

# X-Ray Diffraction Powder Data of Some Thiol Esters of Long Chain Fatty Acids

L. P. WITNAUER and D. A. LUTZ, Eastern Regional Research Laboratory,<sup>1</sup> Philadelphia, Pennsylvania, and G. S. SASIN and R. SASIN, Drexel Institute of Technology, Philadelphia, Pennsylvania

A RECENT PUBLICATION (4) described the preparation of thiol esters of long chain fatty acids. A number of the compounds were solid crystalline materials at ordinary temperatures, suitable for characterization by x-ray diffraction. Although other derivatives (1, 2) of long chain acids have been studied, we were unable to find any reference in the literature that described similar studies on the thiol derivatives. In this paper the x-ray diffraction powder data for the benzyl,  $\beta$ -naphthyl, *n*-amyl, and *n*-hexyl thiol esters of myristic, palmitic, stearic acids, and in some cases lauric acids are reported.

## Experimental

The preparation of the thiol compounds used has been described (4). In order to obtain the same polymorphic form the thiol esters were dissolved in acetone, and the solution was allowed to evaporate to dryness at 26° with the exception of *n*-hexyl myristate and *n*-amyl myristate, which had melting points below room temperature. These were crystallized from acetone at 0° and maintained at this temperature until the diffraction patterns were obtained. X-ray diffraction data were obtained with a General Electric XRD-3 direct recording unit, using filtered Cu K  $\alpha$  radiation ( $\lambda = 1.5405\text{Å}$ ), 1° beam slit, 0.1° detector slit, high resolution soller slit, scanning speed 2°/min., chart speed 60 in./hr., linear scale, 4-sec. time constant. All samples were carefully ground in agate mortar to insure random orientation. The ground samples were gently packed into the recess of a plastic holder. The recess was approximately 0.5 in. square and 0.020 in. deep. Intensities were measured as counts per second at the maximum height of the peaks and then expressed on a relative scale I/I\*, with strongest line, I\*, arbitrarily given a value of 100 (Table I).

## Results and Discussion

The interplanar spacings and relative intensities reported in Table I show that the thiol derivative can be readily distinguished and identified by the x-ray diffraction data. In Figure 1 the corresponding long spacings for the benzyl,  $\beta$ -naphthyl, and *n*-aliphatic thiol esters are plotted against the number of carbon atoms in the aliphatic acid chain. A series of straight lines is obtained; this regular increase in long spacing with increase in hydrocarbon chain length is similar to that observed for other homologous series of long chain aliphatic compounds (2). The values of the long spacings plotted are the averages of at least four orders. The first measurable order was not included in the average because of the limited accuracy with which it could be measured.

The average increase for each additional carbon atom is approximately 2.30 Å. for the benzyl derivatives, 1.85 Å. for the  $\beta$ -naphthyl derivatives, and

TABLE I  
Diffraction Data of Thiol Esters of C<sub>12</sub>-C<sub>18</sub> Aliphatic Acids

| $\beta$ -Naphthyl Thiol Laurate |      | $\beta$ -Naphthyl Thiol Myristate |      | $\beta$ -Naphthyl Thiol Palmitate |      | $\beta$ -Naphthyl Thiol Stearate |      |
|---------------------------------|------|-----------------------------------|------|-----------------------------------|------|----------------------------------|------|
| d, Å                            | I/I* | d, Å                              | I/I* | d, Å                              | I/I* | d, Å                             | I/I* |
| 40.12                           | 91   | 42.03                             | 100  | 46.46                             | 100  | 49.50                            | 100  |
| 19.19                           | 100  | 21.02                             | 27   | 22.94                             | 18   | 24.72                            | 11   |
| 12.80                           | 18   | 14.02                             | 17   | 15.22                             | 14   | 16.50                            | 12   |
| 9.60                            | 31   | 10.52                             | 35   | 11.42                             | 54   | 12.36                            | 90   |
| 6.39                            | 10   | 7.02                              | 3    | 9.13                              | 3    | 9.93                             | 10   |
| 4.79                            | 9    | 5.25                              | 5    | 7.62                              | 6    | 8.24                             | 11   |
| 4.35                            | 5    | 4.67                              | 0.5  | 5.71                              | 6    | 6.19                             | 7    |
| 3.83                            | 15   | 4.48                              | 0.5  | 5.08                              | 0.9  | 4.94                             | 9    |
| 3.29                            | 5    | 4.29                              | 1    | 4.57                              | 2    | 4.21                             | 5    |
| 3.15                            | 5    | 4.21                              | 1    | 4.25                              | 1    | 3.81                             | 11   |
|                                 |      | 3.97                              | 0.7  | 3.93                              | 1    | 3.72                             | 5    |
|                                 |      | 3.83                              | 2    | 3.83                              | 3    | 3.62                             | 3    |
|                                 |      | 3.74                              | 1    | 3.74                              | 2    | 3.53                             | 3    |
|                                 |      | 3.62                              | 0.6  | 3.25                              | 1    | 2.32                             | 2    |
|                                 |      | 2.32                              | 0.5  | 2.40                              | 0.4  |                                  |      |
|                                 |      |                                   |      | 2.28                              | 0.5  |                                  |      |

