seven oxgen atoms involved in nigakilactone L is clarified, indicating the presence of one hydroxyl group in the molecule.

An appearance of signal due to a proton at the lactone terminus (-CH-O-CO-) at δ 4.20[1,3,5] shows that no hydroxyl group is attached to C-14 for nigakilactone L. The ultraviolet (UV) maximum at 263.5 nm showing the absence of hydrogen bond between the hydroxyl at C-11 and the carbonyl group at C-1,[1b] provides evidence for nigakilactone L that no hydroxyl group is located on C-11. An olefinic proton on C-3 resonates at δ 5.25 as a doublet. This shows the presence of a proton (and the absence of hydroxyl group) on C-4 for nigakilactone L. Recently, Hikino, *et al.* isolated from the same plant three bitter principles, picrasin D (IVa), E (IVb)[7] and F (IVc),[10] which have a methylene dioxy moiety in the C ring. Optical rotatory dispersion (ORD) and circular dichroism (CD) data of nigakilactone L agree with those of picrasin E.[7] None of these picrasins, however, is found to be identical with nigakilactone L.

These data along with the observation that nigakilactone L contains three tertiary and one secondary methyl groups should lead to the location of a hydroxyl group on C-13 as in the case of nigakilactone F. Nigakilactone L is considered to be formed biogenetically by oxidation of nigakilactone F (III). The structure IVd is thus given for nigakilactone L.

Department of Chemistry,
Faculty of Science,
University of Tokyo
Bunkyo-ku, Tokyo

Tatsushi Murae
Akihiko Sugie
Takahiko Tsuyuki
Takeyoshi Takahashi

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Structure of Kinamycin C, and the Structural Relationship among Kinamycin A, B, C, and D

In previous papers,[1] we reported fermentation, isolation, and purification of a new quinone antibiotic, kinamycin, which was isolated from the culture broth of *Streptomyces murayamaensis sp. nov.* Hata *et* Ohtani. In this paper we wish to describe the structure of kinamycin C and the structural relationship among kinamycin A, B, C, and D. The infrared (IR) spectra of kinamycins show a sharp absorption of nitrile or isonitrile group at 2155 cm^{-1}. The ultraviolet (UV) and visible spectra of each component show a maximum absorption in the range of 240—260 and 380—450 nm, which are a characteristic absorption in naphthoquinone-type compounds.[2] The presence of phenolic OH is established with a red shift of their absorption in alkaline solution. In the nuclear magnetic resonance (NMR) spectra, three aromatic protons of kinamycins are signaled at 7.02—7.7 δ by a typical absorption of

1) S. Itō, T. Matsuya, S. Ōmura, M. Otani, A. Nakagawa, H. Takeshima, Y. Iwai, M. Ohtani, and T. Hata, *J. Antibiotics*, **23**, 315 (1970); T. Hata, S. Ōmura, Y. Iwai, A. Nakagawa, M. Otani, S. Itō, and T. Matsuya, *J. Antibiotics*, **24**, 353 (1971).
2) I. Singh, R.T. Ogata, R.E. Moore, C.W. Chang, and P.J. Scheuer, *Tetrahedron*, **24**, 6053 (1968).

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ABC splitting pattern, and therefore, the presence of 8-hydroxynaphthoquinone skeleton was confirmed.

The molecular formula and molecular weight of kinamycin C (I), $C_{24}H_{20}N_2O_{10}$, 496, were derived from mass spectra and elementary analyses of the derivatives obtained during structural studies on I. The IR spectrum of I shows a hydrogen-bonding quinone-CO at 1625 cm^{-1}, a free quinone-CO at 1660 cm^{-1}, a OH at 3500 cm^{-1}, and an acetoxyl-CO at 1745 cm^{-1}. The NMR spectrum of I indicated the presence of a *tert*-CH_3 at 1.3 δ (s), three alcoholic AcO groups at 2.0—2.3 δ (s), and vicinal protons on carbon atoms each carrying the alcoholic AcO group at 5.6 and 6.2 δ (d, J=7.2 Hz). Acetylation of I with anhyd. AcONa–Ac_2O on reflux gave a diacetate (II), IR $\nu_{KBr}^{C=O}$ [3] 1655, 1660 cm^{-1} (free quinone-CO). A *tert*-CH_3 signal in I shifted to a lower field at 1.57 δ (s) in II.

Hydrolysis of I with 0.2N NaOH afforded a deacetylkinamycin C (III), IR $\nu_{KBr}^{C=O}$ [3] 1625, 1620 cm^{-1} hydrogen-bonding quinone-CO, which gave an isopropylidene derivative (IV), $C_{20}H_{18}N_2O_7$, on refluxing with anhyd. acetone and a trace of *p*-toluenesulfonic acid as a catalyst.[4] The IR spectrum of IV shows two hydrogen-bonding quinone-CO groups at 1620 cm^{-1}, and this fact suggests that, of the two quinone-CO groups, that in C-1 is in hydrogen-bonding with the phenolic OH at C-8 and that in C-4 with the alcoholic OH at C-4′, both remaining undisturbed by the formation of an isopropylidene grouping. The NMR spectrum of IV shows the presence of three CH_3 groups at 1.4—1.55 δ (s) due to $-O\diagdown\diagup CH_3$ and *tert*-CH_3, vicinal protons at 3.96 and 4.49 δ (d, J=9.0 Hz), and a proton isolated on a carbon carrying the *sec*-OH at 4.83 δ (s). A proton at 3.96 δ in IV seemed to shift to 5.4 δ in the diacetate (V) obtained by acetylation of IV with Ac_2O–pyridine as shown in Fig. 1. IR spectrum of V shows only the absorption of free quinone-CO at 1650 and 1640 cm^{-1}, suggesting acetylation of the OH at C-4′ but not that at C-1′. Consequently, the isopropylidene group in IV must be formed between the *sec*-OH at C-3′ and the *tert*-OH on the carbon carrying the *tert*-CH_3.

