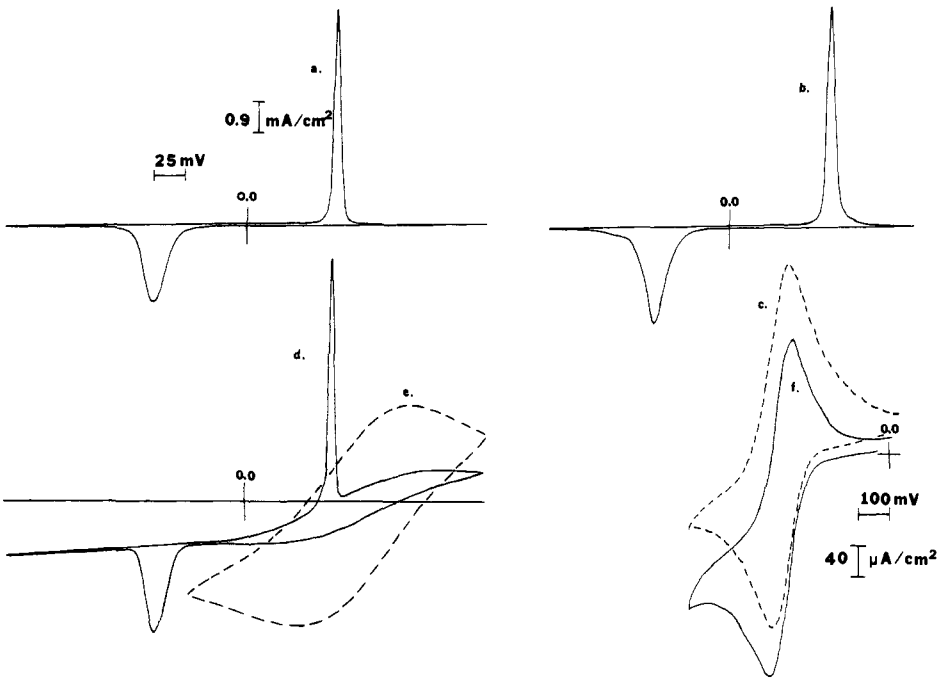

Figure 1. Cyclic voltammograms (10 mV/s) of (a) Pt/Nafion,TTF^+ electrode in 1 M KBr; (b) Pt/TFF (~800-Å thickness) electrode in 1 M KBr; (c) Pt/Nafion,Cp_2FeTMA^+ in 0.2 M Na_2SO_4; (d) Pt/Nafion,TFF^+ electrode in 0.08 M FeY^{2-}, 1 M KBr; (e) Pt electrode in same solution as (d); (f) Pt/Nafion,Cp_2FeTMA^+ electrode in 0.1 M FeY^{2-}, 0.2 M Na_2SO_4. All electrode potentials are given vs. SCE. Current and potentials scales given for (a) also supply to (b), (d), and (e). Potentials are negative to the right and cathodic currents are drawn upward.

covered with Nafion shows currents for FeY^{2-} and $Fe(CN)_6^{3-}$ at least 50 times smaller than that of a bare Pt electrode of the same area, so that transport of species through the film itself or via pin holes[2a] makes only a small contribution.

At this time the effect observed can best be explained as the formation of an internal TTF structure in the polymer film analogous to that found in TTF^+ salts,[5,7] especially after the polymer electrode has been taken through several cycles. Indeed after repetitive electrochemical cycling, observation of the electrode surface by scanning electron microscopy shows the formation of small (<1-μm diameter) needles of crystalline TTF Br on the surface of the polymer exposed to the solution, with some of these embedded into the Nafion surface. The behavior and formation of these crystals is currently under investigation. However, the enhanced conductive properties and color changes in the Nafion,TTF^+ electrodes are found even after a few cycles before large domains of crystalline TTF Br are apparent. One can also contrast the Nafion,TTF^+ electrodes with TTF films prepared by evaporation in terms of stability. The TTF Br film electrodes[7] are stable under cycling for only ~30 min, while the polymer electrodes can be cycled without change for at least several hours.