| <i>n</i> -Amyl Thiol Myristate |      | <i>n</i> -Amyl Thiol Palmitate |      | <i>n</i> -Amyl Thiol Stearate |      |
|--------------------------------|------|--------------------------------|------|-------------------------------|------|
| d, Å                           | I/I* | d, Å                           | I/I* | d, Å                          | I/I* |
| 23.23                          | 100  | 25.96                          | 67   | 28.47                         | 93   |
| 11.78                          | 98   | 12.99                          | 73   | 14.24                         | 100  |
| 7.85                           | 7    | 8.66                           | 7    | 9.50                          | 14   |
| 5.91                           | 18   | 6.51                           | 3    | 5.68                          | 9    |
| 4.72                           | 21   | 5.20                           | 10   | 4.75                          | 12   |
| 3.94                           | 6    | 4.74                           | 28   | 4.48                          | 11   |
| 3.38                           | 3    | 4.44                           | 28   | 4.04                          | 3    |
| 2.97                           | 2    | 4.07                           | 7    | 3.86                          | 6    |
| 2.64                           | 10   | 3.83                           | 13   | 3.80                          | 11   |
| 2.38                           | 20   | 3.75                           | 19   | 3.66                          | 20   |
|                                |      | 3.63                           | 100  | 2.57                          | 2    |
|                                |      | 3.40                           | 5    | 2.43                          | 1    |
|                                |      | 3.16                           | 5    | 2.35                          | 4    |
|                                |      | 2.88                           | 2    |                               |      |
|                                |      | 2.35                           | 3    |                               |      |

| Benzyl Thiol Laurate |      | Benzyl Thiol Myristate |      | Benzyl Thiol Palmitate |      | Benzyl Thiol Stearate |      |
|----------------------|------|------------------------|------|------------------------|------|-----------------------|------|
| d, Å                 | I/I* | d, Å                   | I/I* | d, Å                   | I/I* | d, Å                  | I/I* |
| 21.02                | 60   | 47.75                  | 100  | 53.55                  | 100  | 58.85                 | 54   |
| 14.24                | 34   | 23.86                  | 12   | 26.20                  | 4    | 14.35                 | 100  |
| 10.64                | 100  | 15.91                  | 16   | 17.49                  | 9    | 11.47                 | 16   |
| 7.10                 | 9    | 11.94                  | 74   | 13.09                  | 83   | 9.55                  | 23   |
| 6.06                 | 1    | 9.50                   | 3    | 10.48                  | 7    | 7.18                  | 7    |
| 5.34                 | 25   | 7.96                   | 7    | 8.75                   | 9    | 5.74                  | 18   |
| 4.74                 | 4    | 5.97                   | 19   | 6.55                   | 7    | 5.18                  | 5    |
| 4.46                 | 2    | 5.30                   | 6    | 5.82                   | 2    | 4.74                  | 16   |
| 4.35                 | 8    | 4.78                   | 19   | 5.24                   | 15   | 4.50                  | 5    |
| 4.29                 | 14   | 4.35                   | 4    | 4.77                   | 2    | 4.33                  | 12   |
| 4.09                 | 13   | 4.11                   | 4    | 4.53                   | 3    | 4.13                  | 20   |
| 4.06                 | 11   | 3.97                   | 11   | 4.35                   | 13   | 3.80                  | 13   |
| 3.90                 | 4    | 3.80                   | 2    | 4.13                   | 10   | 3.54                  | 5    |
| 3.78                 | 7    | 3.67                   | 2    | 3.81                   | 5    | 2.58                  | 4    |
| 3.57                 | 6    | 3.40                   | 3    | 3.74                   | 3    | 2.37                  | 12   |
| 2.86                 | 4    | 3.17                   | 2    | 3.08                   | 2    |                       |      |
| 2.78                 | 3    | 2.98                   | 0.9  | 2.61                   | 2    |                       |      |
| 2.68                 | 3    | 2.80                   | 2    | 2.38                   | 6    |                       |      |
| 2.38                 | 15   | 2.65                   | 3    | 2.27                   | 2    |                       |      |
| 2.26                 | 3    | 2.51                   | 2    |                        |      |                       |      |
| 2.14                 | 7    | 2.38                   | 19   |                        |      |                       |      |
|                      |      | 2.67                   | 4    |                        |      |                       |      |

