

heavy overlap of chromium and this oxygen atom in the 100 projection.

The structure is built up of discrete molecules where the chromium atom is surrounded by a somewhat distorted pentagonal pyramid with the oxygen O_5 at the apex. This is the same configuration as described by Stomberg.

Calculation shows that $Cr-O_1-O_3$ are situated in a plane approximately perpendicular to the b -axis, and O_5 is only 0.14 Å out of this plane. Further, the $Cr-N$ bond is almost perpendicular to the plane, and O_2 and O_4 are situated on the opposite side of the plane, 1.16 Å and 1.07 Å away from it.

Calculated interatomic distances and angles are given in Table 2.

The interatomic distances found, seem reasonable and indicate that the molecule is built up of two peroxide groups and one oxide oxygen.

- 1 Stomberg, R. *Nature* **196** (1962) 570.
- 2 Wiede, O. F. *Ber.* **30** (1897) 2178.
- 3 Schwartz, R. and Giese, H. *Ber.* **65** (1932) 871.

Received February 6, 1963.

X-Ray Crystal Data on Some p -Bromophenylhydrazones and p -Bromophenylosazones

KARIN BJÄMER, SVERRE DAHM,
SVEN FURBERG and CHERRY
SCHJANDER PETERSEN

*Institute of Chemistry, University of Oslo,
Blindern-Oslo, Norway*

The hydrazones and osazones are of considerable importance in carbohydrate chemistry, but in spite of this the structure of most of these substances are still incompletely known. As for the hydrazones, both ring and open-chain forms of the sugar have been shown to exist¹. The solid state structure of individual hydrazones is, however, known only in a few cases. For the osazones the evidence is in favour of an open-chain structure stabilized by different types of chelate bonds²⁻⁴, but a direct determination of the structure in the solid state would appear desirable. We have therefore started an investigation of a number of hydrazones and osazones, using

the methods of X-ray crystallography. In order to facilitate the structure determinations the p -bromoderivatives of the compounds were used.

The hydrazones were prepared by mixing equivalent amounts of sugar and p -bromophenylhydrazine in dilute alcohol at room temperature. In order to obtain the osazones, an aqueous solution of the sugar and NaAc was treated with p -bromophenylhydrazine hydrochloride at 80°–100°⁵.

Unit cell dimensions and space groups were derived from X-ray oscillation and Weissenberg diagrams, using copper radiation ($\lambda = 1.542$ Å). The measurements are believed to be accurate to within about 1%. The densities were measured in carbon tetrachloride-bromofrom mixtures, but only approximate values were obtained for the osazones due to the poor quality of the crystals and their solubility in the liquid.

Hydrazones

Ribose-p-Br-phenylhydrazone. Orthorhombic, flat needles, elongated along the c axis, with unit cell dimensions $a = 9.46$ Å, $b = 23.71$ Å, and $c = 5.78$ Å. Space group $P2_12_12_1$. Density 1.63 g/cm³, corresponding to four (calc. 3.98) molecules in the unit cell.

An electron density projection has been calculated (Fig. 1), showing that the ribose probably occurs in its openchain form in this compound. Further work on the structure is in progress.

Arabinose-p-Br-phenylhydrazone. Unit cell dimensions $a = 7.12$ Å, $b = 6.15$ Å, $c = 14.09$ Å, and $\beta = 96^\circ$. Space group $P2_1$.

The crystal structure of this compound has been determined and a full account of the work published⁶. The arabinose occurs in the pyranose chair form, with conformation 1e2e3e4a.

Mannose-p-Br-phenylhydrazone. Small, well-developed triclinic crystals, elongated along a , with (001) as the dominating face. Unit cell dimensions $a = 4.73$ Å, $b = 5.67$ Å, $c = 19.02$ Å, $\alpha = 135^\circ$, $\beta = 106^\circ$ and $\gamma = 73^\circ$. Density 1.70 g/cm³, corresponding to one (calc. 1.00) molecule in the unit cell. Space group $P1$.

The a and b axes are both relatively short. This may indicate that the sugar has an extended, open-chain conformation. A study of models shows that the likely length of such a molecule is in the order of 19 Å, in agreement with the observed length of the c axis.

