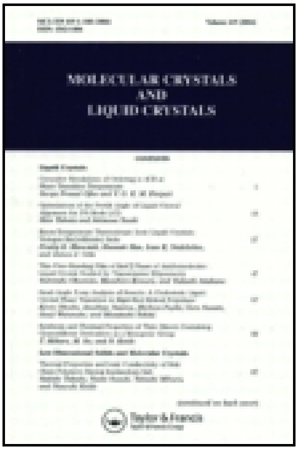

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Optical Behavior of Natural Oils and Fats of Plant Origin

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Optical Behavior of Natural Oils and Fats of Plant Origin

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The paper describes and discusses the results of the observations made on the optical textures exhibited by sixteen naturally occurring oils and fats of plant origin. The textures observed here consist of spherulites, drops, batonnets and maltese crosses which are characteristic of liquid crystals. The refractive indices and the average isotropic polarizabilities of these substances are also discussed. Often it is found that the mesomorphic nature is more pronounced with oils and fats with a high component of saturated triglycerides and with high molecular weights. The paper is illustrated by numerous striking photographs.

Keywords: optical behaviour, mesomorphism, fats, oils

1. INTRODUCTION

Studies have been carried out earlier by others on the optical properties of fatty acid esters[1,2] waxes[3] lard[4] and compounds of related species[5,6] with large content of fatty acid esters. Earlier studies on the optical behaviour of several pure saturated aliphatic esters[3] have clearly shown that they exhibit liquid crystalline behaviour and are significantly birefringent and manifest striking optical textures. The saturated esters of aliphatic acids are relatively simple in their structure, the major portion of the skeleton of the molecule consisting of the zig-zag alkyl chain and the extended molecule may be described as "lath shaped." On the other hand, naturally occurring oils and fats of plant origin have a more complex chemical constitution and consist of mixtures of esters of the trihydric alcohol, i.e., glycerol and fatty acids. Apart from triglycerides, fats also contain a small portion of non-triglyceride constituents.[7] The fatty acid radicals constitute a significant portion of the triglyceride molecule and there can be three branches as shown in Figure 1. The radical "R" represents the fatty acid which in the case of fats of vegetable origin may have widely different constituents of saturated and unsaturated fatty acids. Further, the different molecules of the fat may have different chemical compositions because of the varying nature of R and its coordination at the different sites available. However, it is useful to recognize that here we are dealing with molecules of approximately similar chemical architecture but with different "complexions." Evidently, the molecules of the fatty oils are highly asymmetric and cannot be visualized to be having a simple shape. Under these circumstances, it is quite convenient to associate with each molecule a polarizability ellipsoid. When the polarizability ellipsoids are not randomly oriented in space, the material will exhibit birefringence. Hence, the condensed phases of fatty oils are expected to exhibit birefringence and characteristic textures depending on the nature of the molecular orientation. In the liquid phase, owing to the random orientation of the molecules, the material will be optically isotropic. The present investigation was undertaken with a number of naturally occurring oils of vegetable origin. The studies relate to the optical textures, the birefringence, the refractive indices and densities of a number of fatty oils. The results that have emerged from these studies strikingly confirm our expectations that below the freezing point many naturally occurring fatty oils exhibit mesomorphic behaviour. Further, the X-ray studies carried out by us lend support to the above view. The studies on the refraction of oils have also enabled us to estimate the average polarizabilities in the case of different fatty oils from a knowledge of their average triglyceride composition.

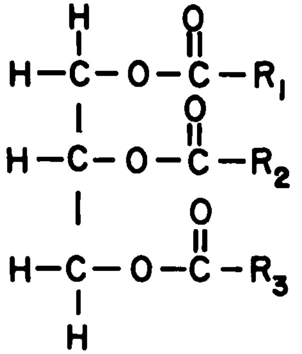


FIGURE 1 Structural formula of a triglyceride molecule.

2. EXPERIMENTAL

The samples of vegetable fats and oils used here were kindly made available to us by the Oil Technological Research Institute, Anantapur, India. The oils and fats investigated by us are listed in Table I which also presents the basic data with regard to the iodine value, saponification value, average molecular weight and the percentage of saturated component esters. The iodine value, saponification value and the percentage composition given in Table I are taken from the data given by the Oil Technological Research Institute. The average molecular weight "M" has been calculated using the well known relation[8] that

$$M = 3 \times 56108 \times (1/\text{saponification value}). \quad (1)$$

The densities of the samples at different temperatures were determined from measurements on the length of a pellet of oil taken in a calibrated capillary tube and maintained at different temperatures in a hot stage. The measured densities are correct to ± 0.0005 gm/cm^3. The refractive indices of the several oils at different temperatures were determined for the sodium D-lines using an Abbe refractometer with thermostatically controlled water circulation. It was also possible to measure the birefringence in the case of the two fats, viz., mango kernel fat and sal seed fat using an interference technique described in one of our earlier papers.[9] The refractive indices and birefringence measurements are correct to ± 0.0005.

The optical textures were observed with a polarizing microscope using specimens of thin films of fats between slide and coverglass and the temperature of the sample could be held static at any desired value by making use of a hot stage as described in one of our earlier papers.[10]

X-ray diffraction photographs/diffractometer traces obtained with different samples also confirm the smectic/β phase type of ordering in several of the samples. Since the nature of such diffraction patterns is very well known,[3,9] diffraction photographs are not reproduced here.