Moreover, incorporation of TTF^+ decreases the "dry" resistance of the Nafion film. The Nafion,TTF^+ layer on Pt was cycled in 1 M KBr, removed from solution, blotted dry, and allowed to dry in air for 10 min. A drop of Hg was placed on the polymer layer as an electrical contact. The i–V curve across the TTF-containing polymer between the Pt and Hg contacts was typically ohmic and independent of v and showed a resistance of ~3 kΩ. A Nafion,TTF electrode which had not been cycled showed a resistance of ~4 MΩ. A "dry" Pt/Nafion electode which does not contain TTF and was subjected to cycling in 1 M KBr shows purely capacitive behavior (i proportional to v and essentially independent of V). While the actual resistivity of the film cannot be computed from these measurements because of uncertainties in the nature of the Hg contact, the results clearly show the dramatic effect of incorporation of TTF^+ into the film.

These Nafion,TTF^+ films may find several applications, e.g., as electrochromic devices and in stabilization of semiconductor electrodes. Experiments with covalently attached polymer layers[9] or electrodeposited polypyrrole[4b] have shown that irradiated semiconductor electrodes (e.g., n-Si) in photoelectrochemical cells can often be stabilized by such layers. A critical factor in the design of such layers is the rate at which photogenerated charge in the semiconductor can be transported through them to solution species. The Nafion,TTF^+ layers look especially attractive for such an application and preliminary experiments have shown similar enhanced charge transport with these layers on semiconductors.[10]

(9) See, e.g.: Fischer, A. B.; Wrighton, M. S.; Umana, M.; Murray, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 3442 and references therein.

(10) The support of this research by the National Science Foundation (CHE 8000682) and the Solar Energy Research Institute is gratefully acknowledged.

Kijanimicin. 1. Structures of the Individual Sugar Components

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Kijanimicin,[1] the major component of a complex of antibiotics produced by *Actinomadura kijaniata* nov. sp.,[2] contains five sugars. Acidic hydrolysis of kijanimicin using 0.5 N methanolic hydrogen chloride at 25 °C for 16.5 h afforded methyl 2,6-dideoxy-4-*O*-methyl-β-L-*ribo*-hexopyranoside (**1**)[3] (Chart), mp 76.0 °C, $[\alpha]_D$ −12.4° (CH_3OH) and the α anomer (**2**) as a gum $[\alpha]_D$ −209.2°. The ^1H NMR (Table I), ^{13}C NMR (Table II) and mass

(1) Isolated from a culture of a soil sample collected in Kenya and named after the Swahili word "kijani" for green, which is the color of the fermentation broth. Kijanimicin is also referred to as SCH 25663.

(2) J. A. Waitz, A. C. Horan, M. Kalyanpur, B. K. Lee, D. Loebenberg, J. A. Marquez, G. Miller, and M. G. Patel, *J. Antibiotics*, in press.

(3) Unless otherwise stated in this and the following paper, all specific rotations were recorded in chloroform at 26 °C (*c* 0.3); IR and NMR spectra were recorded in $CDCl_3$ (reference Me_4Si). All compounds gave either satisfactory microanalyses or high-resolution mass spectral data.

