**• Technical**

# Long Spacings of Six Alkyl Esters of Two Octadecenoic Acids

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## ABSTRACT

X-ray powder diffraction data are presented for some normal alkyl esters of two octadecenoic acids. The crystal long spacings observed for esters of elaidic acid are shown to be linearly related to the length of the carbon chain of the ester group. Little difference in crystal long spacings was observed between esters of *cis* and *trans* acids. Melting points of alkyl esters of elaidic acid are reported.

## INTRODUCTION

Methyl and ethyl esters of the saturated long chain fatty acids have been characterized by X-ray powder diffraction (1,2). Powder diffraction data have also been reported for esters of long chain alcohols with long chain saturated acids (2,3), which are solids at or near room temperature. Powder diffraction data for esters of the unsaturated acids which melt below room temperature have not been reported. Long spacings for alkyl esters of a *cis* and a *trans* acid with 18 carbon atoms are reported herein.

## EXPERIMENTAL PROCEDURES

The pure acids were recrystallized samples prepared by the usual fractional distillation of the methyl esters. The elaidic acid (*trans*-9-octadecenoic) was prepared from pure oleic acid as previously described (4). Esters were prepared from the acids by refluxing with the appropriate anhydrous alcohol in the presence of *p*-toluene-sulfonic acid. Unreacted alcohol was washed from the mixture with water. The ester was dried over anhydrous sodium sulfate and passed through an alumina column to remove residual alcohol and acid, using petroleum ether as an eluant. Freezing points were determined by the thermostatic sealed tube method (5).

A General Electric XRD-5 diffractometer was used to obtain tracings over the 0-50° $2\theta$ range with a strip chart recorder. The instrument was equipped with a copper target X-ray tube, xenon-filled proportional counter tube, and a 0.0007 in. thick nickel filter. A 1° slit was used for collimation. The diffractometer was equipped with a cryostat manufactured by Andonian Association, Inc. (Waltham, MA). The assembly allowed the specimen in the X-ray beam to be easily rotated about the vertical axis. NaCl was used as an internal standard for the diffraction peak locations.

## RESULTS AND DISCUSSION

The diffraction data observed for the esters investigated are presented in Table I and are compared with literature values for the esters of saturated acids containing 18 carbon atoms. Melting points are for the most stable form of the ester. Methyl and ethyl esters of the saturated acids are known to exhibit polymorphism, but polymorphic behavior was not observed for the esters investigated.

The approximate chain length of the esters has been calculated using hydrogen bonding distances 0. . . . .0, van der Waal contact distances C. . . .C, and assuming the carbon chain to be coincident with the *c* axis of the unit cell and the *beta* angle (monoclinic angle) to be coincident equal to 90°. These data have been included in Table I for comparison. As expected, the long spacings increased linearly with the chain length of the ester moiety. The increase, however, was less than would have been predicated by calculation. This indicates that the calculated angle of tilt, ca. 28.5°, is remaining constant with increasing chain length, whereas the *beta* angle (monoclinic angle) is varying with the chain length of the ester group.

The magnitude of the long spacing for methyl petroselinate (*cis*-6-octadecenoate) suggests a dimer, i.e., a double molecule, and is in close agreement with the value reported for methyl stearate, the saturated 18 carbon acid ester, which also crystallizes as a dimer (Table I). The difference between the calculated long spacing and the observed value indicates that the carbon chain is not coincident with the *c* axis and therefore could be expected to have an angle of tilt and *beta* angle very different from the longer chain esters.

The position of the unsaturation, i.e., whether the primary carbon atom is of an odd or even number, has been shown to affect the molecular packing in the unit cell (6,7). The data reported herein are inconclusive with regard to this point. Very little difference was also noted between the long spacings of the *cis* and *trans* butyl esters.

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[Received July 3, 1975]

TABLE I

Diffraction Data for Esters of Elaidic and Petroselinic Acids

| Name of compound | Melting point (C) | Long spacing (Å) | Stearic acid ester[a] (Å) | Calculated chain length (Å) |
|---|---|---|---|---|
| Ethyl elaidate | 5.1 | 29.72 | 25.8 | 28.75 |
| Propyl elaidate | -12.5 | 29.93 | 30.1 | 30.01 |
| Butyl elaidate | 10.6 | 30.63 | 31.5 | 31.27 |
| Amyl elaidate | 11.4 | 31.21 | 32.5 | 32.53 |
| Methyl petroselinate | 0.4 | 47.82 | 47.95 | 54.90 |
| Butyl petroselinate | --- | 29.45 | 32.5 | 31.27 |

[a] See ref. 1.