3. REFRACTIVE INDICES AND POLARIZABILITIES

The refractive indices and the values of molar refraction derived therefrom, may also be used as a characteristic property for identification of chemical compounds. Attempts have been made by earlier

TABLE I

Name of the oil/fat	Botanical name of the species	Iodine value	Saponification value	Mean molecular weight	Weight % of saturated esters
Palm Kernel		16	244	689.85	
Date Seed	Phoenix Sylvertris	50	212	793.98	53.6
Palm	Elacis Guineensis Jaca	66	198	850.12	50
Sal Seed	Shorea robusta	36	193	872.14	55.3
Mango Kernel	Mangifera indica	50	191	881.28	50.8
Neem	Azardirachta indica	67	195–204	865.66[a]	43
Lime Seed	Satrus Auruintifolia	102.2	197.2	853.57	36.5
Subabul	Leucaena leucocephala	133	187.3	898.69	24.3
Chilli seed	Capsicum annum	136	192	876.69	18.9
Karanj	Pongamia Pinnata	82.9	187.5	897.73	
Tamarind Seed	Tamarindus indica	186.4	192	876.69	27.4
Gonkhru Seed	Xanthium strumarium	133	188	895.34	10.5
Ambadi Seed	Hibiscus cannabinus	93–107	189–193	883.68[a]	21
Rice bran	Oryza sativa	85–104	179–195		
Cotton seed	Gorsypium	103–115	189–198		21–25
Groundnut	Arachis hypogaea	84–100	188–196		
Hydrogenated rice bran		28			
Hydrogenated ambadi seed		54			

[a] Approximate value of Molecular weight calculated from the triglyceride composition of the oil.

investigators to correlate refractive index with the characteristic constants of fatty acid esters and oils. For example, Hammond and Lundberg[1] have developed equations for the calculation of molar refraction, molar volume (or density) and refractive index for liquid fatty acid and some simple derivatives of fatty acids. These equations involve two parameters, viz., carbon chain length and unsaturation. However, they suggest that in the case of fatty oils a linear relationship between refractive index and iodine value has a rather limited applicability. Making use of the values of group refractivities obtained from data on hydrocarbons, Tels *et al.*,[2] have derived an empirical relation between iodine value, saponification value and the specific refraction of fatty oils, namely,

$$r_D^{20} = (n^2-1)(n^2+2)^{-1}d^{-1}$$

$$= 0.3307 + 1.68 \times 10^{-5}\, I{\cdot}V - 1.41 \times 10^{-4}\, S.V. \quad (2)$$

In the present investigations, the values of specific refraction of fatty oils determined experimentally are in good agreement with the values calculable from the above relation.

Using the calculated values of the molecular weight (Eq. (1)), it is possible to estimate the average values of the molar refraction and the mean molecular polarizability for each natural oil, using the well-known Lorentz-Lorenz relation. These values are presented in Table II. It may be assumed that the increase in molecular weight in the case of different oils arises mainly due to the additions of methylenes involving an increase in the length of the alkyl chains. Therefore, one should expect that the increase in the average molecular polarizability with the molecular weight has to be attributed mainly to the average number of methylene groups added. That this interpretation is correct is confirmed by a graphical plot of the mean molecular polarizability "α" versus the average molecular weight "M." The graph exhibits the linear variation, as shown in Figure 2. In particular, it should be pointed out that the increase in the average molecular polarizability (of 1.79×10^{-24} cm^3) for every 14.027 gms (calculable from Figure 2) corresponds to the polarizability associated with the methylene group, in pleasing agreement with the value of 1.84×10^{-24} cm^3 reported in the literature.[2] Further, the observed values of the molecular polarizability in the case of several pure triglycerides are in good agreement with the values found from an extrapolation of the graph in Figure 2. It may be noted that in Figure 2, the point corresponding to palm oil (M = 850.12) is very much out of alignment

TABLE II

Name of the oil/fat	Density at 30°C	Ref. index at 30°C	Specific refraction	Mean molecular polariza-bility $\alpha(10^{-24}cm^3)$	Molar refraction (cm^3)
Palm kernel oil	0.9060	1.4590	0.3017	82.512	208.15
Date seed oil	0.9273	1.4610	0.2959	92.157	232.49
Palm oil	0.9428	1.4610	0.2910	98.077	247.42
Sal seed oil	0.9032	1.4620	0.3044	105.235	265.48
Mango Kernel fat	0.8953	1.4586	0.3051	106.574	268.85
Neem oil	0.9091	1.4738	0.3090	106.047	267.52
Lime seed oil	0.9126	1.4683	0.3048	103.121	260.14
Subabul oil	0.9096	1.4696	0.3065	109.182	275.43
Chilli seed oil	0.9140	1.4732	0.3070	106.701	269.17
Karanj oil	0.9243	1.4770	0.3086	108.785	274.43
Tamarind seed oil	0.9342	1.4761	0.3019	104.934	264.72
Ambadi seed oil	0.9224 (26.5°C)	1.470	0.3025	105.954	267.29
Gonkhru seed oil	0.9120	1.4735	0.3079	109.269	275.65

