bacterial cells had been destroyed with 30 percent hydrogen peroxide.

The bacterial cells range in diameter from a little less than 0.4 to nearly 0.7 μ , the larger ones being jet black and the smallest ones dark brown. In addition to these there are a very few short rods and a few larger cells (about 1 μ in diameter) that are clear and highly refringent. These larger cells suggest bacterial spores.

The evident similarity between the Lower Cretaceous Newark Canyon lake beds, especially the black limestone, which consists of minute calcite crystals and black bacterial cells, and the black mud from Green Lake, which consists of calcite crystals, black bacterial cells, and diatom valves, suggests that the Newark Canyon black limestone was originally a black mud nearly identical with that now forming in Green Lake. Because the Green Lake mud is so unusual it seems reasonably safe to infer that the Newark Canyon black mud also accumulated in a relatively deep, meromictic, fresh-water lake, which supported a luxuriant growth of photosynthetic sulfur bacteria at or near the base of its epilimnion. This inference, of course, carries with it the assumption that the black bacteria in each sediment are predominantly the remains of pigmented sulfur bacteria. This is an assumption that has not been tested for Green Lake and cannot be tested for the Lower Cretaceous lake unless, perhaps, infrared spectra of the bacteria from each locality should show similar and highly distinctive characteristics.

One further speculation seems warranted. The fact that many of the calcite crystals in the Green Lake mud contain enormous numbers of black bacterial cells must mean that those crystals grew in the mud and occluded the bacteria as they grew (Fig. 3). Indeed, not only are the bacteria distributed all through these crystals but in some they are concentrated in closely spaced planes parallel to the crystal faces. Occlusion of such motes of organic matter in a crystal appears to be a nearly perfect mechanism for preserving them intact. Might it not be that the Newark Canyon bacteria, and the scraps of organic matter to which they clung, were similarly occluded in calcite crystals that grew in the mud of the Lower Cretaceous lake? That they are not now within the calcite crystals but are concentrated in films between the crystals (Fig. 4) is

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not an argument against this suggestion because the calcite crystals were all recrystallized during diagenesis, and it is well known that crystals rid themselves of inclusions during such a regeneration.

The unmineralized bacteria of the Newark Canyon Formation are more than 100 million years old, whereas the bacteria in the calcite crystals in the Green Lake mud may have become fossilized last year, or within the past decade. The processes by which the Green Lake bacteria are entombed still go on, though we do not yet know exactly how they operate. The important point is we can observe and measure these present-day

processes. Geologists are continually on the alert for present-day analogs because they help us understand and explain what we find in the geologic record (7).

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- 3 July 1963

Sucrose: Precise Determination of Crystal and Molecular Structure by Neutron Diffraction

Abstract. This analysis provides the first precise molecular parameters for sucrose. All hydrogen atoms are included. Carbon-carbon distances are 1.51 to 1.53 Å; carbon-oxygen 1.40 to 1.44 Å; carbon-hydrogen 1.08 to 1.11 Å; oxygen-hydrogen 0.94 to 0.99 Å. The furanose ring conformation differs from that in sucrose sodium bromide dihydrate. Hydrogen bonds (two of them intramolecular) utilize every hydroxyl group except one.

The structure of the molecule of sucrose (C12H22O11) has not previously been determined with the precision that modern diffraction techniques afford. An x-ray determination by Beevers and Cochran (1) in 1947 of the structure of sucrose sodium bromide dihydrate (SSBD) confirmed the chemically assigned relative configurations (2) of the asymmetric carbon atoms of the molecule. A subsequent x-ray determination of the structure of sucrose itself (3) was somewhat less satisfactory, since refinement was terminated at an early stage because the data were felt to be of poor quality; the agreement between calculated and observed structure factors was just close enough to suggest that the phase problem had been essentially solved, without, however, furnishing conclusive proof of the structure proposed (4).

This report concerns a precise threedimensional neutron-diffraction analysis of the structure of crystalline sucrose, for which the starting point was the rough structure of Beevers et al. (3). The neutron technique was chosen because it, unlike the x-ray technique, allows determination of coordinates of hydrogen atoms with nearly the same precision that can be attained for the

coordinates of the heavier atoms (5). Determination of this structure is by far the largest problem ever undertaken in neutron-diffraction analysis, both with respect to the number of structural parameters determined and with respect to the number of data obtained. The results demonstrate clearly the power of the neutron-diffraction method in structural studies of complex crystals.

