Tetrahedron Letters No.8, pp. 627-630, 1969. Pergamon Press. Printed in Great Britain.

CRYSTAL STRUCTURE OF ONE OF THE POSITION ISOMER OF CAPAURIMINE BY X-RAY ANALYSIS

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(Received in Japan 30 November 1968; received in UK for publication 15 January 1969)

Capaurimine, one of the protoberberine alkaloids isolated from Corydalis species, was assigned to (I) through chemical degradations by Manske[1]. We have synthesised the compound (I), but there were some significant differences in the n.m.r. and i.r. spectra between the synthetic product and natural one[2]. It has been reported[2] that methylation of the synthetic substance (I) with diazomethane gave the 1,2,3,9,10-pentamethoxyprotoberberine (II) and that the i.r. spectrum was not identical with that of O,O-dimethylcapaurimine. On the other hand the i.r. spectrum of the latter compound was the same as that of O-methylcapaurine. We have, therefore, investigated[3] the structure of the hydrobromide of natural capaurine (III) and it has been found that the plane formula given by Manske is correct but the quinolizidine ring system in this molecule takes rather unusual cis-conformation.

In the present work natural capaurine was purified as its hydrobromide, and the base, recovered from the preceding salt, was then treated with diazomethane to give O-methyl derivative, whose i.r. spectrum and R_f value were identical with those of synthetic O,O-dimethylcapaurimine (II)[4] [colourless needles (Found: C, 68.27; H, 6.90. $C_{22}H_{27}O_5N$ requires C, 68.55; H, 7.06 %), m.p. 140 - 141°, n.m.r. (τ) (in $CDCl_3$): 6.18, 6.17, 6.15, 6.15 (15H, 5 x $OC\underline{H}_3$), 3.57 (1H, aroma-

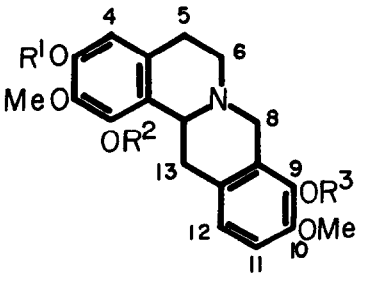
tic proton), 3.21 (2H, aromatic protons)]. Furthermore, methylation of 5,6,13 13a-tetrahydro-3,9-dihydroxy-1,2,10-trimethoxy-8H-dibenzo[a,g]quinolizine (IV)[2] afforded the compound (II). Thus an X-ray analysis of the hydrobromide of IV was undertaken in order to determine its conformation in the crystal state.

Recrystallisation of the hydrobromide of IV from methanol-ether gave pale yellow prisms, whose crystallographic and physical data are: $C_{20}H_{24}O_5NBr$, M = 438.31, m.p. 195 - 197°(decomp.), ρ_c = 1.4308 g. cm.$^{-1}$, ρ_o = 1.4745 g. cm.$^{-1}$, monoclinic, a = 17.43, b = 13.01, c = 8.97Å, β = 93.5°, space group Ic, Z = 4.

The intensity data were collected by the multiplefilm equi-inclination Weissenberg photographs using Cukα radiation. Relative intensities were estimated visually. The structure was solved by the heavy-atom method. Early Fourier synthesis has clearly indicated that the main skeleton of the molecule is cis-dibenzo[a,g]quinolizidine. The structure was refined by successive Fourier syntheses and least-squares method. After two cycles of least-squares refinement, the R factor was 0.23. Further refinements are in progress.

The perspective drawing of the structure is shown in Fig. 1.

It seems to be plausible that the cis-conformation would be preferentially formed in case of capaurine (III) and our synthetic sample (IV) because of the repulsion between the oxygen substituent at the C_1-position and C_{13}-hydrogen.



