Table III. $\Delta\delta_H$ Values for H_2 and H_4

H	$\delta_H(15)$	$\delta_H(9)$	stereochemistry[a]	$\Delta\delta_H$ (15 → 9)	H	$\delta_H(16)$	$\delta_H(17)$	stereochemistry[a]	$\Delta\delta_H$ (16 → 17)
H_{2eq}	1.76	2.69	cis	+0.93	H_{2eq}	2.05	3.02	cis	+0.97
H_{2ax}	1.38	1.54	trans	+0.16	H_{2ax}	1.59	1.56	trans	−0.03
H_{4eq}	3.45	4.44	cis	+0.99	H_{4ax}	4.64	4.60	trans	−0.04

[a] Stereochemistry of the protons at C_2 and C_4 relative to the heterosubstituent at C_3.

Table IV. $\Delta\delta_C$ Values for C_2 and C_4

carbon	δ_C (15)[10]	δ_C (9)	$\Delta\delta_C$ (15 → 9)	δ_C (18)[12]	δ_C (17)[12]	$\Delta\delta_C$ (18 → 17)
C_2	39.7	35.8	−3.9	43.3	39.4	−3.9
C_4	57.6	53.9	−3.7	77.8	77.4	−0.4

$[\theta]_{234}$ −326, $[\theta]_{280}$ +340 (CF_3CH_2OH); ν_{max} 3430, 2980, 2950, 2940, 2900, 2840, 1735, 1550, 1508, 1230, 1123, 1055 cm^{-1}; and the β anomer (**9**), mp 180.5–181.5 °C, $[\alpha]_D$ +34.1° (CH_3OH); λ_{max} (CF_3CH_2OH) 199 nm (ϵ 4909); $[\theta]_{234}$ −962, $[\theta]_{282}$ +2308 (CF_3CH_2OH); ν_{max} 3440, 3000, 2955, 2900, 2860, 1730, 1550, 1515, 1315, 1235, 1065 cm^{-1}. The ^1H NMR (Table I) and ^{13}C NMR data (Table II) were in agreement with the proposed 2,3,4,6-tetradeoxy-4-(methoxycarbonylamino)-3-*C*-methyl-3-nitro-D-*xylo*-hexopyranosyl structures **8** and **9** ($^4C_1$ conformation). The chemical shift of the 3-methyl (δC 26.4, 25.4) in **8** and **9** was in agreement with published values[9] for an equatorial *C*-methyl nitro sugar. Independent proof for the stereochemistry at C_3 was obtained as follows. Methyl β-L-mycaroside (**14**) was converted by standard techniques into the 4-methoxycarbonylamino derivative (**15**). Comparison of the ^1H NMR data for **15**[10] with that of **9** (Table III) revealed marked deshielding of the vicinal cis protons H_{2e} and H_{4e} in going from the 3-axial hydroxy compound **15** to the 3-axial nitro compound **9**, while little effect was observed on the vicinal trans proton H_{2a}. This was in excellent agreement with the results obtained in going from **16**[11] to **17**[11] (Table III). Comparison of the ^{13}C NMR data for **15**[10] with those of **9** (Table IV) revealed pronounced shielding of C_2 and C_4, both of which bear vicinal cis protons to the axial nitro group.[12] These data were in excellent agrement with the observed shielding at C_2, which bears a vicinal cis proton, and the complete absence of any marked shielding at C_4, which does not bear a vicinal cis proton to the 3-*O*-acetate, in going from **18**[12] to **17**[12] (Table IV). Thus kijanose has the xylo configuration.

The EI mass spectra of **8** and **9** revealed no molecular ions, but ions at *m/e* 184, 172, 156, 140, and 128 were diagnostic for structures **8** and **9**. The CIMS gave MH^+ ions for **8** and **9** at *m/e* 263. Chemical proof for the presence of the nitro group was obtained by reduction of **8** and **9** by using Raney nickel to give **10** and **11** ($M^{+\cdot}$, *m/e* 232),[10] which on acetylation afforded **12** and **13**.[10]

