

References and Notes

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11. Unpublished data of K. Kneipp cited in W. A. Pryor and T. F. Fiske, *Intra-Sci. Chem. Rep.* **3**, 249 (1969) and in W. A. Pryor and U. Tonellato, *J. Phys. Chem.* **73**, 850 (1969).
12. The bond dissociation energies (in kilocalories per mole) are $D(\text{CH}_3\text{S}-\text{H}) = 88$ and $D(\text{C}_6\text{H}_5\text{S}-\text{H}) = 75$ [J. A. Kerr, *Chem. Rev.* **66**, 465 (1966)]. The value of $D(\text{t-C}_4\text{H}_9\text{S}-\text{H})$ also is 88 [H. Mackle, *Tetrahedron* **19**, 1159 (1963)]. The bond dissociation energy of the RS-H bond determines the reactivity of the thiyl radical toward QH; see W. A. Pryor, *Mechanisms of Sulfur Reactions* (McGraw-Hill, New York, 1962), pp. 88-93; C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.* **81**, 1137 (1959).
13. Reaction 4 is a more complex process for thiophenol, consisting of the addition of a deuterium atom to the ring to form a cyclohexadienyl radical which then reacts with a second D atom to form HD and $\text{C}_6\text{H}_4\text{DSD}$. In method II the ring positions of thiophenol become tritiated by a similar mechanism.
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17. The data from aqueous radiolysis of methanol, ethanol, and isopropanol give a reactivity per hydrogen for primary, secondary, and tertiary hydrogens which is not at all what should be expected of the hydrogen atom. Our data obtained by method II yield relative rates for the attack of the H atom on these alcohols which closely parallel the data for the methyl radical. Since the methyl radical and H atom form bonds with hydrogen of the same strength (104 kcal/mole), it would be expected that they would show similar selectivity (10). These points are discussed in a review [W. A. Pryor and J. P. Stanley, *Intra-Sci. Chem. Rep.*, in press].
18. Supported in part by grant GM-11908 from PHS-NIH. J.P.S. is a postdoctoral fellow supported on the NIH grant. M.G.G. was a NASA predoctoral trainee from 1963 to 1966 and a research associate on the NIH grant from 1966 to 1967.

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Calcium Oxalate: Crystallographic Analysis in Solid Aggregates in Urinary Sediments

Abstract. A relationship between crystallographic structure and morphological form of calcium oxalates in urinary sediments is established. The common tetragonal bipyramids have been confirmed as weddellite from their electron diffraction patterns. Other solid forms, such as needles, biconcave disks, and dumbbell forms, that can appear in hyperoxalurias, of both metabolic and alimentary origin, have been identified as whewellite. Micrographs reveal fibrous structure on those whewellite polycrystalline aggregates.

Urinary calcium oxalate sediments of healthy persons and patients with renal stones have been studied by electron microscopy (Siemens Elmiskop IA), and the different crystalline types have been identified by diffraction analysis of selected areas. Specimens were pre-

pared as follows. Immediately after the urine was collected, it was centrifuged in warm, conical glass tubes (1500 rev/min, 1 minute), and the sediment was washed with distilled water and dried. Crystals were observed directly and by replica with the Bradley method (1).