Oxidation of III with $NaIO_4$ in dioxane gives VI, IR $\nu_{KBr}^{C=O}$ [3] 1660 (free quinone-CO), 1620 (hydrogen-bonding quinone-CO), 1700 cm^{-1} (aldehyde-CO), whose NMR spectrum (Fig. 2) shows the presence of an aldehyde proton attached to unsaturated bond at 10.52 δ (s), a

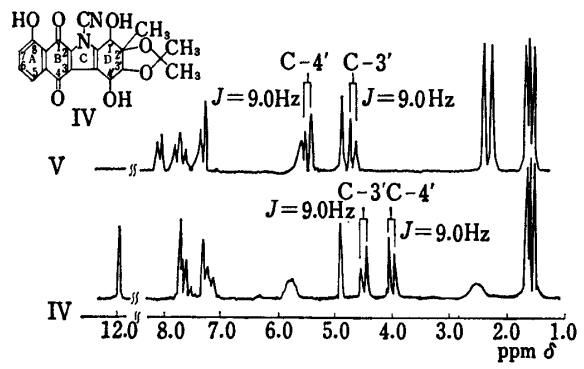

Fig. 1. NMR Spectra of Isopropylidene Kinamycin (IV) and Isopropylidene Kinamycin Diacetate (V) (100 MHz; $CDCl_3$)

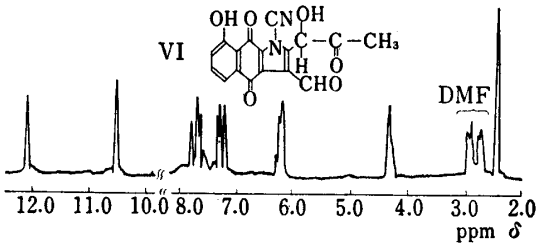

Fig. 2. NMR Spectrum of Kinamycin $NaIO_4$ Oxide (VI) (100 MHz; DMF-d_7)

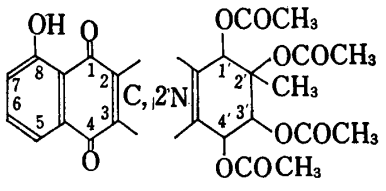

Fig. 3. Partial structure of Kinamycin C

3) quinone-CO.

4) M. Miyamoto, K. Morita, Y. Kawamatsu, S. Noguchi, R. Marumoto, M. Sasai, A. Nohara, Y. Nakadaira, Y.Y. Lin, and K. Nakanishi, *Tetrahedron*, **22**, 2761 (1966).

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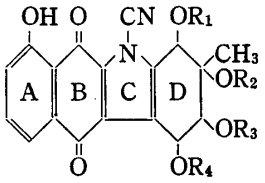
CH_3 adjacent to the carbonyl produced by oxidation at 2.4 δ (s), and a *sec*-OH and a proton on the same carbon at 6.28 δ and 4.28 δ. These observations suggest that I has a partial structure shown in Fig. 3.

The remaining structure was determined by X-ray crystallography[5] on a *p*-bromobenzoate derivative (VII), obtained by treatment with *p*-bromobenzoyl chloride in $CHCl_3$–Pyridine and a structure with a nitrile or isonitrile group attached to N atom on pyrole ring was presumed.

Hydrolysis[6] of III by refluxing with 30% KOH for 1 hr liberated ammonia but not formic acid and, therefore, kinamycins were confirmed to have the nitrile group.

Other components, A (VIII), $C_{24}H_{20}N_2O_{10}$ (M^+=496), B (IX), $C_{20}H_{16}N_2O_8$ (M^+=412), and D (X), $C_{22}H_{18}N_2O_9$ (M^+=454), were assumed to have difference in the number and position of functional groups in the D ring from NMR, IR, and mass spectra. From the NMR spectra, kinamycins have three AcO groups in VIII, one AcO in IX, and two AcO groups in X. *Tert*-CH_3 groups in VIII and IX are shifted to lower field, and appear at 1.58 δ and 1.54 δ, respectively, compared to those in I and X. Therefore, VIII and IX are assumed to possess an AcO instead of *tert*-OH. Acetylated substances of components IX, I, and X were confirmed to be the same from their IR spectra and thin-layer chromatography. From the comparison of spectrometric data, the structure of each component was determined as shown in Chart 1.



Component	R_1	R_2	R_3	R_4
A (Ⅷ)	$COCH_3$	$COCH_3$	$COCH_3$	H
B (Ⅸ)	H	$COCH_3$	H	H
C (I)	$COCH_3$	H	$COCH_3$	$COCH_3$
D (X)	$COCH_3$	H	$COCH_3$	H

Chart 1. Structures of Kinamycin A (VIII), B (IX), C (I), and D (X)

Kitasato University[*1] *and*
Kitasato Institute[*2]
Minato-ku, Tokyo 108

Satoshi Ōmura[*1,*2]
Akira Nakagawa[*1]
Haruki Yamada[*1]
Tōju Hata[*1,*2]

Kwansei gakuin University
Nishinomiya, Hyogo-ken 662

Akio Furusaki
Tokunosuke Watanabe

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6) D.B. Borders, K.J. Sax, J.E. Lancaster, W.K. Hausmann, L.A. Mitscher, E.R. Wetzel, and E.L. Patterson, *Tetrahedron*, **26**, 3123 (1970).

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