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Table I. ^{1}H NMR Data

compd	1	2	3	8	9
H_1	4.73 dd	4.79 dd	4.78 dd	4.59 dd	4.47 dd
H_{2eq}	2.19 ddd	2.21 ddd	2.24 ddd	2.71 dd	2.69 ddd
H_{2ax}	1.62 ddd	1.87 ddd	1.81 ddd	1.78 dd	1.54 dd
H_{3eq}	4.28 ddd	4.24 ddd	5.76 ddd		
H_4	2.88 dd	2.87 dd	3.00 dd	4.40 dd	4.44 ddd
H_{5ax}	3.77 dq	3.99 dq	3.94 dq	4.22 dq	3.60 dq
6-CH_3	1.30 d	1.33 d	1.36 d	1.19 d	1.23 d
1-OCH_3	3.48 s	3.47 s[a]	3.49 s	3.19 s	3.51 s
3-CH_3				1.52 s	1.59 s
3-OH	2.34 s	1.61 bs			
3-OBz			7.40 m		
4-OCH_3	3.42 s	3.40 s[a]	3.37 s		
4-N*H*$COOCH_3$				5.00 d	5.14 d
4-NHCOO*C*H_3				3.70 s	3.75 s
$J_{1,2eq}$[b]	2.5	1.5	2.5	1	2.5
$J_{1,2ax}$	9.5	3.5	9	4	10
$J_{2eq,2ax}$	14	14	14	15	15
$J_{2eq,3eq}$	3.5	3	3.5		
$J_{2ax,3eq}$	3	3.5	3		
$J_{2eq,4eq}$					1
$J_{3eq,4ax}$	3	3	3		
$J_{4,5ax}$	9.5	10	9	1	1
$J_{4eq,4-NH}$				10	10
$J_{5ax,6}$	6	6	6.5	6	6

[a] May be interchanged. [b] J is in Hz.

Table II. ^{13}C NMR Data

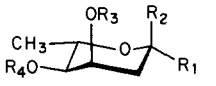
carbon	1	2	3	4	5	6	7	8	9	10	11
C_1	99.0	98.4	99.2	98.4	99.0 (d)	105.3	105.5	96.9 (d)	99.9	99.1	100.4
C_2	36.7	35.2	35.9	35.2	37.7 (t)	42.0	42.7	34.6 (t)	35.8	37.4	40.2
C_3	64.0	63.5	66.4	67.4	68.0 (d)	67.7	68.7	86.0 (s)	90.7	59.3	57.8
C_4	82.8	82.4	81.4	72.6	73.2 (d)	90.9	91.1	52.8 (d)	53.9	50.7	53.0
C_5	68.2	62.4	69.7	64.4	69.6 (d)	71.2	71.1	62.3 (d)	68.9	61.4	68.2
C_6	18.2	18.0	18.3	17.8	18.1 (q)	18.6	18.9	16.9 (q)	16.9	17.4	17.2
1-OCH_3	56.5	55.1	56.4	55.1	56.5 (q)	54.8	55.4	55.0 (q)	56.6	55.2	56.4
3-CH_3								26.4 (q)	25.4	23.1	30.7
3-O*C*OC_6H_5[a]			165.7								
4-OCH_3	57.3	56.5	57.5								
4-NH*C*OOCH$_3$								157.4 (s)	157.4	157.6	157.6
4-NHCOO*C*H_3								52.8 (q)	52.7	52.3	52.3

[a] Five signals were observed for the six aromatic carbons in 3 at 133.6, 133.1, 130.2, 129.8, and 128.5.