The application of Hudson's Rules of Isorotation to **8** and **9**, $[M]_{D\alpha} - [M]_{D\beta} = 340.6° - 89.3° = 251.3°$, and **10** and **11**, $[M]_{D\alpha} - [M]_{D\beta} = 281.7° - (-11.4°) = 292.1°$, indicated a D-configuration. Recently L-rubranitrose (**19**)[13] was claimed to have the L-configuration by comparison of the CD of **19** with that of L-evernitrose.[14] The published rotation of **19** did not agree with an L-sugar.[13] Comparison of the CD data for **9** with that reported for 1-*O*-acetyl-β-L-rubranitrose (**19**) (R = Ac)[13] clearly indicates that both compounds have the same absolute stereochemistry. The published rotation for **19**[13] is also in agreement with a D-configuration. We therefore propose that rubranitrose is a D-sugar and that the correct structure is **20**. D-Kijanose represents the third naturally occurring nitro sugar to be discovered from an antibiotic.[15] The structure of the tetrasaccharide moiety and the location of the sugars on the aglycon in kijanimicin will be described in the following paper.

(9) K. Sato, M. Matsuzawa, K. Ajisaka, and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, **53**, 189 (1980).
(10) Full details will be published in *J. Chem. Soc., Perkin Trans. 1.*
(11) R. S. Jaret, A. K. Mallams, and H. Reimann, *J. Chem. Soc., Perkin Trans. 1*, 1374 (1973).
(12) P. Bartner, D. L. Boxler, R. Brambilla, A. K. Mallams, J. B. Morton, P. Reichert, F. D. Sancilio, H. Suprenant, G. Tomalesky, G. Lukacs, A. Olesker, T. T. Thang, L. Valente and S. Omura, *J. Chem. Soc., Perkin Trans. 1*, 1600 (1979).
(13) S. A. Mizsak, H. Hoeksema, and L. M. Pschigoda, *J. Antibiot.*, **32**, 771 (1979).
(14) A. K. Ganguly, O. Z. Sarre, A. T. McPhail, and K. D. Onan, *J. Chem. Soc., Chem. Commun.*, 313 (1977).
(15) Recently a nitro sugar having the same composition as D-kijanose has been isolated from the tetrocarcins,[7] but no structure has yet been published.

Kijanimicin. 2.[1] Structure and Absolute Stereochemistry of Kijanimicin

Alan K. Mallams,* Mohindar S. Puar, and Randall R. Rossman

Research Division, Schering-Plough Corporation Bloomfield, New Jersey 07006

Andrew T. McPhail*

Paul M. Gross Chemical Laboratory, Duke University Durham, North Carolina 27706

Ronald D. Macfarlane

Department of Chemistry, Texas A&M University College Station, Texas 77843

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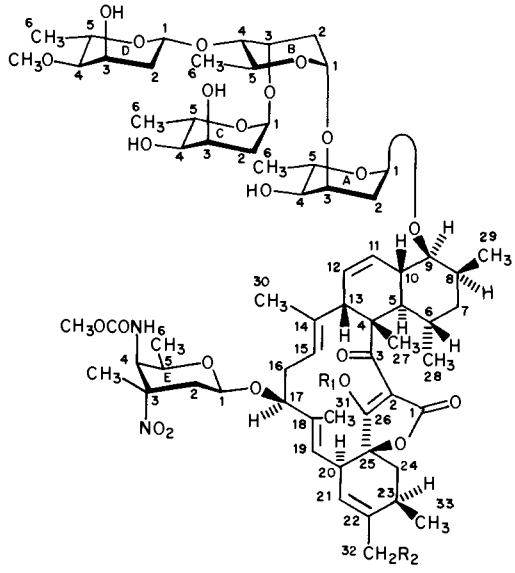
Kijanimicin[1] has been shown to have the novel tetronic acid structure **1**. Kijanimicin (**1**) was purified by preparative HPLC on silica gel using dichloromethane–methanol–triethylamine (98:1:1) as the eluant, affording a colorless amorphous solid, mp 174.5 °C dec; $[\alpha]_D$ −124.2° (CH_3OH); pK_a 5.0, λ_{max} (CF_3CH_2OH) 200 nm (ϵ 42 832), 241 (8946), 264 (sh) (9697), 274 (9446); λ_{max} (CH_3OH + 0.1 N HCl) 205 nm (ϵ 38 313), 258 (9881); λ_{max} (CH_3OH + 0.1 N NaOH) 236 nm (ϵ 14 677), 266 (sh) (12 002), 276 nm (12 002); ν_{max} ($CHCl_3$) 3625, 3550, 3480, 3440, 2980, 2940, 2910, 1755, 1730, 1605, 1545, 1510, 1230, 1130, and 1058 cm^{-1}. The above data suggested the presence of a tetronic acid moiety and hydroxyl, carbonyl, lactone, carbamate, nitro, and ether functions in the molecule. The ^1H NMR spectrum of **1** revealed methyl groups at δ_H ($CDCl_3$) (220 MHz) 0.65 (3 H, d, J = 5 Hz, 6-CH_3), 1.07 (3 H, d, J = 7 Hz, 8-CH_3), 1.18 (3 H, d, J = 6 Hz, 6^E-CH_3), 1.20–1.40 (envelope of CH_3 signals), 1.60 (3 H, s, 3^E-CH_3), 1.64 (3 H, s, 4-CH_3), 3.45 (3 H, s, 4^D-OCH_3) and 3.76 (3 H, s, 4^E-$NHCOOCH_3$). The ^{13}C NMR spectrum of **1** (Table I) revealed 67 carbon atoms of which five were anomeric carbons, indicating that **1** contains five sugars.[1] Although a satisfactory analysis (C, H, N) for **1** for $C_{67}H_{100}N_2O_{24}$ was obtained, it could not be used to unambigously establish the molecular composition. An EIMS of **1** gave the highest mass fragment ion at *m/e* 552 (2.1%). Kijanimicin (**1**) was therefore converted into 26-*O*-methylkijanimicin (**2**) by treatment with diazomethane. The 26-*O*-methyl group occurred as a singlet at δ_H ($CDCl_3$) (600 MHz) 4.12.[3] The EIMS, CIMS, and FDMS