Three different crystal specimens, weighing approximately 80, 10, and 5 mg, were employed. For the intense reflections, data from the smaller crystals only were used, in order to minimize extinction errors. About 5800 individual intensity measurements were made to provide averaged data for some 2800 independent reflections accessible to measurement on the Oak Ridge automatic neutron diffractometer (6). Before averaging, the intensity data were corrected for absorption effects and the Lorentz effect, then placed on an absolute scale by comparison with data from a standard crystal of NaCl.

From the coordinates of the 12 carbon and 11 oxygen atoms in the asymmetric unit of the structure of Beevers et al. we calculated reasonable coordinates for the 14 hydrogen atoms at-

tached to carbon atoms (7). Refinement by the method of least squares (8) was started at once, though the remaining eight hydrogen atoms of the asymmetric unit had not been placed. From three-dimensional Fourier maps, one of which was computed (9) after each cycle of least-squares refinement, all of the eight remaining hydrogen atoms were eventually found; and rather gross misplacements of atoms C'_{6} and O'_{6} were corrected (see Figs. 1 and 2 for the key to the numbering of carbon atoms). All other shifts were effected by the least-squares calculations. The last one of ten cycles of least-squares refinement included adjustment of individual anisotropic thermal parameters. The value of the reliability index R, defined by the equation

$$R = \Sigma \mid F^{2}_{\text{obs.}} - F^{2}_{\text{calc.}} \mid /\Sigma \quad F^{2}_{\text{obs.}},$$

where F is the structure factor, is now 0.083.

Standard errors in the coordinates (10) are about 0.002 Å for the carbon atoms and the oxygen atoms of the ether linkages 0.002 to 0.004 Å for the oxygen atoms of the hydroxyl groups, 0.004 to 0.007 Å for hydrogen atoms attached to carbon, and 0.005 to 0.010 Å for hydrogen atoms of hydroxyl groups. Coordinates of the carbon and oxygen atoms, especially the y coordinates, are considerably different from those of the starting structure, corresponding to an average radial shift of position for the oxygen and carbon atoms of 0.28 Å; minimum, 0.06 Å; maximum, 0.91 Å (11).

Packing of the sucrose molecules is largely determined by hydrogen bonds O-H...O, of which there are seven per asymmetric unit, including two intra-molecular bonds (Fig. 1). Although the O₄ hydroxyl group does not participate in hydrogen bonding, its hydrogen atom is loosely fixed in position through two fairly close contacts with oxygen atoms in other molecules (see single dashed lines of Fig. 1). The observed cleavage parallel to (100) is neatly explained by the pattern of hydrogen bonds, since only one of the 7 bonds extends across the plane $\frac{1}{2}$, y, z (see also 3).

General features of the structure of the sucrose molecule can be seen from the two views of Figs. 1 and 2. The conformation of the molecule about the bonds of the glycosidic linkage, $C_1-O_1-C'_{2}$, is surprisingly similar to



Fig. 1. The sucrose structure viewed in projection along the b axis, showing hydrogen bonding. The smallest circles represent hydrogen atoms. The molecule is shown in correct absolute configuration (14).



Fig. 2. The reference molecule (asymmetric unit) in the sucrose crystal structure viewed in projection along the *a* axis. The insert shows a clearer view of a portion of the molecule, projected along a line in the plane of **a** and **b**, 30° from **a**. Numbers attached are bond lengths (Å).

that in SSBD (1), even though the hydrogen bonding is completely different—in the latter structure there are no intramolecular hydrogen bonds. The only significant difference, about 10°, is in the conformation about the C_1-O_1 bond. Conformations about the bonds C_5-C_6 and $C'_5-C'_6$ are also very nearly the same in sucrose and in SSBD. However, the conformation about the bond $C'_2-C'_1$ differs by 135° between the two structures.

