$\times 10^{-5}$ sec^{-1} [1 atm of N_2] and $k_D = 4.2 \times 10^{-2}$ l. mole^{-1} sec^{-1}. Since $k_m[N_2] \ll k_D[Ru(NH_3)_5OH_2^{2+}]$ in the experiments performed, the steady state concentration of the monomeric species is established with a half-time determined by the pseudo-first-order constant $k_D[Ru(NH_3)_5OH_2^{2+}] \cong 4.2 \times 10^{-3}$ sec^{-1} at 0.1 *M* $Ru(NH_3)_5OH_2^{2+}$ (a typical concentration); for this condition $t_{1/2} \cong 3$ min. Measurements of heat production after ~10 min correspond, therefore, to the overall reaction.

$$N_2(g) + 2Ru(NH_3)_5OH_2^{2+} \longrightarrow (H_3N)_5RuN_2Ru(NH_3)_5^{4+} + 2H_2O \quad (3)$$

Observations were made over a total of 1–2% reaction. No account was taken of reversibility of the reactions, which were studied kinetically[3] to much greater extent of reaction than employed here. Experiments were run on two concentrations of the aquo complex, 0.1 and 0.03 *M*. Different partial pressures of nitrogen were also used so that various rates of nitrogen uptake were followed. The results for the steady state heat/mol of N_2 are given in Table I. As can be seen from these

Table I

Concn, *M*	$\Delta N_2/\Delta t$, μmol/sec	Heat/mol of N_2, kcal/mol
0.1	0.0020	−25 ± 2
0.1	0.0033	−26 ± 2
0.1	0.0036	−27 ± 2
0.03	0.0014	−22 ± 2
0.03	0.0011	−23 ± 2

results a value of −25 ± 2 kcal is obtained. The range of error must be regarded as an indication of the difficulty of measuring the small heats attending this reaction. There is no significant effect of the threefold concentration change outside of experimental error in these measurements. We therefore believe that conditions were clearly established where the heat effect is due to dimer formation and the enthalpy value of reaction 3 is −25 ± 2 kcal/mol.

The heat of reaction of dissolved nitrogen with the aquo ruthenium complex may be calculated from the above results. The heat of nitrogen dissolution

$$N_2(g) + aq \longrightarrow N_2(aq)$$

is estimated as −3.2 kcal at 25° from the temperature dependence of the Henry's law constants.[7] Therefore the reaction

$$N_2(aq) + 2Ru(NH_3)_5OH_2^{2+} \longrightarrow [(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$$

has a ΔH value of −22 ± 2 kcal at 25°.

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(7) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 256.

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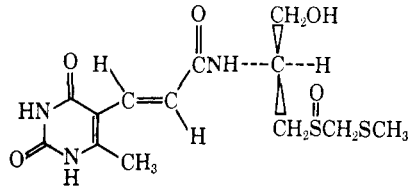
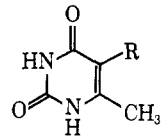
The Structure of Sparsomycin[1]

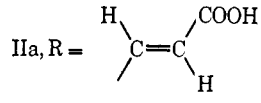
Sir:

The isolation of the antibiotic, sparsomycin, was reported some years ago by Argoudelis and Herr.[2] This communication presents evidence which establishes the structure of sparsomycin to be that represented by the expression I.

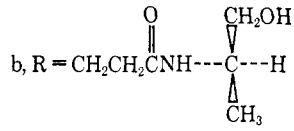


I





IIa, R =



b, R = CH_2CH_2CNH---C---H (with O and CH_2OH, CH_3)

c, R = CH_2CH_2COOH

The previously reported molecular formula for sparsomycin was $C_{13}H_{19-21}N_3O_6S_2$. It has been found that material which gives an analysis corresponding to the suggested molecular formula contains about 0.75 mol of water per mol of sparsomycin. Antibiotic dried under high vacuum at room temperature for 48 hr or more loses 80–90% of its water and gives analytical values[3] corresponding to the molecular formula $C_{13}H_{19}N_3O_5S_2$ which must be the correct one.