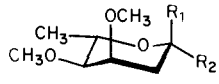
(1) Part 1: A. K. Mallams, M. S. Puar, and R. R. Rossman, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) R. D. Macfarlane and D. F. Torgerson, *Science (Washington, D.C.)*, **191**, 920 (1976). One of us (R.D.M.) gratefully acknowledges NIH Grant GM-26096.
(3) Full details will be published in *J. Chem. Soc., Perkin Trans. 1.*

0002-7863/81/1503-3940$01.25/0

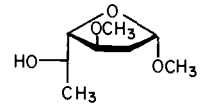
Chart I



1, R_1 = H; R_2 = OH
2, R_1 = CH_3; R_2 = OH
3, R_1 = H; sugars A–D = H; R_2 = OH
4, R_1 = CH_3; sugars A–D = H; R_2 = OH
5, R_1 = H; sugars A–D and E = H; R_2 = OH
6, R_1 = H; sugars A–D and E = H; R_2 = Cl
7, R_1 = H; sugars A–D and E = H; R_2 = OCH_3
8, R_1 = CH_3; sugars A–D and E = H; R_2 = OCH_3
9, R_1 = H; sugars A–D and E = CH_3; R_2 = OCH_3
10, R_1 = H; sugars A–D and E = Ac; R_2 = OCH_3
11, R_1 = CH_3; sugars A–D and E = Ac; R_2 = OCH_3
12, R_1 = H; sugar C = H; R_2 = OH



13, R_1 = OCH_3; R_2 = H
14, R_1 = H; R_2 = OCH_3



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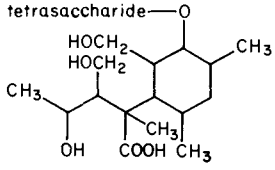
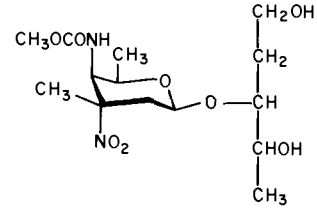


16



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on **2** all failed to give the molecular ion, and we therefore turned to ^{252}Cf-plasma desorption mass spectrometry (^{252}Cf-PDMS)[2] which gave a molecular weight for **2** of 1331.1 ± 0.4 which was in excellent agreement with a molecular composition of $C_{68}H_{102}N_2O_{24}$ (M_r 1330.68). The molecular weight of kijanimicin (**1**) was therefore unambiguously established, suggesting a molecular formula $C_{67}H_{100}N_2O_{24}$.

