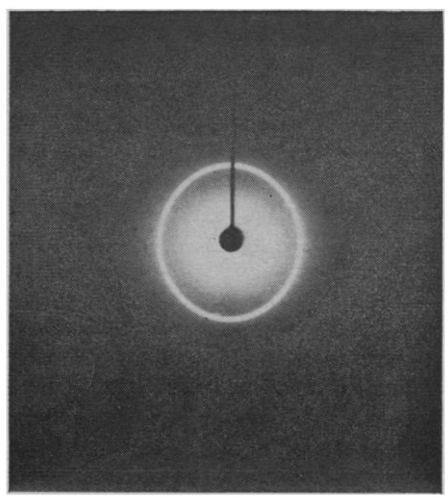
Uric Acid Dihydrate in Bird Urine

Abstract. *X-ray diffraction analysis shows that the white excrement from a budgerigar consists mainly of uric acid dihydrate. Initially this material is in the form of a smectic (or cholesteric) phase, which transforms to the normal crystalline phase either on aging or on removal of the minor (soluble) constituents of the excrement with water or dilute acids.*

In recent reports (*1, 2*) Folk has claimed, on the basis of his x-ray diffraction patterns from bird urine, "that it [bird urine] does not consist largely of uric acid, as has frequently been parroted" (*1*). He has observed that the white part of the droppings (urine) of birds consists, when fresh, of minute spheres which are optically uniaxial and of very high birefringence. Their x-ray diffraction pattern, he found, consists of a single very sharp, very intense peak at 3.20 to 3.23 Å. These droppings show none of the other lines characteristic of uric acid, uric acid dihydrate, or sodium urate, some of which might be expected to be of higher intensity. We have confirmed this observation, using the white part of the excrement of a parakeet (budgerigar) (Fig. 1), but we also find a weak second-order line at 1.60 Å, which defines the position of the main spacing more accurately as being at 3.20 Å. This single spacing, we find, is given both when the dropping is fresh and soft and when it has become hard and dry, after several days. Folk believes that the absence of all spacings except this one shows conclusively that the material is not mainly uric acid. But this is not so. Both the optical behavior and the single, sharp spacing (first and second orders) show that the material is in the form of a disordered layer structure, like a pack of cards, the orientation of each card in its own plane being random, but with a constant spacing from one card to the next. The polar direction is normal to the layers. The birefringence can be very large indeed. The best-known example of this type of structure is pyrolytic graphite, which can exist with varying degrees of disorder, but for which the main spacing is unaltered unless the carbon (001) planes become tilted, the crystallite size becomes very small, or foreign atoms are intercalated. A similar single periodicity is typical of some "plastic crystals" of the smectic or cholesteric types (mesomorphic phase P_1P_0R or even SSR) (*3*).

The main layer spacing (021) of uric acid dihydrate crystals is almost precisely that found for the specimens of bird droppings (3.195 Å as compared with 3.20 Å), and a "plastic crystal" or disordered form of uric acid dihydrate cannot therefore be ruled out on the basis of the x-ray analysis alone. Moreover, the birefringence and the refractive indices of uric acid dihydrate are high {α along (010), 1.508; β and γ [in (010)], 1.691, 1.728}. In the uric acid dihydrate structure the molecules are tilted at about $\pm 30°$ to (020). In a mesomorphic layer structure having a spacing of 3.20 Å the molecules would tend to be parallel to the layers and the negative birefringence could be even larger than that of uric acid dihydrate.



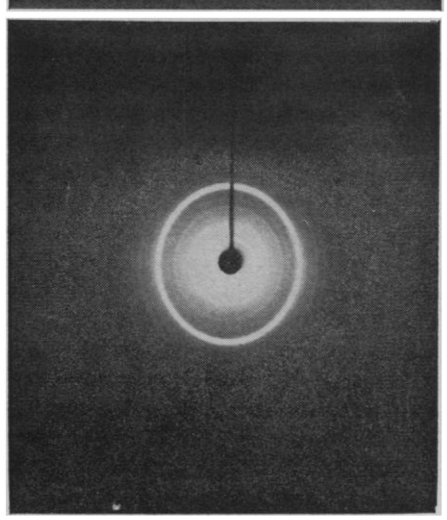


Fig. 1 (top). X-ray diffraction pattern of white excrement (camera radius, 3 cm; CuKα radiation; exposure time, 2 hours). Fig. 2 (bottom). X-ray diffraction pattern of uric acid dihydrate into which the white excrement is transformed after washing and drying (technical details are the same as for Fig. 1).

