as found with smaller ketones (8), occurs with loss of the smaller alkyl chain:

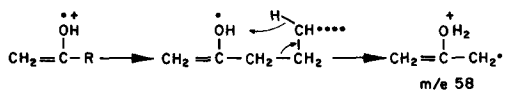
$C_{15}H_{31}COC_{14}H_{29}$ → $C_{15}H_{31}CO^+$ m/e 239 (94%); $C_{14}H_{29}CO^+$ m/e 195 (15%)

Where the side chain is unsaturated, less preference is observed:

$C_{15}H_{31}COC_{17}H_{33}$ → $C_{15}H_{31}CO^+$ m/e 239 (35%); $C_{17}H_{33}CO^+$ m/e 265 (30%)

The McLafferty rearrangement in the spectrum of a methyl ketone yields a base peak at m/e 58. This peak also is observed characteristically in the spectrum of other ketones, but arises from a second rearrangement of the McLafferty rearrangement ion. The peak occurs at ca. 20-30% abundance in the spectra of the ketones given in Scheme II:

SCHEME II

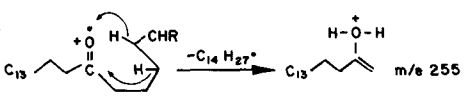


The McLafferty rearrangement ion itself does not appear as a major fragmentation ion in the spectra of these compounds and yields peaks of relatively low abundance at m/e 254 in palmitone (35%) and 15-triacontanone (28%). In the unsymmetrical ketones, the McLafferty ion does not appear at all in the spectrum of 18-tritriaconta-9-enone and only for the longer alkyl chain in the 15-triacontanone spectrum.

Fragmentation γ to the carbonyl group accounts for a moderately abundant peak present at m/e 267 (Table I). In this case, as with α-cleavage, cleavage is preferred in the smaller side chain, and where unsaturation is present in the unsaturated chain.

The presence of an abundant peak at m/e 255 in palmitone (Fig. 4) results from a concerted double hydrogen transfer which may occur from different positions on the alkyl chain. This reaction is due to β-cleavage in the long chain with one hydrogen transfer from the γ-carbon (McLafferty rearrangement) and one from another position ("McLafferty + 1") yielding m/e 255 (Scheme III):

SCHEME III



The "McLafferty + 1" rearrangement has been observed previously in low abundance in the spectrum of several smaller ketones (9). In this study, however, the mass spectra of several even and uneven dialkyl ketones of long chains have indicated relatively intense peaks arising from this rearrangement. These peaks were as abundant as the classic single hydrogen McLafferty rearrangement ion and, in some cases, more intense (Table I). In the spectrum of 15-triacontanone the "McLafferty + 1" rearrangement yield peaks at m/e 255 (35%) and m/e 241 (38%).

In the spectrum of 18-tritriaconta-9-enone, several major fragmentations were found corresponding to both sides of the carbonyl group. Peaks at m/e 239 and 267 correspond to simple cleavage at sites α and γ to the carbonyl group of unsaturated alkyl chain, respectively. Cleavage at the site β to the carbonyl group yields the "McLafferty + 1" rearrangement. This fragmentation gives rise to peaks at m/e 255 (18%) corresponding to the ion $[C_{15}H_{31}COOH_2CH_2]^+$ and m/e 283 (5%) corresponding to $[C_{17}H_{33}COOH_2CH_2]^+$. Simple cleavage on the saturated alkyl chain fragmentations yields peaks at m/e 265 (α), 293 (γ), 307 (δ) and 321 (ϵ) (Table I).

Propanediol Diesters

In the mass spectra of the propanediol diesters with the same fatty acid group, two major fragmentations occur which are similar to those of triglycerides (6), giving rise to an acylium ion, $[RCO]^+$, and a parent minus acyloxy ion $[M\text{-}RCOO]^+$, in both the 1,2 and 1,3 isomers. The $[M\text{-}RCOO]^+$ apparently is the base peak in both configurations.