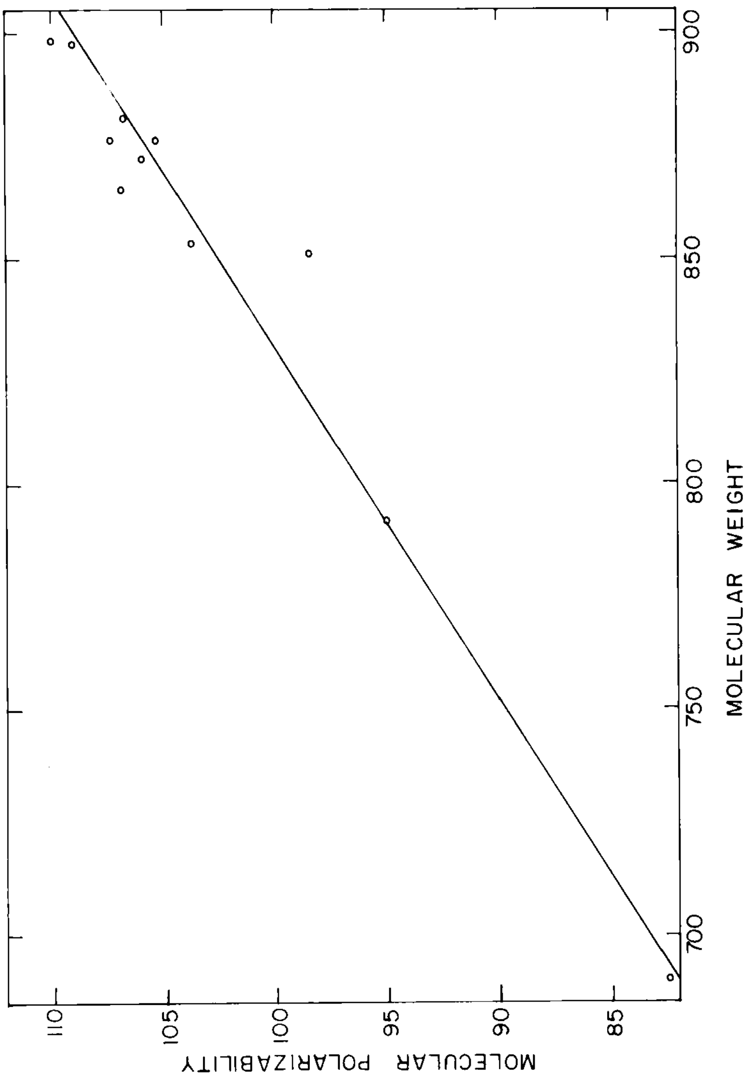


FIGURE 2 Variation of molecular polarizability (10^{-24} cm^3) of fatty oils with the molecular weight. λ = 589 nm.

of the linear curve. This is ascribable to the very large percentage of unesterified fatty acid component (acid value = 40) present in the sample. It is known that in oils high in free fatty acids, the refractive index will be lower.[7]

The values of molar refraction in the case of different fats/oils calculated from the values of molar refraction of pure triglycerides (using the principle of additivity of molar refractions) agree with the experimentally determined values within the limits of experimental error.

Birefringence at different wavelengths was determined in the case of the two fats, viz., mango kernel fat and sal seed fat using the interference technique described in one of our earlier papers[9] and the values are given in Table III.

4. OPTICAL TEXTURES

Systematic investigations on the optical textures of natural vegetable oils and fats do not appear to have been carried out and data are scanty. However, it must be mentioned here that studies on the optical textures of pure triglycerides were first reported by Malkin, who has observed the occurrence of non-ringed spherulites in the case of α-

TABLE III

Birefringence of fats

Sal seed fat at about 30°C		Mango kernel fat at about 43°C	
Wavelength (nm)	Birefringence	Wavelength (nm)	Birefringence
640.0	0.0144	640.0	0.0270
622.5	0.0148	622.0	0.0277
604.5	0.0150	605.0	0.0281
588.0	0.0153	588.5	0.0284
573.0	0.0157	574.2	0.0288
557.3	0.0159	561.3	0.0291
545.1	0.0161	546.5	0.0294
531.5	0.0163	537.1	0.0296
520.2	0.0165	524.3	0.0299
507.5	0.0167	512.5	0.0301
498.1	0.0169	501.1	0.0303
488.5	0.0171	480.5	0.0305
478.0	0.0173	-	-
468.2	0.0174	-	-
457.5	0.0175	-	-

phases of trilaurin and tristearin[11] and of ringed spherulites in symmetrical mixed triglycerides.[12] Quimby[13] has reported the observations on optical textures in the case of different phases of pure triglycerides. Non-ringed spherulites are also observed in the α- and β-phases of tristearin by Barrall[14] *et al.* Spherulitic and needle like textures in the case of the animal fat, viz., lard, are observed by Herb[4] *et al.*, using phase contrast and polarized light microscopy. In the case of natural vegetable oils, optical textures are generally observable only after leaving the substance for long periods and in the following, we report our observations in the case of natural vegetable fats and oils.

The natural oil/fat is taken in the form of a thin film (thickness ~25μ) between slide and cover glass for examination under a polarizing microscope. The molten fats and the oils which are in liquid phase are optically isotropic and do not exhibit any birefringence. However, the thin films of oils in the slides (maintained at room temperature varying around 25°C), in course of time over a period, from a few days to a few months (depending on the nature of the oil), develop areas of birefringence in regions where segregation of the different major constituents have taken place with preferential orientation of the molecules. This is evidenced by the appearance of the birefringent patterns under the polarizing microscope in some regions, whereas in other regions the esters are in the liquid phase and hence exhibit optical isotropy. On the other hand, in the case of natural fats which are solids or semi-solids at ordinary temperatures, the birefringence is invariably observed without any difficulty. In the case of oils, the birefringence patterns appear sooner with some oils than with others. Actually it is found that the greater the saturated component in the triglycerides the sooner does the formation of the birefringent patterns take place. Table IV gives a broad summary of the types of optical textures/patterns observed with different oils and fats. The several oils are listed serially in the table such that the rate of formation of the patterns, of the successive fats/oils are slower and slower.

The birefringence patterns observed in the case of different oils and fats may be classified as follows:

(a) "drops,"
(b) spherulites (ringed and non-ringed)
(c) batonnets
(d) clusters of needle like regions and
(e) spherulites developing into fan-shaped texture along the radial directions.

TABLE IV

Typical textures exhibited by different oils/fats

Name of the oil/fat	Typical textures observed
1) Hydrogenated rice bran oil	batonnets
2) Hydrogenated and ambadi seed oil	batonnets, "drops"
3) Mango kernel fat	streaks of radially arranged bright spots, batonnets, fan shaped texture
4) Sal seed oil	irregular ringed spherulites, clusters of needle like regions, "drops," spherulites developing into fan shaped textures along radial directions
5) Palm oil	ringed spherulite with zig-zag maltese cross
6) Palm kernel oil	ringed spherulite with zig-zag maltese cross
7) Neem oil[a]	faintly ringed spherulites
8) Lime seed oil	ringed spherulites
9) Karanj oil[a]	faintly ringed spherulites
10) Date seed oil	"drops"
11) Subabul	"drops"
12) Rice bran oil	"drops," ringed spherulites, stepped-drop like growth
13) Chilli seed oil	irregular ringed spherulites
14) Tamarind seed	irregular ringed spherulites and thin batonnets
15) Cotton seed oil	batonnets
16) Gonkhru seed oil	irregular ringed spherulites

[a]In the slides prepared with the specimens settled at the bottom of the container, batonnets, maltese crosses and crystals were observed.

