Tetrahedron Letters No.25, pp. 2367-2370, 1967. Pergamon Press Ltd. Printed in Great Britain.

STUDIES ON THE MONOTERPENE GLUCOSIDES: V.[1]
THE X-RAY INVESTIGATION OF MONOTROPEIN MOLECULE.

Norio Masaki, Masakazu Hirabayashi, Kaoru Fuji,
Kenji Osaki and Hiroyuki Inouye
Faculty of Pharmaceutical Sciences, Kyoto University,
Sakyo-ku, Kyoto, Japan.

(Received 13 March 1967)

Recently, Inouye and his collaborators clarified the structure of monotropein, but the stereochemistry of C-8 remained unsolved. Although the absolute configuration of C-1 tentatively proposed at that time was later supported on the basis of NMR spectral investigation of daphylloside[1], a related substance, some ambiguity still remained.

In order to solve these problems an X-ray analysis of the rubidium salt of monotropein was attempted. This compound was recrystallized from the aqueous ethanol in the form of colourless prisms elongated along the c-axis, the composition of which was found to be $C_{16}H_{21}O_{11}Rb \cdot 2H_2O$. These crystals are orthorhombic, space group $P2_12_12_1$, with a = 10.14, b = 24.57 and c = 8.10 Å. The calculated density is 1.688 g cm^{-3}, which indicates that there are four formula units per unit-cell. Three-dimensional diffraction intensities were visually estimated on the Weissenberg photographs and on the precession photographs taken with the c-axis crystal.

The coordinates of rubidium atom are found immediately on the Patterson map. The other atoms except for hydrogen are clearly revealed after several cycle applications with the usual Fourier method. Further refinement is now in progress, the R-value being 0.213 at the present stage.

The molecular structure derived in this investigation is shown in Fig. 1, where all the atoms in the asymmetric unit of this crystal, excluding hydrogen,

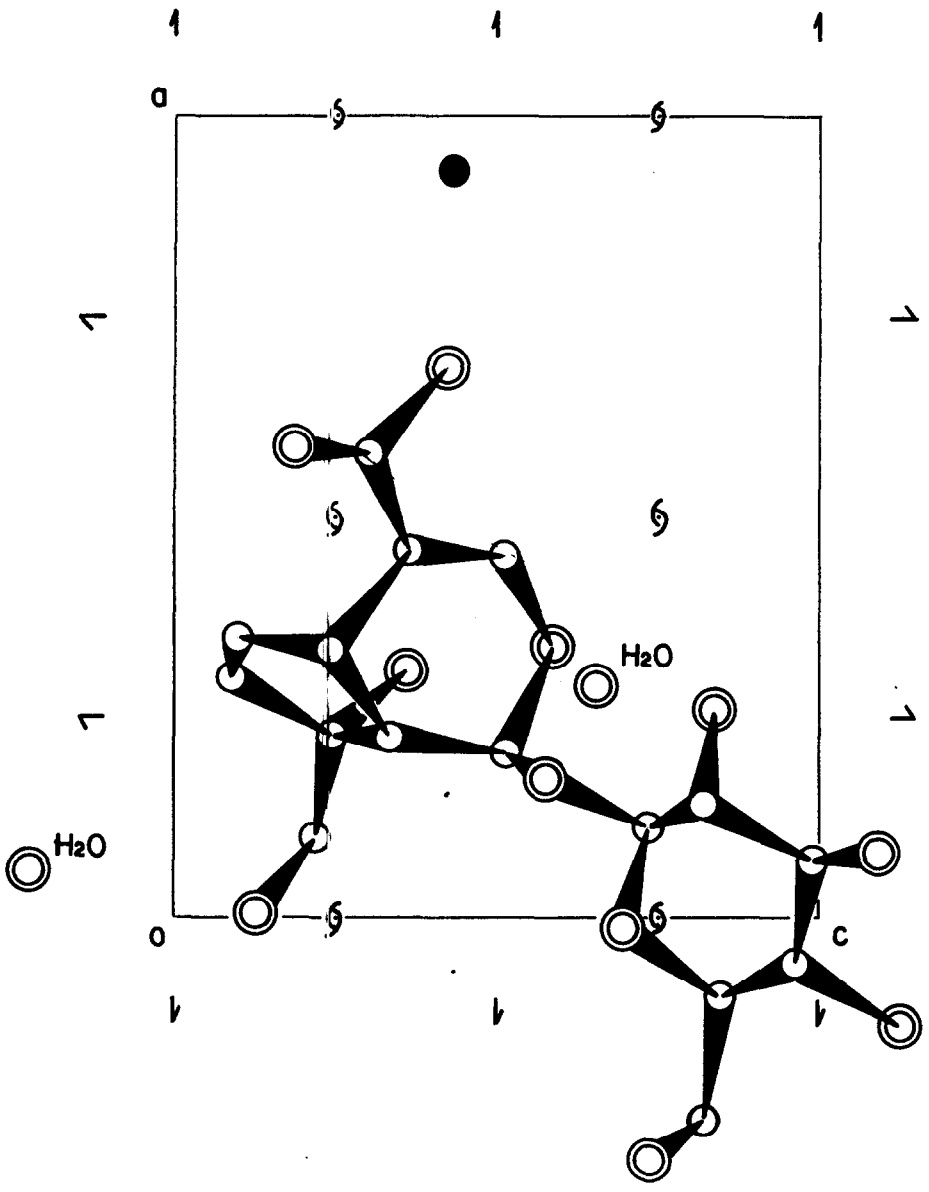
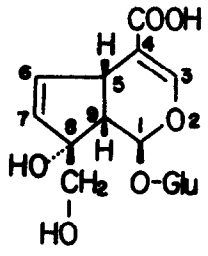
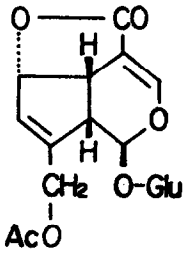