In the mixed propanediol diesters, four major fragmentations occur giving rise to ions $[RCO]^+$, $[RCO]^+$, $[M\text{-}RCOO]^+$ and $[M\text{-}RCOO]^+$ in both isomers (Fig. 5). The pattern of fragmentations of propanediol diesters containing the unsaturated ester were similar to those containing the saturated esters. In all the cases, the acyl fragmentation of the unsaturated ester resulted in a less abundant acyl ion compared to those of the saturated ester fragmentation (Fig. 5). Furthermore, in the spectra of a propanediol diester containing the unsaturated ester, a relatively intense peak is present at a mass that is one unit less than that of the corresponding acylium ion $[RCO]^+$. The mechanism involved in this fragmentation probably is similar to the fragmentation of M-32 ion from monounsaturated long chain methyl esters (2). The ion $[RCO\text{-}1]^+$ was as intense

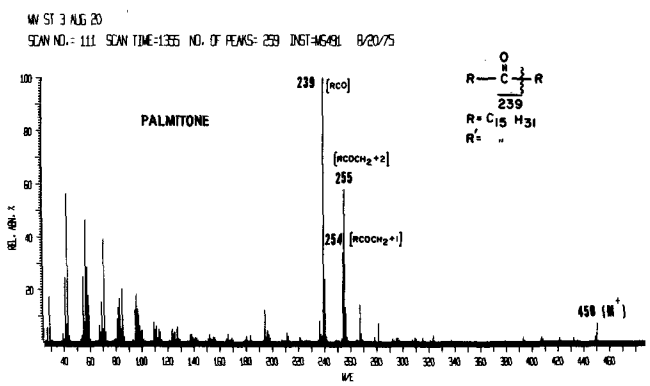


FIG. 4. Mass spectrum of palmitone.

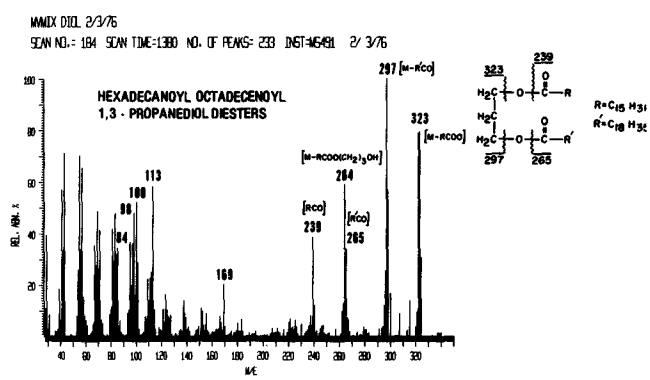
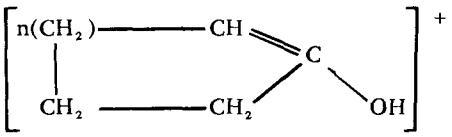


FIG. 5. Mass spectrum of hexadecanoyl octadecenoyl 1,3-propanediol diesters.

as the corresponding acylium ion $[RCO]^+$ (Fig. 5).

In all cases, a distinct pattern of fragmentation was noted for all the propanediol diesters studied. A base peak corresponding to the ion $[M\text{-}RCOO]^+$ was observed in all the spectra obtained. Another fragmentation typical of propanediol diesters is due to a common ion of the structure:



and giving rise to m/e 84 and 98 corresponding to n of 1 and 2, respectively. Additional peaks of low intensities (287, 315, 341, 343) arising from the loss of the acyl group from the compound and capture of two hydrogens also were found in the spectra (Table II). In general, the pattern of fragmentations obtained in the spectra of propanediol diesters was in agreement with those of ethanediol diesters reported previously (2).

ACKNOWLEDGMENT

J.H. Cornell synthesized the ketones and helped prepare the propanediol diesters.

