microscope slide holding the specimen. A felt pad attached to the bottom of the device will eliminate the possibility of scratching the condenser lens.

With the ¼-inch hole in position beneath the specimen, a deep black background is provided even when the specimen is strongly illuminated with flood lamps. Thus, in the case of predominantly "black" insects, sufficient contrast is provided between the reflective "black" of the insect and the nonreflective black of the background formed by the cavity.

As it was constructed, the device (Fig. 1) is 1¼ inch in diameter and has a depth of ¾ inch. However, the use of any properly blackened box with flat, removable lids having various hole sizes will serve a similar purpose when objects of greater dimensions are to be photographed.

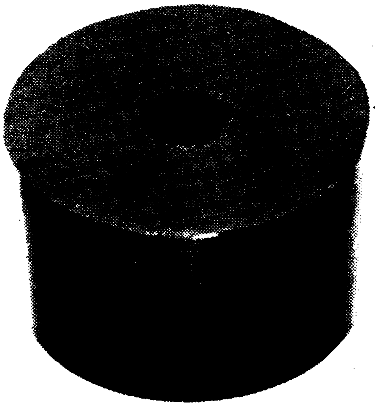

FIG. 1

Crystalline Dihydrate of Calcium Ascorbate

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Szent-Györgyi (*3*), in investigating vitamin C, mentioned that the solubility of the calcium salt excluded its identity with that of the acid studied by Bertrand and others.

Hirst, *et al.* (*1*) prepared the calcium salt by adding a slight excess of calcium carbonate to the aqueous solution of ascorbic acid. The solution was evaporated to dryness in a desiccator. The dry residue was then triturated with alcohol when a neutral salt was obtained which had a pale yellow color and gave an aqueous solution with a rotation of $[\alpha]^{19}_{D}$ + 91. Analysis showed a calcium content of 9.9 per cent, as compared with the theoretical 10.2 per cent, for $(C_6H_7O_6)_2$. No analysis of the carbon or hydrogen was stated, and apparently the substance was not crystalline.

Calcium ascorbate, prepared as a cream-colored dry powder, has been made in considerable quantites for medicinal preparations. However, because of its hygroscopic property, this soon took up moisture when exposed to a humid atmosphere and became gummy, decomposing to an orange-colored product. It was thus unsuitable for practical use.

One of the writers (S. L. R.) developed the stabilized solutions of calcium ascorbate which have since been widely used. Study was continued, however, to secure a stable, dry form of calcium ascorbate that could be employed for oral therapy. This has apparently been attained in the dihydrate of calcium ascorbate.

While investigating the production of a more stable form of calcium ascorbate we have succeeded in crystallizing this important salt from water. The crystals obtained are white, are much more stable than the uncrystallized salt, and have remained dry and white when exposed for several months to the humid atmosphere of the laboratory.

Due to the known tendency of ascorbic acid solutions to oxidize and undergo further decomposition, solutions of the calcium ascorbate were were not allowed to stand for long periods in water or alcohol, nor was the temperature of the solutions allowed to rise much above 30°. It was found necessary to dry the crystals with absolute alcohol and to remove the alcohol quickly to avoid oxidation of the crystals, with subsequent coloration.

METHOD

The first product to approach the crystalline salt in composition was obtained by precipitation in acetone. Sixty grams of ascorbic acid was dissolved in 140 cc. of hot water, the solution cooled to 30°, and 16.3 grams (a little less than ⅙ mole) of calcium carbonate added slowly with stirring. The solution was filtered with suction to remove a small residue and the excess of carbon dioxide. The aqueous solution was run in a thin stream by means of a pipette into 3,000 cc. of acetone with constant stirring. Some gum, in addition to a flocculent precipitate which at first was in suspension, formed on the bottom of the beaker. The gum was kneaded with the stirring rod and, on standing overnight, became brittle. This was broken up, the acetone decanted, and the precipitate washed with 300 cc. of fresh acetone. The material was filtered, ground in a mortar, rubbed up in about 200 cc. of ether to remove the excess of acetone, and filtered with suction to remove ether. When dry, it contained 9.3 per cent calcium.

One gram of the calcium ascorbate obtained by precipitation from acetone was rubbed up in 0.5 cc. of water. Crystals formed which, under the microscope, appeared as prisms.

Crystalline calcium ascorbate was next prepared from water, using as seed the first crystals obtained. One hundred and twenty grams of ascorbic acid was dissolved in 280 cc. of hot water, the solution cooled to about 25°, and 32.6 grams (a little less than ⅓ mole) of calcium carbonate added with stirring. The solution was filtered with suction, as before, to remove the small residue and excess carbon dioxide, and the filtrate was evaporated *in vacuo* to a thin syrup of about 170-cc. volume. On seeding and stirring, a crystalline mass was obtained which, after standing no longer than an hour, was filtered with suction, the crystals then being rubbed up with 200 cc. of absolute alcohol, refiltered, and washed with an additional 50 cc. of alcohol to remove excess moisture. Alcohol was removed by drawing air through the filter and then spreading the crystals on filter paper to dry. The yield was 71.9 grams, or 49.5 per cent of the theoretical. Higher yields were obtained when the solution was evaporated to a thicker syrup.

The crystals remained white and dry for months on exposure to the humid atmosphere of the laboratory.

The analysis of these crystals indicates a calcium ascorbate dihydrate.