Mild acidic hydrolysis of **1** gave *O*-β-D-kijanosyl-(1→17)-kijanolide (**3**),[1] $[\alpha]_D$ −37.6° (CH_3OH); pK_a 4.8; λ_{max} (CH_3OH) 204 nm (ε 27738), 240 (10366), 266 (8244), 276 (7625); ν_{max} 3680, 3615, 3440, 2940, 1755, 1730, 1605, 1545, 1510, 1235, and 1060 cm^{-1}. The highest mass ion in the EIMS of **3** was at *m/e* 552. The ^{13}C NMR data for **3** are given in Table I, and it is evident from the $\Delta\delta_C$ values in going from **3** to **1** that the four digitoxose units are part of a tetrassaccharide moiety that is glycosidically linked to a secondary hydroxyl group at C_9 of the aglycone. Treatment of **3** with diazomethane gave the methyl ether **4**. The ^{252}Cf-PDMS of **4** indicated a M_r 796.8 ± 0.2 which was in agreement with a composition of $C_{43}H_{60}N_2O_{12}$ (M_r 797.0). The differences in composition between **4** and **2**, and between their ^{13}C NMR spectra, indicated that the tetrasaccharide was comprised of one 2,6-dideoxy-4-*O*-methyl-L-*ribo*-hexopyranose unit and three 2,6-dideoxy-L-*ribo*-hexopyranose units. The 600 MHz ^{1}H NMR spectrum[4] of **4** in $CDCl_3$ revealed a doublet of doublets at δ_H 4.46 ($J_{1^Eax,2^Eax}$ = 9.5 Hz, $J_{1^Eax,2^Eeq}$ = 1.9 Hz) due to H_{1^Eax}, indicating that the D-kijanosyl unit has a β-glycosidic linkage to the aglycon. The 600 MHz ^{1}H NMR spectrum[4] of **2** in CD_3CN revealed three additional doublet of doublet signals at δ_H 4.72 ($J_{1eq,2ax}$ = 4.5 Hz, $J_{1eq,2eq}$ < 0.5 Hz), 5.06 ($J_{1eq,2ax}$ = 4.0 Hz, $J_{1eq,2eq}$ < 0.5 Hz) and 5.13 ($J_{1eq,2ax}$ = 3.3 Hz, $J_{1eq,2eq}$ < 0.5 Hz) arising from the three equatorial anomeric protons of the L-digitoxose units, indicating that they were all present as α-glycosides. A doublet of occurred at δ_H 4.88 ($J_{1^Dax,2^Dax}$ = 10.0 Hz, $J_{1^Dax,2^Deq}$ = 1.9 Hz) due to H_{1^Dax} indicated that the 2,6-dideoxy-4-*O*-methyl-L-*ribo*-hexopyranose was present as a β-glycoside.

Acidic hydrolysis[1] of **3** gave methyl α- and β-D-kijanoside,[1] traces of kijanolide **5**, and also 32-chloro-32-deoxykijanolide (**6**).[3] Extensive decomposition of the aglycon occurred. Kijanimicin (**1**) was therefore exhaustively permethylated by using sodium hydride and methyl iodide in DMF, and the resulting per-N,O-methylated product was subjected to acidic hydrolysis by using 0.5 N hydrogen chloride in methanol at 25 °C for 20 h. The latter afforded **13**,[3] the β anomer **14**,[3] methyl 2,6-dideoxy-4-*O*-methyl-β-L-*ribo*-hexopyranoside,[1] the α anomer,[1] methyl 2,6-dideoxy-α-L-*ribo*-hexopyranoside,[1] the β anomer,[1] methyl 2,6-dideoxy-α-L-*ribo*-hexofuranoside,[1] and the β anomer,[1] which indicated that the tetrasaccharide moiety has a branch point. The acidic hydrolysis also produced *O*-(4^E-*N*-methyl-β-D-kijanosyl)-(1→17)-32-*O*-methylkijanolide[3] and some 32-*O*-methykijanolide (**7**). By increasing the reaction time to 43 h the yield of **7** was greatly improved, $[\alpha]_D$ −11.6° (CH_3OH); λ_{max} (CF_3CH_2OH) 245 nm (ε 7090), 262 (7976); ν_{max} 3610, 2960, 2920, 2880, 1748, 1058 cm^{-1}; *m/e* 566 (M^+·). The ^{13}C NMR data for **7** (Table I) indicated that no rearrangements had occurred during the acidic hydrolysis. The isolation of **7** enabled us to prepare 26,32-di-*O*-methylkijanolide **8**,[3] 9,17,32-tri-*O*-methylkijanolide (**9**),[3] 9,17-di-*O*-acetyl-32-*O*-methylkijanolide (**10**),[3] and 9,17-di-*O*-acetyl-26,32-di-*O*-methylkijanolide (**11**).[3] Analysis of the ^{13}C NMR data[3] and the fully decoupled 600-MHz ^{1}H NMR data[3,4] for **7**–**11** enabled us to assign all but two of the protons in kijanolide and revealed the structures of all of the proton containing fragments of the aglycone.

