

minor product in 2 further runs (final pH=7.03 and 7.43, $E_h = -186$ and -193). In all cases djurleite was admixed with either covellite or chalcocite. In the 6 runs where djurleite was a major product, it was consistently indexable on the orthorhombic cell with $a=26.9$, $b=15.5$, $c=13.3$ Å.

The X-ray powder data obtained were similar to those shown in Table I for C201. No consistent evidence was found for any change in the nature of the product on drying. The Guinier films showed generally weaker and broader reflections than the 11 cm films, and reflections absent from the Guinier films were generally very weak on the 11 cm film. A very broad band about 4 Å on the Guinier films was caused by the tape in sample holder, and masked possible reflections in this region. Inconsistencies in relative intensities between the films are possibly caused by some degree of sample orientation in the Guinier camera.

The very strong 046 reflection* ($d=1.924$ Å) was not observed as a discrete line on any film. It is thought that the $d=1.935$ (C201) line, which is relatively broad on all films, includes both the 080 and 046 reflections. That this line was the strongest discrete djurleite line on all films, is consistent with this interpretation.

The chemical implications of the results will be discussed in detail in a further paper.⁴ However, the identification of djurleite, rather than chalcocite, as the primary product of the aqueous reaction between Cu_2O and Na_2S is consistent with observed data on natural minerals^{21b} which indicate that djurleite is rather more abundant than chalcocite, especially in the supergene enrichment zones of copper ore deposits. The reason for the formation of djurleite, in place of the apparently more reduced chalcocite is unknown. It seems to have a relatively stable structure with, possibly, little deviation from the $\text{Cu}_{1.67}\text{S}$ formula. The admixture of covellite or chalcocite with the synthetic material may indicate that Cu^{2+} or Cu^+ ions, present in excess of that required for the $\text{Cu}_{1.67}\text{S}$ formula, are rigorously excluded from the structure, and form the end-member phases.

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The Molecular and Crystal Structure of Dehydroascorbic Acid

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The molecular structure of the biologically important dehydroascorbic acid with the empirical formula $\text{C}_6\text{H}_6\text{O}_4$ has been disputed for some time. Several structural formulae have been proposed, including monomers, dimers¹⁻³ and polymers.⁴

We have studied crystals grown from dimethyl sulfoxide and from a mixture of 5% 0.2 N hydrochloric acid in glacial acetic acid as recommended by Staudinger and Weis.⁵

The soft crystals grown from dimethyl sulfoxide give an X-ray pattern typical of a polymer.

The commercially available dehydroascorbic acid is, however, crystalline, and gives very small, but well developed crystals when recrystallized from the mixture mentioned above.

We wish to give a preliminary report on the structural analysis of crystalline dehydroascorbic acid. It crystallizes in the monoclinic system with the space group

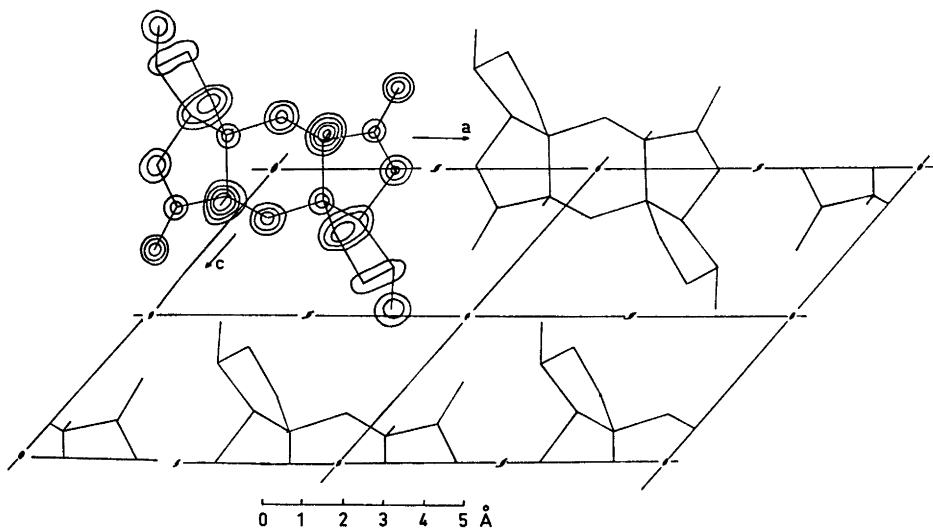


Fig. 1. View of the structure of dehydroascorbic acid as seen along the monoclinic b axis. Contours are at arbitrary intervals.

C_2 , and there are four empirical formula units in the unit cell. The cell dimensions are: $a = 15.69$, $b = 5.55$, $c = 9.47$ Å, $\beta = 130.2^\circ$.

Using the $(h0l)$ X-ray data, the structure was solved by direct methods. The molecular arrangement emerging from the subsequent refinements is shown in Fig. 1, which represents the contents of the unit cell as seen along the b axis.

Our findings confirm that crystalline dehydroascorbic acid is in a dimeric form, and should thus be assigned the empirical formula $C_{12}H_{12}O_{12}$.

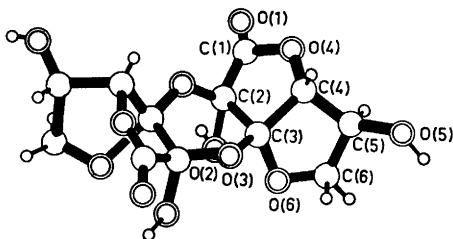


Fig. 2. Perspective drawing of the dehydroascorbic acid molecule. The atoms are numbered in accordance with the convention for ascorbic acid.

The molecule has a two-fold axis, and consists of one six-membered and four five-membered rings fused together as shown in Fig. 2. The six-membered ring is a dioxan ring in the skew boat configuration. The five-membered rings adjacent to the dioxan ring are non-planar γ -lactone rings, while the residual rings are semiketal rings, probably with the characteristic envelope configuration.

The numbering of the atoms in one-half of the molecule corresponds to that in ascorbic acid itself.⁶

Further details of the structure will be given when the full account of the three-dimensional X-ray analysis is published shortly.

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