ones. Another important factor is the steric hindrance of the bulky carboxyl groups. The parallel orientation of the carboxyl groups is energetically disadvantageous. In the case of *n*-fatty acid *A*-super and A_2 forms adopting the triclinic subcell with parallel skeletal planes (*T*∥), the carboxyl groups take two different orientations in order to reduce the steric hindrance. The formation of an O⊥-like subcell of the HM phase seems to have an analogous effect of promoting the perpendicular packing of carboxyl groups.

The thermal factors of the C atoms increase gradually from the *cis*-olefin group as the methyl terminal is approached. This tendency has been also found in the γ_1 phase of erucic acid, which shows a reversible phase transition accompanied by conformational disorder at the methyl terminal (Kobayashi & Kaneko, 1990). The thermal motion of the methyl-terminal chains may be activated by the insertion of the *cis*-olefin group. However, the thermal factor of the methyl C atom is relatively small in comparison to that of the γ_1 phase. It is inferred that the thermal motion of the methyl-terminal chain is depressed by two factors, the relatively long chain length and the even number of C atoms in the methyl-terminal chain. Petroselinic acid contains three more methylene units in the methyl-terminal chains than erucic acid. The even–odd effect of the number of C atoms on the melting points and crystal structures of *n*-alkanes and *n*-fatty acids is well known. This dynamical property of the HM phase probably relates to the fact that there is no order–disorder-type phase transition as found in the other *cis*-monoenic acids.

In both molecules *A* and *B*, the carboxyl groups are located nearly coplanar to the skeletal planes of the carboxyl-terminal chains. The O···O hydrogen-bond length is 2.662 (3) Å for molecule *A* and 2.633 (4) Å for molecule *B*.

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Structure of the γ_1 Phase of Erucic Acid

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Abstract. *cis*-13-Docosenoic acid, $C_{22}H_{42}O_2$, M_r = 338.57, triclinic, $P\bar{1}$, a = 5.462 (1), b = 5.197 (1), c = 44.16 (1) Å, α = 91.20 (1), β = 90.85 (2), γ = 117.32 (2)°, V = 1113.0 (5) Å^3, Z = 2, D_x = 1.01 g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, μ = 4.4 cm^{-1}, $F(000)$ = 380, T = 266 K, $R(F)$ = 0.054, $wR(F)$ =

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0.074 for 2387 unique reflections with $F > 3\sigma(F)$. Polymethylene segments form a triclinic subcell with parallel skeletal planes. The chains are inclined towards the interface of dimer layers by 42° for the methyl-terminal chain and by 43° for the carboxyl-terminal chain. The torsion angles of the C—C=C—C *cis*-olefin group are 98, 2, 95° from the carboxyl side.

Introduction. It is well known that *cis*-unsaturated fatty acids are widely distributed in biological tissues and increase the fluidity of biomembranes. Recently, we showed that reversible solid-state phase transitions occur between the α and γ phases of oleic, palmitoleic and erucic acids and between the α_1 and γ_1 phases of erucic acid (Suzuki, Ogaki & Sato, 1985; Suzuki, Sato, Yoshimoto, Tanaka & Kobayashi, 1988). The two phase transitions are of reversible order–disorder type, with the higher temperature phases (α and α_1) being conformationally disordered in the vicinity of the methyl terminal of the *cis*-unsaturated hydrocarbon chains (Kobayashi, Kaneko, Sato & Suzuki, 1986). This partial melting phenomenon at the interface of dimer layers is probably closely related to the high mobility of *cis*-unsaturated acyl segments of phospholipids in biomembranes, since this phenomenon has not been found in *n*-fatty acids. Previous work on erucic acid showed that there were several differences in transition behavior between the $\gamma \rightarrow \alpha$ and $\gamma_1 \rightarrow \alpha_1$ phase transitions. For example, the γ_1 phase transforms to the α_1 phase at a rather higher temperature (282 K) than the transition point of the γ phase (272 K). Detailed structural information on the ordered phases (γ and γ_1) is important for a full understanding of these phase transitions. The structure of the γ phase of oleic acid has already been determined by Abrahamsson & Ryderstedt-Nahringbauer (1962).* Therefore, we have determined the structure of the γ_1 phase of erucic acid.