The diacetate **10** crystallized from chloroform–methanol.[5] The crystals belong to the orthorhombic system, space group $P2_12_12_1$, with a = 11.897 (5), b = 28.423 (11), c = 10.282 (4) Å; U = 3447 Å^3; Z = 4; d_{calcd} = 1.243 g cm^{-3}. The structure was solved by use of the MULTAN 76[6] program package incorporating the magic integer approach.[7] Approximate positions for 34 nonhydrogen atoms were obtained from an E map evaluated by use of the 400 largest $|E|$ values and a set of phase angles which yielded one of the highest combined figures of merit. The remaining 13 nonhydrogen atoms were then located in an F_o Fourier synthesis phased by this 34-atom fragment. Full-matrix least-squares refinement of positional and thermal parameters for all nonhydrogen atoms[8,9] converged at R = 0.067[10] over 1871 statistically significant [$I > 2.0\sigma(I)$] reflections measured[11] on an Enraf–Nonius CAD-3 automated diffractometer (Ni-filtered Cu K_α radiation, = 1.5418 Å θ-2θscans). A view of the structure and solid-state conformation

(4) The 600-MHz ^{1}H NMR spectra were recorded at Carnegie-Mellon University, Pittsburgh, PA, and NIH Grant RR00292 is gratefully acknowledged.

(5) A variety of salts, metal complexes, and iodobenzoyl derivatives of **1** and **3** had been prepared, and although some were crystalline, the crystals were not acceptable for X-ray analysis.

(6) P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J.-P. Declerq, "MULTAN 76, a System of Computer Programmes for the Automatic Solution of Crystal Structures", Universities of New York and Louvain, 1976.

(7) L. Lessinger and T. N. Margulis, *Acta Crystallogr., Sect. B* **B34**, 578 (1978).

(8) See paragraph at end of paper regarding supplementary material.

(9) Hydrogen atoms, save those on methyl carbons C(30), C(31), C(38), C(42), and C(45), were included at their calculated positions, but were not refined.

(10) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(11) R. W. Miller and A. T. McPhail, *J. Chem. Soc., Perkin Trans. 2*, 1527 (1979).

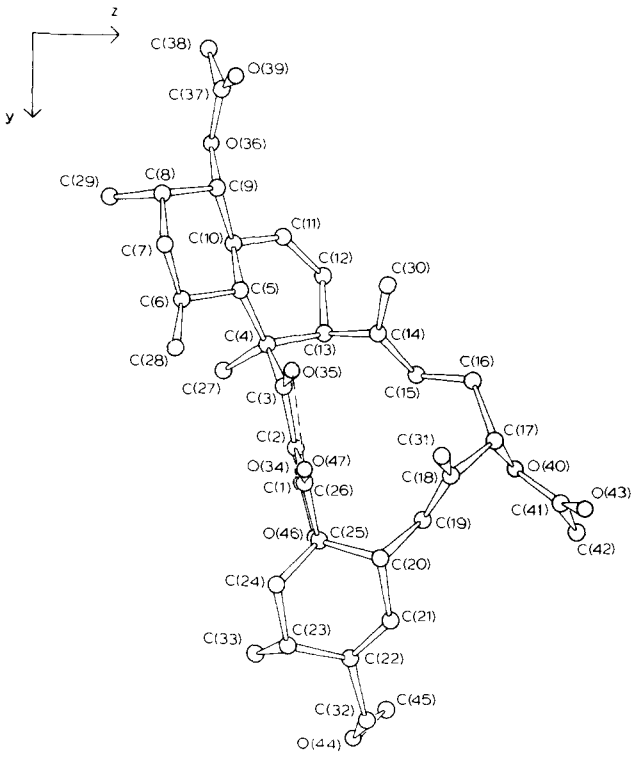

Figure 1. Structure and solid-state conformation of **10**.

is shown in Figure 1. The basic ring system in **10** differs from that found recently in tetronolide[12] only in the location of the double bond in one of the cyclohexene rings. The 600-MHz ^{1}H NMR data[3,4] indicate that a similar conformation exists in solution.