Glucose-p-Br-phenylhydrazone. Big prisms were obtained, with m.p. 165°C and density 1.67 g/cm³. They are orthorhombic, with $a = 6.82$ Å, $b = 32.52$ Å and $c = 6.19$ Å. Space group $P2_12_12_1$. Four (calc. 3.97) molecules in the unit cell.

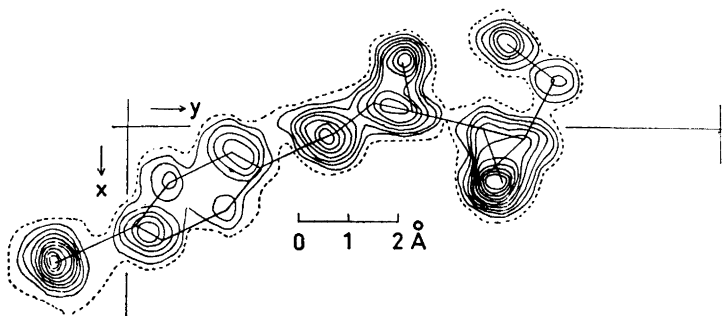


Fig. 1. Electron density projection in direction of c axis of ribose- p -Br-phenylhydrazone. Contours at arbitrary intervals.

A complete structure determination of this compound is in progress.

Osazones

Xylose- p -Br-phenylosazone. Recrystallization from aqueous alcohol yielded flat yellow needles, melting in the range 190° – 210° C and having a density of about 1.75 g/cm 3 . The crystals are monoclinic, with b as the needle axis and (001) as the dominating face. The unit cell dimensions are $a = 15.91$ Å, $b = 5.65$ Å, $c = 20.84$ Å and $\beta = 96^{\circ}$. There are four molecules in the unit cell (calculated density 1.74 g/cm 3). The space group appears to be $P2_1$, with two molecules in the asymmetric unit. The $h0l$ reflections are very weak for odd values of h and in the b projection the structure

may be approximately described by a pseudo-cell containing two molecules. On this basis the electron density projection shown in Fig. 2 has been determined. The sugar appears to have an open-chain structure and the relative position of the two phenylhydrazine residues corresponds in this projection to a chelate bond between nitrogen atoms.

Further work on the structure is in progress.

Ribose- p -Br-phenylosazone. The compound was prepared as described by Levene and Jacobs 7 . Yellow needles elongated along b were obtained, with m.p. 180° C (approx.) and a density of about 1.70 g/cm 3 . The unit cell dimensions are $a = 16.52$ Å, $b = 5.30$ Å, $c = 21.08$ Å and $\beta = 101^{\circ}$. Four (calc. 3.82) molecules in the unit cell. The discrepancy is

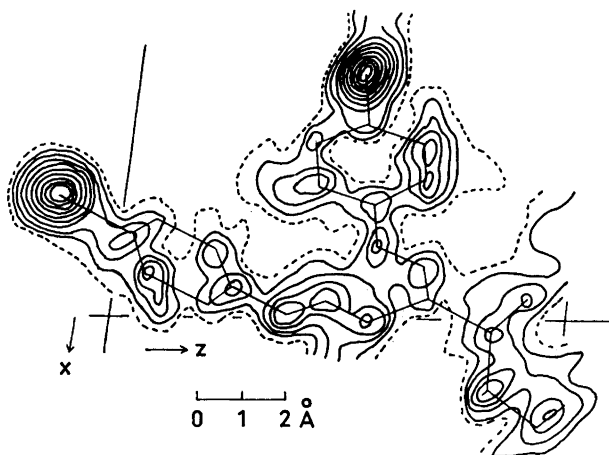


Fig. 2. Electron density projection in direction of b axis of xylose- p -Br-phenylosazone. Contours at arbitrary intervals.

probably due to inaccuracy in the density determination. Reflections $h0l$ are absent for h odd and there appear to be glide planes a in the crystal. The osazone was, however, prepared from D-ribose and must be optically active. The true space group is probably $P2_1$ with the two molecules in the asymmetric unit, as found for the xylose derivative. There must, in fact, be a very close resemblance between the crystal structures of these two compounds, as is evident both from the cell dimensions and from the striking similarity in the intensity distribution of the $h0l$ diagrams.