REFERENCES

1. Baumann, W.J., H.H.O. Schmid, H.W. Ulshoffer, and M.R. Mangold, Biochim. Biophys. Acta 144:355 (1967).
2. Baumann, W.J., J. Seufert, H.W. Hayes and R.T. Holman, J. Lipid Res. 10:703 (1969).
3. Vajdi, M., W.W. Nawar and C. Merritt, Jr., JAOCS 55:849 (1978).
4. Vajdi, M., W.W. Nawar and C. Merritt, Jr., Ibid. 56:611 (1979).
5. Gilman, H., and J.F. Nelson, Recl. Trav. Chim. 55:518 (1936).
6. Ryhage, R., and E. Stenhagen, J. Lipid Res. 5:361 (1960).
7. McLafferty, F.W., Interpretation of Mass Spectra, W.A. Benjamin, Inc. 1973, p. 134.
8. Sharkey, A.G., J.L. Shultz and R.A. Friedel, Anal. Chem. 28:934 (1956).
9. Edon, G., C. Djerassi, J.H. Beynon and M. Caprioli, Org. Mass Spectrom. 5:917 (1971).

[Received July 18, 1980]

Cocoa Butter Substitutes from Mango Fat

B.P. BALIGA and A.D. SHITOLE, Research and Development Laboratories, M/s, The Tata Oil Mills Company Limited, Sewri, Bombay, 400 033, India

ABSTRACT

Mango fat obtained by solvent extraction of the kernels of the mango fruit (*Magnifera indica*) has been studied for its suitability in making cocoa butter substitutes. The fat has been fractioned from acetone at low temperatures in one and/or two stages in order to segregate suitable solid fractions having physical properties closer to cocoa butter. The data pertaining to the solidification characteristics and dilatometric behavior of the mango fat, its acetone-fractionated products and their admixtures with cocoa butter in equal proportions have been determined in order to assess their compatibility with cocoa butter. Fractionated mango fat can serve as a good partial substitute for cocoa butter.

INTRODUCTION

Cocoa butter is a unique, naturally occurring fat containing mainly monounsaturated and diunsaturated glycerides in which palmitooleostearin constitutes a single dominant glyceride. Several workers have attempted to prepare cocoa-butter-like products from other fats which have some degree of resemblance to cocoa butter and which could be modified into cocoa-butter-like fats. The various methods tried (1-12) include esterification, (inter-, trans- and directed), hydrogenation (selective or homogeneous), fractionation (dry, with solvent or water containing a surface-active agent) or combination of these in order to have a product with a melting point (mp) around 36 C and a sufficient degree of hardness and brittleness so that the finished product retains its shape at normal room temperatures.

All of these routes, except for fractionation alone, have some obvious disadvantages, such as randomization, isomerization and *trans* acid formation, which preclude exact simulation of a cocoa-butter-like product. Or, if the physical properties are reproduced, the product might be incompatible with cocoa butter when used in blends. Fractionation is considered the most suitable method for segregating glyceride fractions in their natural form/configuration which could have cocoa-butter-like properties, and which could be blended with cocoa butter without adversely affecting the original characteristics of cocoa butter. The preparation of Coberine (12) by solvent fractionation of palm oil is an ideal example of this method.

In India, a number of indigenous fats that are rich in monounsaturated and disunsaturated glycerides and low in linoleic acid content are available which can serve as good starting materials for making cocoa butter substitutes. Examples are sal (*Shorea robusta*), dhupa (*Vateria indica*), kokum (*Garcinia indica*), mowrah (*Bassia latifolia*) and mango (*Magnifera indica*). The reported fatty acid and glyceride compositions of these fats and of cocoa butter are given in Table 1 (14-20). Cocoa butter substitutes have been prepared from sal, kokum and mowrah fats (6-11).

In this study, an attempt has been made to prepare cocoa-butter-like products from mango fat by fractionation.

At least 1,000 varieties of mango are available in India, of which about 25 varieties are commercially important (13). The mango kernels contain 6-15% fat. The composition of the fat varies among sources (Table II, ref. 21). The glyceride composition reported by Pathak et al. (20) shows that the fat contains 14% trisaturated glycerides. The proportion of disaturated to monosaturated glycerides is very low (0.4:1) compared to that of cocoa butter (3.7:1). It is therefore necessary to fractionate the fat in order to segregate a suitable fraction having properties similar to cocoa butter. Some work has been reported in this area (22,23).

In this study, acetone fractionation of mango fat in a single stage and in two stages has been done to obtain suitable hard fractions. A detailed evaluation of the physical properties of the individual fractions, original mango fat and their blends with cocoa butter in equal proportions