Communications to the Editor

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THE STRUCTURE OF A NEW DITERPENE ALKALOID: SANYONAMINE

Shin-ichiro Sakai,*[,a] Keiichi Yamaguchi,[a] Hiromitsu Takayama,[a] Ichiro Yamamoto,[a] and Toshihiko Okamoto[b]

Faculty of Pharmaceutical Sciences, Chiba University,[a] 1-33, Yayoi-cho, Chiba 260, Japan and Faculty of Pharmaceutical Sciences, Tokyo University,[b] Hongo, Bunkyo-ku, Tokyo 113, Japan

The structure and absolute configuration of sanyonamine (I), which is found widely as a minor diterpene alkaloid in *Aconitum sanyoense* Nakai and *A. s. var. tonense* Nakai collected at various places in Japan, were established on the basis of X-ray analysis of (I) and a CD spectral study on 15-dehydrosanyonamine (II).

KEYWORDS —— diterpene alkaloid; *Aconitum sanyoense* Nakai; *Aconitum sanyoense* Nakai *var. tonense* Nakai; *Ranunculaceae*; sanyonamine; X-ray analysis; CD spectrum; absolute configuration

Dōgo base, $C_{20}H_{27}NO_2$ (mp 276 – 278°C, $[\alpha]_D$ + 62.9°), was originally isolated as a minor base of *Aconitum sanyoense* Nakai collected at Mt. Dōgo, Hiroshima prefecture and Mt. Giboshi, Okayama prefecture.[1] The same alkaloid was recently isolated from *Aconitum sanyoense* Nakai *var. tonense* Nakai (Zyōsyu-torikabuto), collected at Kuzure, Matsumoto, Nagano prefecture.[2] The mass and NMR spectra of Dōgo base and Katsuyama base I[3] isolated from *A. sanyoense* Nakai (Katsuyama-bushi or Sanyo-torikabuto), collected at Katsuyama, Fukui prefecture, have revealed that the two alkaloids were identical. We have given the name sanyonamine to this widely distributed diterpene alkaloid.

Sanyonamine has the following spectral data; IR ν_{max}^{KBr} cm^{-1}: 3350, 3305 (each OH), NMR ($CDCl_3$) δ_{ppm}^{400MHz} 4.98, 4.96 (each 1H, s. $=CH_2$), 4.31 (1H, br s. C_2-H), 4.07 (1H, s. C_{15}-H), 3.63 (1H, br s. C_6-H), 3.50 (1H, d. J= 12Hz, C_{19}-Ha), 2.77 (1H, d. J= 12Hz, C_{19}-Hb), 3.67 (1H, s. C_{20}-H), 1.06 (3H, s. C_{18}-H_3), MS: m/z(%), 313 (M^+, 100), 296 (M^+ - OH, 50). Deshielding of C_{19}-Ha and C_{20}-H signals in the NMR spectrum is explained by the anisotropic effect of an axial α-hydroxy group on the C_2-position.[4] Structure (I) (2-α-hydroxynominine) was assigned to sanyonamine according to the above spectral data, and to confirm this a single crystal X-ray diffraction analysis was performed.

Crystals of (I) belong to a monoclinic space group, $P2_1$, with the cell parameters of a= 13.151(7), b= 13.590(7), c= 9.375(8)Å, Z= 4, and Dx= 1.26 g/cm^3. The structure was solved by the direct method MULTAN and the result was refined by a block diagonal least squares procedure to R= 0.071 for 3467 unique reflections with $Fo > 2\sigma(Fo)$ measured on a Rigaku AFC-5 diffractometer with CuKα radiation. The ORTEP drawing and stereoscopic view of the structure of sanyonamine (I) are shown in Fig. 1 and 2.