| <i>n</i> -Hexyl Thiol Myristate |      | <i>n</i> -Hexyl Thiol Palmitate |      | <i>n</i> -Hexyl Thiol Stearate |      |
|---------------------------------|------|---------------------------------|------|--------------------------------|------|
| d, Å                            | I/I* | d, Å                            | I/I* | d, Å                           | I/I* |
| 25.22                           | 100  | 28.04                           | 100  | 30.44                          | 100  |
| 12.80                           | 51   | 14.02                           | 69   | 15.25                          | 68   |
| 6.41                            | 7    | 9.35                            | 2    | 10.16                          | 4    |
| 5.12                            | 3    | 7.02                            | 7    | 7.62                           | 3    |
| 4.27                            | 1    | 5.60                            | 6    | 6.09                           | 6    |
| 4.07                            | 2    | 4.69                            | 1    | 5.06                           | 3    |
| 3.69                            | 6    | 4.11                            | 1    | 4.46                           | 5    |
| 3.22                            | 2    | 3.72                            | 0.4  | 4.31                           | 13   |
| 2.86                            | 1    | 3.13                            | 1    | 4.11                           | 60   |
| 2.34                            | 7    | 2.55                            | 0.4  | 3.38                           | 70   |
|                                 |      | 2.34                            | 6    | 3.74                           | 38   |
|                                 |      |                                 |      | 2.34                           | 7    |

1.21 Å. for the *n*-aliphatic derivatives. The values for the two aromatic series are greater than the expected projected C-C distance, 1.27 Å. It appears that the measured spacings of the aromatic deriva-

<sup>1</sup> One of the laboratories of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

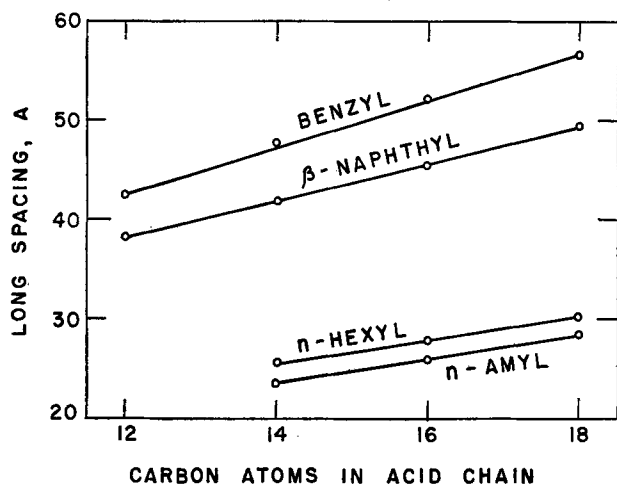


FIG. 1. Long spacings of thiol esters of  $C_{12}$ - $C_{18}$  aliphatic acids.

tives are the projection of double the molecular length on [d 001]. Thus these aromatic thiol esters must crystallize in bimolecular layers like the methyl esters of the *n*-aliphatic acids. The increase in long spacing for each additional carbon atom is  $2.30/2 = 1.15$  A. and  $1.85/2 = 0.92$  A. for the benzyl and  $\beta$ -naphthyl derivatives, respectively. This is much lower than the expected projected distance, 1.27 A., of a C-C bond. Thus these derivatives must be tilted with respect to the 001 plane.