Folk found that eagle droppings, even in the dry state, are unstable and change from spheres to "large crystals." He did not say whether he made any attempt to identify these crystals by x-ray analysis; this is unfortunate, because this transition resembles a typical disorder-to-order transition and the final crystalline form could well reveal the nature of the original material, although not necessarily so, as "aging" will sometimes cause a chemical reaction in the solid state involving molecular rearrangement (*4*).

Droppings from other birds (for example, those from members of the parrot family) are, according to Folk, "rapidly soluble in water and immediately reprecipitate as crystals" (*1*, p. 1518). Here again, he does not appear to have identified these crystals, because he infers that the very fact of "solubility" proves that they cannot be uric acid, which is very insoluble at ordinary temperatures, both in water and in weak acids. We do not question Folk's interesting observations, some of which we have repeated, but we do question his interpretation of them. The fact that in some cases the tiny spheres disappear when water (or acid) is added and that crystals immediately precipitate does not prove that true solution has taken place. True solution would not result in any immediate precipitation; a solution of some soluble constituent of the spheres could take place which would result in a breaking up of the spheres, the insoluble part remaining momentarily in suspension in a finely divided form and then recrystallizing, possibly in another crystalline modification of the original material. In other words, a small part of the material of white bird excretion is truly soluble, and the remainder is insoluble but is easily transformed once the original spheres have been disintegrated. Our x-ray diffraction pattern (Fig. 2) shows conclusively that this transformed (crystalline) material is uric acid dihydrate, the main layer spacing of which is almost identical with the unique spacing of the original excrement. Not only the positions, but also the intensities, of first- and second-order lines agree very closely. Anhydrous uric acid is not found, nor is sodium urate. These have sufficiently different main layer spacings to be ruled out. If the true solution (solvent : water or acid) is evaporated to dryness, a very small white deposit is obtained, which gives an "amorphous" x-ray diffraction pattern, and which we have not identified.

We have extended Folk's experiments as follows: (i) Some of the white excrement was ashed. This gave a small quantity of white (mineral) powder, from which an excellent x-ray diffraction pattern could be obtained, with lines corresponding to spacings of 7.57 (weak), 6.26 (medium), 5.21 (medium-weak), 4.34 (weak), 4.04 (medium-weak), 3.143 (strong), 2.965 (medium-strong), 2.720 (medium-weak), 2.588 (medium-strong), 2.371 (medium), and 2.252 Å (medium). (ii) A white chunk of dry excrement giving only the 3.20-Å spacing, was placed in water, stirred thoroughly, removed, and dried. In a second experiment, the sample was thoroughly washed after removal and before drying. In both cases, the dried chunk was found to be covered with glistening crystals of uric acid dihydrate, easily identifiable by x-ray diffraction. (iii) A similar chunk boiled in excess water yielded an insoluble residue which was crystalline uric acid dihydrate. The boiled solution, evaporated to dryness (by heating), gave a very small white deposit which showed only one weak x-ray diffraction line. The solubility of uric acid increases with temperature, but is never large. (iv) A chunk placed in 1*N* HCl, then removed and dried, gave the x-ray diffraction pattern of uric acid dihydrate. The evaporated solution gave a very small quantity of material which was amorphous, the amorphous pattern being similar to that obtained by evaporation of a cold aqueous solution.

