Calcium palmitate and α-palmitic acid in gallstones

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SUMMARY Calcium palmitate occurred in 20% of the gallstones studied in this laboratory by x-ray diffraction and was the most important crystalline constituent after the different forms of cholesterol and calcium carbonate. Only one calculus contained α-palmitic acid. The gallstones came from America, England, Australia, Sweden, and South Africa, and, as far as is known, this represents the first time these compounds have been found in stones from countries other than Japan.

In a recent paper describing the composition of gallstones as determined by the x-ray powder method (Sutor and Wooley, 1969), the presence of two crystalline long-chain compounds in some stones from England and Australia was reported. At the time, identification was not possible because the one diffraction pattern was not listed in the American Society for Testing Materials (ASTM) index of powder patterns, and the other pattern which was obtained from only one stone could not be unambiguously resolved from the first. The first compound has subsequently been found in gallstones from Sweden, South Africa, and America and better photographs have now enabled the two substances to be identified.

Long-chain compounds pack in the crystal in such a way that the chains of molecules are parallel. In the powder pattern the line corresponding to the distance between the planes of successive chains is very intense and its spacing is nearly constant for a particular series of long-chain compounds. The spacing corresponding to the length of the chain varies from one member to the next by some increment which depends on the particular series. Knowledge of these two spacings may be sufficient, in the first instance, to assign a compound to a series. Comparison of the powder pattern with that of the known material will then show if the correct choice has been made.

The two relevant spacings for the first long-chain compound are 45 Å and 4.4 Å. The corresponding spacings for calcium caprate, laurate, myristate, and stearate given in the ASTM index suggested that the material was calcium palmitate. A powder photograph of the commercial compound taken on the Nonius-Guinier powder camera (camera radius 57.3 mm) confirmed this identification. The d-spacings and their relative intensities for calcium palmitate are listed in the Table. They differ considerably from the values given in the ASTM index which may correspond to another form of calcium palmitate belonging to a different series.

Once this pattern was established the other long-chain compound was identified as α-palmitic acid.

As far as is known, neither calcium palmitate nor α-palmitic acid have been reported previously in gallstones from countries other than Japan. In the stones studied in this laboratory calcium palmitate was the most important constituent after the different forms of cholesterol and calcium carbonate. It has been identified in about 20% of the Australian stones examined, in 15% of the English, 20% of the Swedish, 20% of the American, and 17% of the South African ones. No pure stone was found1. The material occurred with one or sometimes several of the usual constituents of gallstones (Sutor and Wooley, 1969).

1Several pure stones have now (June 1970) been found.
Calcium palmitate and o-palmitic acid in gallstones

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>I</th>
<th>d (Å)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>Strong</td>
<td>4-40</td>
<td>Very strong</td>
</tr>
<tr>
<td>15.15</td>
<td>Very strong</td>
<td>4-35</td>
<td>Very strong</td>
</tr>
<tr>
<td>11.25</td>
<td>Medium weak</td>
<td>4-10</td>
<td>Medium</td>
</tr>
<tr>
<td>9.00</td>
<td>Medium</td>
<td>4-03</td>
<td>Medium</td>
</tr>
<tr>
<td>6.42</td>
<td>Very weak</td>
<td>3-85</td>
<td>Weak</td>
</tr>
<tr>
<td>5.83</td>
<td>Weak</td>
<td>3-39</td>
<td>Medium</td>
</tr>
<tr>
<td>5.71</td>
<td>Very weak</td>
<td>3-34</td>
<td>Weak</td>
</tr>
<tr>
<td>5.46</td>
<td>Very weak</td>
<td>3-28</td>
<td>Very weak</td>
</tr>
<tr>
<td>5.21</td>
<td>Very weak</td>
<td>2-90</td>
<td>Weak</td>
</tr>
</tbody>
</table>

Table. Spacings (d) and relative intensities (I) of the lines in the x-ray powder photograph of calcium palmitate

1 As an internal standard was not used there may be a small zero error in the d-values.

In seven calculi it was the major component. In 12 other calculi it was present as small white spheroids which were usually scattered through the stone but formed only a small part of it. The latter stones invariably consisted of loose aggregates of material in the regions where the spheroids occurred. α-Palmitic acid was identified with calcium palmitate and anhydrous cholesterol in one calculus from a female English patient.

Palmitic acid, together with oleic and linoleic acids, make up 80% of the fatty acid content of the human gallbladder and hepatic bile (Blomstrand and Ekdahl, 1960). Approximately 90% of the total fatty acids are conjugated to lecithin. In a study of the composition of bile from stone formers and non-stone formers, Blomstrand and Ekdahl (1960) found no difference in the fatty acid content, but unfortunately the number of controls and patients studied was too small for the results to be significant. The occurrence of calcium palmitate and palmitic acid in gallstones might suggest an increase in the bile concentration of free palmitic acid in some cases of cholelithiasis. On the other hand, the difference between a stone former and non-stone former might also be attributed to the absence in stone formers’ bile of a particular compound (commonly referred to as an inhibitor of crystallization) which prevents calcium palmitate from crystallizing or from growing on a stone already present.

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References
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