Crystal Structure of DL-12-Hydroxystearic Acid

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(Received February 23, 1996)

12-Hydroxystearic acid was stacked to give a lamellar structure. 12-Hydroxy groups formed hydrogen bond sequences along the a-axis. The hydrocarbon chains took approximately an *all-trans* conformation, but might be slightly bent because of the 12-hydroxy group.

The physicochemical properties of racemic 12-hydroxy-stearic acid(DL-12-HSA), such as melting point,[1] monolayer isotherm,[2] subcell type,[2] ability of formation of solid solution with stearic acid, and X-ray powder diffraction patterns with and without stearic acid,[1,2] have been discussed mainly in comparison with those of optically active 12-hydroxystearic acid (D-12-HSA). D-12-HSA is usually prepared from ricinoleic acid by acetylation[3] and is widely used as a solidifying agent for disposal of waste edible or engine oils.[4,5] Electron micrographs have demonstrated that the D-12-HSA formed left-handed twisted fiber crystals whilst the DL-12-HSA separated out as plate-shaped crystals.[1,2,6] Monolayer studies have suggested that the DL-12-HSA is packed in a manner similar to that in the B-form of stearic acid and a part of hydroxy groups are left free by steric hindrance.[2]

DL-12-HSA was synthesized by the reduction with sodium borohydride from 12-ketostearic acid which was derived by Johns oxidation of D-12-HSA purchased from SIGMA. Crystals were grown by slow evaporation from a chloroform/hexane solution. A tranpparent colorless, plate-like crystal of 0.7x0.4x0.02 mm in size was used for the X-ray analysis.[8]

The crystal structure was solved by direct method and refined by full-matrix least squares analysis. All calculations were performed using the teXsan crystallographic software package.[7]

Figure 1 shows a view of D-12-HSA in racemic crystals with atomic numbering. The hydrogen atom of 12-hydroxy group could not be observed with a difference Fourier synthesis. Figure 2 shows the packing of DL-12-HSA without hydrogen atoms viewed nearly along the acyl chain. The hydrogen bond sequences, formed by the 12-hydroxy groups, extended zigzag along the a-axis. The distance between the O3 atom and O3 atom of neighboring molecules associated by an a-axial glide plane was 2.87(1) Å (see broken line in Figure 2) and the angle of C12-O3---O3 was 117(1)°. The acyl chain took approximately an *all-trans* conformation and formed orthorhombic packing O⊥ subcell type with average parameters (from C12 to C18) of as=5.00 Å, bs=7.83 Å, cs=2.55 Å. The subcell was set according to Abrahamsson *at al.* [9] In comparison with polymorphism of stearic acid, namely C-form,[10] B-form[11] and E-form,[12] the molecular conformation and packing type of the E-form was more similar to these of DL-12-HSA. The values of as and cs of DL-12-HSA were equal to those(as=5.02 Å; cs=2.55 Å) of the E-form but bs was 7.36 Å, being longer than that of the E-form by 0.47 Å, where as and bs were interchanged from the definition in the literature of the E-form. The elongation of bs, which is parallel to the b-axis, was caused by the 12-hydroxy group. Figure 3 shows drawings of D-12-HSA in a racemic crystal and E-form of stearic acid viewed from the C18 side. The drawings were made using a Nemesis software package.[13] The torsion angles from C4-C5-C6-C7 to C15-C16-C17-C18 were equal to 180° within e.s.d. ×3 except for torsion angle; C10-C11-C12-C13, which was 173(2) °. The deviation from 180° might cause the molecule to bend. Such bending was not observed in the structures of the stearic acids. The DL-12-HSA was probably forced to bend in order to fill up the space expanded by 12-hydroxy group in crystal. The molecules of DL-12-HSA formed lamellae and bound to form dimers with the enantiomer in neighboring lamella through the hydrogen bond between the carboxyl groups. The molecular axis was tilted by 25.7 ° from the layer normal and the angle was nearly equal to the chain tilt (26 °) of E-form of stearic acid. The O1---O2 distance between the carboxyl groups was 2.62(2) Å. The value was slightly shorter than that (2.67 Å) of the E-form. The closest intermolecular O1---O2 distance of non hydrogen bonded carboxyl groups of DL-12-HSA was 3.21 Å. The distance was slightly longer than that (3.14 Å) of the E-form. The calculated density of DL-12-HSA was 1.052 g/cm^3. The value was slightly greater than that (1.044) of the E-form. This indicates that the DL-12-HSA may form a more packed structure than the E-form of stearic acid. The more packed structure was probably brought about by the bending of the molecules.

