probably due to inaccuracy in the density determination. Reflections *h*0*l* 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 *h*0*l* 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 $a = 17.33$ Å, $b = 42.3$ Å and $c = 5.43$ Å. There are eight molecules in the unit cell, corresponding to a calculated density of 1.72 g/cm³. Reflections *hk*0 are present only for $h = 2n$, 0*k*0 for $k = 2n$ and *h*00 for $h = 4n$, whereas there are no systematic absences in the *hk*1 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 Å. They all have a long axis of 20 – 21 Å (42 Å for the glucose osazone) and a somewhat shorter one of 16 – 17 Å, 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 laboratory [1]. 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°/min., column: 125°→250°, 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

$$CH_3CH_2COCH_2CH_2CH_2CH_2NCS$$

I

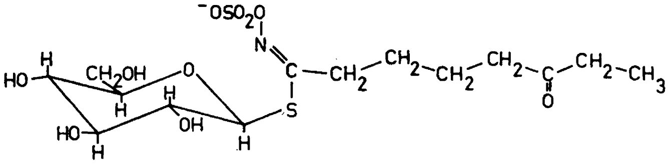
$$CH_3CH_2COCH_2CH_2CH_2CH_2COOCH_3$$

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.



III

by treatment of the isothiocyanates with ammonia, gave identical UV-spectra ($\lambda_{\max}^{\mathrm{EtOH}}$ 242 mμ, 207 mμ), but could easily be separated by paper chromatography in water-saturated chloroform or carbon tetrachloride: 30 % acetic acid (1:1). The mass spectrum of the new isothiocyanate, purified by vapour phase chromatography, provided the clue to its structure *. The molecular weight 171, in conjunction with strong peaks at *m/e* 29, 57 (base peak), 72, 114, and 142, clearly indicated that the new mustard oil was 5-oxoheptyl isothiocyanate (I) **.

Upon hydrolysis with 20 % HCl (60°, 3 h), the glucoside fraction afforded a mixture of acids,[2] which was converted into methyl esters by Fischer-esterification. On vapour phase chromatography (silicone rubber, 11°/min., column: 100°→300°, He: 70 ml/min.), the ester corresponding to the minor glucoside appeared first, cleanly separated from 6-oxononanoic acid methyl ester which was previously demonstrated to derive from glucocappasalin.[1] The first methyl ester afforded a crystalline semicarbazone, m.p. 94–95° (from water), alone or in admixture with an authentic specimen of the *semicarbazone* of *6-oxooctanoic acid methyl ester* (II). The two preparations exhibited coinciding infra-red spectra. The synthetic semicarbazone, m.p. 97° (Found: C 52.14; H 8.30; N 18.32. Calc. for $C_{10}H_{19}N_3O_3$: C 52.38; H 8.35; N 18.33), was produced from methyl 6-oxooctanoate (II), an ester repeatedly reported in the literature and here prepared in 70 % yield from the acid chloride of methyl hydrogen adipate and ethylcadmium bromide according to the general conditions reported for analogous reactions.[3]

A solution of the new glucoside, free from glucocappasalin, was produced by band chromatography on Whatman 3 MM paper. Upon acid hydrolysis of this solution (60°, 3 h, 20 % HCl), hydroxylamine was formed and identified by paper chromatography.[2] Another portion of the eluate was subjected to enzymic hydrolysis with myrosinase in a citrate buffer (pH 6.0) and the formation of sulphate was established. Thin layer chromatography, according to Stahl and Kaltenbach,[4] was employed to demonstrate the simultaneous liberation of glucose during the enzymic hydrolysis.

The gluconorcappasalin ion * hence possesses the usual structure (III), thus representing a lower homologue of glucocappasalin.[1]

A full account of the present work will appear in a forthcoming paper.

---

* The authors are much indebted to Dr. R. Ryhage, Stockholm, for performing the mass spectra.

** A systematic study of the mass-spectral behaviour of isothiocyanates has been carried out in cooperation with Dr. C. Djerassi, Stanford University. The results will appear in this journal as a joint contribution from the two laboratories.

* In the semi-systematic nomenclature recently proposed for glucosides of this type,[5] the gluconorcappasalin ion (I) is denoted 5-oxoheptyl glucosinolate.

1. Kjær, A. and Thomsen, H. *Acta Chem. Scand.* **16** (1962) 2065.
2. Ettlinger, M. G. and Lundeen, A. J. *J. Am. Chem. Soc.* **78** (1956) 4172.
3. Cason, J. and Prout, F. S. *Org. Syn.* **28** (1948) 75.
4. Stahl, E. and Kaltenbach, U. *J. Chromatog.* **5.** (1961) 351.
5. Ettlinger, M. G. and Dateo, Jr., G. P. *Studies of Mustard Oil Glucosides*, Final Report, Contract DA 19-129-QM-1059, Rice Institute, Houston, Texas (1961) 17.

Received February 8, 1963.