	Found	Calculated for $(C_6H_7O_6)_2Ca2H_2O$
Calcium	9.42	9.40
Carbon	33.48	33.81
Hydrogen	4.24	4.25

Titration of 0.4000 gram of the calcium ascorbate in 100 cc. of N/1 acetic acid solution required 37.34 cc. of N/10 iodine, giving a value of 82.15 per cent ascorbic acid (theory for the dihydrate, 82.63 per cent).

From the above analysis one may conclude that the calcium ascorbate is a dihydrate, although drying of 0.6447 gram of the substance in vacuum at the temperature of boiling toluene for 6 hours resulted in a loss of only 0.65 per cent. At this temperature a slight decomposition occurred, with the substance turning a light yellow color, and no higher temperature was attempted in drying the calcium ascorbate. It is well known, however, that many calcium salts are combined with water, which is difficult to remove, and this crystalline calcium ascorbate is undoubtedly such a hydrate.

The specific rotation of the crystalline calcium ascorbate obtained in water was $[\alpha]^{20}_{D} + 95.6$ (C2.4). That obtained by Hirst for his product was $[\alpha]^{19}_{D} + 91$.

A study of the crystallographic and optical properties of the dihydrate of calcium ascorbate was conducted by Wilbur G. Valentine.

The material consisted of two lots: a dry sample, and a supersaturated liquor in which crystals were forming. The problem was to determine the type of crystals, assign them to the proper system, and determine the optical properties in so far as a petrographic inspection would allow.

General Results

The dry sample appears to be uniform in crystallization. The crystals, which have rather definite crystal boundaries, show no evidence of deterioration on the boundaries, even after standing for a month in contact with air. In general, they are somewhat elongated triclinic crystals, with the principal optical directions oblique to all edges between crystal faces and to the general elongation of the crystals. The faces appear to be in pairs on opposite sides of the crystals.

Crystals from the concentrated liquor were also observed. In general, those forming on the sides and bottom of the vessel were larger than those in the dry sample and did not have well-formed external faces. Optically, they behaved in the same manner as those from the dry sample and are assumed to have the same triclinic crystallization. A thin skin of crystals also formed on top of the liquid. A short examination of these crystals showed that they are quite different from the others. They are distinctly elongated, being 5 to 10 times as long as they are wide. The cross-section of the prismatic crystals appears to be square. If this is true, they are almost certainly tetragonal in crystallization. The terminations are usually simple pinacoids, but partly developed pyramids were noted in a few instances.

Optical Properties

Triclinic form. In most cases the greater index vibration direction was across the crystal, and the lesser more nearly parallel to the direction of elongation. In some instances, however, this situation is reversed. Hence, the elongation of the mineral is more nearly parallel to the vibration direction of the intermediate index, β. The greatest dimension perpendicular to the elongation is closest to the vibration direction of the greatest index, γ, and the shortest dimension is most nearly parallel to the vibration direction of least index, α. Because of this orientation, the determination of α in the liquid media of low viscosity used in the inspection is least certain, but the determination of γ should be fairly accurate. The best determination of α is that it lies between 1.530 and 1.535 and is nearer 1.530; γ is very close to 1.680; β was not measured directly, but should lie at about the midpoint between the two extremes. The birefringence, γ-α, is 0.150. That this is very high is borne out by the high colors shown by the small crystals observed.

Many crystals give very poor optical figures because of small size and poor orientation. All figures are definitely biaxial. In all cases where the determination seemed definite, they are biaxial negative. A few optic axis figures were seen, and the isogyre has only a slight flexure in the diagnonal position. Hence, the optical angle is nearly 90°. The isogyres and color bands are sharp, indicating very little dispersion.

Tetragonal form. The study of these crystals was not extensive enough to allow as much certainty of the results as in the case of the triclinic crystals. The vibration direction of greater index is parallel to the length of the prisms and seems to be slightly higher than 1.535. The lesser index is very close to 1.530. Hence, the birefringence falls between 0.005 and 0.010. The birefringent colors check with this determination, being low gray for most crystals. No satisfactory optical figures were seen, all being flash figures. This agrees with the interpretation that these are uniaxial crystals with the C axis in the plane of the field. From the index data, the mineral should be uniaxial negative.

Other Data

The material was studied under high power with a Bausch and Lomb petrographic microscope. The mineral grains were immersed in liquid media whose indices are within 0.001 of the stated amount. The crystals of the dry sample ranged from about 0.01 to 0.05 mm. in length, and from about 0.005 to 0.03 mm. in width. The triclinic crystals from the liquor were much larger, but the tetragonal crystals were about comparable in size to the triclinic crystals from the dry sample.

X-ray diffraction studies, which were carried out by Dr. Fankuchen, showed that the material is clearly crystalline. The diagram was taken with a 57.3-mm.-radius camera with nickel-filtered copper radiation (± 1.54 A.). The spacings of the first 16 lines, shown below, are in Angstrom units:

d/n	7.20	5.73	5.38	4.82	4.67	4.19	4.05	3.92
Intensity	vs	wm	w	m	w	s	m	wm
d/n	3.72	3.49	3.27	3.15	2.99	2.95	2.79	2.71
Intensity	ms	ms	ms	m	vw	w	s	w

s = strong, m = medium, v = very, w = weak.

References

1. Hirst, J. *et al.* *J. chem. Soc.*, 1933, 1279.
2. Ruskin, S. L. U. S. Pat. #2,400,171.
3. Szent-Györgyi, A. *Biochem. J.*, 1928, 22, 1387.