(I) R^1= Me , R^2= R^3=H

(II) R^1= R^2= R^3= Me

(III) R^1= R^3=Me , R^2=H

(IV) R^1= R^3=H , R^2=Me

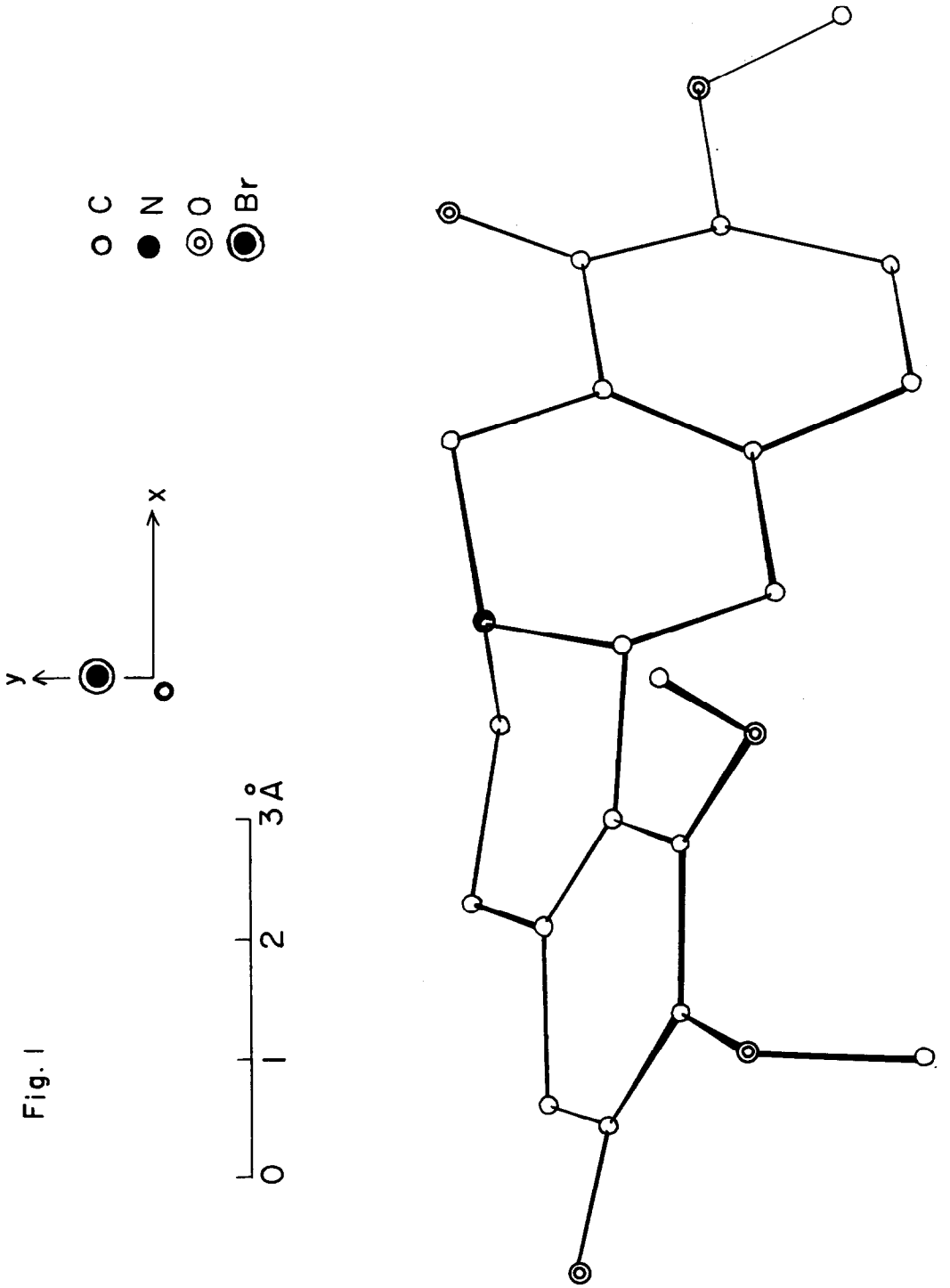


Fig. 1

Acknowledgement We thank President A. Yanagisawa, Director O. Takagi and Dr. K. Kigasawa of the Grelan Pharmaceutical Co. Ltd., Prof. H. Iida of Tokyo College of Pharmacy, Dr. K. Fukumoto and Dr. H. Yagi of Pharmaceutical Institute, Tohoku University for their assistance.

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4 It is considered that the discrepancy with the previous report[2] would be due to either of the following reasons. First, the conformation of natural compounds is different from that of synthetic one but the salt formation of both specimens seems to afford the same conformation. Secondary, since we have purified the natural capaurine through its hydrobromide, the i.r. spectra of natural O-methylcapaurine and synthetic O,O-dimethylcapaurimine seem to be identical each other, but further investigation could not be done because of no available natural sample.