There is a significant difference in the conformation of the furanose ring between sucrose and SSBD. In the SSBD crystal, atoms C'2, C'3, C'5, and O'2 are very nearly coplanar, and atom C'₄ is about 0.5 Å from their average plane. The furanose ring in the sucrose crystal cannot be described so simply. We prefer to describe it by specifying an angle of twist about each ring bond. Consider four successive atoms around the ring, as C'_5 , C'_4 , C'_3 , C'_2 . We define the conformation angle of the directed bond $C'_{4} \rightarrow C'_{3}$ as the angle, measured counterclockwise, that the projection of bond $C'_4 \rightarrow C'_5$ makes relative to the projection of bond $C'_{3} \rightarrow C'_{2}$ when one looks in the direction of the bond $C'_{4}\rightarrow C'_{3}$. In the furanose ring of sucrose the conformation angles for the various bonds are: $C'_{4} \rightarrow C'_{3}$, 34.9°; $C'_{5} \rightarrow C'_{4}$, -27.4°; $O'_2 \rightarrow C'_5$, 8.3°; $C'_2 \rightarrow O'_2$, 14.5°; $C'_3 \rightarrow C'_2$, -31.0° . Corresponding values for SSBD are 36.5°, -34.5°, 22.9°, -1.5°, and -21.1° .

The pyranose ring, as in SSBD, is in the chair form, with $-CH_2OH$ and -OH groups in requatorial positions and O₁ and 5 hydrogen atoms in axial positions. The six conformation angles of the ring, alternating in sign, fall within the range of magnitude 54.5° to 55.5°. The range is wider, 51.3° to 64.0°, in SSBD, probably reflecting the larger coordinate errors.

Lengths (12) of C-C bonds (Fig. 2) show remarkably small deviations from the mean of 1.524 Å, regardless of environment. The short C-C bonds, averaging 1.44 Å, reported by Beevers and Cochran, in the furanose ring in SSBD can hardly be correct. Variations of length among the C-O bonds are slightly greater. In each ring, the C-Obond adjacent to the glycosidic linkage appears significantly shorter than the other C-O bond of the ring. The C-H bond lengths range from 1.08 to 1.11 Å; the average, 1.10 Å, is the normal value expected for saturated molecules.

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The O-H bond lengths show the largest range of values, probably because of perturbing effects of hydrogen bonding and because of widely varying effects of thermal motion on apparent bond lengths. For the O₄ hydroxyl group, thermal motion has an especially large effect, since this group is not clamped in orientation by hydrogen bonding, and torsional motion about the C₄-O₄ bond is relatively free.

The apparent bond length of 0.89 Å was approximately corrected (13) for the thermal motion to 0.94 Å, on the assumption that the H atom "rides" the oxygen atom. We have not yet analyzed the thermal motion in enough detail to make corrections for other bonds.

The oxygen valence angles in the ether linkages are: $C_1-O_1-C'_2$ (glycosidic linkage), 114.6°; $C_1-O_5-C_5$, 116.0°; $C'_2-O'_2-C'_5$, 111.5°. Carbon valence angles inside the pyranose ring range from 108.2° to 111.2°; inside the furanose ring, from 102.2° to 105.8°. Other carbon valence angles range from 105.0° to 116.0°. Oxygen valence angles in the hydroxyl groups range from 104.6° to 111.6°.

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 A table of coordinates will appear in the com-
- 10. A table of coordinates will appear in the complete account of this work to be published later. It will be furnished earlier to anyone interested.
- 11. In least-squares refinement for space group $P2_1$, the y coordinate of one atom must be held constant to fix the origin of the coordinate system. We have fixed the y coordinate of atom C_1 at the value reported by Beevers *et al.* (3). The coordinate shifts given must be considered with this constraint in mind.
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Interpretation of the 3- to 4-Micron Infrared Spectrum of Mars

Abstract. Infrared reflection spectra have been recorded for a large number of inorganic and organic samples, including minerals and biological specimens, for the purpose of interpreting the 3- to $4-\mu$ spectrum of Mars. A previous suggestion that the Martian bands indicated the presence of carbohydrates is shown not to be a required conclusion. However, no satisfactory explanation is advanced and the problem remains unresolved.

The nature of the Martian surface and the possibility of life existing there has for decades stimulated considerable speculation and research. A notable contribution to the rather meager quantitative data on the planet was made recently by Sinton (1, 2) when he observed "absorption bands" in the 3- to 4-micron radiation reflected by the dark areas which were less pronounced in the radiation from the light areas. The spectral curves he obtained with the 200-inch (508 cm) telescope at Mt. Palomar Observatory are shown in Fig. 1. Because of the low available energy, the resolution on the disc was poor, being at best half a planetary diameter, and the accepted area for the nominal Syrtis Major spectrum, in fact, included large expanses of bright areas. The associated spectral resolution calculated from the slit width and dispersion was 90 cm⁻¹ (0.11 μ) for some of the recordings and 45 cm⁻¹ (0.056 μ) for the remainder.

The significant observation was of a

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