The molecular order in the different birefringent patterns listed above are those usually encountered with mesomorphic substances. They may be briefly summarized as follows:

(a) *Drops:* The so called "drops" are birefringent regions arising due to the molecular order wherein spherical shells of smectic layers are arranged like the layers of an onion to form a droplet.[15] In the smectic layers, the molecules have their long axis along the local normal to the surface of each layer.

(b) *Spherulites:* It is well known that in spherulites, molecules are arranged radially about centres of nucleation, such that the directions of maximum refractive index are either parallel or transverse to the radial directions. In a ringed spherulite, the direction of the maximum refractive index is transverse to the radial direction and there exists a helicoidal arrangement of molecules along each radial direction giving rise to a periodic variation of the refractive index along any radius, for light polarized transverse to the radial direction and hence concentric alternate bright and dark rings are discernible when the specimen is observed through crossed polars.[9]

(c) *Batonnets:* In the case of batonnets the direction of maximum refractive index lies either along or perpendicular to the central axis of symmetry.[16]

(d) Clusters of needle like regions are also observed. These birefringent patterns are formed due to crystallization around nucleation centres.

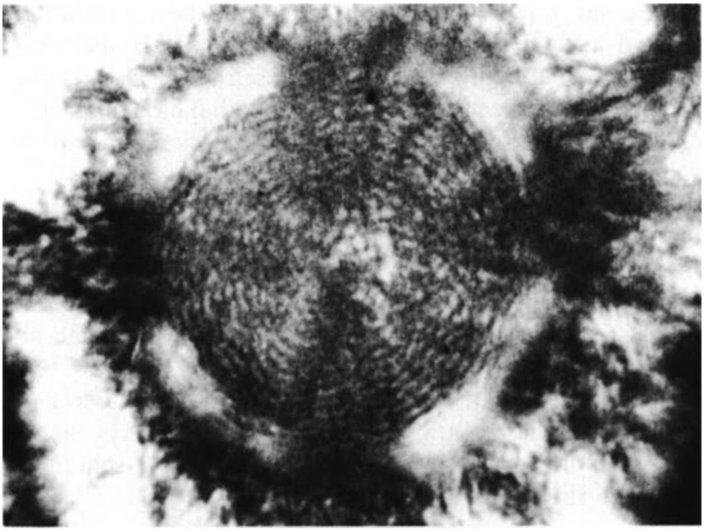
(e) The spherulites observed in oils/fats are metastable and correspond to the α-phase of triglycerides.[11] They gradually develop into fan-shaped textures along the radial directions of the spherulite and correspond to the β-phase of triglycerides.

5. EVOLUTION OF TEXTURES IN OILS/FATS

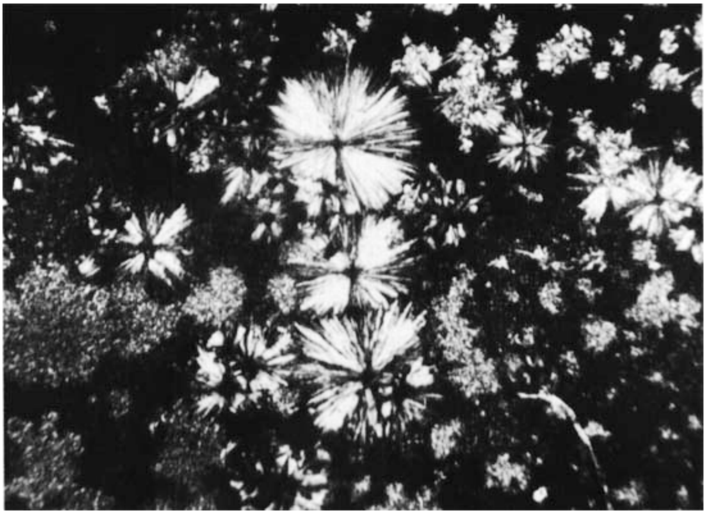
In the case of oils containing more than 50% of unsaturated fatty acid esters, segregation of the saturated part of the relevant esters takes place slowly at room temperature over a period of about two to three months, resulting in the formation of "drops." Gradually some of these "drops" develop into ringed spherulites, which remain stable for about 2 to 4 months and slowly develop into the fan-shaped texture along the radial directions before ultimately passing over to the crystalline phase (e.g., lime seed oil, tamarind seed oil, chilli seed oil, gonkhru seed oil etc.) On the other hand, in the case of oils containing relatively larger proportions of saturated esters, batonnets and radial streaks are observed in addition to "drops" and spherulites. These textures also transform into a fan-type texture, over a period of 2 to 4 months, before crystallizing, (e.g., sal seed oil, palm oil, palmkernel oil, neem oil etc.) That the textures are due to the segregation of the more saturated components is confirmed from the following observations.

(a) It is easy to disturb the cover glass and observe the tumbling and displacements of the "drops" within the isotropic liquid.

(b) On melting the specimen, the birefringence vanishes and on cooling, the textures do not appear immediately and it requires a long time before the entire process of evolution of segregation and texture formation is repeated.

