X-Ray Study of Hydrogenated Jojoba Wax

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ABSTRACT AND SUMMARY

Crystallographic analysis of hydrogenated jojoba wax ester shows the crystal structure to be monoclinic with orthorhombic perpendicular, $O_\perp$, chain packing. Cell dimensions are: a = 4.99, b = 7.44, c = 55.2Å, β = 90°. A larger secondary unit cell is observed and identified as permitting the hydrocarbon ester chains freedom of rotation. Hydrogenated jojoba wax ester is crystallographically similar to polyethylene.

INTRODUCTION

Jojoba oil has recently attained industrial importance. In addition to its chemical and physical similarity to sperm whale oil, hydrogenated jojoba wax is used in making smokeless hard candles (1,2). Hydrogenated jojoba wax has also been found to be miscible with polyethylene in all proportions (3). The mixture at all ratios produces a solid of increased hardness and lower melting point than pure polyethylene (4). Jojoba oil is not a chemically pure compound. Its composition consists of 43% docosanyl eicosanoate, 31% eicosanyl eicosanoate, and numerous other was esters (3-5). Interest in the physical properties of jojoba oil led to examining hydrogenated jojoba wax ester crystallographically. The objectives were to establish the chain conformation, unit cell, and angle of tilt of the chains, and to compare the structure to that of polyethylene. Hydrogenated jojoba wax was examined rather than its predominant component ester, docosanyl eicosanoate, because of probably crystallographic differences between the molecular pure and impure substances.

EXPERIMENTAL PROCEDURES

Gas chromatography and mass spectrometry indicated the ester composition of hydrogenated jojoba wax to be 43% docosanyl eicosanoate, 31% eicosanyl eicosanoate, 8% eicosanyl docosanoate, and 18% random long-chain esters (3-4).

Debye-Scherrer X-ray diffraction film data were gathered with a cylindrical powder camera (radius = 57.296 mm) equipped with Ni-filtered Cu radiation (λ = 1.5405 Å). Aluminum powder was used for calibration. Low angle diffraction data were taken with a Warhus camera at a sample to film distance of 29 cm using Ni-filtered Cu radiation. The low angle data were not calibrated. Weissenberg and precession camera photography of single crystals aided in reflection indices assignments. Single crystals were obtained as very thin platelets by evaporation of a benzene solution at room temperature and pressure. Numerous single crystals and a mixture of single crystals were examined crystallographically. Only one pattern was discernible. Using a hot stage microscope, the crystals were observed to melt completely within a one degree range, 71.5 to 72.5 C. Reflection intensities were visually estimated, and the film spacings were read on an illuminated film measuring device. Computer calculations were performed on an IBM 1130 computer and a Modular Computer System 2.

Crystal data are: unit cell = monoclinic; molecules per unit cell = 2; a = 4.99 ± 0.01 Å; b = 7.44 ± 0.01; c = 55.2 ± 0.2; β = 90.3 ± 0.5°; absent reflections $h0\ell$ (h = odd), $0kl$ (k = odd); probable space group = Pa; molecular formula = $C_{42}H_{83}O_2$ (docosanyl eicosanoate); molecular weight = 620; calculated density = 1.00 g/cc.

RESULTS AND DISCUSSION

Unit cell dimensions were obtained by least-squares treatment of the powder diagram data of Table I. Single crystal photographs provided assignment of the majority of reflections. Low angle X-ray diffraction aided in indexing the 00ℓ reflections. Comparisons of the crystallographic dimensions to those of previous single crystal investigations of normal long-chain fatty acid esters are presented in Table II. The esters include methyl, ethyl, and propyl stearate and hexadecyl hexadecanoate (6-10).

The jojoba crystal is considered isostructural to the monoclinic esters, because the unit cells have near identical chain packing areas and the X-ray diffraction patterns are nearly identical.

