

X-RAY DIFFRACTION STUDIES OF GALL STONES

K. C. NAGPAL, T. A. K. GHORI AND S. Z. ALI
National Physical Laboratory, New Delhi 110 012, India.

ABSTRACT

X-ray diffraction analyses of 13 gall stones of patients in the age group 20–74 years were carried out. Anhydrous cholesterol, the chief ingredient of gall stones, was present in 62% of calculi whereas the monohydrate was present in 46%. Calcium carbonate, identified as calcite and aragonite, was present in 23 and 8% of the calculi respectively. Apatite was found in 38% of calculi.

INTRODUCTION

BILIARY calculi are well known concretions formed under certain pathological conditions inside the gall bladder. These are usually heterogeneous^{1,2}. Inflammation, stasis and stagnation predispose to the precipitation of these 'stone' forming materials, thus initiating the 'stone' process. The nucleus of the gall stones can either be pigment or protein with traces of bile salts and cholesterol. Once it is formed, growth may continue by deposition of either the original substance or another on a matrix formed by microprotein. Conditions governing the crystallization of each constituent are not clearly understood. However, epitaxy³ contributes to the development of a mixed calculus; and calculations of the dimensions of prominent crystal faces show that anhydrous cholesterol, calcite, aragonite, vaterite and apatite can grow on each other. The biliary constituents can be precipitated anywhere in the biliary tract and the gall bladder only modifies the final form.

X-ray diffraction analysis has been widely used in identifying the crystalline components present in biliary calculi. In the present study, this technique was used to determine the crystalline components present in gall stones.

MATERIALS AND METHODS

X-ray diffraction analyses of gall stones of 13 patients (11 women and 2 men) in the age group 20–74 years,

which were supplied by the L.L.R.M. Medical College, Meerut, were carried out. The stones were crushed to a fine powder in an agate mortar and pestle. The powders were studied by making cylindrical samples, after mixing with an amorphous binder. A Philip's Debye-Scherrer powder camera of 114.6 mm diameter, with fine colimator enabling the recording of maximum Bragg-spacing of 40 Å was used for taking the powder photographs. CuK_α radiation at 35 kV and 12 mA was used.

The d-spacings corresponding to the lines of the pattern were calculated by using the Bragg-equation.

RESULTS AND DISCUSSION

The present analyses relate to the composition of the calculi irrespective of size, shape and weight. The crystalline components identified in these stones were found to be anhydrous cholesterol, cholesterol monohydrate, calcium carbonate as aragonite, calcite and apatite (table 1).

The crystalline components of gall stones can usually be identified readily because the diffraction patterns of different components have very few lines in common and masking of a minor component by a major one is unlikely to occur. The minimum amount of a minor component of a mixture which can be detected is variable because of the large difference in the absorption coefficients for x-rays of the different compounds present in the gall stones. However, ill-crystallized materials or disordered and very small crystallite-sized

TABLE I
Crystalline phases identified in gall stone by x-ray powder method

Case No.	3	4	5	7	8	9	12	14	17	25	40	44	49
Phases present	N —	—	—	A ₁ B	A ₁ C ₂	A ₂ ,B	—	—	—	U	—	A ₂ ,C ₂	—
	O —	—	—	A ₁	A ₁ ,B	A ₂ ,B	—	—	—	A ₂ ,C ₂	—	A ₂ ,C ₂	—
	W A ₁	A ₁ ,A ₂	C ₁	—	—	—	A ₁	A ₁	A ₁ ,A ₂ ,B	—	A ₂	—	A ₁ ,A ₂ ,B

Key words:

A₁ = Anhydrous cholesterol, A₂ = Cholesterol monohydrate, B = Apatite, C₁ = Aragonite, C₂ = Calcite, N = Nucleus of stones, O = Outer layers of stones, W = Overall stones, U = Unidentified phase.

phases are very difficult to detect in the presence of large amounts of other phases⁴.