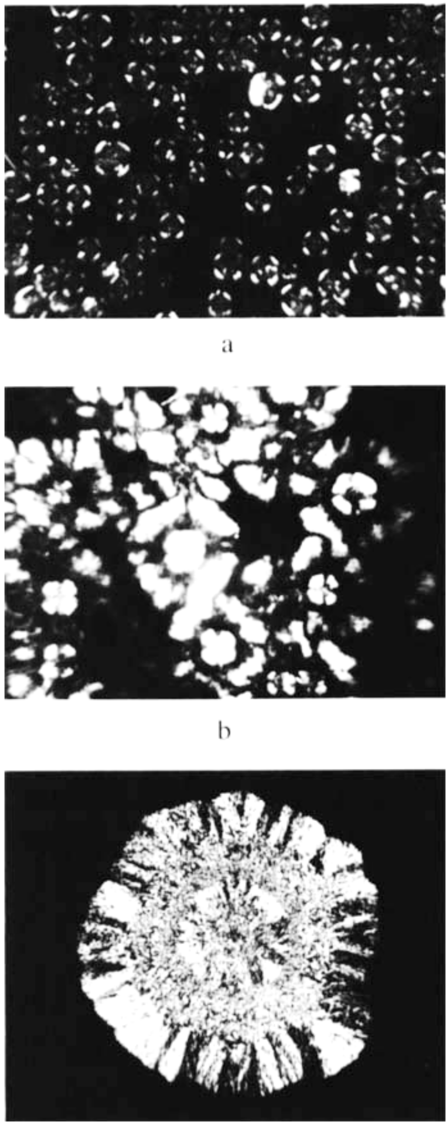


a



b

FIGURE 3 Microphotographs of textures exhibited by sal seed oil as observed between crossed polars: (a) Irregular ringed spherulite 1570× (b) Clusters of needle-like bright regions around nucleation centers 260×.



c

FIGURE 4 Microphotographs of textures exhibited by sal seed oil under crossed polars: (a) "drops," 250× (b) "drops" growing in size, 545× (c) Spherulite changing into fan type texture along radial directions, 405×.

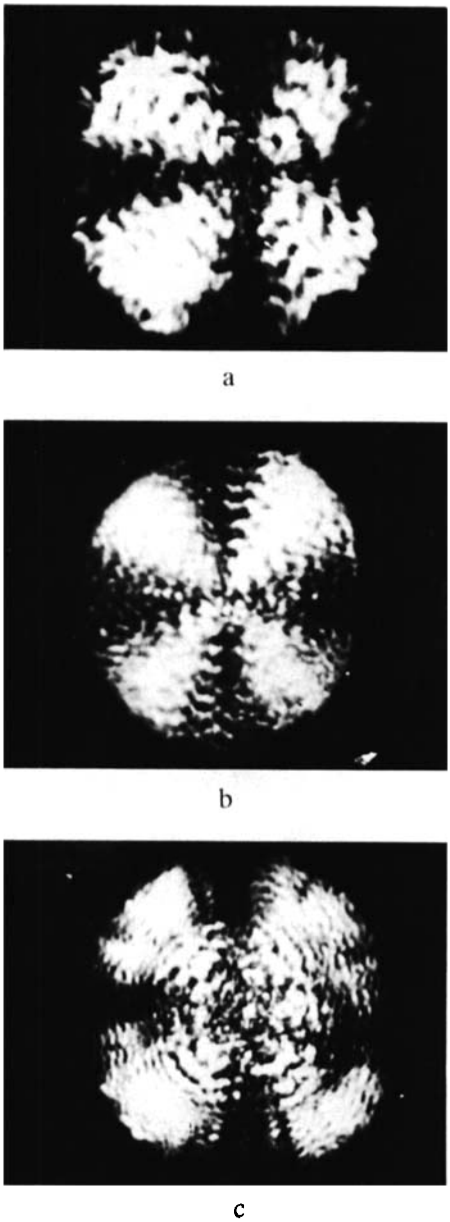


FIGURE 5 Microphotographs of ringed spherulites with zig-zag maltese cross observed between crossed polars, in the case of: (a) palm oil, 790× (b) palm kernel oil, 760× (c) ringed spherulite of lime seed oil observed under crossed polars, 1180×.

(c) From materials which have been left standing for about three months, it is possible to use the portions of the liquid which have settled down at the bottom to prepare slides. With such slides batonnets are immediately observed and after a lapse of about three months time, well-formed crystals appear at several places in the slide.

In the following, a brief account of the observations on typical textures in the case of some oils/fats is given.

Sal seed oil: When the specimen is cooled from the isotropic melt, an irregular weakly birefringent pattern appears at about 52°C (titer point of sal seed oil being 52.8°C). As the specimen is cooled slowly in the hot stage and allowed to remain at room temperature for about 12 hours, irregular ringed spherulites (Figure 3a) are observed over some parts of the slide. In some other regions, clusters of needle shaped bright regions diverging radially from centres of nucleation (Figure 3b) are also observed. After 2–3 days, small "drops" are also observed over a large region of the slide (Figure 4a). These gradually grow in size (Figure 4b) and also develop into irregular ringed spherulites. Optical diffraction pattern in the form of a diffuse halo is also observable with the ringed spherulitic texture. The ringed spherulites are found to be unstable and collapse over a period of one week and develop into fan-shaped texture along the radial directions (Figure 4c) and finally pass over to the crystalline phase in the course of about 6 months. On the other hand, when the specimen is quenched from the isotropic melt, very small batonnets are observed, which appear to be radially arranged around nucleation centres, although in a highly irregular fashion.

Palm oil: As the sample is set, an irregular weak birefringent pattern is observed. After a period of about six weeks, well defined irregular spherulites with zig-zag maltese crosses (Figure 5a) are observed at some places. In some other regions, clusters of needle like regions are also observed.

Palm Kernel oil: When the specimen is set, no birefringence is observed immediately. However, well defined ringed spherulites with zig-zag maltese crosses (Figure 5b) are observed in some regions after a period of about two months, as in the case of palm oil. After about six months, such spherulites are seen over a large area of the slide.

Here, it may be pointed out that, although palm kernel oil has a larger proportion of saturated esters compared to sal seed oil and palm oil, it takes a longer time for the birefringent textures to be observed in palm kernel oil. This is explainable as due to the presence of large percentage of shorter chain fatty acid ester. The percentage of shorter chain lauric ester present in palm kernel oil is more than that of the longer chain esters of stearic and arachidic acids. The latter two are present in greater proportions in sal seed oil, whereas the palmitic ester is present in greater proportion in palm oil.