Experimental. The high-purity (>99.9%) erucic acid sample was supplied by the Nippon Oil and Fats Co. Crystals of the γ_1 phase were grown from an acetonitrile solution by cooling. Structure analysis was carried out on a crystal of dimensions $\sim 0.8 \times 0.3 \times 0.1$ mm. Intensity data from a Rigaku–Denki AFC-5 automated four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation from a rotating anode; unit-cell parameters refined using angular values of 25 centered reflections in the range $19 < 2\theta < 50°$. Reflections in the range $3 < 2\theta < 120°$ ($-5 \le h \le 5$, $0 \le k \le 5$, $-49 \le l \le 49$) were measured by ω-scan mode with scan speeds of $6° \text{ min}^{-1}$ ($3 \le 2\theta \le 90°$) or $4° \text{ min}^{-1}$ ($90 < 2\theta \le 120°$). In order to avoid interference from neighboring reflections, which increases with θ, two scan-width ranges were used, $(2.3-0.8\tan\theta)°$ for reflections with $3 \le 2\theta \le 90°$ and $(1.95-0.45\tan\theta)°$ for reflections with $90 \le 2\theta \le 120°$. 3748 reflections measured, of which 3289 were unique ($R_{\text{int}} = 0.032$). 2387 reflections with $|F_o| > 3\sigma(|F_o|)$ were used in the refinement; no significant intensity variation for three standard reflections; no absorption correction. The molecular model was initially built for 13 C and two O atoms based on a three-dimensional Patterson calculation; all other non-H atoms located in the Fourier map after several cycles of block-diagonal least-squares refinement; H atoms located by difference Fourier syntheses; full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic thermal parameters for all non-H atoms; 42 H atoms refined isotropically; 385 parameters, $R = 0.054$, $wR = 0.074$, $S = 1.09$, $w = [\sigma(F)^2 + 0.0217F + 0.0003F^2]^{-1}$, maximum $\Delta/\sigma = 0.016$; largest peak in final difference Fourier map less than 0.12 e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computations were carried out on an ACOS-S930 system at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University. Program *MFPA* (Tanaka & Yasuoka, 1979) was used for the Patterson map, *HBLS*-V and *FMLS* (Ashida, 1979) for the least-squares refinements, and *ORTEP*II (Johnson, 1971) for plotting the crystal structures.

Discussion. The atomic coordinates for the non-H atoms are given in Table 1* and the overall crystal structure is shown in Fig. 1. The bond lengths, bond angles and torsion angles are listed in Table 2.

The structure of the γ_1 phase is very different from that of the γ phase, as expected from a previous spectroscopic study (Kobayashi, 1988). The two polymethylene chains linked to the *cis*-olefin group adopt all-*trans* conformations and form a triclinic subcell with parallel skeletal planes ($T\|$), as often found in long-chain compounds (Abrahamsson, Dahlén, Löfgren & Pascher, 1978); in contrast, the γ phase adopts an orthorhombic subcell with parallel skeletal planes ($O'\|$) characteristic of *cis*-unsaturated fatty acids (Abrahamsson & Ryderstedt-Nahringbauer, 1962). The average subcell

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* The low-melting form of oleic acid reported by Abrahamsson & Ryderstedt-Nahringbauer is referred to here as the γ phase.

* Lists of structure factors, anisotropic thermal parameters, bond distances, bond angles, torsion angles, H-atom parameters and least-squares planes, together with the procedure for obtaining subcell parameters, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54820 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0523]