The angle of tilt of the long chain is then considered. Lutz et al. have surveyed a series of normal alkyl esters of long chain fatty acids via X-ray powder diffractometry (11). The data were least-squared to provide an equation relating carbon chain number to long spacing. The equation is:

$$d = (3.1440 \pm 0.9588) + (1.1205 \pm 0.0298)x \tag{I}$$

where x is the number of carbon atoms. A value of 50.2 Å is predicted for docosanyl eicosanoate. The observed result was 55.2 Å, a difference of 5 Å. The reason lies in the magnitude of the monoclinic β-angle. Lutz et al. had examined hexadecyl hexadecanoate, which Kohlhaas showed to have a β-angle of 118.5° (9), thus indicating the series consisted of structures bearing a large β-angle. The three monoclinic stearate single crystal studies give β-angles ranging from 113.5° to 119.2° (6-8). Assuming a β-angle of 115° for docosanyl eicosanoate, straightening of the predicted oblique cell to a rectangular cell results in a long spacing (c-dimension) of 55.4 Å, in good agreement with the experimental value.

The probable space group of hydrogenated jojoba wax is Pa. Rationalization for this choice is as follows. The number of molecular units in the unit cell is two. Molecular size and expected straight chain conformation yield this result in view of the observed unit cell dimensions. Single crystal diffractometry established the unit cell lengths and angles. Investigation of the long axis by low angle X-ray diffraction gave no evidence that the long axis was doubled in length as was observed for hexadecyl hexadecanoate (9) and for the methyl and ethyl stearate structures (6,7), with only propyl stearate being a "monomer" (8). Calculations of expected intensities using docosanyl eicosanoate show the 001 reflection to be very intense with subsequent alternating increased intensities for 00ℓ with ℓ = odd. The calculations coincide with the jojoba wax low angle observation of a very intense reflection at 54.8 Å. The length of the long chain molecule is asymmetric due to the ester linkage. The above factors confine the fundamental space group symmetry to be either monoclinic or triclinic. Furthermore, the virtual identity of the jojoba X-ray pattern to the previously studied single crystal structures indicates the chain packing must be orthorhombic perpendicular, $O_\perp$.

A monoclinic unit cell system is most probable. All previously determined normal long chain ester structures have been monoclinic. Space group possibilities are Pm, P2, $P2_1$, and Pa.

TABLE I

X-Ray Powder Diagram Data for Hydrogenated Jojoba Wax

Spacing (Å)	Intensity		Unit cell index (calculated spacing, Å)
	Observed[a]	Calculated	
54.8	(ES)[b]	>1000	001 (55.2)
27.4	(W)[b]	262	002 (27.6)
18.2	(MS)[b]	941	003 (18.4)
13.7	W	71	004 (13.8)
11.0	WM	256	005 (11.0)
9.22	VW	39	006 (9.20)
7.89	EW	95	007 (7.89)
6.00	EW	39	009 (6.13)
4.57[c]	WM		
4.27	EW	7	0013 (4.25)
4.11[c]	VS	>1000	110 (4.14), 111, 112 (4.10)
3.98	EW	---	114 (3.96)
3.72	VS	429	020 (3.72), 021, 022 (3.69)
3.62	WM	---	024 (3.59)
3.54[c]	W		
2.98	M	11	120 (2.98), 121, 122 (2.96)
2.49	M	779	200 (2.49), 201, 202 (2.48)
2.36	W	44	210 (2.37), 211, 212 (2.36), 0122 (2.38)
2.31	VW	--	1021 (2.32)
2.27	EW	2	0123 (2.28)
2.22	MS	50	130 (2.22), 131, 132, 1022 (2.24)
2.15	VW	---	1023 (2.16)
2.13	VW	79	1122 (2.14)
2.09	WM	---	1024 (2.08), 0222 (2.08)
2.07	W	96	220 (2.07), 221, 222
2.06	VW	---	223 (2.06)
1.95	VW	1	1221 (1.97)
1.93	W	20	1222 (1.92)
1.87	EW	2	1223 (1.87)
1.86	WM	7	040 (1.86), 041, 042
1.73	W	--	140 (1.74), 141, 142
1.70	VW	4	2122 (1.71)
1.68	WM	---	2123 (1.68)
1.66	EW	3	1322 (1.66)
1.62	W	29	310 (1.62), 311, 312
1.52	VW	10	320 (1.52), 321, 322
1.50	W	---	240 (1.49), 241, 242
1.44	EW	2	2322 (1.44)
1.38	VW	2	330 (1.38), 331, 332

[a] Intensity scale: S = strong; M = medium; W = weak; WM = weak to medium; ES = extremely strong; EW = extremely weak; VS = very strong; VW = very weak.