Lime seed oil: Spherulites with well defined ring systems (Figure 5c) and (Figure 6a) are observed with the specimen of lime seed oil, after standing for about four months. When the spherulite formed in the specimen of lime seed oil (shown in Figure 6a) is observed in plane polarized light (without introducing the analyzer) the ring structure becomes invisible along the direction of vibration of the incident light and the visibility of the rings is maximum in a perpendicular direction (as may be seen from Figure 6b). This indicates the existence of a helicoidal arrangement of the molecules, associated with the spherulitic texture.[9]

Neem oil: With specimens of neem seed oil, only small spherulites could be observed after a period of about 3–4 months (Figure 6c). However, when a slide was prepared using the liquid portion at the bottom of the container (after settling for about three months), maltese crosses, "drops" and small batonnets (Figure 6d) could be easily seen to develop within a few hours.

In the case of specimens of date seed oil and subabul oil only small "drops" (shown in Figure 6e and Figure 6f respectively) could be observed after a period of about 4–5 months. The specimens of rice-bran oil exhibited spherulites with less distinct ring systems (Figure 7b). In addition, a few "drops" having stepped-growth like pattern (Figure 7a) were also observed.

A slide with a specimen of Karanj oil settled down at the bottom of the container, exhibited features similar to the case of neem oil discussed above. Well-formed crystals (Figure 7c) could be observed in the specimen after about a month.

Ringed spherulites obtained with specimens of chilli seed oil and tamarind seed oil after a lapse of about 5–6 months are shown in Figure 8a and Figure 8b respectively. Thin batonnets which gradually develop into the fan-type texture (Figure 8d) were observed with the specimens of the highly unsaturated tamarind seed oil also. Batonnets were also observed with the specimen of cotton seed oil (Figure 8c), although they developed at a very slow rate over a period of about 8 months. It is well-known that batonnets are often observed in the smectic mesophase. In the case of gonkhru seed oil, irregular ringed

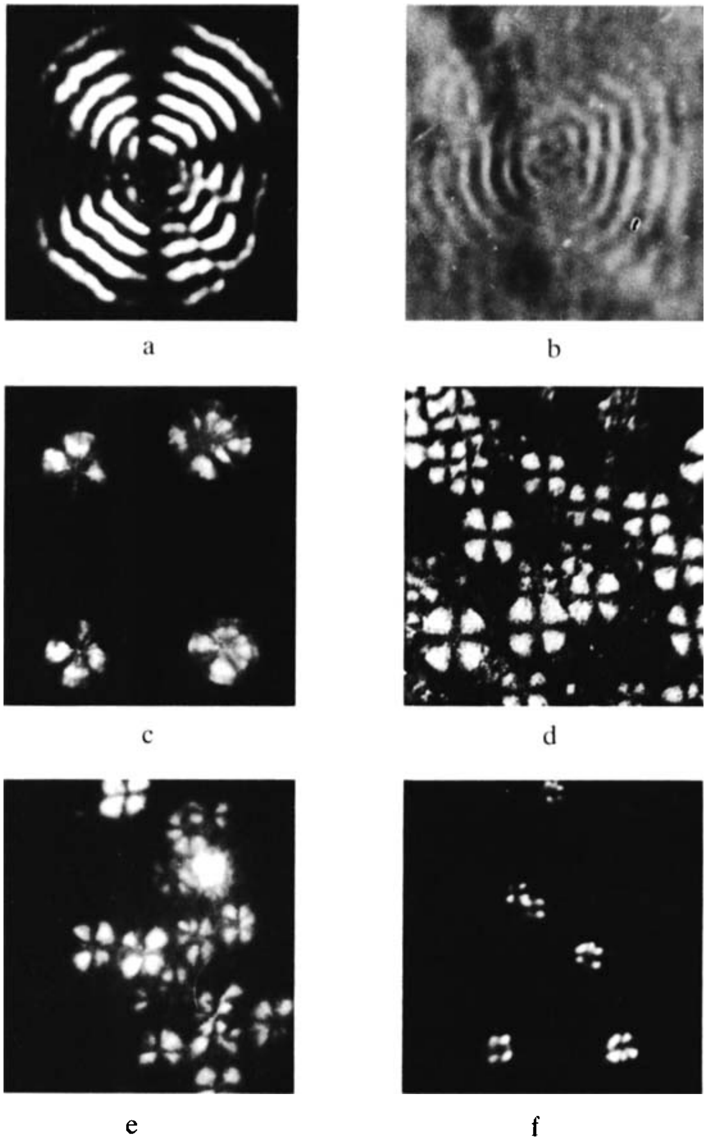


FIGURE 6 Microphotographs of ringed spherulite exhibited by lime seed oil as observed through: (a) crossed polars 1830× (b) using incident polarized light with the electric vector along the vertical. The rings are indistinct along the vertical direction, 1830× (c) Faint ringed spherulite observed with neem oil crossed polars, 690× (d) Maltese crosses exhibited by a sample of neem oil settled at the bottom of the container observed under crossed polars, 195× (e) "drops" observed in the case of date seed oil under crossed polars, 360× (f) "drops" exhibited by subabul oil under crossed polars, 605×.