It remained now to complete the structure of the tetrasaccharide moiety and to determine the absolute stereochemistry of kijanolide. Controlled sodium metaperiodate oxidation of **1** afforded the monodesdigitoxosyl derivative **12** after treatment with Dowex 50W-X8 (H^+) resin. The ^{13}C NMR data for **12** are given in Table I. Exhaustive permethylation of **12** followed by acidic hydrolysis using 0.5 N hydrogen chloride in methanol afforded **13**,[3] the β anomer (**14**),[3] methyl 2,6-dideoxy-4-*O*-methyl-β-L-*ribo*-hexopyranoside,[1] the α anomer,[1] and **15**.[3] This hydrolytic data, coupled with that obtained when per-*N*,*O*-methylkijanimicin was subjected to acidic hydrolysis, could only be accommodated with two possible branched chain tetrasaccharide structures. One of these did not fit the ^{13}C NMR data (Table I) and was therefore excluded, leaving us with only one possible structure. The carbons of the terminal sugar D were readily assignable. The other terminal sugar C showed the expected chemical shifts for C_2–C_6. The anomeric carbon, however, was strongly shielded (δ_C 92.2). It was also apparent in going from **1** to **12** that almost no change was observed in δ_C for C_3 of the sugar B, in spite of the fact that the sugar C had been removed. The marked shielding of C_2 in sugar B in **1** was also removed when sugar C was removed to give **12**. These results are in excellent agreement with what one would expect from previous ^{13}C NMR studies carried out on 1-, 3-, and 5-*epi*-aminoglycoside antibiotics.[13,14] It is evident in **1** that the deshielding at C_3 of the sugar B resulting from the glycosidic linkage of sugar C is being cancelled out by the shielding produced by sugar C due to its conformation about the glycosidic linkage.[13,14] It is also apparent that similar shieldings are present at C_1 in the sugar B as well as at C_3 and C_2 in the sugar A in **1** and **12**. From the data in Table I it is evident that the tetrasaccharide moiety is glycosidically linked to kijanolide at C_9, while the D-kijanose moiety is located at C_{17}. Chemical proof for the location of the

Table I. ^{13}C NMR Data[d]

