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BITTER PRINCIPLES OF PHYSALIS ALKEKENGI VAR FRANCHETI : X-RAY ANALYSIS OF 5α-ACETOXY-6β-BROMOHEXAHYDROPHYSALIN A

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Physalin A ($C_{28}H_{30}O_{10}$), the bitter principle of Physalis Alkekengi var Francheti was converted into its tetrahydro-derivative ($C_{28}H_{34}O_{10}$), which was treated with Br_2-AcONa/AcOH, affording an acetoxy bromide ($C_{30}H_{37}O_{12}Br$) (I).[1] In order to establish the structure of physalin A, X-ray crystal structure analysis of this bromine derivative (I) has been performed.

The crystallographic data are as follows: Formula, $C_{30}H_{37}O_{12}Br \cdot 2CH_3OH$ (crystallized from methanol); Space group, $P2_1$ (monoclinic); Z = 2; Cell constants, a = 24.09Å, b = 7.60Å, c = 8.74Å, β = 96.0°; Density, D_{obs} = 1.53g cm^{-3}, D_{calc} = 1.537g cm^{-3}. The intensities of 3716 independent reflections were visually estimated from the Weissenberg photographs about the b- and c-axes with Cu-Kα radiation.

The bromine position, deduced from a three-dimensional Patterson synthesis, was used to calculate the first three-dimensional Fourier distribution. Though the Fourier map was partly complicated by pseudosymmetry, a reasonable model containing more than three fourths of other atoms than hydrogen could be assumed referring to the standard bond lengths and angles. The parameters of the atoms included in the model were refined through six cycles of least-squares calculations treating all the atoms as carbon. During these calculations most of the remaining atoms were added from chemical considerations.

Another three-dimensional Fourier synthesis was prepared, from which all the non-hydrogen atoms of the empirical formula including those of two methanol molecules, were located and were assigned either to carbon or to oxygen, considering the values of individual temperature factors and Fourier peak heights as well as chemical evidences. Four cycles of least-squares calculations reduced the R-value to 0.09 for 1110 reflections ($0.43 \geq \sin\theta/\lambda \geq 0.16$). Further refinements were made through three cycles of block diagonal least-squares calculations[2] with anisotropic temperature factors for bromine, using all the observed reflections. The final

R-value was 0.100 for all the observed reflections and 0.105 including $F_o = 0$.

The absolute configuration was determined by the anomalous dispersion of Cu-Kα radiation due to bromine atom. Figure 1 is the perspective drawing of a chemical unit along the c-axis. The bond lengths and angles, shown in Figures 2 and 3 respectively, are quite consistent with the structure (I) except for the neighbourhood of C_{27} position, where rather short C-C bond length and large bond angles are observed. The cause of this anomaly is still not certain. Anyway the chemical structure (I) has been established for this bromine derivative, which we now call 5α-acetoxy-6β-bromohexahydrophysalin A.[1)]

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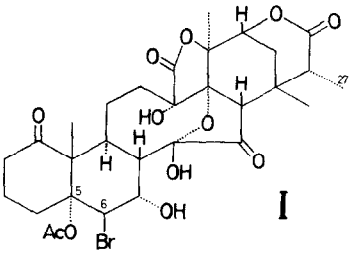

I

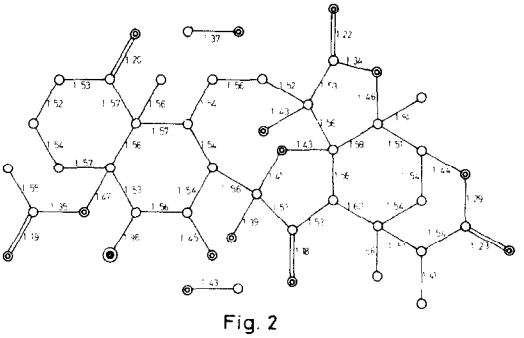

Fig. 2

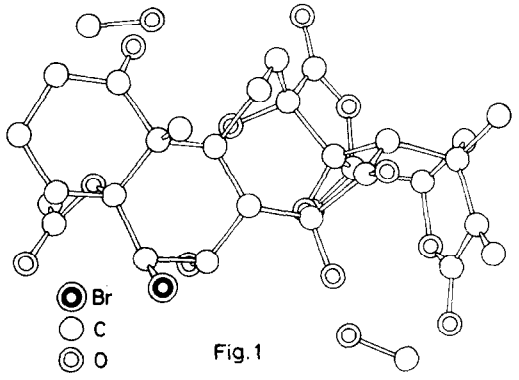

Fig. 1

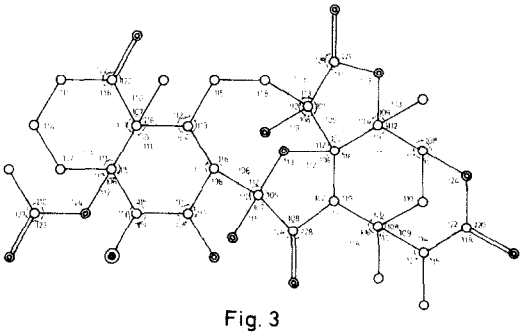

Fig. 3

REFERENCES

1) T. Matsuura, M. Kawai, R. Nakashima and Y. Butsugan: preceding communication.
2) Program: HBLS by T. Ashida.