

transition characteristics of *cis*-monounsaturated acids, which is induced by conformational disordering in the methyl-terminal chain (Kobayashi, Kaneko, Sato & Suzuki, 1986).

The carboxyl group is nearly coplanar with the skeletal plane of the carboxyl-terminal hydrocarbon chain, and the C—C—C=O group of the LM phase is recognized to have a *cis* conformation. The distance between the hydrogen-bonded O atoms is 2.68 (1) Å.

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## Structure of the High-Melting Phase of Petroselinic Acid

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**Abstract.** *cis*-6-Octadecenoic acid, C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>,  $M_r = 282.47$ , triclinic,  $P\bar{1}$ ,  $a = 5.359$  (1),  $b = 8.874$  (2),  $c = 41.391$  (5) Å,  $\alpha = 90.49$  (1),  $\beta = 89.12$  (2),  $\gamma = 113.81$  (2)°,  $V = 1800.7$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.04$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 4.7$  cm<sup>-1</sup>,  $F(000) = 632$ ,  $T = 263$  K,  $R(F) = 0.068$ ,  $wR(F) = 0.087$  for 3927 unique observed reflections with  $F > 3\sigma(F)$ . There are two crystallographically independent molecules *A* and *B* in the asymmetric unit. The methyl-terminal hydrocarbon chains of both molecules form a monoclinic subcell with parallel skeletal planes. Torsion angles of the C—C=C—C olefin group are 91, 1 and 130° from the carboxyl side for molecule *A*, and 137, 1 and 119° for molecule *B*.

**Introduction.** Recently, we have demonstrated that *cis*-monounsaturated fatty acids crystallize in various modifications and that they undergo several types of solid-state phase transition (Kobayashi & Kaneko, 1990). Most *cis*-monounsaturated fatty acids whose methyl-terminal hydrocarbon chains contain an odd number of C atoms have two crystalline phases  $\alpha$  and  $\gamma$  in common. Between the  $\alpha$  and  $\gamma$  phases, there is a reversible phase transition accompanied by conformational disorder in the vicinity of the methyl terminal. We found an additional order–disorder phase transition between the  $\alpha_1$  and  $\gamma_1$  phases of erucic acid (Suzuki, Sato, Yoshimoto, Tanaka & Kobayashi, 1988). These phase transitions are one of the important characteristics of *cis*-monoenoic acids.

Petroselinic acid, which contains an even number (12) of C atoms in the methyl-terminal chain, exhibits very different polymorphism from that of the other *cis*-monoenoic acids (Sato, Yoshimoto, Suzuki, Kobayashi & Kaneko, 1990). There are two solid phases, a high-melting (HM) and a low-melting (LM) phase, both of which melt at higher temperatures (HM 303.7 K, LM 301.7 K) than oleic and asclepic acids consisting of the same number (18) of C atoms. Furthermore, there is no reversible order-disorder-type phase transition in petroselinic acid. In the previous paper, we showed that the LM phase forms a characteristic crystal structure considerably different from the crystal structures of other previously determined *cis*-unsaturated fatty acids (Kaneko, Kobayashi, Kitagawa, Matsuura, Sato & Suzuki, 1992). Two bimolecular layers form a double-layered polytype structure (Orth II), in which the crystallographic repeating unit along the stacking direction of the layers is twice the thickness of one layer (Kobayashi, Kobayashi, Itoh & Sato, 1984), and the polymethylene chains at both sides of the *cis*-olefin groups are packed in the orthorhombic subcell with perpendicular skeletal ( $O\perp$ ) planes (Abrahamsson, Dahlén, Löfgren & Pascher, 1978). Both characteristics have not been reported previously in *cis*-unsaturated lipid-related compounds. A preliminary study using vibrational spectroscopic and X-ray diffraction methods on the HM phase (Kaneko, 1989) suggested that this phase also has a unique crystal structure with the asymmetric unit containing two independent molecules. An understanding of the detailed structure of the HM phase is of fundamental importance for studies of polymorphism in *cis*-unsaturated fats and lipids.

