THE STEREOCHEMISTRY OF (±)-6a-β-ETHYL-1,2,5,6,6a,7,8,9,9a-α,9b-α-DECAHYDRO-4H-PYRROLO[3,2,1-i,j]QUINOLIN-9β-OL

Kyoyu Sasaki
Department of Chemistry, Faculty of Science, Nagoya University,
Nagoya, Japan
and
Yuji Sendo,[*] Masao Akagi,[**] and Yoshio Ban[***]
Faculty of Pharmaceutical Sciences, Hokkaido University,
Sapporo, Japan

The methiodide (V) of the entitled compound was submitted to X-ray analysis, and the structure was established to be the one shown in Fig. 1, which is represented by the formula (V).

(±)-6a-β-Ethyl-1,2,5,6,6a,7,8,9,9a-α,9b-α-decahydro-4H-pyrrolo-[3,2,1-i,j]quinolin-9-one (IIIa) was prepared by Ban et al. (1) as an intermediate for the total synthesis of dl-aspidospermine (I), the other stereoisomer of which had been synthesized by Stork

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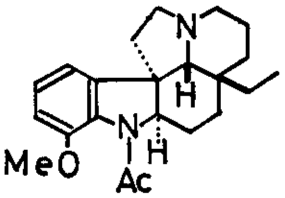
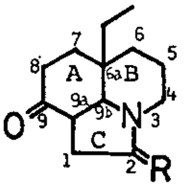
[*] The present address: Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushimaku, Osaka.

[**] The present address: Osaka Pharmaceutical College, Matsubarashi, Osaka.

[***] Inquires should be addressed to Y. Ban.

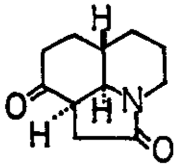


(I)

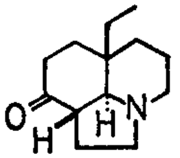


(II) R=O

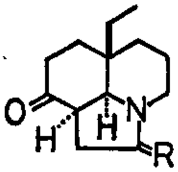
(III) R=H_2



(IV)

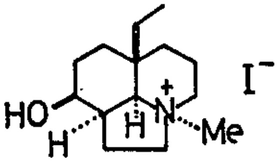


(IIIa)

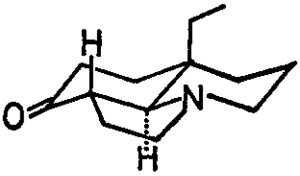


(IIb) R=O

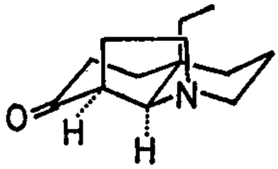
(IIIb) R=H_2



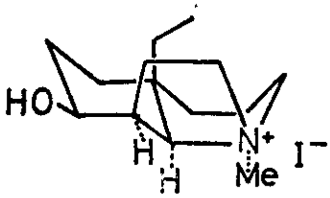
(V)



(IIIa)



(IIIb)



(V)

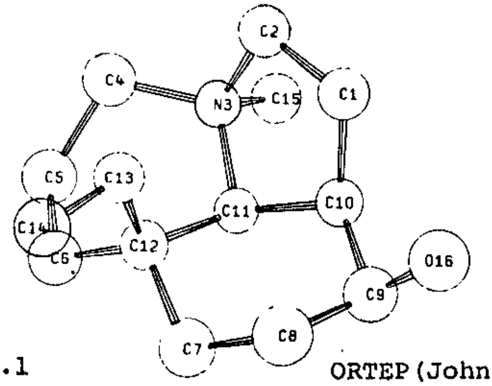
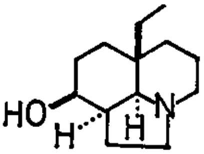


Fig.1 ORTEP(Johnson, 1965) diagram of the methiodide(V)



(VI)

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*Each formula demonstrates one enantiomer of the racemic compound.

et al. for the same achievement (2). The stereochemistry of our compound was proposed to be IIIa on revision of the initial assignments made by Stork (2) and by Ban et al.(1). The assignment was mainly based upon the n.m.r. spectrum of IIb on direct comparison with that of IV, whose A/B ring juncture had been known to be *trans* (3). This proposal was further supported by spectral data of the related compounds in addition to the X-ray analysis of the final product (4,5). Thus, it also indicated that the ketone(IIIa, A/B:*trans*, A/C:*trans*) was exclusively produced from the alcohol(VI) of the different stereochemistry(A/B:*trans*, A/C:*cis*) on chromic acid oxidation or the Oppenauer oxidation. The unique feature of this transformation could not but be ascribed to an acute 1,3-diaxial repulsion between 6a-β-ethyl group and the five-membered ring pictured in IIIb which actually could not exist and should be immediately converted to IIIa through the enolization process. Thus, the elucidation of the stereochemistry of the compound(VI) should be significant to prove this stereochemical change (6).

In this paper, we report an X-ray analysis of the methiodide(V) derived from our intermediate(VI), which comfirms the correctness of the above proposal about the stereochemistry of this series of compounds II~VI.

A single X-ray analysis was executed to verify the structure of the methiodide(V) ($C_{14}H_{26}NOI$, m.p. 260-262°C, recrystallized from methanol), whose transparent needles were mounted in capillaries. Preliminary photographs showed a 2/m Laue symmetry, with systematic absence for $h0l(l=2n+1)$ and $0k0(k=2n+1)$. The space group is therefore, $P2_1/c$. The observed crystal density of 1.55 g.cm.$^{-3}$ indicated four molecules of V per unit cell (ρ calcd. =1.56 g.cm.$^{-3}$). The unit cell dimensions and intensities were measured by use of an automatic four-circle diffractometer Y-290. The unit cell constants are a=7.807Å, b=23.989Å, c=9.742Å and β=125.5°. Intensities of the reflections with $\theta \leqq 60°$ were recorded with Cu-Kα radiation. After correction for background, Lorentz and polarization factors, and 1393 reflections, for which $I \geqq 3\sigma$, were used for the analysis. The structure was solved by the heavy-atom method. The structural parameters were refined by the block-diagonal least-squares method with an anisotropic temperature factor for iodine and isotropic one for the remaining 16 nonhydrogen atoms, and the final R-factor reduced to 11.3%.

The molecular shape (A/B:*trans*, A/C:*cis*) of the methiodide(V) is shown in Fig. 1, which demonstrates that the hydrogen at C(9b) [corresponding to C11 of the crystal diagram] and the methyl group at nitrogen(N 3) are in *cis*-configuration, and the B-ring is in a boat form. With the parent compound(VI), however, the relationship between the lone pair of the nitrogen and C(9b)-H could not be concluded to be the same, since the inversion of the substituent in trivalent nitrogen is known to be a process of low activation energy (7).

REFERENCES AND NOTES

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6. With the keto-lactam(IIb, m.p. 165-166°) (1) which substantially exists in a form of A/B:*trans*, A/C:*cis*, a similar 1,3-diaxial repulsion pictured in IIIb could be relieved by taking a planar(sp^2) structure for the lactam part[C(2) and N(3)] and a twist boat form for A-ring.(See Ref. 4).
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