

was identified by column chromatography according to a modified Swim and Krampitz procedure,<sup>12</sup> by paper chromatography of the ammonium salt<sup>13</sup> ( $R_F = 0.30, 0.35, 0.40,$  and  $0.35$  for the ammonium salts of formic, acetic, propionic acids and acid from fucoxanthin, respectively) and by paper chromatography of the hydroxamic derivative ( $R_F = 0.60, 0.41, 0.60,$  and  $0.75$  for the unknown, formic, acetic and propionic acid derivatives, respectively).

Fucoxanthin thus contains an acetoxy group, and the analytical data of the fucoxanthols previously reported by us<sup>9</sup> showed too high oxygen contents and led us to the erroneous conclusion that fucoxanthin could not be an ester. The fact that fucoxanthin is an acetate explains why Karrer *et al.*<sup>3</sup> obtained seven moles of acetic acid upon chromic acid oxidation of one mole fucoxanthin, as against six moles of acetic acid per mole of lutein and  $\beta$ -carotene.

The present evidence indicates that the oxygen functions of fucoxanthin are: one secondary (or primary) hydroxyl group, one conjugated keto function, one acetoxy group and two tertiary hydroxyl functions. The presence of the last mentioned is inferred from the partition data of fucoxanthol b acetate, and is compatible with the infra-red spectra of fucoxanthin and its derivatives.<sup>8</sup>

A detailed report of this work will be given elsewhere. Further studies on the structure of fucoxanthin are in progress.

- Willstätter, R. and Page, H. J. *Ann.* **404** (1914) 237.
- Karrer, P. *Z. angew. Chem.* **42** (1929) 918.
- Karrer, P., Helfenstein, A., Wehrli, H., Pieper, B. and Morf, R. *Helv. Chim. Acta* **14** (1931) 614.
- Heilbron, I. M. and Phipers, R. F. *Biochem. J.* **29** (1935) 1369.
- Torto, E. G. and Weedon, B. C. L. *Chem. Ind. (London)* **1955** 1219.
- Retrovsky, R. *Collection Czech. Chem. Commun.* **13** (1948) 631.
- Liaaen, S. and Sørensen, N. A. in Braarud, T. and Sørensen, N. A. *2nd Intern. Seaweed Symposium*, Pergamon Press, London 1956, p. 25.
- Jensen, A. *Acta Chem. Scand.* **15** (1961) 1604.
- Jensen, A. *Acta Chem. Scand.* **15** (1961) 1605.

- Varian NMR Spectra Catalog*, Varian Associates, Palo Alto 1960.
- Roth, H. *Pregl-Roth Qualitative Organische Mikroanalyse*. Springer Verlag, Wien 1958, p. 239.
- Swim, H. E. and Krampitz, L. O. *J. Bacteriol.* **67** (1954) 419.
- Kennedy, E. P. and Barker, H. A. *Anal. Chem.* **23** (1951) 1033.

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## The Crystal Structure of L-Ascorbic Acid, "Vitamin C"

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The crystal structure of vitamin C as proposed by Cox and Goodwin<sup>1</sup> in 1936 has been considered to be insufficiently accurate by modern standards. A revision seemed therefore appropriate, also in view of the biological importance of the substance. The author's main interest lies in the field of hydrogen bonding as studied by neutron diffraction methods, and it was felt that vitamin C might reveal some interesting features also in this respect.

In addition to X-ray data, neutron data were collected with the intention to study the positions of the hydrogen atoms. To permit a detailed investigation of the hydrogen atoms attached to oxygen atoms, and to avoid overlap in projections of these hydrogens with other atoms, two sets of neutron data were collected. The first set was recorded from a single crystal of the usual L-ascorbic acid. The second set was recorded from a crystal where the hydrogen atoms attached to oxygen were exchanged by deuterium atoms. The scattering amplitudes for these isotopes of hydrogen have different values and even different signs. A Fourier synthesis based upon the difference between the structure factors of these compounds is thus expected to give only the scattering density from the hydroxyl hydrogen atoms.

The space group is  $P2_1$ , as found by Cox and Goodwin. The unit cell dimensions

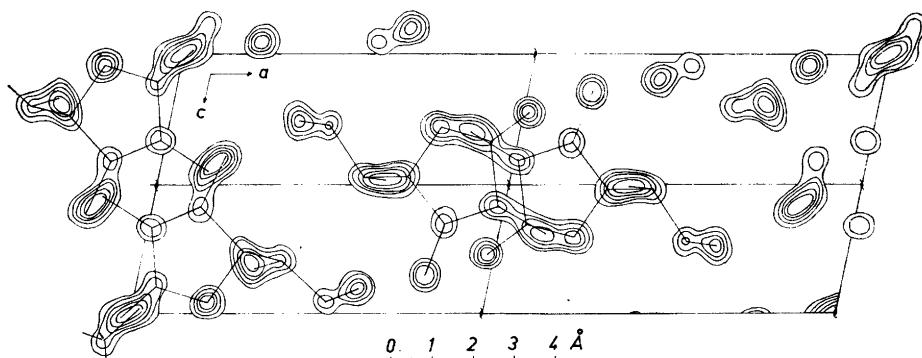
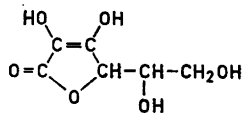


Fig. 1. This Fourier map shows the contents of the unit cell of L-ascorbic acid as seen along the monoclinic  $b$ -axis. Contours are at arbitrary intervals.

found by the present author are:  $a = 17.20$  Å;  $b = 6.37$  Å;  $c = 6.40$  Å and  $\beta = 102^{\circ}05'$ . There are four molecules in the unit cell, but as pointed out by Cox and Goodwin, these are related to each other in pairs by pseudo symmetry operations. In the  $b$ -axis projection, one molecule of the asymmetric unit is nearly transferred into the position of the second molecule by translation of  $1/2$  along the  $a$  axis and  $1/4$  along the  $c$  axis.

Using the ( $h0l$ ) X-ray data, a study of the Patterson projection along the  $b$  axis enabled the author to discard the molecular arrangement proposed by Cox and Goodwin. After many vain attempts, the structure was established by the use of a combination of sharpened Patterson functions and direct methods. The signs of the structure factors could not be determined by inequality relations, but the use of statistical methods gave a number of possible sign combinations for the strongest reflections. The corresponding Fourier maps were now calculated, and in one of these maps the weak contour of the five-membered rings could be seen. Of the sign set, comprising 52 reflections, 6 signs turned out to be wrong; after correcting these, the  $R$  index dropped from 52% to 17% in the course of 8 Fourier refinements. Fig. 1 shows the Fourier map at this stage. A subsequent least squares refinement gave a final  $R$  value of 9.4%. The hydrogen atoms were not included.

From the Fourier map it could be inferred that L-ascorbic acid is built up according to the generally accepted structure formula:



The five-membered ring seems to be nearly planar, and assuming the plane of the ring to be normal to the  $b$  axis, the distances in this ring and in the side chain are normal for this type of compound. More precise information on the distances and angles in the ascorbic acid molecule will be deduced from three-dimensional X-ray data. Such work is now in progress. However, the arrangement of the hydrogen bond system has already been partly established by means of the neutron data.

A full account of the three-dimensional analysis, including the neutron diffraction study will appear later.

1. Cox, E. G. and Goodwin, T. H. *J. Chem. Soc.* 1936 769.

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