**Experimental.** Petroselinic acid supplied by the Nippon Oil and Fats Co. Crystals of the HM phase prepared from an acetonitrile solution at 299 K by slow evaporation. Structural analysis with a crystal of dimensions  $0.15 \times 0.40 \times 0.25$  mm. The crystal was cooled in dry air. Intensity data from a Rigaku AFC-5 four-circle diffractometer with Ni-filtered  $Cu K\alpha$  radiation from a rotating anode. Lattice parameters from 15 reflections in the range  $18 < 2\theta < 50^\circ$ . 10 610 reflections with  $3 < 2\theta < 120^\circ$  ( $-6 \leq h \leq 6$ ,  $-9 \leq k \leq 9$ ,  $-46 \leq l \leq 46$ ) measured, of which 5305 were unique ( $R_{int} = 0.035$ );  $\omega$ -scan mode with scan speed  $12^\circ \text{ min}^{-1}$ , scan width  $(1.4 + 0.15 \tan \theta)^\circ$ ; 3927 reflections with  $|F_o| > 3\sigma(|F_o|)$  used in the refinement; no significant intensity variation for three standard reflections; no absorption correction. The molecular model was initially built for 30 C and two O atoms based on combined Patterson and direct-methods (*SHELXS86*; Sheldrick, 1986) results; 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; 68 H atoms refined isotropically; 634 parameters,  $R = 0.068$ ,  $wR = 0.087$ ,  $S = 1.52$ ,  $w = [\sigma(F)^2 + 0.0008F^2]^{-1}$ , maximum  $\Delta/\sigma = 0.180$ , maximum and minimum heights in  $\Delta\rho$  map were 0.15 and  $-0.16 \text{ e \AA}^{-3}$ . 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. Programs *HBL5-V* and *FMLS* (Ashida, 1979) were used for the least-squares refinement, and *ORTEPII* (Johnson, 1971) for plotting the crystal structure.

**Discussion.** Refined 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 asymmetric unit consists of two independent molecules *A* and *B* whose structures differ from each other in the arrangement of the portion of the molecule from the olefin group to the carboxyl group.

The lateral packing of acyl chains in the HM phase is quite unique (Fig. 2). The skeletal planes of the methyl-terminal chains of molecules *A* and *B* are arranged nearly parallel to each other (the deviation from a parallel orientation is about  $15^\circ$ ). If only the long methyl-terminal chain is considered, the repeating unit along the *b* axis can be taken as half of the main lattice. From this point of view, the main lattice of the HM phase can be regarded as a superstructure such as the *A*-super (von Sydow, 1956; Goto & Asada, 1978), and *A*<sub>2</sub> and *A*<sub>3</sub> forms (Kobayashi, Kobayashi & Tadokoro, 1984) of *n*-fatty acids. Judging from the average subcell dimensions,  $a_s = 4.44$ ,  $b_s = 4.75$ ,  $c_s = 2.54 \text{ \AA}$ ,  $\alpha = 89^\circ$ ,  $\beta = 91^\circ$  and  $\gamma = 118^\circ$ , the methyl-terminal chains form a monoclinic subcell with parallel skeletal planes ( $M\parallel$ ), a structure rarely found in long-chain compounds (Abrahamsson *et al.*, 1978). The  $a_s$  axis is parallel to the *b* axis of the main lattice and the  $c_s$  axis (*i.e.* the methyl-terminal chain) is inclined towards the basal plane by  $31^\circ$ . In contrast, the carboxyl-terminal chain is packed in an arrangement

\* Lists of structure factors, anisotropic thermal parameters, bond distances, bond angles, torsion angles, H-atom parameters and selected 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 54819 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0527]

Table 1. Atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) for non-H atoms
$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i a_j$$