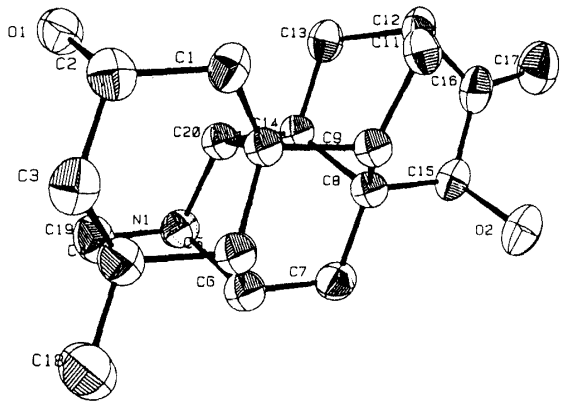


Fig. 1. An ORTEP Drawing of the Structure of (I)

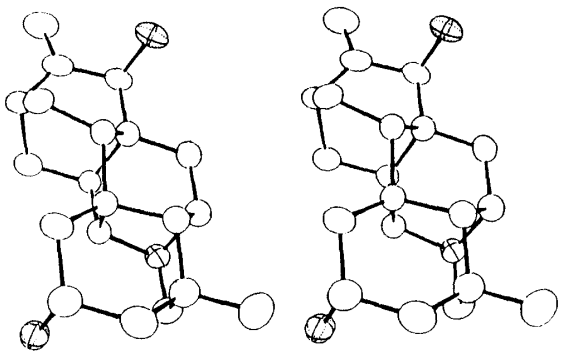
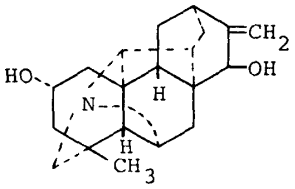
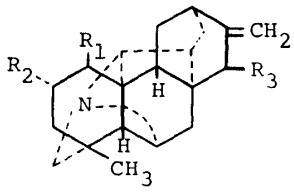


Fig. 2. Stereoscopic View of the Structure of (I)



(I)



(II) R_1= H R_2= OH
R_3= =O

(III) R_1= R_2 = H
R_3= =O

(IV)[5]
R_1= $OCOCH_3$
R_2= $OCOC_6H_5$
R_3= =O

Next, the absolute configuration of sanyonamine (I) was studied. Sanyonamine (I) was oxidized to the α,β-unsaturated ketone derivative, 15-dehydrosanyonamine (II), [mp 296 – 300°C, $C_{20}H_{25}NO_2$, (m/z; M^+ Calcd 311.188, Found 311.188), IR (KBr); 1700 (C=O), 1635 (conj. C=C), CD (dioxane); λ_{ext}nm(Δε) 235 (+2.03), 260 (+0.40), 330 (+0.13 sh.), 337 (+0.19 sh.), 353 (+0.30), 368 (+0.26), 388 (+0.10 sh.)], with active MnO_2 in $CHCl_3$ at r.t. under stirring for 24 h. 15-Dehydronominine (III),[6] [mp 136 – 138°C, $C_{20}H_{25}NO$, (m/z; M^+ Calcd 295.194, Found 295.192)] and acetylhypognavinone (IV) exhibited CD spectra of the carbonyl chromophores very similar to those of (II) as shown in Fig. 3. These observations indicate that the absolute configuration of sanyonamine (I) is the same as those of (III) and (IV).

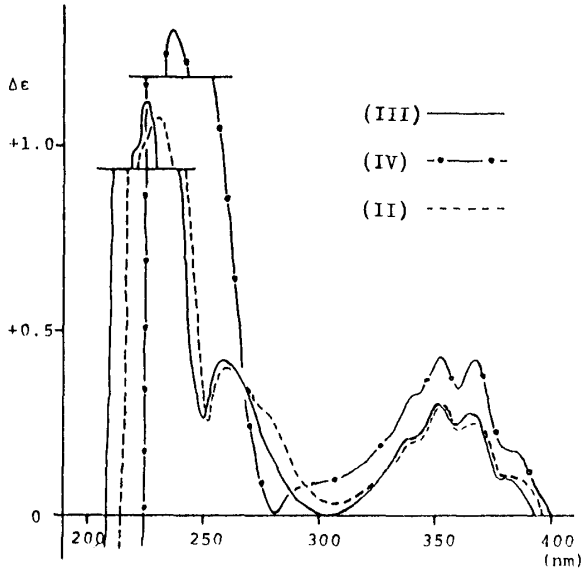


Fig. 3. CD Spectra of (II), (III) and (IV) in Dioxane

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REFERENCES AND NOTE

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5) See the proceding communication. "submitted."
6) See the following communication. "submitted."

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