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Reactions in Inclusion Compounds: A Solid-state Regio-Specific and Stereo-Specific Hydroxylation of Desoxycholic Acid

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Reactions in Inclusion Compounds

A Solid-State Regio-Specific and Stereo-Specific Hydroxylation of Desoxycholic Acid

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In recent years there has been increased interest in organic chemistry to mimic the enzymatic reactions of nature in order to increase the power of synthetic methods.[1] Molecular crystals are very convenient vehicles for the performance of such reactions, since in them as in an enzyme, the geometrical contacts between reacting centers of the rigid molecules are strictly defined by the packing of the crystal.

In the present approach we describe here we have used molecular complexes of steroids, of which there are a great variety known, of various types, and with a large number of small molecules.[2] Here we describe a one-step hydroxylation of desoxycholic acid **1**. This acid forms a well-defined 4:1 crystalline complex, m.p. 160–1°, when crystallised with the di-t-butyl diperoxymonocarbonate **2**.

When a polycrystalline sample of this inclusion complex is heated at 90°C for 120 hours, the guest molecule decomposes inside the steroid channel and reacts with the host to give two major products **3** (15%) and **4** (15%), and traces of **5**. (See Figure 1). Products were identified by mass spectrometry and by N.M.R. Similar results are also obtained when the crystalline powder is exposed to irradiation ($\lambda > 300$ nm). The X-ray intensity data on the complex were collected at room temperature on a diffractometer.

The host molecule, including almost all hydrogens, were readily found as shown in Figure 2. The guest molecule has not yet been located; presumably since it lies in the inclusion channel on a twofold axis and is disordered about this axis.

† This work is taken from the Ph.D. thesis of R. Popovitz-Biro and C. P. Tang, to be submitted to the Feinberg Graduate School, The Weizmann Institute of Science.

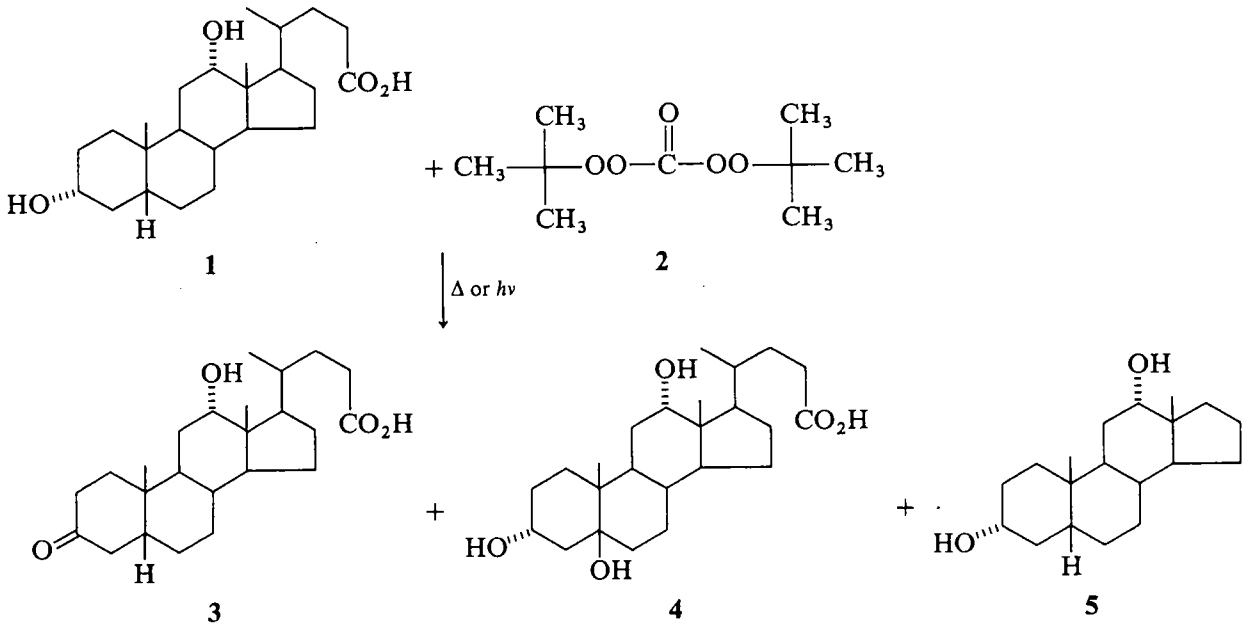

FIGURE 1

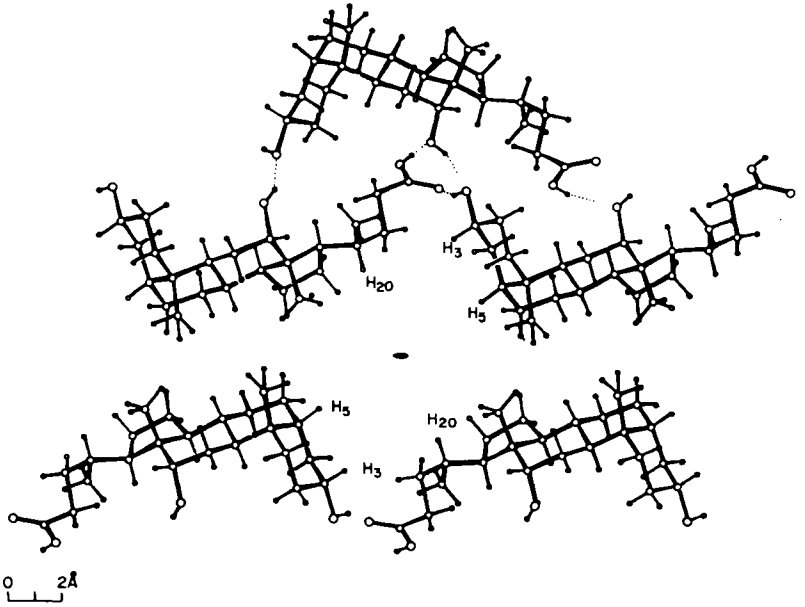

FIGURE 2

The hydrogen bonding structure of the steroid is very similar to that of other reported desoxycholic acid complexes.[3,4] The host channel structure shows that only a limited number of tertiary hydrogens of the steroid on the inner wall of the channel are exposed to the guest and therefore available for abstraction. Consequently only these sites are oxidised.

In this context it is noteworthy that previous work in solution on similar systems has led to unselective attacks on the various positions of the steroid.[5]

Studies on apocholic acid, which forms similar complexes, will be described as well.

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