[b] Low angle diffraction data.

[c] Secondary cell reflection.

TABLE II

Crystallographic Cell Dimension Data

Name of compound	Monoclinic cell system	a(Å)	b(Å)	c(Å)	β(°)	Chain packing area (Å^2)[a]
Methyl stearate (6)	A 2/a	5.61	7.33	106.6	116.8	36.7
Ethyl stearate (7)	Aa	5.59	7.40	55.0	113.5	37.9
Propyl stearate (8)	Pa	5.59	7.39	30.0	119.2	36.1
Hexadecyl hexadecanoate (9)	P2	5.61	7.415	88.8	118.5	36.6
Hydrogenated jojoba wax	(Pa)	4.99	7.44	55.2	90.3	37.1
	Orthorhombic cell system					
Polyethylene (12)	Pnam	7.40	4.93	2.534	---	36.5
Methyl stearate (10)	Pnab	5.61	7.35	95.2	---	41.2

[a] Calculated as area of plane normal to the c-axis.

Further elimination is made on assumption that chain packing is orthorhombic perpendicular, O⊥. This packing was observed in the stearate structures, hexadecyl hexadecanoate, and in Bunn's normal paraffin structure (6-10,12). The latter is the prototype for polyethylene, with which hydrogenated jojoba ester is miscible in all ratios (3).

Space group Pm was eliminated because it has a mirror plane and will not result in O⊥ chain packing.

P2 was also eliminated for the same reason. In addition, P2 would also require antiparallel or inverted chains. Although this is feasible, the earlier investigations all indicated parallel chains.

$P2_1$ and Pa both can accommodate the expected O⊥ packing. They are distinctive in that the former necessitates antiparallel unit cell chains whereas space group Pa results in parallel alignment. Pa agrees with the observed systematic reflection absences, and is therefore the most probable space group.

The intensities of Table I were calculated using Pa symmetry. The calculations were obtained using a model docosanyl eicosanoate molecule placed in the unit cell in a position such that the chain axis was parallel to the c-axis. The first two carbon atoms of the ester were located at

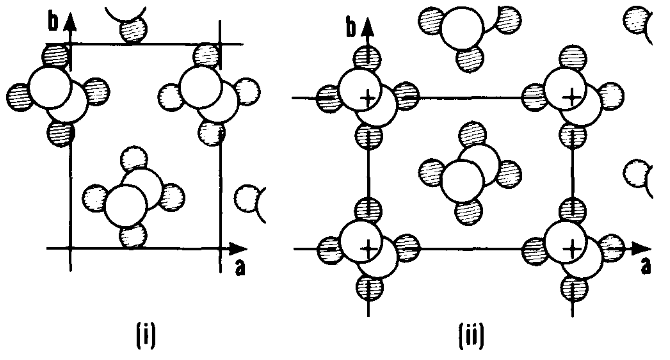

FIG. 1. (i) Projection of hydrocarbon chain methylene units on the a-b plane of the hydrogenated jojoba wax unit cell. Chain axes positions are taken from the structure of propyl stearate.

(ii) Projection of hydrocarbon chain methylene units on the a-b base plane of the polyethylene unit cell.