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	0.1961 (6)	−0.1057 (6)	0.02975 (6)	4.75
C(2)	0.3394 (6)	−0.2025 (7)	0.05240 (7)	5.08
C(3)	0.6054 (6)	0.0325 (7)	0.06648 (7)	4.90
C(4)	0.7137 (6)	−0.0867 (7)	0.09160 (7)	5.03
C(5)	0.9814 (6)	0.1360 (6)	0.10692 (7)	4.90
C(6)	1.0797 (6)	0.0172 (7)	0.13293 (7)	5.04
C(7)	1.3463 (6)	0.2362 (7)	0.14852 (7)	5.14
C(8)	1.4426 (6)	0.1185 (7)	0.17459 (7)	5.09
C(9)	1.7079 (6)	0.3377 (7)	0.19032 (7)	5.27
C(10)	1.8016 (6)	0.2200 (7)	0.21684 (7)	5.34
C(11)	2.0660 (6)	0.4454 (7)	0.23266 (7)	5.38
C(12)	2.1506 (8)	0.3345 (9)	0.26035 (8)	6.56
C(13)	2.4058 (7)	0.5603 (8)	0.27620 (7)	6.66
C(14)	2.4126 (8)	0.7178 (9)	0.30027 (8)	6.85
C(15)	2.1691 (8)	0.6987 (10)	0.31709 (9)	7.19
C(16)	2.1023 (8)	0.5038 (9)	0.34416 (8)	6.71
C(17)	1.8524 (8)	0.4756 (10)	0.36123 (9)	7.08
C(18)	1.7751 (9)	0.2662 (10)	0.38685 (10)	7.29
C(19)	1.5296 (9)	0.2330 (11)	0.40438 (10)	7.84
C(20)	1.4495 (10)	0.0203 (11)	0.42947 (10)	8.19
C(21)	1.2041 (14)	−0.0066 (15)	0.44707 (14)	10.5
C(22)	1.122 (3)	−0.2247 (19)	0.47174 (18)	12.6
O(1)	0.3018 (4)	0.1341 (5)	0.01877 (5)	6.11
O(2)	−0.0546 (4)	−0.2998 (5)	0.02303 (5)	6.08

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

C(1)—O(1)	1.222 (4)	C(1)—O(2)	1.299 (4)
C(1)—C(2)	1.492 (4)	C(12)—C(13)	1.498 (6)
C(13)—C(14)	1.318 (6)	C(14)—C(15)	1.497 (7)
C(2)—C(2)—O(1)	123.6 (3)	C(11)—C(12)—C(13)	113.1 (4)
C(2)—C(1)—O(2)	113.5 (3)	C(12)—C(13)—C(14)	125.7 (4)
O(1)—C(1)—O(2)	122.9 (3)	C(13)—C(14)—C(15)	126.4 (4)
C(10)—C(11)—C(12)	113.7 (3)	C(14)—C(15)—C(16)	112.9 (4)
O(1)—C(1)—C(2)—C(3)	12.4 (4)	C(12)—C(13)—C(14)—C(15)	1.7 (7)
C(1)—C(2)—C(3)—C(4)	173.6 (3)	C(13)—C(14)—C(15)—C(16)	94.9 (6)
C(10)—C(11)—C(12)—C(13)	−178.3 (3)	C(14)—C(15)—C(16)—C(17)	−178.8 (4)
C(11)—C(12)—C(13)—C(14)	98.0 (5)		

parameters† of γ_1 are $a_s = 4.23$, $b_s = 5.20$, $c_s = 2.55$ Å, $\alpha = 81$, $\beta = 105$ and $\gamma = 120°$ for the carboxyl-terminal chain and $a_s = 4.34$, $b_s = 5.20$, $c_s = 2.54$ Å, $\alpha = 81$, $\beta = 105$ and $\gamma = 120°$ for the methyl-terminal chain. The subcell orientation in the methyl-terminal portion is different from that of the carboxyl-terminal portion (Fig. 2). Although the (101) plane of the subcell is located parallel to the basal *ab* plane of the main lattice for both sides, the methyl-terminal b_s axis is parallel to the *b* axis and the carboxyl-terminal b_s axis points in the opposite direction. As a result, the methyl- and carboxyl-terminal hydrocarbon chains make an angle of 30° viewed along the c^* axis. The hydrocarbon chain tilts by 42° on the methyl side and by 43° on the carboxyl side. These angles are rather larger than those of any other modification (*A*, *B*, *C* and *E* forms) of even-numbered *n*-fatty acids. The acyl chain of the *A* form adopting the same $T\|$ subcell is inclined by 25° (Small, 1986). It is inferred that the γ_1 phase constructs a lamellar interface whose structure is considerably different from that of *n*-fatty acids and that this structure has a large influence on the dynamical properties of the acyl chains.

