

X-RAY STRUCTURE DETERMINATION OF A NATURALLY OCCURRING  $\gamma$ -LACTONE

GLUCOSIDE FROM HELLEBORUS FOETIDA L.

R. A. Mariezcurrena, S. E. Rasmussen, J. Lam

Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

and

E. Wollenweber

Botanical Institute, Technical University of Darmstadt, D 6100

Darmstadt, Germany.

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In a recent publication Tschesche et al.<sup>1</sup> report about lactone glucosides from ranunculaceous plants. A glucoside, ranuncoside, was isolated from Ranunculus repens and Helleborus foetidus, from which plant we have also isolated a glucoside. This compound is identical with one of those reported by Tschesche et al.<sup>1</sup>

The melting point is 205-208°C. According to the elementary analysis it contains 45.37% C, 6.19% H, and 48.44% O.  $M = 294 (C_{11}H_{16}O_8 \cdot H_2O)$ .

The compound crystallizes in the monoclinic system. The crystals are piezoelectric and reflections  $0k0$  were absent for  $k = 2n+1$ . Hence the space group is  $P2_1$ . The cell parameters are:  $a = 11.41 \text{ \AA}$ ,  $b = 10.82 \text{ \AA}$ ,  $c = 5.33 \text{ \AA}$ ,  $\beta = 95.70$ .

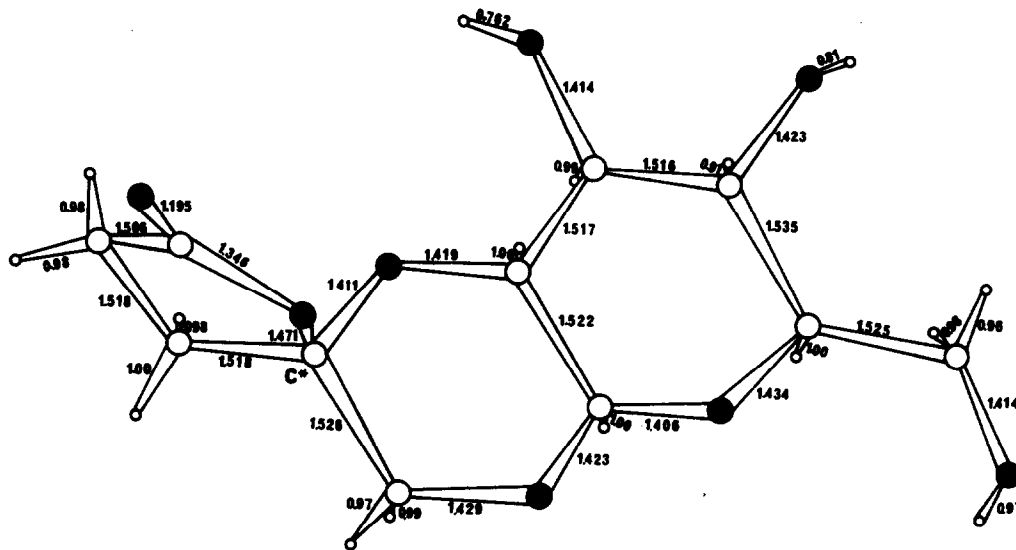
Professor Tschesche kindly sent us crystals isolated in his laboratory. Oscillation and Weissenberg X-ray photographs of his and our samples exhibited complete identity both in lattice spacings and in relative intensities. Hence the identity of the two samples is established without doubt. The melting points of the two samples differed less than 1°C and a mixture melted at a temperature intermediate between the melting points of the two samples.

The structure was solved by direct methods and refined to a conventional R-value of 0.046. All atoms were located.

Fig. 1 is an axonometric projection of the molecule. It contains a  $\beta$ -glucose unit fused on to a dioxane ring. A saturated  $\gamma$ -lactone ring is connected to the dioxane ring in a spiro arrangement. Bond lengths are shown in the figure. Standard deviations of bond lengths between the heavier atoms are about 0.003 Å. The  $\gamma$ -lactone ring deviates significantly from planarity.

Tschesche et al.<sup>1</sup> suggested a similar structure. The X-ray determination establishes the stereochemistry at C\* besides quantitative results for bond lengths etc. The crystallographic evidence is in complete agreement with chemical evidence based on hydrolysis experiments and with data obtained by infrared and mass spectroscopy. The infrared spectrum of the glucoside shows a saturated  $\gamma$ -lactone response at  $1780\text{ cm}^{-1}$ , besides hydroxyl group frequencies in the regions from  $3610$  to  $3360\text{ cm}^{-1}$  and from  $1115$  to  $1015\text{ cm}^{-1}$ . The infrared spectrum of the aglucone obtained after acid hydrolysis is identical with that of  $\delta$ -hydroxylevulinic acid.

Fig.1



REFERENCES

1. R. Tschesche, K. Welmar, C. Wullf, and G. Snatzhe, *Chem. Ber.*, 1972, **105**, 290 - 300.