Folk (*2*, p. 99) claimed that "the spectacular microscopic display" seen when parrot excrement is mixed with vinegar proves that the nature of the bird droppings has been changed. The truth of this statement depends on the meaning given to the word "nature." All the x-ray and microscopic evidence, for wet and dry samples, is compatible with the following statement of the composition and behavior of the white, soft part of bird excrement: (i) The little uniaxial birefringent spheres (or clumps of spheres) observed by Folk consist of at least two constituents, the major part being uric acid dihydrate in a disordered, layer form, and the minor part being some soluble material which includes those salts giving the mineral ash. (ii) Wetting of a sphere, whether with water or weak acid, can break up the sphere (probably by penetration parallel to the aligned polar axes) and dissolve out the minor constituent(s). The disordered uric acid dihydrate "needles," no longer bound together in bundles, readily transform to normally ordered uric acid dihydrate crystals. Such a disorder-to-order transformation can be quite spectacular as seen under the microscope and would give exactly the change of x-ray diffraction pattern illustrated in Figs. 1 and 2. (iii) Aging alone could well produce the same change of order, both textural and structural. It is not surprising that this happens in some cases. In others, it could possibly be accelerated by mild heating. But such textural and structural changes are not a change of "nature"; the separation of soluble minor constituents from insoluble major constituents would involve a major textural change.

What is not changed is the substance of the major constituent. Disordered or ordered, in the plastic (liquid crystal or "pyrolytic") form or recrystallized as clear, glistening single crystals, it is still uric acid dihydrate, according to the most probable interpretation of all the x-ray evidence. We do not know why the disordered form crystallizes as spheres in the first place, but even well-ordered crystalline materials sometimes do the same (for example, $CaCO_3$ plus organic matter in pearls, H_2O in hailstones, and a variety of substances grown in gels).

Note added in proof: A quantitative analysis of the carbon, hydrogen, and nitrogen content of the white bird urine, before "treatment" of any kind, was carried out by placing the material in a furnace at 800°C; carbon was determined as CO_2, hydrogen as H_2O, and nitrogen as N. The results are shown below by comparison with values calculated for uric acid dihydrate and uric acid, respectively.

		C(%)	H(%)	N(%)
Uric acid dihydrate	Obs.	29.36	3.48	27.39
	Calc.	29.41	3.92	27.45
Uric acid	Calc.	35.7	2.37	33.3

There is no reason to suppose, therefore, that urates or purines other than uric acid dihydrate are present in more than trace quantities.

KATHLEEN LONSDALE*
D. JUNE SUTOR
University College, London, W.C.1, England

References and Notes

1. R. L. Folk, *Science* **166**, 1516 (1969).
2. ———, *ibid.* **170**, 98 (1970).
3. C. Herman, *Z. Kristallogr.* **79**, 186 (1932); *ibid.*, p. 337; A. Mabis, *Acta Crystallogr.* **15**, 1152 (1962).
4. J. Z. Gougoutas, J. C. Clardy, A. M. Glazer, L. Lessinger, S. Singh, *Acta Crystallogr. Sect. A* **25**, S232 (1969) (abstract only); J. Z. Gougoutas, *J. Pure Appl. Chem.*, in press.
5. The x-ray photographs were taken by Mrs. S. Wooley. All work done at University College, London, referred to here was supported by the Nuffield Foundation.
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Intelligence and Blood Pressure in the Aged

Abstract. *Diastolic hypertension was related to significant intellectual loss over a 10-year period among individuals initially examined in their 60's. Such loss was not found in their age peers in association with normal or mild elevations of blood pressure. Of the subjects initially examined at 70 to 79 years of age, none with hypertension completed the follow-up program, and those with normal and mildly elevated blood pressure showed some intellectual decline over the decade. At the initial examination, hypertension was related to lower intelligence test scores only among those subjects who subsequently did not complete the follow-up program. The results suggest that hypertension is related to intellectual changes among the aged.*

The incidence of hypertension increases with age and is frequently complicated by cardiovascular disease and strokes (*1, 2*). Among middle-aged adults and the aged, hypertension may also be related to psychomotor slowing (*3, 4*), lowered flicker fusion threshold (*5*), and organic brain impairment (*6*). Despite these findings, however, relatively little attention has been paid to the long-term behavioral effects associated with hypertensive disorder.

This report examines the relation between blood pressure (BP) and intelligence, as measured by the Wechsler