	x	y	z	$B_{\text{eq}}$
O(1A)	0.2100 (5)	0.0078 (3)	0.03036 (5)	5.31
O(2A)	-0.0028 (5)	0.1729 (3)	0.02204 (5)	5.69
C(1A)	0.1672 (6)	0.1282 (4)	0.03764 (7)	4.52
C(2A)	0.2993 (6)	0.2405 (4)	0.06566 (7)	4.67
C(3A)	0.4580 (7)	0.1818 (4)	0.08803 (7)	4.84
C(4A)	0.6228 (6)	0.3164 (4)	0.11182 (7)	4.76
C(5A)	0.7433 (7)	0.2567 (4)	0.13934 (7)	5.23
C(6A)	0.9403 (6)	0.3944 (4)	0.15900 (7)	4.87
C(7A)	0.8877 (6)	0.4634 (4)	0.18490 (7)	4.75
C(8A)	0.6192 (7)	0.4211 (4)	0.20156 (7)	5.05
C(9A)	0.6279 (6)	0.3979 (4)	0.23782 (7)	4.79
C(10A)	0.3538 (7)	0.3565 (4)	0.25467 (7)	5.13
C(11A)	0.3567 (7)	0.3303 (4)	0.29081 (7)	5.21
C(12A)	0.0840 (7)	0.2890 (5)	0.30754 (8)	5.64
C(13A)	0.0830 (7)	0.2590 (5)	0.34375 (8)	5.54
C(14A)	-0.1864 (7)	0.2200 (5)	0.36045 (8)	5.71
C(15A)	-0.1877 (7)	0.1891 (5)	0.39625 (8)	5.67
C(16A)	-0.4557 (7)	0.1508 (5)	0.41340 (8)	5.93
C(17A)	-0.4540 (8)	0.1187 (5)	0.44925 (8)	6.34
C(18A)	-0.7240 (9)	0.0811 (6)	0.46634 (9)	7.84
O(1B)	0.0503 (5)	0.5566 (3)	0.03958 (5)	5.60
O(2B)	0.3421 (5)	0.6313 (3)	-0.00135 (5)	6.39
C(1B)	0.2807 (7)	0.6323 (4)	0.02904 (7)	4.32
C(2B)	0.5156 (6)	0.7357 (4)	0.04958 (8)	4.95
C(3B)	0.4642 (6)	0.7113 (4)	0.08529 (7)	4.73
C(4B)	0.7147 (6)	0.8084 (4)	0.10512 (7)	4.50
C(5B)	0.6758 (6)	0.7759 (4)	0.14076 (7)	5.15
C(6B)	0.9187 (6)	0.8760 (4)	0.16055 (7)	4.58
C(7B)	0.9207 (6)	0.9517 (4)	0.18795 (7)	4.60
C(8B)	0.6798 (7)	0.9542 (5)	0.20627 (7)	5.21
C(9B)	0.6475 (7)	0.8817 (4)	0.23995 (7)	4.93
C(10B)	0.3965 (7)	0.8776 (4)	0.25801 (7)	5.12
C(11B)	0.3698 (7)	0.8125 (5)	0.29233 (8)	5.32
C(12B)	0.1159 (7)	0.8027 (5)	0.30994 (8)	5.41
C(13B)	0.0908 (7)	0.7434 (5)	0.34447 (8)	5.57
C(14B)	-0.1628 (7)	0.7309 (5)	0.36222 (8)	5.45
C(15B)	-0.1830 (7)	0.6766 (5)	0.39698 (8)	5.76
C(16B)	-0.4385 (7)	0.6599 (5)	0.41499 (8)	5.75
C(17B)	-0.4530 (8)	0.6065 (5)	0.44964 (8)	6.49
C(18B)	-0.7115 (8)	0.5865 (6)	0.46729 (9)	7.54

Table 2. Selected bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

	Mol. A	Mol. B	Mol. A	Mol. B	
C(1)—O(1)	1.214 (4)	1.218 (4)	C(1)—O(2)	1.311 (4)	1.296 (4)
C(1)—C(2)	1.508 (5)	1.495 (5)	C(2)—C(3)	1.498 (5)	1.501 (5)
C(3)—C(4)	1.527 (5)	1.519 (5)	C(4)—C(5)	1.518 (5)	1.501 (5)
C(5)—C(6)	1.496 (5)	1.497 (5)	C(6)—C(7)	1.313 (5)	1.311 (5)
C(7)—C(8)	1.492 (5)	1.494 (5)	C(8)—C(9)	1.521 (5)	1.518 (5)
O(1)—C(1)—C(2)	124.0 (3)	123.6 (3)	O(1)—C(1)—C(2)—C(3)	-9.3 (5)	12.8 (5)
O(2)—C(1)—C(2)	112.8 (3)	114.1 (3)	O(2)—C(1)—C(2)—C(3)	169.8 (3)	-168.0 (3)
O(1)—C(1)—O(2)	123.2 (3)	122.3 (3)	C(1)—C(2)—C(3)—C(4)	170.0 (3)	175.4 (3)
C(1)—C(2)—C(3)	115.9 (3)	114.7 (3)	C(2)—C(3)—C(4)—C(5)	168.4 (3)	-175.3 (3)
C(2)—C(3)—C(4)	111.5 (3)	112.9 (3)	C(3)—C(4)—C(5)—C(6)	170.5 (3)	-177.8 (3)
C(3)—C(4)—C(5)	114.3 (3)	114.1 (3)	C(4)—C(5)—C(6)—C(7)	90.9 (4)	136.5 (4)
C(4)—C(5)—C(6)	113.0 (3)	114.3 (3)	C(5)—C(6)—C(7)—C(8)	0.8 (6)	1.0 (6)
C(5)—C(6)—C(7)	127.6 (3)	127.4 (3)	C(6)—C(7)—C(8)—C(9)	130.2 (4)	119.3 (4)
C(6)—C(7)—C(8)	127.8 (3)	127.2 (3)	C(7)—C(8)—C(9)—C(10)	179.4 (3)	-177.6 (3)
C(7)—C(8)—C(9)	113.5 (3)	113.6 (3)			