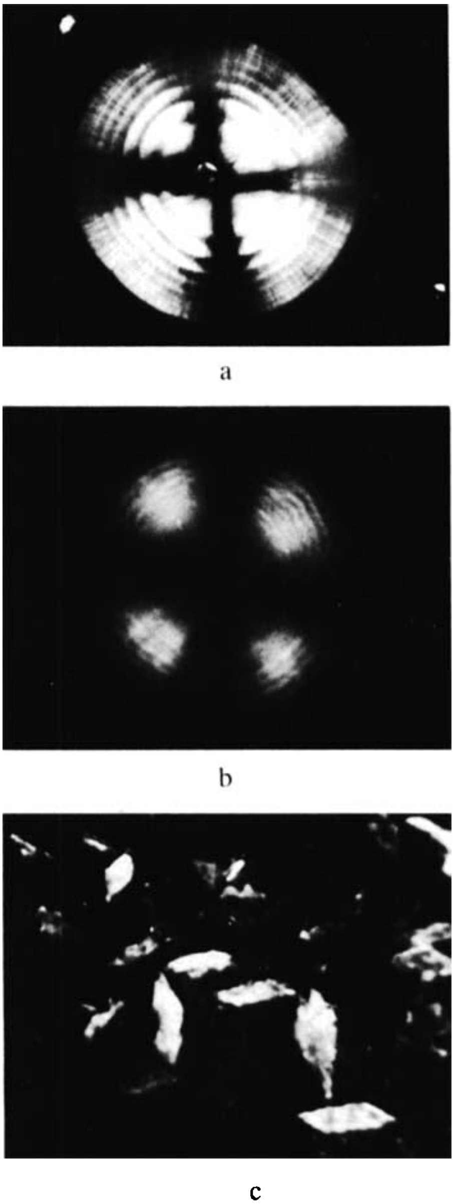


FIGURE 7 Microphotographs of (a) Circular stepped-drop-like growth exhibited by rice bran oil, observed through crossed polars, 880× (b) Faintly ringed spherulite observed in the case of rice bran oil, crossed polars 1820× (c) Crystals developed in a slide prepared with a sample of Karanj oil settled at the bottom of the container crossed polars, 1710×.

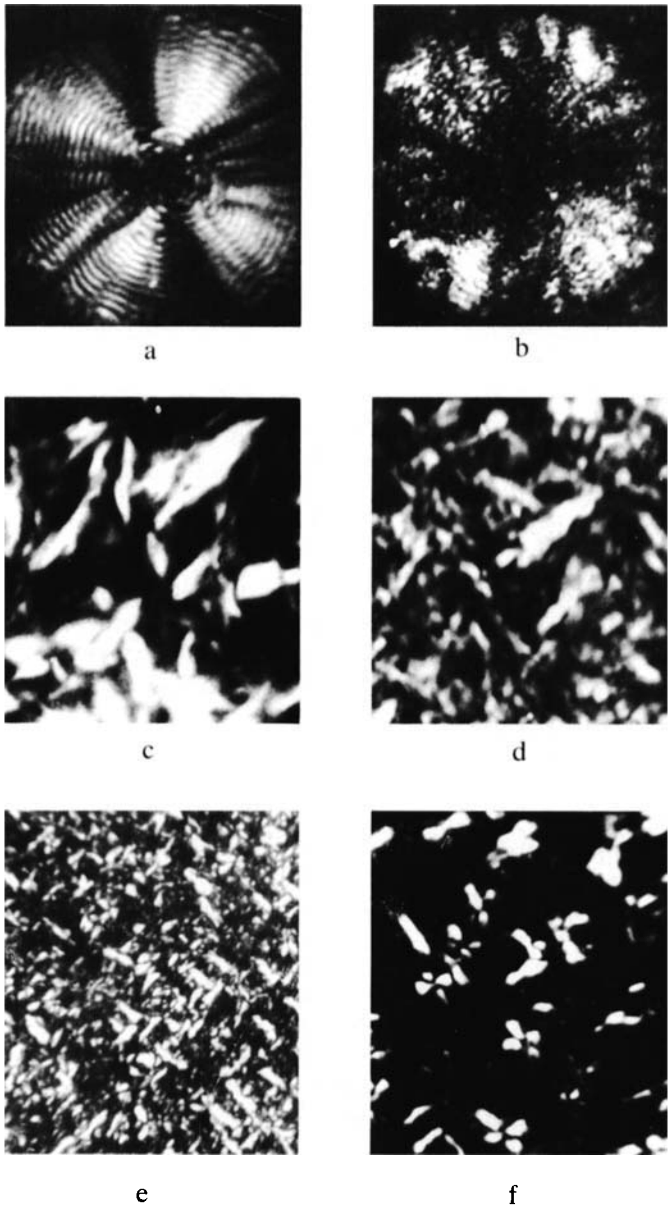


FIGURE 8 Microphotographs of textures of different oils observed under crossed polars: (a) ringed spherulite of chilli seed oil, 1450× (b) ringed spherulite of tamarind seed oil, 1040× (c) batonnets of cotton seed oil, 1040× (d) batonnets of tamarind seed oil, 260× (e) batonnets of hydrogenated rice bran oil, 1350× (f) batonnets and "drops" exhibited by hydrogenated ambadi seed oil, 1300×.

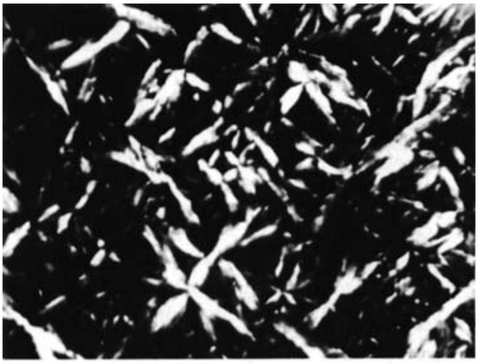
spherulites were observed at a few regions of the slide after a period of about one year. However, no birefringent texture could be observed with ground nut oil (which has a very low setting point of about 0.3°C) even after 18 months.