positions numerically equivalent to the fractional x- and y-coordinates for the two end carbons of the propyl stearate structure, also of Pa space group symmetry. The carbon zigzag distance was 2.534 Å, as determined by Bunn (12) for hydrocarbon chain structures. Tetrahedral bonding was assumed. The ester linkage carbon-carbon distance was 2.67 Å with the average carbon-oxygen bond length 1.48 Å. The values were obtained from the three stearate structures cited. Construction of the molecule yielded an ester of 53.3 Å. Taking into account the 55.2 Å c-dimension, there remains a 1.9 Å distance between endgroup planes, less than that observed for the stearate structures, 3.1 Å. Part of the discrepancy is due to the molecule being "bent" at the ester linkage. Propyl stearate is the best example available. The angle of "bend" in this molecule is about 12°. A 12° correction of the docosanyl eicosanoate c-axis altitude brings about a decrease of 0.6 Å to an apparent molecular height of 52.7 Å. The end-group planes now separate by 2.5 Å, in modest agreement with the value of 3.1 Å for the stearate structures and a 2.6 Å value observed in a like long chain hydrocarbon-type structure, the low melting form of oleic acid (13). In fact, 12° is all that is required to correct a linear jojoba molecule to a 52.1 Å height. The conclusion drawn here is that the jojoba structure demonstrates less end chain inclination than the previous structures. However, a more detailed analysis is necessary to confirm this belief.

The intensities were calculated as: $I = (F_{hk\ell})^2 \times (Lp)$. $F_{hk\ell}$, the hkℓ reflection structure factor, is the amplitude brought about by the diffraction of the proposed molecule located in the unit cell for the hkℓ indexed reflection. Lp is the Lorentz polarization correction to compensate for the loss in intensity due to polarization of the X-ray beam upon reflection: $Lp = (1 + \cos^2 2\theta)/(\sin^2 \theta \cos\theta)$.

Despite assumed ideality of the fatty acid ester, the agreement between observed and calculated intensities is good. No values were calculated for reflections that were not observed. The 00ℓ calculations were higher due to the crystals not being pure docosanyl eicosanoate, the existence of probable voids, and possible inadvertent inversion of the ester.

The intensity calculations show that the 0kℓ (k = odd) absences were likely the result of molecular conformation and packing. The h0ℓ (h = odd) calculated absences were forced as a result of the Pa structure factor symmetry. It was obvious, though, that the result would be the same without the forced absences.

Hydrogenated jojoba ester is miscible in all proportions with polyethylene (4). Molecular similarity extends also to the crystalline state. Both compounds exhibit near identical powder patterns. Table II compares the unit cell dimensions and chain packing areas. The major reflections at 4.1 and 3.7 Å for both solids suggest isomorphism. This if further indicated because the 4.1 Å reflection indexes as the 110 reflection for both compounds and the 3.7 Å reflection indexes as the 200 reflection for polyethylene and the 020 reflection for jojoba. The difference is due only to the choice of axes in the polymer structure (12). A comparison of chain unit packing environments for jojoba and polyethylene can be made using Figure 1. The jojoba ester approximates the propyl stearate structure as reasoned earlier, and the stearate structure is therefore used as a model. Both cells each exhibit orthorhombic O⊥ packing. Superimposition of the chain planes is accomplished by mere 90° rotation of one coordinate set followed by translation of the unit cell axes. The chain packing compatability of the two compounds is then readily recognized.

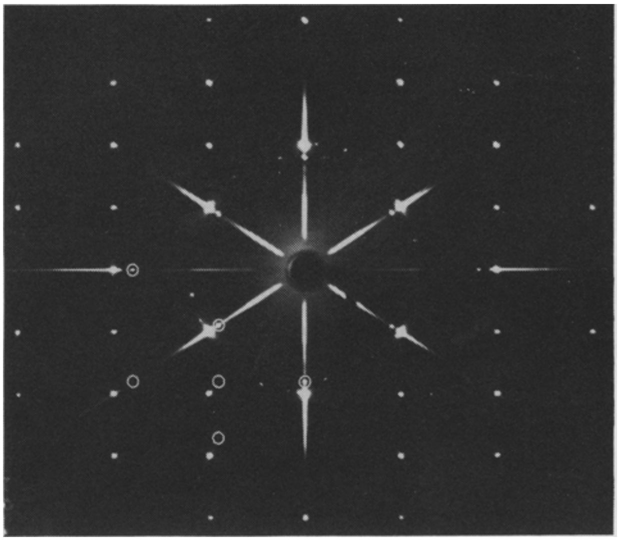

FIG. 2. X-ray single crystal precession photograph of hk0 data for hydrogenated jojoba ester. The circles denote location of secondary cell lattice reflection.