carbon	1	3	7	12
C_1	167.1 (s)	167.1 (s)	167.3 (s)	167.2
C_2	101.9 (s)	102.0 (s)	102.2 (s)	101.8
C_3	206.2 (s)	206.5 (s)	206.5 (s)	206.3
C_4	51.0 (s)	51.1 (s)	51.1 (s)	51.0
C_5	31.3 (d)[a,e]	31.2 (d)[a,e]	31.2 (d)[a,e]	31.3[a,e]
C_6	27.9 (d)[a]	28.0 (d)[a]	27.7 (d)[a]	27.9[a]
C_7	41.6 (t)	41.9 (t)	41.8 (t)	41.8
C_8	38.5 (d)	39.3 (d)	39.2 (d)	38.5
C_9	84.5 (d)	76.1 (d)	76.1 (d)	83.9
C_{10}	34.8 (d)	34.8 (d)	34.8 (d)	34.3
C_{11}	125.8 (d)	125.8 (d)	125.6 (d)	126.1
C_{12}	126.7 (d)	126.5 (d)	126.6 (d)	126.3
C_{13}	53.2 (d)	53.3 (d)	53.3 (d)	53.3
C_{14}	135.7 (s)	135.9 (s)	135.8 (s)	135.8
C_{15}	123.6 (d)	123.4 (d)	123.1 (d)	123.5
C_{16}	31.1 (t)	31.2 (t)	32.1 (t)	31.1
C_{17}	78.4 (d)	78.6 (d)	72.9 (d)	78.1
C_{18}	137.1 (s)	137.0 (s)	141.3 (s)	137.1
C_{19}	121.5 (d)	121.5 (d)	123.9 (d)	121.6
C_{20}	43.1 (d)[e]	42.9 (d)[e]	42.9 (d)[e]	43.2[e]
C_{21}	119.3 (d)	119.4 (d)	117.6 (d)	119.3
C_{22}	141.5 (s)	141.5 (s)	138.6 (s)	141.5
C_{23}	40.2 (d)	40.3 (d)	40.1 (d)	40.3
C_{24}	35.5 (t)	35.4 (t)	35.3 (t)	35.6
C_{25}	83.3 (s)	83.3 (s)	83.3 (s)	83.4
C_{26}	201.5 (s)	201.5 (s)	201.0 (s)	201.7
C_{27}	20.2 (q)	20.2 (q)	20.0 (q)	20.2
C_{28}	22.2 (q)	22.3 (q)	22.3 (q)	22.2
C_{29}	14.0 (q)	13.0 (q)	13.1 (q)	14.2
C_{30}	15.1 (q)	15.2 (q)	14.8 (q)	15.1
C_{31}	13.7 (q)	13.7 (q)	13.7 (q)	13.8
C_{32}	64.4 (t)	64.9 (t)	74.7 (t)	64.0
C_{33}	15.1 (q)	15.0 (q)	15.2 (q)	15.1
32-OCH_3			58.0 (q)	
C_1A	98.2 (d)			98.1
C_2A	29.9 (t)[b]			30.2
C_3A	66.8 (d)[c]			66.0[b]
C_4A	71.8 (d)			71.5
C_5A	65.1 (d)[c]			65.0[b]
C_6A	17.9 (q)			17.9[c]
C_1B	90.8 (d)			91.1
C_2B	29.7 (t)[b]			34.4
C_3B	62.6 (d)			62.1
C_4B	79.6 (d)			77.3
C_5B	67.1 (d)[c]			65.5[b]
C_6B	17.9 (q)			17.8[c]
C_1C	92.2 (d)			
C_2C	34.4 (t)			
C_3C	67.5 (d)			
C_4C	72.4 (d)			
C_5C	64.9 (d)			
C_6C	17.9 (q)			
C_1D	99.8 (d)			98.4
C_2D	36.8 (t)			36.9
C_3D	63.8 (d)			64.0
C_4D	82.6 (d)			82.3
C_5D	68.1 (d)			68.4
C_6D	18.4 (q)			18.3
4[D]-OCH_3	57.3 (q)			57.3
C_1E	97.1 (d)	97.1 (d)		96.9
C_2E	35.7 (t)	35.8 (t)		35.6
C_3E	91.0 (s)	91.2 (s)		91.1
C_4E	53.8 (d)	53.8 (d)		53.8
C_5E	69.1 (d)	69.2 (d)		69.1
C_6E	17.0 (q)	17.0 (q)		17.0
3[E]-CH_3	25.3 (q)	25.3 (q)		25.3
4[E]-$NHCOOCH_3$	157.4 (s)	157.4 (s)		157.7
4[E]-$NHCOOCH_3$	52.7 (q)	52.6 (q)		52.7

[a] May be interchanged in any vertical column. [b] Same as footnote *a*. [c] Same as footnote *a*. [d] Spectra recorded in $CDCl_3$. SFOR multiplicities are indicated in parentheses. [e] Same as footnote *a*.

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glycosidic linkages to the aglycon was obtained by subjecting **1** to ozonolysis followed by reduction with sodium borohydride to give **16** and **17**.[3]

Finally as a consequence of knowing the absolute stereochemistry of sugar A (L) and the nature of the glycosidic linkage to the aglycone (α),[15] as well as the relative stereochemical environment at C_8, C_9 and C_{10},[14] we were able to deduce the absolute stereochemistry of kijanimicin (**1**) from the observed glycosylation shifts in the ^{13}C NMR spectra in going from **3** to **1**. Thus the observed deshielding at C_9 (+8.4) coupled with the shielding at C_8 (-0.7) and absence of any shielding at C_{10} were in excellent agreement with the expected glycosylation shifts for an α-L-deoxysugar glycosidically attached to an aglycone having the stereochemical features present at C_8, C_9, and C_{10} in **1**.[14] It therefore follows that C_9 has the *S* configuration. Had the configuration at C_9 been *R*, then marked shielding would have been predicted at C_8, C_9, and at C_1 for sugar A[13,14] which was not the case.

It is therefore concluded that the total structure and absolute stereochemistry of kijanimicn may be represented by **1**. Kijanimicin (**1**) has antitumor activity and is active against *P.acnes* and is a member of a new class of tetronic acid containing antibiotics of which the tetrocarcins[12,16-18] and antlermicins[19,20] are the only other known members. The latter differ in the structure of the aglycon as well as in the structures of some of the glycosidic components, and full structures for these antiobiotics have not yet been published.