Hydrogenated oils: The process of hydrogenation involves reduction of the unsaturation of oils and in the case of the two hydrogenated oils, viz., rice bran oil and ambadi seed oil, batonnets (Figures 8e and 8f) were immediately formed, throughout the slide, when the specimens were cooled from the isotropic melt. Small "drops" were also observed at some places, as may be seen from Figure 8f. These textures exhibit typical 4-leaf clover shaped optical scattering patterns, indicating that along each radial direction the molecules are arranged with two of their principal vibration directions parallel and perpendicular to the radii.[17,18]

Mango Kernel fat: The textures in the case of mango kernel fat were somewhat different from those observed in the case of other oils/fats discussed above, in that neither "drops" nor spherulites could be observed. Being a hard fat at room temperature, the mango kernel fat exhibits only large batonnets and fan shaped textures (Figure 9a) throughout the slide prepared by cooling the specimen slowly in a hot stage from the isotropic molten phase. On the other hand, when the specimen was rapidly quenched from the isotropic melt, streaks of bright spots diverging radially from nucleation centres (Figures 9b and 9c) were observed. These bright spots may be recognized as small batonnets as may be seen from Figure 9b, corresponding to a slower rate of quenching. A weak diffuse optical diffraction halo could be observed in the case of the quenched specimens, the diffraction being associated with the particulate nature of the medium.

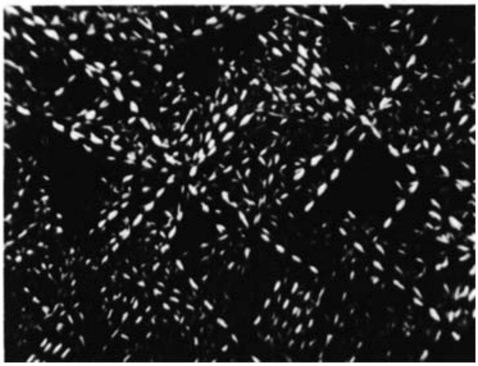
6. MIXTURES OF OILS WITH CHOLESTERIC COMPOUNDS

In view of the fact that many of the oils discussed above, exhibit optical textures similar to the ones exhibited by cholesteric compounds, it was thought worthwhile to study the textures of the mixtures of the oils/fats and the cholesteric compounds. As anticipated, these mixtures give rise to striking optical textures indicative of the spiral/helicoidal twisted arrangements of long molecules. The spiral formed outside the cover glass, when a mixture of sal seed oil with about 35% of cholesteryl stearate is slowly cooled from the isotropic melt is shown in Figure 10a. A spiral arrangement could also be observed (out-side the cover glass) in a mixture of mango kernel fat



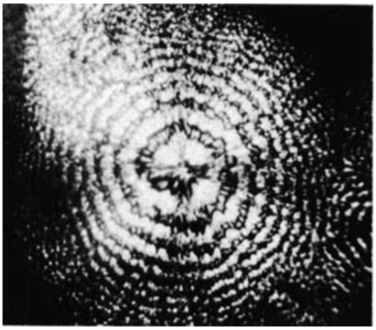
a

b



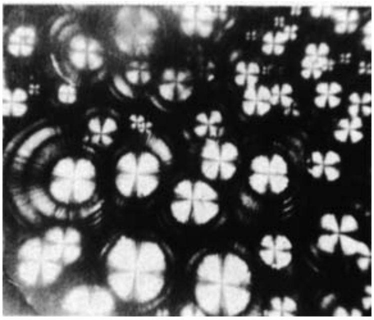
c

FIGURE 9 Microphotographs of textures of mango kernel fat observed under crossed polars (a) batonnets exhibited by a slowly cooled specimen, 90 × (b) radially arranged batonnets observed with the sample quenched at a slower rate, 95 × (c) streaks of radially arranged bright spots, exhibited by rapidly quenched sample, 245 × .



a

b



c

FIGURE 10 Microphotographs of textures exhibited by mixtures of oils with cholesteric compounds. Spiral growth exhibited by mixture of (a) sal seed oil with 35% cholesteryl stearate (specimen with free-surface) crossed polars, 115× (b) Mango kernel fat with 37% of cholesteryl myristate (specimen with a free surface) with polarizer only, 215× (c) Periodic condensation around maltese crosses observed with a mixture of neem oil with 25% cholesteryl stearate crossed polars, 155×.

with about 37% of cholesteryl myristate and Figure 10b exhibits the spiral as observed in plane polarized light (using no analyzer in the polarizing microscope). The texture observed in the case of a mixture of the sample of neem seed oil settled at the bottom of the container with cholesteryl stearate (Figure 10c) exhibits concentric circles of periodic condensation around maltese crosses. In addition to the above textures, very well formed ringed spherulites were also observed in the solid phase, in the case of a number of mixtures containing sal seed oil and various amounts of cholesteryl stearate, cholesteryl palmitate and also the non-mesogenic long chain compound, viz., cetyl alcohol. Similar well defined spherulites were also observed with mixtures of mango kernel fat with various proportions of cholesteryl myristate. The well defined ringed spherulites obtained in the above cases exhibit very good optical diffraction patterns also, from which the pitch of the helicoidal arrangement can be estimated.

7. CONCLUDING REMARKS

Natural vegetable oils/fats consisting of long chain triglyceride molecules exhibit striking optical birefringence patterns, under a polarizing microscope. Segregation of heavier components of the oils are responsible for the appearance of optical textures, characteristic of the liquid crystalline state. The batonnets, drops and fan-shaped textures observed in the case of these oils/fats are typical of the mesomorphic smectic state. The ringed spherulites observed here, resemble those observed with cholesteric compounds. X-ray diffraction studies on these oils/fats also give supporting evidence indicating the existence of liquid crystal like molecular order in these natural products. From the observations on the evolution of textures in the several oils, the following general conclusions may be drawn.

(a) The rapidity of formation of textures increases with increasing percentage of saturated components in the oils.

(b) Oils with larger values of the average molecular weight generally exhibit the ringed spherulitic texture.

(c) In the case of oils with higher setting points/melting points the formation of texture will be more rapid.

(d) Relatively heavier and more saturated components of the oils tend to segregate and give rise to optical textures that resemble the textures normally observed with smectic liquid crystals and also with the β-phase of triglycerides.

(e) Hydrogenation of the oils decreases the proportion of unsaturated components and the hydrogenated oils readily exhibit smectic like textures.

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