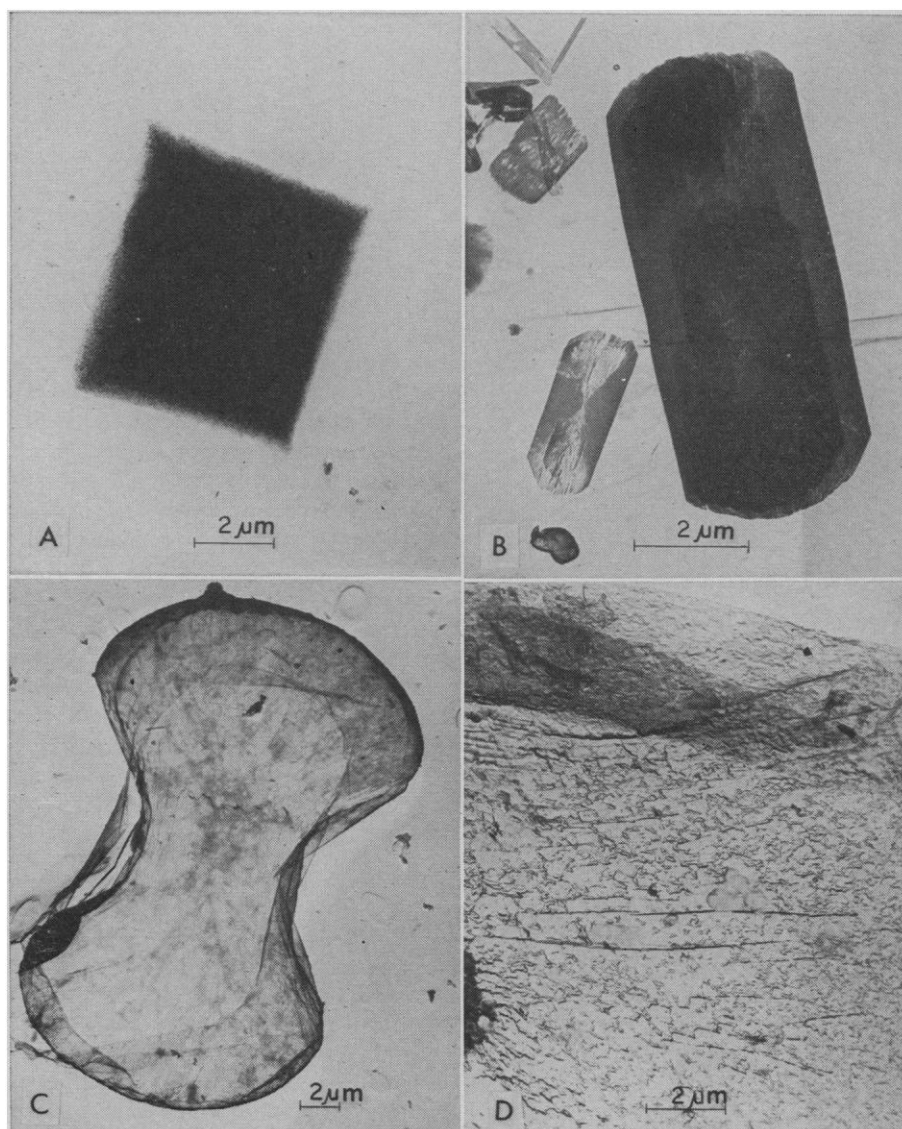


Fig. 1. (A) Bipyramid tetragonal crystal of weddellite. (B) Aggregated prismatic crystals. (C) Carbon replica of a typical dumbbell form of polycrystalline aggregates. (D) Replica of a dumbbell form with high magnification. On its surface the fibrillar structure is observed.

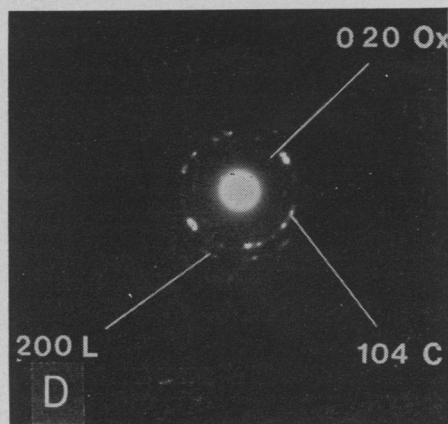
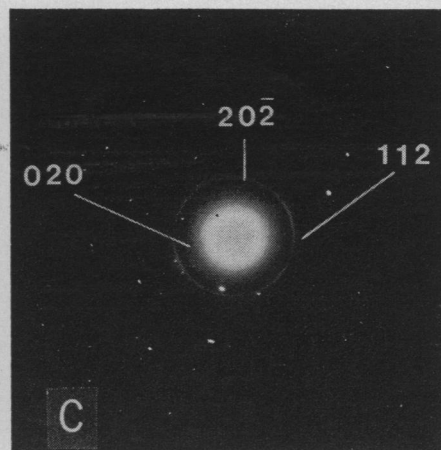
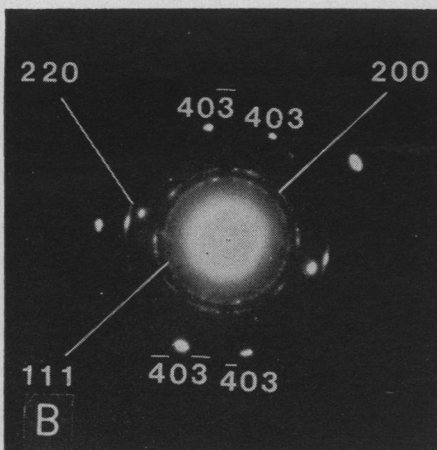
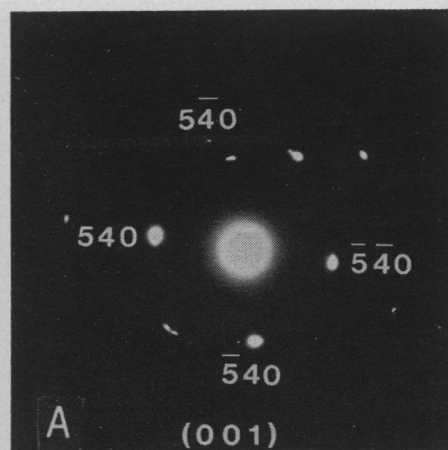