A sample of 2:1 mixture of polyethylene and hydrogenated jojoba ester was examined by X-ray powder diffractometry. The sample had been prepared by melting, mixing, and resolidification of the components at room temperature. High angle photography gave a pattern identical to the common pattern of the two constituents. The predominant 4.1 and 3.7 Å reflections were present. Low angle diffraction yielded only a diffraction halo extending from 86 to 102 Å. Obviously, the halo was due to the existance of chain folding lamella resulting from the polymer. No long spacings characteristic of long chain fatty acid ester crystallites were observed. This was taken as evidence the jojoba ester had not crystallized in independent domains, but had crystallized with the polymer.

The powder patterns of polyethylene and saturated jojoba wax bear another similarity. Both compounds exhibit unindexed reflections at 4.57, 4.11, and 3.54 Å. The unindexed 4.11 Å reflection was observed in precession single crystal photographs. Polyethylene investigators have attempted to index these reflections in a secondary lattice (14-16). Gieniewski and Moore indexed these reflections using a monoclinic cell ($\gamma = 95.6°$, c-axis = long axis) with the packing of hydrocarbon chains skewed from their orthorhombic cell packing locations (14). The hk0 precession photograph of jojoba shows the 4.57 and 4.11 Å reflections to be the dominant reflections of a secondary unit cell (Fig. 2). Lesser hk0 reflections are also apparent, confirming the existence of a secondary cell lattice structure network. By their proximate positions to the primary cell lattice reflections, the secondary reflections are indexed as 110 and 200,

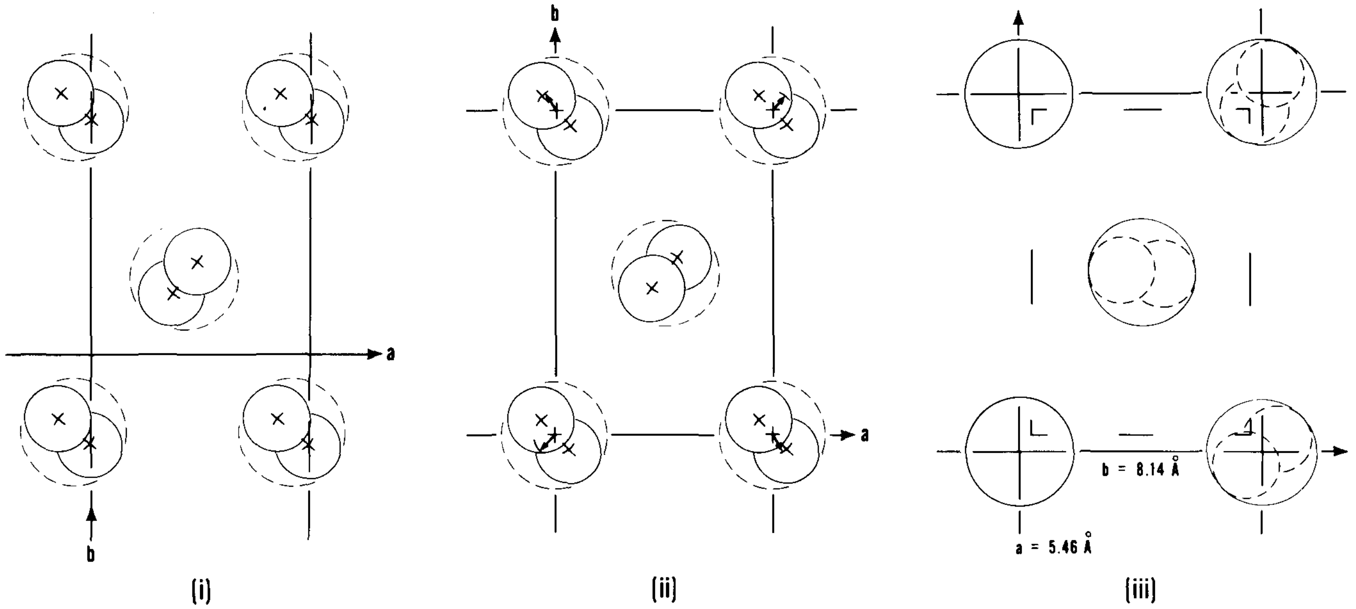

FIG. 3. (i) Projection of methylene carbons of hydrogenated jojoba ester on the a-b plane. Chain axes positions correspond to those of propyl stearate. The dashed circles represent freedom of axis rotation for the hydrocarbon chain.