similar to the  $O\perp$  subcell. The skeletal plane of molecule *A* is nearly parallel to the *b* axis and that of molecule *B* is perpendicular to *b*.

One of the important factors leading to this composite lateral packing is the flexibility of the structure around the *cis*-olefin groups. Our structural study on *cis*-monounsaturated fatty acids and their derivatives indicated the conformational diversity of the *cis*-olefin group (Kobayashi & Kaneko, 1990). In the HM phase, the torsion angles of the C(5)—C(6)=C(7)—C(8) groups are 91, 1 and 130° for molecule *A* and 137, 1 and 119° for molecule *B*. Although the rotational angle of the C(5)—C(6) bond deviates considerably from the standard skew angle of 120°, especially in molecule *A*, the whole molecular shape can be recognized as a skew, *cis*, skew type in both molecules. The large difference in the torsion angle of the C(5)—C(6) bond between molecules *A* and *B* makes it possible for the carboxyl-terminal chain to form an array perpendicular to the nearest-neighbor

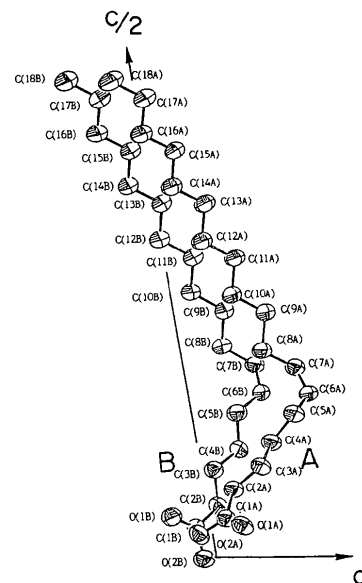


Fig. 1. ORTEP view of the high-melting phase of petroselinic acid. Thermal ellipsoids are plotted at the 50% probability level.

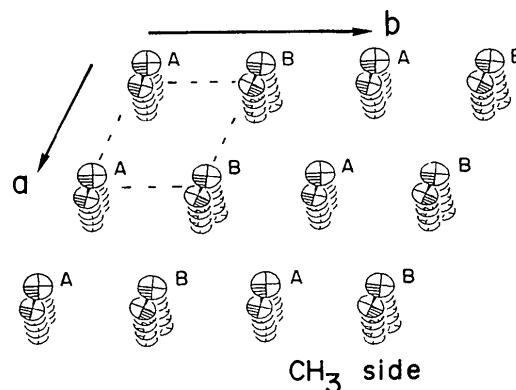


Fig. 2. Lateral packing of the methyl-terminal chains.

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*<sub>2</sub> 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  $\gamma_1$  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  $\gamma_1$  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*-monoenoic 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 $\gamma_1$ Phase of Erucic Acid

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**Abstract.** *cis*-13-Docosenoic acid, C<sub>22</sub>H<sub>42</sub>O<sub>2</sub>, *M<sub>r</sub>* = 338.57, triclinic, *P* $\bar{1}$ , *a* = 5.462 (1), *b* = 5.197 (1), *c* = 44.16 (1) Å,  $\alpha$  = 91.20 (1),  $\beta$  = 90.85 (2),  $\gamma$  = 117.32 (2)°, *V* = 1113.0 (5) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.01 g cm<sup>-3</sup>,  $\lambda$ (Cu *K* $\alpha$ ) = 1.5418 Å,  $\mu$  = 4.4 cm<sup>-1</sup>, *F*(000) = 380, *T* = 266 K, *R*(*F*) = 0.054, *wR*(*F*) =

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