THE CONFIGURATION CONCERNING THE MODE OF BIPHENYL LINKAGE OF BISAKNADININE[1)]

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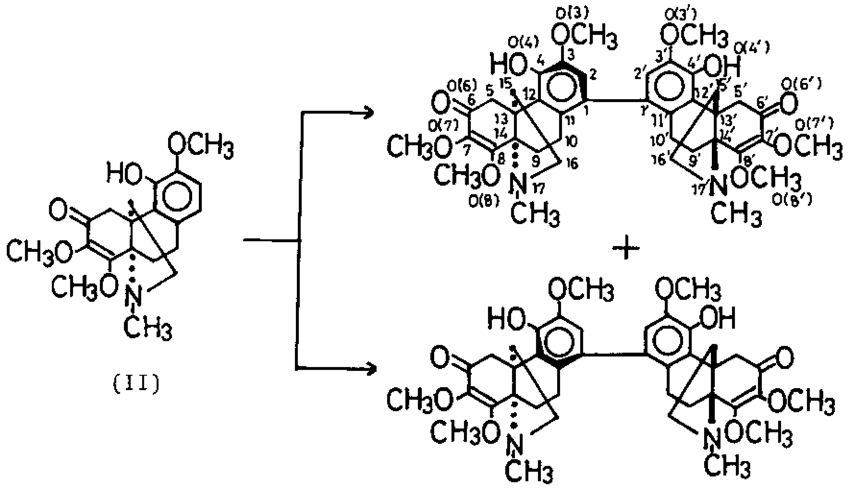
The crystal structure of natural bisaknadinine has been determined by X-ray diffraction method demonstrating the absolute configuration concerning the mode of biphenyl linkage has been confirmed to be R-configuration (Ia).

In part XI[2)], we reported the isolation of bisaknadinine, a new dimeric hasubanan type alkaloid containing biphenyl linkage, from *Stephania Sasakii* Hayata. Its structure was deduce as Ia or Ib from various spectral data, especially by the application of nuclear Overhauser effect and internuclear double resonance. The chemical oxidation of monomer aknadinine (=4-desmethylhasubanonine)(II)[3)] with



(II)

(Ia)

(Ib)

silver nitrate solution gave two species of dimeric compounds which were identified respectively with natural bisaknadinine and its stereoisomer due to the newly introduced axial chirality concerning the mode of biphenyl linkage. It was impossible to decide from only its ORD and CD data whether the structure of natural bisaknadinine is Ia or Ib. Therefore, we have determined the crystal structure of natural bisaknadinine by X-ray diffraction method and decided its structure as R-configuration (Ia).

Crystal data: Recrystallization of bisaknadinine from acetone gave the well formed columnar crystals, mp 198∿200°, $C_{40}H_{48}N_2O_{10}\cdot C_3H_6O$[4], orthorhombic with space group $P2_12_12_1$, a=10.330(2), b=12.279(2), c=31.441(4) Å, V=3987.9(9) $Å^3$, D_x=1.291 $g\cdot cm^{-3}$, z=4. The intensity data were collected on a Rigaku four-circle automated diffractometer with graphite monochromated Cu Kα radiation. 3749 independent reflections ($|F_o|>3.0\sigma(|F_o|)$) within sinθ/λ less than 0.588 $Å^{-1}$ were obtained and corrected for Lorentz and polarization factors, but not for absorption because of the smallness of the used crystal. The structure was solved by MULTAN 78[5]. The resulting E map revealed the positions of all non-hydrogen atoms of bisaknadinine. All hydrogen atoms and the solvent molecule (acetone) were located by the difference systheses. Block-diagonal least-squares refinement of positional and thermal parameters reduced R-factor to 0.057. The stereoscopic view of the molecular conformation is shown in Figure. On the basis of the absolute configuration of aknadinine (II)[3], the natural bisaknadinine is confirmed to have the structure of Ia (R-configuration) concerning the mode of bipheny

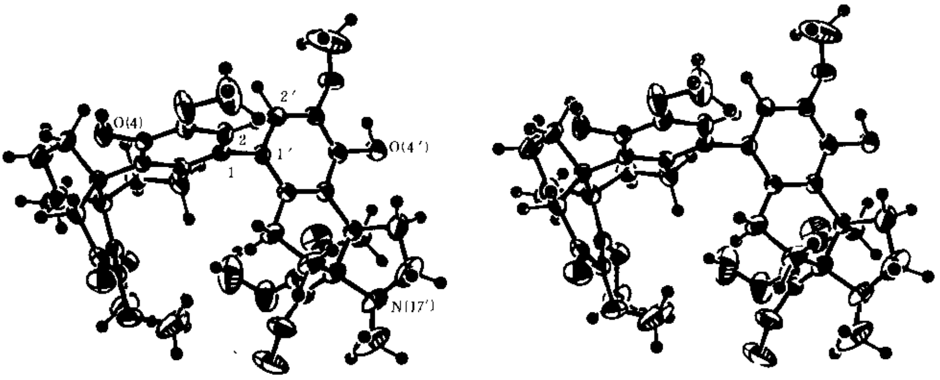


Fig. A stereoview of the molecular structure of bisaknadinine linkage. The dihedral angle between both the benzene portion is 77.5° and the torsion angle of C(2')-C(1')-C(1)-C(2) is -77.1°. The C(1)-C(1') bond length of 1.498(7) Å is quite normal in sp^2-sp^2 biphenyl bond, compared with biphenyl itself (1.496 Å)[6]. The remaining bond parameters are also in good agreement with those values of the related compounds[6,7]. In crystal, the bisaknadinine molecule is held by a hydrogen bond [O(4)(*x*,*y*,*z*)---N(17')(*x*,*-1+y*,*z*), 2.836(7) Å] and by normal van der Waals contacts with the neighboring molecules. The oxygen atom of acetone is hydrogen-bonded to the O(4') atom of bisaknadinine (2.748(6) Å) and stabilize the molecular packing.

References and Foodnotes

1) This paper constitutes Part 269 in the series "Studies on the Alkaloids of Menispermaceous Plants" The Alkaloids of *Stephania Sasakii* Hayata XII. (Part 268, XI: Ref. 2).

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4) The analytical results and formula in the previous paper[2] should be corrected as follows. Found: C,66.36; H,6.79; N,3.66. Calcd. for $C_{40}H_{48}N_2O_{10}\cdot C_3H_6O$: C,66.64; H,7.02; N,3.62.

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