Supplementary Material Available: Table of positional parameters for the nonhydrogen atoms in **10** (2 pages). Ordering information is given on any masthead page.

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Electron-Impact-Induced Fragmentation of Quaternary Ammonium Cations

Mamoru Ohashi,† Robert P. Barron,* and Walter R. Benson

Food and Drug Administration, Division of Drug Chemistry Washington, D.C. 20204

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Recently Stoll and Röllgen as well as Cotter and Yergey have shown that tetraalkylammonium salts are evaporated and dissociated to yield the corresponding quaternary ammonium cation by simply heating the sample,[1] whereas Lee et al. proposed that electron impact is necessry to cause dissociation of gaseous quaternary ammonium salts to give the corresponding ammonium cation.[2] These reports prompted us to present our recent results on in-beam EI (desorption from extended probes) mass spectrometry[3] of these compounds. The series tetraethyl-, tetrapropyl-, tetrabutyl-, and tetrapentylammonium bromide was selected as typical and studied by the techniques of in-beam EI mass spectrometry and mass-analyzed ion kinetic energy spectrometry (MIKES) or the direct analysis of daughter ions (DADI).[4] Our results are summarized as follows:

(i) When the compound was loaded on a metal tip and inserted into the hot ion source (ca. 280 °C) and heated to 350 °C by the sample heater, or the compound was deposited on an unactivated FD wire of 10-μm diameter tungsten and quickly heated, only the corresponding tetraalkylammonium cation was recorded. Without an electron beam, no fragment ions were detected. This observation is consistent with that of Röllgen or Cotter and not with the results of Lee et al.

(ii) Then the electron beam (filament) was turned on and the in-beam EI spectra were recorded. A significant increase in the abundance of the quaternary ammonium cation was observed, which appears to be consistent with the observation of Lee et al. Two possible explanations are proposed for this increase: (a thermal dissociation of gaseous neutral molecules such as $(R_4N^+X^-)_n$ to the cation R_4N^+ on the hot surface[5] or (b) dissociation induced by electron bombardment.[2] Both processes are conceivable, but from observations at different positions of the tip relative to the electron beam, process b appears to be the major contributing factor. The in-beam EI spectrum of tetrabutylammonium bromide is shown in Figure 1 as a typical example. In addition to these peaks, weak but remarkable cluster ions were observed at *m/z* 563, 565 $[(R_4N^+)_2Br^-]^+$ and *m/z* 320, 322 $(R_4NBr - H)^+$. The major spectral features are very similar to those obtained by field desorption,[6] ^{252}Cf plasma desorption,[7] laser desorption,[7] and flash desorption.[2] If quaternary ammonium salts undergo thermal decomposition prior to electron impact[8] or chemical ionization[9] in the ion source as hitherto believed, fragment ions observed in this study are considered to be produced by electron-impact ionization of thermally degraded products such as tributylamine. However, the in-beam EI spectra exhibit very weak peaks corresponding to the molecular ion of butyl bromide,

Table I. MIKES and IKES of Tetraalkylammonium Cation

R	transition[a]	fragment ion (*m/z*)	E/E_0[b]	V/V_0[c]
Et	1	102 (a)	0.781	1.275
	2	101 (b)	0.776	1.288
	3	100 (c)	0.766	1.301
	4	86 (d)	0.659	*e*
Pr	1	144 (a)	0.774	1.290
	2	143 (b)	*d*	1.300
	3	142 (c)	0.762	1.309
	4	114 (d)	0.611	1.633
	5	43 (f)	0.229	*e*
Bu	1	186 (a)	0.768	1.302
	2	185 (b)	*d*	1.306
	3	184 (c)	0.761	1.314
	4	142 (d)	0.588	1.703
	5	57 (f)	0.233	*e*
Pn	1	228 (a)	0.765	1.307
	2	227 (b)	*d*	1.311
	3	226 (c)	0.757	1.317
	4	170 (d)	0.570	*e*

[a] See Figure 1. [b] MIKES of tetraalkylammonium cation. [c] IKES obtained by acceleration voltage scanning (V_0 = 1 kV). [d] Overlapping peaks. [e] No data obtained.

† Visiting scientist on leave from The University of Electro-Communications, Chofu, Tokyo 182, Japan.

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