(ii) Projection of the methylene carbons of hydrogenated jojoba ester on the a-b plane following translation of coordinate axes origin to coincide with chain axis. Arrows illustrate the shift of the hydrocarbon axis necessary to alleviate the intermolecular repulsion encountered by the free rotation or twisting of the chain.

(iii) Projection of free rotation hydrogenated jojoba methylene units upon movement of the chain axes to allow for hydrocarbon chain rotation. A new unit cell is assumed at the axes of the hydrocarbon chain positions. The original unit cell is inscribed with dashed lines.

respectively. The 3.54 Å spacing was not observed in jojoba single crystal data. It will be discussed later.

The secondary a- and b- unit cell dimensions are 5.50 and 8.22 Å. We consider the larger secondary cell to arise from hydrocarbon chain rotation or twisting with subsequent elimination of the prependicular packing of hydrocarbon chain planes. This idea is not new. Chapman has cited the concept that rotation or random orientation about its axis is responsible for the 4.6 Å reflection (17). Figure 3 illustrates the concept. The chains are considered cylindrically shaped. This produces increases in interchain interactions. Movement of the chains alleviates the stress. A neighboring chain shifts a distance equal to the radius of the hydrocarbon chain base vector (0.426 Å). Resultant axes corrections are $\Delta a = 0.47$ Å and $\Delta b = 0.70$ Å. The new cell dimensions are 5.46 and 8.14 Å in very good agreement to the observed data. Whether the result for jojoba is true for polyethylene is only conjecture at this stage. An absolute indexing of the polymer secondary cell is required.

The 3.54 Å reflection, although of weak intensity in powder photographs, was not observed in the single crystal photographs bearing the secondary unit cell. The conclusion reached is that the 3.54 Å spacing is characteristic of yet another secondary unit cell, possibly the triclinic octadecane cell found by Muller and Lonsdale (18). They observed the 3.54 Å spacing to be of prominent intensity. The fact that it appears with lesser intensity in the jojoba powder data would be in accord with the above conclusion that it represents a minor constituent of the diffracting medium.

The conclusions reached in this study are the following. First, the chain conformation is fully extended with orthorhombic perpendicular O⊥ packing. Aside from the ester linkage, the jojoba conformation appears to be indistinguishable from that of polyethylene. Second, the unit cell of jojoba is essentially rectangular and approximates that of polyethylene, whereas it contrasts to the oblique monoclinic unit cells of previously studied long chain esters. Thirdly, the hydrogenated wax ester study indicates moderate chain tilt with respect to the ab plane. This is in accordance with its similarity to polyethylene and again contrasts to the previously studied esters. Lastly, as a result of the above, hydrogenated jojoba wax appears to be crystallographically more common to polyethylene than to its own chemical genre.

Here arises a remaining question on the physical propensity of the wax ester towards polyethylene. As has been cited, the compound studied is a broad mixture of esters, even though docosanyl eicosanoate predominates. The question is whether ester purity governs solid state properties. If so, the result may be uniformly produced by any mixture of normal long chain fatty acids. Available evidence would indicate a negative answer. In the study of normal alkyl esters of long chain acids, Lutz et al. (11) found three compounds that did not match their least-squares curve of chain carbon atom number vs. long spacing. However, as demonstrated earlier, if the cell in question is assumed to be rectangular, the long spacing calculated from the curve is in good agreement with the observed data. Sample purity would be of interest. Noteworthy is the fact that the three compounds were all even-numbered carbon esters, as is docosanyl eicosanoate. A single crystal investigation of pure docosanyl eicosanoate would be of great interest. Knowledge of the elements differentiating the perpendicular and tilting packing modes of the long chain esters is yet to be obtained. The importance of the problem is in the possible major effect the ratio of ester mixtures may have on the structural and physical macro properties.

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