Fig. 2. Electron diffraction patterns of (A) a bipyramid tetragonal crystal of weddellite (calcium oxalate dihydrate) with (001) orientation; (B) the same diagram as (A), after electron bombardment, which still presents spots of weddellite (403) and rings which correspond to lime (111) (200) (220); (C) the crystalline aggregate of (B) which presents the principal rings (020), (202), (112) of whewellite (calcium oxalate monohydrate); (D) a dumbbell form (like that in Fig. 1C) which presents a weak ring (020) Ox of whewellite even though very low beam intensity has been used in order to delay the transformation to calcite (104) C and lime (200) L.

To prevent the decomposition of the crystals during observation, the specimens were cooled with liquid nitrogen.

Tetragonal bipyramids are the most abundant forms observed but others with less well-defined crystallization (ellipsoid, biconcave disks, needles, spherulites, and dumbbell forms) were also found, especially in cases of metabolic hyperoxalurias or in healthy individuals on a rich oxalate diet. Tetragonal bipyramids (Fig. 1A) have been recognized as weddellite (2). Our analysis by electron diffraction (Fig. 2A) confirms this. The increase in temperature produced by electron bombardment and the high vacuum rapidly convert the weddellite crystals to calcite and then to calcium oxide (Fig. 2B).

Dumbbell forms have been identified as whewellite on the basis of their shapes (3). Electron-diffraction ring patterns corresponding to whewellite crystals (Fig. 2, C and D) have been observed in the prismatic crystal aggregates (Fig. 1B), dumbbell-shaped (Fig. 1C), and spherulite forms of calcium oxalate. The patterns of dumbbell forms do not have very sharp rings because low-intensity electron beams are used to delay the transformation to cal-

cite. Dumbbell forms are polycrystalline aggregates with fibrous structures (Fig. 1D).

Dumbbell or sandglass shapes are not exclusive of whewellite. They have also been found in mineral substances of fibrillar structure like hematite (4), in some organic polymers (5), and in non-polymeric substances (6).

Such aggregates may be produced through a branching or fanning mechanism during the growth of needles in length. The aggregates gradually approach the spherical form with cavities in the center which may remain noticeable in the final spherulite.

Needles, isolated or aggregated in fascicles with irregular morphology, do not have crystalline structures as perfect as those from plant cells (7). Dumbbell forms and spherulites with hollowed central areas such as those found in the

urinary sediments are stages of the same well-defined development, peculiar to many fibrous crystals.

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Attine Fungus Gardens Contain Yeasts

Abstract. *Yeasts were detected in the fungus gardens of Atta cephalotes and Acromyrmex octospinosus by scanning electron microscopy and by microbiological techniques.*

Attine ants, by supplying organic substrate, maintain a symbiotic relationship with fungi which in turn serve both as a food source (1) and energy reserve for the colony. In this symbiosis the ants and their fungi have developed an efficient means of utilizing

plant carbohydrates as an energy source (1). The fungus gardens of attine ants consist of organic matter loosely held together by fungus mycelium (2). The organisms accepted as true ant fungi are the Basidiomycetes *Agaricus gongylophora*, *Lepiota* sp., and *Auricularia*