Cholesterol, the chief ingredient of gall stones, is a chemically complex molecule with several side chains. It has triclinic symmetry and its content varies from 57.3 to 99.7% of the dry substance⁵. Three forms of cholesterol have been reported in literature^{6,7}. However, difficulties⁶ occur in differentiating these forms. Cholesterol and cholesterol monohydrate are readily interchangeable, suggesting that water can enter and leave the lattices without difficulty. Cholesterol deposits freshly removed from man were invariably found to be cholesterol monohydrate⁸, suggesting that cholesterol is originally laid down as monohydrate. When cholesterol monohydrate crystallised in man is kept in air for some time, it loses its water and transforms into anhydrous cholesterol. Thus anhydrous is formed from monohydrate, but whether this is always the case or whether it is deposited as such is not yet understood. Besides the formation of an anhydrous crystal form, the x-ray powder patterns reported by Bogren and Larsen⁷ also indicated that cholesterol was transformed into an amorphous state when water left the lattice.

Cholesterol is almost insoluble in water⁹. It is, therefore, remarkable that crystals of anhydrous cholesterol undergo a transition into monohydrate in the presence of water. Crystals of the hydrate are stable up to five years under certain conditions, whereas samples consisting of very small crystallites have been found, where a large part is transformed after a few days.

Calcium carbonate as aragonite has been found only in one stone whereas calcite is present in the nucleus and outer layers with other crystalline compounds in three stones. Vaterite could not be detected in any of the stones.

Indication of apatite in the nucleus and the other layers of five stones has also been noticed. Due to small crystallite size, the apatite gives diffuse and weak

patterns. On the basis of its strongest lines in the region of 2.82 to 2.88 Å, it has been identified.

The incidence of gall stones increases with advancing years and the disease has a high frequency in females in all ages. In our series the female-to-male ratio was 6.5:1. This ratio was similar to that observed by others¹⁰⁻¹². This disease in females is highest between 50 and 59 years and in males between 70 and 79 years. The maximum number of patients have been found in the age group of 36 to 40 years and the majority of them (70.6%) were vegetarians. This conforms to the general dietary habits of Meerut area. In the majority of the patients the fat intake was comparatively high. The consumption of high calorie diet with a large amount of fat containing saturated fatty acid has been supposed to be the cause for the formation of stones.

Authors thank Dr. A. M. Nagar, Department of Surgery, L.L.R.M. Medical College, Meerut for supplying the gall stones.

1. Sutor, D. J. and Wooley, S. E., *Gut*, 1969, **10**, 681.
2. Sutor, D. J., *Gut*, 1970, **11**, 618.
3. Lonsdale, K., *Nature (London)*, 1968, **217**, 56.
4. Sutor, D. J., *Br. J. Urol.*, 1968, **40**, 29.
5. Nishimura, C., *Ch. Ztbl. I.*, 1939, 2441.
6. Sutor, D. J. and Wooley, S. E., *Gut*, 1971, **12**, 55.
7. Sutor, D. J. and Gaston, P. J., *Gut*, 1972, **13**, 64.
8. Bogren, H. and Larson, K., *Biochem. Biophys. Acta*, 1963, **75**, 65.
9. Ekwall, P. and Mandell, I., *Acta Chem. Scand.*, 1961, **15**, 1404.
10. Horn, G., *Br. Med. J.*, 1956, **2**, 732.
11. Rains, A. F. J. H., *Gallstone*, William Heinmann Medical Book Ltd., (Pergamon Press, Oxford, U.K. 1964).
12. Friedman, G. G., *J. Chronic Disease*, 1966, **19**, 273.

REACTION OF TETRAPHENYLDITIN DIACETATE WITH N-PHENYL-BENZOHYDROXAMIC ACID AND 8-HYDROXYQUINOLINE

B. PRADHAN* AND A. K. GHOSH

Department of Chemistry, North Bengal University, Darjeeling 734 430, India.

* Present Address: Department of Chemistry, Raiganj University College, Raiganj 733 134, India.

ABSTRACT

The Sn—Sn bond in tetraphenylditin 1,2-diacetate is cleaved when reacted with N-phenylbenzohydroxamic acid (PBHA); but the bond is retained when reacted with 8-hydroxyquinoline (Ox). In the former the characterised product is diphenyl tin bis (N-phenyl-benzohydroxamate) and in the latter the product has been characterised as diacetate ditin bis (oxinate).

INTRODUCTION

IN recent years, coordination compounds of organotin moieties have been extensively studied.

But coordination compounds of organoditin compounds have not been studied in detail due to the cleavage of Sn—Sn bond by various reagents. An attempt is made here to prepare coordination com-