The same crystals were obtained from D-arabinose.

Glucose-p-Br-phenylosazone. Long flat needles were obtained from the reaction mixture, elongated along c , with (010) predominant. Weissenberg diagrams about c were taken. The reflections had the shape of narrow sharp lines 5–10 mm long. The crystals are orthorhombic, with $a = 17.33 \text{ \AA}$, $b = 42.3 \text{ \AA}$ and $c = 5.43 \text{ \AA}$. There are eight molecules in the unit cell, corresponding to a calculated density of 1.72 g/cm^3 . Reflections $hk0$ are present only for $h = 2n$, $0k0$ for $k = 2n$ and $h00$ for $h = 4n$, whereas there are no systematic absences in the hkl reflections. It is hoped that the determination of the structure of the xylose derivative may throw some light on the crystallographic implications of these peculiar extinction rules.

Discussion. Several crystallographic features are common to the three osazones described above. The crystals are needle-shaped and the corresponding axis is short, lying in the range $5.3 - 5.7 \text{ \AA}$. They all have a long axis of $20 - 21 \text{ \AA}$ (42 \AA for the glucose osazone) and a somewhat shorter one of $16 - 17 \text{ \AA}$, the latter being halved in the pseudo-cell present. It seems reasonable to assume that the general shape of the molecules, as well as their arrangement in the crystals, are approximately the same for all three osazones, corresponding to that given in Fig. 2 for the xylose derivative.

1. Mester, L. and Major, A. *J. Am. Chem. Soc.* **77** (1955) 4297.
2. Fieser, L. F. and Fieser, M. *Organic Chemistry* (2nd. Ed.) Reinhold Publishing Corp., New York 1950.
3. Mester, L. *Advan. Carbohydrate Chem.* **13** (1958) 105.
4. Henseke, G. and Köhler, H. *Ann.* **614** (1958) 105.
5. Vogel, A. I. *Elementary Pract. Org. Chemistry*, Longmans Green and Co., Ltd. 1957.

6. Furberg, S. and Petersen, C. S. *Acta Chem. Scand.* **16** (1962) 1539.

7. Levene, P. A. and Jacobs, W. A. *Ber.* **42** (1909) 3247.

Received February 7, 1963.

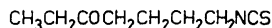
Gluconorcappasalin, a Thioglucoside Producing 5-Oxoheptyl Isothiocyanate on Enzymic Hydrolysis*

ANDERS KJÆR and HELENE THOMSEN

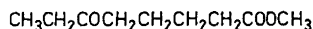
Department of Organic Chemistry, Royal Veterinary and Agricultural College, Copenhagen, Denmark

Seeds of the South-American tree *Capparis salicifolia* Griseb. (family Capparidaceae) contain two thioglucosides; the structure of glucocappasalin, the predominant of these, was recently established in this laboratory¹. We now present evidence that the minor thioglucoside constitutes a lower homologue, for which we accordingly suggest the name *gluconorcappasalin*.

A purified mixture of the two thioglucosides** was subjected to enzymic hydrolysis in the usual way. The resulting isothiocyanates were cleanly separated by vapour phase chromatography (silicone rubber, programme: $11^\circ/\text{min.}$, column: $125^\circ \rightarrow 250^\circ$, He 38 ml/min.). The two constituents gave almost identical infra-red spectra with strong C=O-bands at 1720 cm^{-1} . The corresponding thiourea-derivatives, prepared



I



II

* Part XLVIII of a series of papers on naturally derived isothiocyanates; (part XLVII: *Acta Chem. Scand.* **17** (1963) 279).

** The authors are much indebted to Dr. U. Weiss, N.I.H., Bethesda, Md. for drawing our attention to this plant, and to Professor V. Deulofeu, University of Buenos Aires, and Dr. N. Fock, The Ethnographic Division of The Danish National Museum, for their help in providing seed material for the present study.