On the other hand, the measured increase in long spacing for each additional carbon atom for the *n*-amyl and *n*-hexyl derivatives is 1.21 A., slightly less than the expected projected C-C bond distance. Thus these *n*-aliphatic thiol acid esters, like the ethyl esters of the *n*-aliphatic acids, crystallize in apparent monomolecular layers. If the measured long spacings of these compounds are plotted against the total number of carbon atoms in the chain, the data form two separate, approximately parallel, lines. The only difference between the two sets of derivatives is in the number of carbon atoms; one, *n*-amyl, contains an odd number of carbon atoms while the other, *n*-hexyl,

contains an even number. This even-odd alternation in long spacing is characteristic for long chain compounds that possess tilted chains in the solid state (3). The previously reported long spacings of odd alternating compounds are always slightly greater, in proportion, than even. However in the present case the reverse is true. The reason for this is not apparent at the present time.

Because of the multiplicity of lines in the low angular region, it is difficult to isolate the side spacings of these derivatives. However a side spacing common to each derivative in a particular series can be found for the  $\beta$ -naphthyl-, *n*-amyl-, and benzyl-derivatives. For example, in the four  $\beta$ -naphthyl derivatives each show a relatively strong diffraction line at about 3.83 A. However for the *n*-hexyl series there appears to be no correspondence. This probably results from the difficulty in obtaining the material in good crystalline form because of the low melting temperatures of the myristate and palmitate members of the series, 20.5 and 28.5°C., respectively.

### Summary

X-ray diffraction powder data were obtained for 14 thiol esters of long chain fatty acids including benzyl,  $\beta$ -naphthyl, *n*-amyl, and *n*-hexyl thiol myristates; thiol palmitates; thiol stearates; and in some cases thiol laurates. All the individual compounds can be readily distinguished and identified by the diffraction data. Long spacings increase regularly with increase in hydrocarbon chain length. The benzyl and  $\beta$ -naphthyl thiol esters crystallize in tilted bimolecular layers while the *n*-amyl and *n*-hexyl thiol derivatives crystallize in tilted monomolecular layers.

### REFERENCES

1. Francis, F., Collins, F. J. E., and Piper, S. H., Proc. Roy. Soc. London, **4158**, 691-718 (1937).
2. Francis, F., and Piper, S. H., J. Am. Chem. Soc., **61**, 577-581 (1939).
3. Malkin, T., Nature, **127**, 126-127 (1931); J. Chem. Soc., **1931**, 2796-2805.
4. Sasin, G. S., Sasin, R., and Capron, N., J. Org. Chem., **21**, 852 (1956).

[Received July 9, 1956]

## Some Laboratory Investigations of Degummed Cottonseed Oil

JAMES K. SIKES, Plains Cooperative Oil Mill, Lubbock, Texas

IN A PAPER presented by W. C. Whittecar at the April, 1955, meeting of the American Oil Chemists' Society in New Orleans (7) the mechanics of cottonseed oil degumming, its primary and secondary benefits were discussed. There has been little change in the mechanics of the operation since that time, and we now believe that the principle is a thoroughly sound and profitable one.

One innovation however has been tried experimentally, that of miscella degumming, or degumming the oil while still in the miscella stage. Oil was taken from a French basket-type of extractor to the usual pre-evaporator but, instead of going directly to the final still to remove the last of the hexane, the oil went to the degumming stage. This miscella contained 8.0% hexane. The oil was degummed in the

usual way, *i.e.*, it was mixed with 2.5% water, heated to 120°F. (49°C.), and centrifuged through two De Laval VO 194 hermetically sealed machines. Oil was pumped from the centrifuges to the vacuum still to remove the hexane and finally to a four-car dryer to remove the moisture.

This process worked quite well. The cup loss of the oil produced by this method is comparable to straight degumming but is somewhat more stable in color, as verified by an eight-month storage test. This results, we assume, from the fact that the total gossypol content of the miscella-degummed oil is lower than that of regularly degummed oil, as shown in Table I.

Some tests were run to determine the solubility of gossypol in *n*-hexane, commercial grade, in an effort