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Revised Structure for an Alkaloid from *Streptomyces* sp. NA-337

An alkaloid from *Streptomyces* sp. NA-337, whose structure was assigned previously as (E,E)-4-methyl-2-pentadienyl-1-pyrroline, is re-investigated and revised as (E,E)-2-pentadienyl-3,4,5,6-tetrahydropyridine.

We previously reported the isolation and structure elucidation of the alkaloids (**1**) and (**2**) from *Streptomyces* sp. NA-337.[1] The alkaloid (**1**) was identified as abikoviromycin by comparison of a derivative of **1**, 4,4a-epoxy-5-ethylidene-1-methyl-2,3,4,4a,5,7a-hexahydro-1*H*-1-pyrindine methiodide, with an authentic sample derived from abikoviromycin. The alkaloid (**2**) was assigned as (E,E)-4-methyl-2-pentadienyl-1-pyrroline ($C_4H_8=CH_2CH(Me)CH_2$ in Chart 1) by its chemical reactions and the physico-chemical method. After that, however, the optical rotation of **2**, which was a main factor to decide the structure, was recognized incidentally to be zero. We now wish to revise the structure of **2** on the basis of results obtained by re-investigation.

It was established that **2**, $C_{10}H_{15}N$, contained the *trans, trans*-pentadienyl group conjugated with the imino group in a ring by its chemical reactions and the nuclear magnetic resonance (NMR) and ultraviolet spectra (UV).[1] The remaining unit, C_4H_8, was assigned as the $CH_2CH(Me)CH_2$ group consisted of the 4-methyl-1-pyrroline ring by the optical activity of **2** and the spectral data of **2** and its derivatives.[1] Since, now, re-examination of the optical rotation at the D line[2] and the optical rotatory dispersion[3] showed the hydrochloride of **2** to be optically inactive, the C_4H_8 unit might not be the $CH_2CH(Me)CH_2$ group. The ^{13}CNMR spectrum[4]

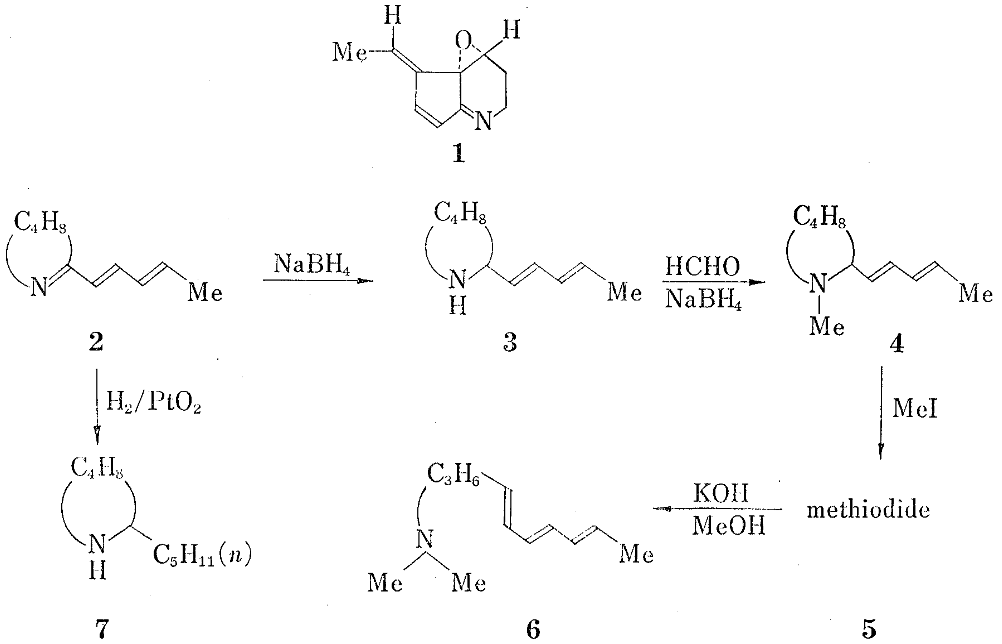

Chart 1

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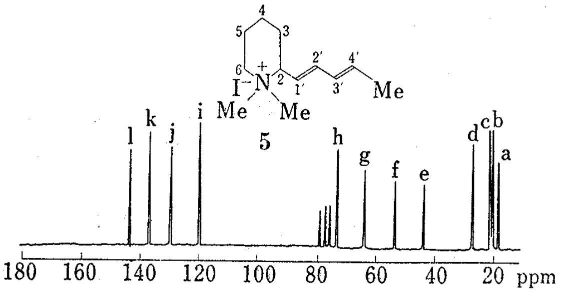
[1] M. Onda, Y. Konda, Y. Narimatsu, H. Tanaka, J. Awaya, and S. Ōmura, *Chem. Pharm. Bull.* (Tokyo), 22, 2916 (1974).

[2] JASCO DIP-SL; $c=1.0\%$, EtOH.

[3] JASCO J-20; $c=0.001\%$ (EtOH).

[4] JEOL JNM PS-100/PFT-100; 25.1 MHz; $CDCl_3$; tetramethyl silane (TMS) as reference.

of the compound (**5**) was carefully examined by using off-resonance technique, indicating no methyl carbon except two N-methyl and one methyl in the side chain (Fig. 1). Further, re-examination of the ^{13}CNMR spectrum of the hydrochloride of **2** showed only one methyl carbon (δ 19.18) in the side chain. On reappraisal of the NMR data,[1,5] the signals (**2**, δ 2.00; **3**, 1.77; **5**, *ca.* 1.93) can be reasonably assigned to the methylene group rather than the methyl group in question. From these facts, conclusively, **2** should be revised as (E,E)-2-pentadienyl-3,4,5,6-tetrahydropyridine which shows a series of the chemical reactions as depicted in Chart 1 ($C_4H_8=(CH_2)_4$). The alkaloid (**2**) is believed to be the same as 1-[2-(3,4,5,6-tetrahydropyridyl)]-1,3-pentadiene (THPP) which was recently isolated from *Actinomyces* strain MD 736-C6[6] by comparison of the physical properties and physicochemical data.[7]



a.	18.39 q	4′-Me		g.	63.87 t	C-6
b.	20.72 t	C-4		h.	73.48 d	C-2
c.	21.21 t	C-5		i.	119.10 d	C-4′
d.	27.13 t	C-3		j.	129.69 d	C-3′
e.	43.53 q	NMe$_2$		k.	136.39 d	C-2′
f.	53.73 q			l.	142.41 d	C-1′

Fig. 1. ^{13}C NMR Spectrum of **5**

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5) Compound (**6**): δ 1.70—1.30 (m, $4\times$H). Compound (**7**): 1.90—1.20 (m, $14\times$H).

6) Y. Kumada, H. Naganawa, M. Hamada, T. Takeuchi, and H. Umezawa, *J. Antibiotics* (*Tokyo*), **27**, 726 (1974).

7) The hydrochloride of **2** showed a wide range of mp which sintered at 155—160°, changed to brown at 170°, and melted at 190—200° to give a dark brown melt. The hydrochloride of THPP and its admixture with the hydrochloride of **2** displayed the same pattern of mp as that mentioned above. The infrared spectrum was directly compared. The UV, NMR, and ^{13}CNMR spectra were compared with those described in lit.[6]