The difference in subcell structure between γ and γ_1 is ascribed to the conformation of the *cis*-olefin group. In the case of the γ phase of oleic acid, the C(8)—C(9)=C(10)—C(11) torsion angles are 132, 2 and −128° (*i.e.* skew, *cis*, skew′ type) and the molecule as a whole assumes a planar form. However, the C(12)—C(13)=C(14)—C(15) torsion angles in the γ_1 phase are 98, 2 and 95°. Although these values deviate significantly from the standard skew angle of 120°, the overall configuration of the γ_1 phase can be regarded as skew, *cis*, skew (the two alkyl chains are located at the opposite sides of the *cis*-olefin plane, in contrast to their linkages to the same side in the

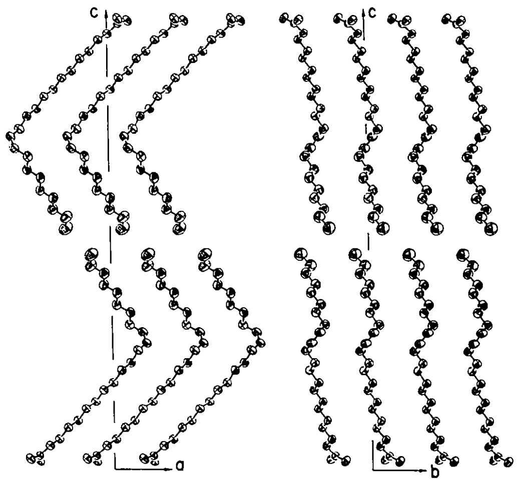

Fig. 1. *ORTEP* view of the γ_1 phase of erucic acid. Thermal ellipsoids are plotted at the 50% probability level.

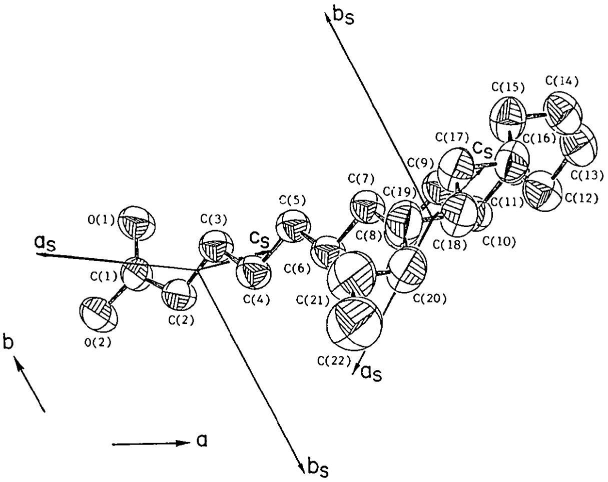

Fig. 2. Relationship between the molecular structure and the subcell orientation, projected along the normal of the basal *ab* plane.

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† The subcell axes were set according to standard conventions; see, for example, Abrahamsson, Dahlén, Löfgren & Pascher (1978).

skew, *cis*, skew′ conformation). It becomes impossible for molecules taking this twisted structure in the γ_1 phase to form a highly symmetric subcell structure such as O′||.

The thermal factors of the C atoms increase gradually from the *cis*-olefin group towards the methyl terminal, whereas those of the carboxyl-terminal chain (positions 2–11) are almost identical. This shows that the introduction of the *cis*-double bond increases the mobility of the methyl-terminal chains. It is concluded that this dynamical behavior of the acyl chains in the γ_1 phase is an important factor for the reversible order–disorder phase transition accompanied by conformational disordering in the methyl-terminal chain.

The carboxyl group is somewhat twisted with respect to the skeletal plane of the carboxyl-terminal chain (Table 2). The O···O hydrogen-bond distance is 2.652 (3) Å. The carbonyl group and the C(2)—C(3) bond take *cis* geometry.

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Structure of (4*Z*,6*Z*)-6-Acetyl-7-hydroxy-2,4,6-octatriene-4-olide

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Abstract. $C_{10}H_{10}O_4$, $M_r = 194.2$, monoclinic, $P2_1/c$, $a = 9.266$ (7), $b = 14.570$ (10), $c = 7.404$ (5) Å, $\beta = 108.60$ (6)°, $V = 947$ (2) Å^3, $Z = 4$, $D_m = 1.35$ (1), $D_x = 1.362$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.66$ mm^{-1}, $F(000) = 408$, $T = 293$ K, final $R = 0.050$ for 869 unique observed reflections. The molecule exists as the enolic tautomer and consists of two planar fragments oriented at an angle of 61.4 (2)° to one another. The main stabilizing factor of the enol form appears to be a strong intramolecular O—H···O hydrogen bond of 2.422 (3) Å. The structural results are compared with those of other similar analogues reported previously.

Introduction. The title compound (II) was prepared by acid hydrolysis of the 2-(5-phenoxy-2-

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