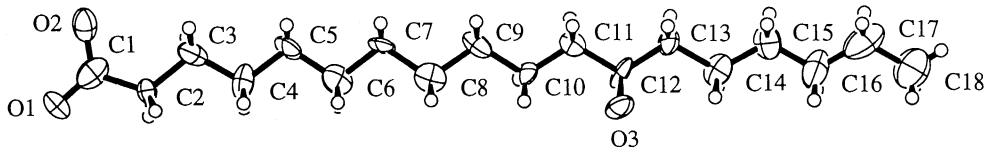

Figure 1. Numbering of atoms and conformation of DL-12-hydroxystearic acid.

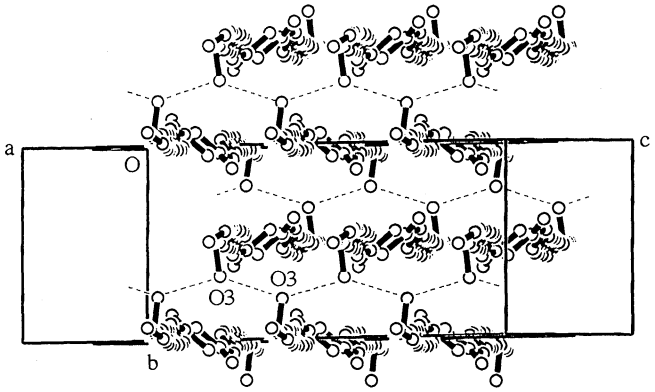

Figure 2. Hydrogen bond sequences along the a-axis of DL-12-hydroxystearic acid. O3---O3 : 2.87Å.

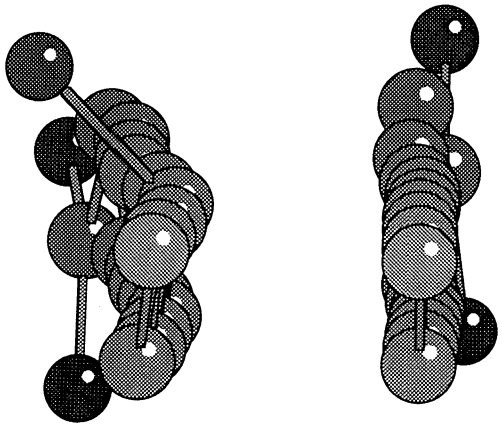

Figure 3. The molecular structures of DL-12-hydroxy-stearic acid (A) and E-form of stearic acid(B).

References and Notes

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8 Crystal data : $C_{18}H_{36}O_3$, M=300.48, monoclinic, space group $P2_1/a$, a=5.488(2), b=7.831(2), c=44.24(1) Å, β=93.64(2)°, V=1897.3(9) Å^3, Z=4, D_c=1.052 g/cm^3. Intensity data were measured on a Rigaku AFC7R diffractometer using ω scan technique with graphite monochromated Cu Kα radiation (=1.54178 Å). 1854 unique reflections within $3 \leq 2\theta \leq 100.1$ ° were collected. The non-hydrogen atoms were refined anisotropically Hydrogen atoms were included but not refined. R=0.126 (R_w=0.160) for 791 reflections [I>σ1.50(I)]. The relatively high R-value is supposed to be a result of the poor quality of the crystal.

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