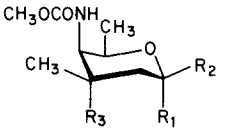
spectral data were in agreement with the proposed structures of these novel deoxysugars **1** and **2**. Benzoylation of **1** afforded the 3-*O*-benzoate **3**, mp 58–60.5 °C; $[\alpha]_D$ −31.4°; ν_{max} 1720, 1280 cm^{-1} (Tables I and II). The acidic hydrolysis also afforded methyl 2,6-dideoxy-α-L-*ribo*-hexopyranoside (methyl α-L-digitoxoside) (**4**), $[\alpha]_D$ −170.7°, the β anomer **5**, $[\alpha]_D$ +33.2°, methyl 2,6-dideoxy-α-L-*ribo*-hexofuranoside (**6**), $[\alpha]_D$ −135.8°, and the β anomer **7**, $[\alpha]_D$ +98.4°, as oils. The ^{1}H NMR data were consistent with data reported for methyl D-digitoxosides,[4] and only the ^{13}C NMR data (Table II) are reported here. In all of the above digitoxose derivatives the absolute stereochemistry was shown to be L by application of Hudson's Rules of Isorotation. This sugar was reported independently to occur in three polyene antibiotics,[5] as well as in the tetrocarcins[6] and antelermicins,[6,7] which are closely related to kijanimicin. The acidic hydrolysis also afforded *O*-β-D-kijanosyl-(1 → 17)-kijanolide.[8] From the ^{13}C NMR data of kijanimicin and the above compound,[8] it was evident that kijanimicin contains a tetrasaccharide unit comprised of one 2,6-dideoxy-4-*O*-methyl-β-L-*ribo*-hexopyranosyl unit and three α-L-digitoxosyl units.

Acidic hydrolysis of O-β-D-kijanosyl-(1 → 17)-kijanolide by using 5 N hydrogen chloride in methanol at 65 °C for 3 h afforded

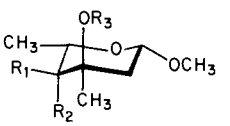
Chart I



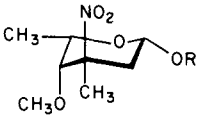
1, R_1 = OCH_3; R_2 = R_3 = H; R_4 = CH_3
2, R_1 = R_3 = H; R_2 = OCH_3; R_4 = CH_3
= OCH_3; R_2 = H; R_3 = Bz; R_4 = CH_3
4, R_1 = R_3 = R_4 = H; R_2 = OCH_3
5, R_1 = OCH_3; R_2 = R_3 = R_4 = H



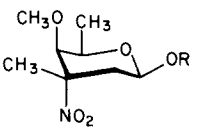
8, R_1 = OCH_3; R_2 = H; R_3 = NO_2
9, R_1 = H; R_2 = OCH_3; R_3 = NO_2
10, R_1 = OCH_3; R_2 = H; R_3 = NH_2
11, R_1 = H; R_2 = OCH_3; R_3 = NH_2
12, R_1 = OCH_3; R_2 = H; R_3 = NHAc
13, R_1 = H; R_2 = OCH_3; R_3 = NHAc



14, R_1 = OH; R_2 = R_3 = H
15, R_1 = R_3 = H; R_2 = $NHCOOCH_3$
16, R_1 = OPr; R_2 = R_3 = H
17, R_1 = OPr; R_2 = H; R_3 = Ac
18, R_1 = OAc; R_2 = R_3 = H



19



20

the novel nitro sugars methyl α-D-kijanoside (**8**) as a viscous gum, $[\alpha]_D$ +130.0° (CH_3OH); λ_{max} (CF_3CH_2OH) 199 nm (ε 4968);

(4) A. Zeeck, *Liebigs Ann. Chem.*, 2079 (1975).
(5) J. Zielinski, E. Jereczek, P. Sowinski, L. Falkowski, A. Rudowski, and E. Borowski, *J. Antibiot.* **32**, 565 (1979).
(6) F. Tomita, T. Tamaoki, K. Shirahata, M. Kasai, M. Morimoto, S. Ohkubo, K. Mineura and S. Ishii, *J. Antibiot.* **33**, 668 (1980).
(7) K. Kobinata, M. Uramoto, T. Mizuno and K. Isono, *J. Antibiot.* **33**, 244 (1980).
(8) The structure and physical data are given in the following paper.

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

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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 42832), 241 (8946), 264 (sh) (9697), 274 (9446); λ_{max} (CH_3OH + 0.1 N HCl) 205 nm (ϵ 38313), 258 (9881); λ_{max} (CH_3OH + 0.1 N NaOH) 236 nm (ϵ 14677), 266 (sh) (12002), 276 nm (12002); 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