Fig. 1. Perspective drawing of a chemical unit in the monotropein rubidium salt dihydrate. Black, open and double circles represent rubidium, carbon and oxygen atoms respectively.

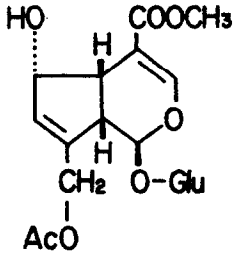
are drawn. As this molecule has a β-D-glucose unit, the absolute configuration of the molecule was easily established. The atomic arrangements around the atom C-1 and around the atom C-8 were determined without ambiguity. The other part of the obtained molecular structure agreed with that proposed[2] for the monotropein molecule. It was also found in this crystal that the sugar moiety takes an quasi-axial conformation towards the heterocyclic ring of the aglycone.



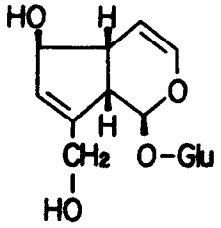
(I)



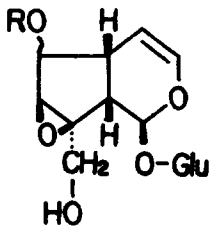
(II)



(III)



(IV)



(V)

Glu = β-D-glucopyranose

Ac = CH_3CO-

R = HO-⟨O⟩-CO-

Since the absolute configuration of C-1 of monotropein (I) was determined as described above, that of asperuloside (II)[2], daphylloside (III)[1], aucubin (IV)[3] and catalposide (V)[3,4], whose structures had chemically been correlated to monotropein (I), was established as it had been proposed. Accordingly, it was confirmed that they are represented as shown.

We are grateful to Dr. T. Arai, Dr. Y. Amano and Mr. T. Taga of our institute for their kind help in this work.

REFERENCES

[1] Part IV, H. Inouye, S. Ueda, M. Hirabayashi and N. Shimokawa, Yakugaku Zasshi 86, 943 (1966).

[2] H. Inouye, T. Arai and Y. Miyoshi, Chem. & Pharm. Bull. 12, 888 (1964).

[3] H. Inouye and K. Fuji, ibid. 12, 901 (1964).

[4] J. M. Bobbitt, D. W. Spiggle, S. Mahboob, H. Schmid and W. von Philipsborn, J. Org. Chem. 31, 500 (1966).