Mild acid hydrolysis of sparsomycin (2 *N* acid on the steam bath) resulted in isolation of a compound (IIa) having the molecular formula $C_8H_8N_2O_4$; mp 265° dec; pK_a's (DMF–60% EtOH) 7.90 and 11.35; $\lambda_{max}^{H_2O}$ 293 mμ (ε 14,210); $\lambda_{sh}^{H_2O}$ 270 mμ (ε 12,700); ν_{max} 3420, 3010, 1750, 1700, 1645, 1590, 1345, 1315, 1200, 1095, 1030, 992, 886, 785, and 722 cm^{-1}; nmr (DMF-d_7) δ 2.40 (s, 3 H), 7.25 (d of d, 2 H, J = 16 Hz), 10.0–11.6 (broad exchangeable H). The mass spectrum showed no molecular ion, but the methyl ester (prepared by the Fischer procedure, mp 305–307° dec) gave 210.0676. The spectral and analytical data derived from the eight-carbon acid are consistent with structure IIa which was synthesized by the following sequence. Chromic oxide oxidation of 5-hydroxymethyl-6-methyluracil gave 5-formyl-6-methyluracil, dec above 200°; infrared carbonyl band at 1740 cm^{-1}; $\lambda_{max}^{H_2O}$ 231 mμ (ε 6440) and 283 mμ (ε 9500); nmr (DMF-d_7) δ 2.54 (s, 3 H), 9.98 (s, 1 H). A Wittig reaction of the aldehyde with carbethoxymeth-

(1) This work was supported by Contracts PH43-62-168 and PH43-68-1023, with Chemotherapy, National Cancer Institute, National Institutes of Health, Bethesda, Md.
(2) A. D. Argoudelis and R. R. Herr, *Antimicrob. Ag. Chemoth.*, 780 (1962).
(3) All compounds gave either satisfactory combustion analyses or molecular formulas by mass spectrometry.

ylidenetriphenylphosphorane gave the ethyl ester of IIa, mp 299–302° dec; λ_{max}^{EtOH} 303 mμ (ε 17,875); λ_{sh}^{EtOH} 270 mμ (ε 9400); nmr (DMSO-d_6) δ 1.20 (t, 3 H, J = 7 Hz), 2.28 (s, 3 H), 4.13 (q, 2 H, J = 7 Hz), 7.13 (d of d, 2 H, J = 16 Hz), 11.27 (s, 2 H, exchangeable). Alkaline hydrolysis of the ester followed by acidification gave an acid which was identical with the eight-carbon acid from sparsomycin as judged by infrared, ultraviolet, and nmr spectra and by tlc in three solvent systems.

Heating a mixture of sparsomycin, water, and Raney nickel under reflux resulted in isolation of 2 mol of methane per mol of sparsomycin and a compound (IIb) having the molecular formula $C_{11}H_{17}N_3O_4$ (established by high resolution mass spectrometry) and melting at 231° dec. Alkaline hydrolysis of IIb followed by acidification gave another eight-carbon acid (IIc) which appeared to be the analog of IIa in which the *trans*-olefin system is reduced. The physical properties of IIc are mp 302–304° dec; $\lambda_{max}^{H_2O}$ 266 mμ (ε 8237); ν_{max} 3050, 1720, 1630, 1530, 1375, 1340, 1280, 1210, 1175, 870, 815, 792, and 725 cm^{-1}; nmr (DMSO-d_6) δ 2.08 (s, 3 H), 2.26–2.60 (m, 4 H), 10.63 (s, 1 H), 10.91 (s, 1 H); mass (*m/e*) 198.0646. The product was identified as 5-(β-carboxyethyl)-6-methyluracil (IIc) by comparison with an authentic sample synthesized by the procedure of Johnson and Heyl[4] for the carboxymethyl analog.

Freeze drying of the filtrate from IIc followed by treatment of the residue with benzoyl chloride in pyridine on the steam bath gave a compound which was purified by chromatography on silica gel using chloroform as the eluting agent. The compound, mp 87–89°, $[\alpha]_D$ −61.4° (*c* 1, $CHCl_3$), had a molecular formula of $C_{24}H_{21}NO_4$ established by high-resolution mass spectroscopy. The ir spectrum had no bands in the NH–OH region but had bands at 1720, 1660, 1595, and 1575 cm^{-1}. The synthetic tribenzoyl derivative of L-2-aminopropanol, mp 90–92°, $[\alpha]_D$ +63.2° (*c* 2, $CHCl_3$), nmr ($CDCl_3$), δ 1.59 (d, 3 H), 4.50–5.60 (m, 3 H), 7.0–8.0 (m, 15 H), mass (*m/e*) 387.1495, had an ir spectrum superimposable on that of the benzoyl derivative from sparsomycin. The two compounds also had identical R_f values (0.75) in tlc on silica using chloroform–methanol (95:5). These results establish that D-2-aminopropanol was formed by hydrolysis of IIb. The absence of a basic group in sparsomycin indicates that D-2-aminopropanol and IIc must be combined by an amide linkage to give a compound having the structure indicated in expression IIb. The nmr spectrum of sparsomycin shows two signals for methyl groups, both of them being singlets. Consequently it is apparent that the methyl group of D-2-aminopropanol is not present as such in sparsomycin as its nmr would contain a doublet for a CH_3C in such case. From this it seems that the atoms of sparsomycin removed by Raney nickel treatment must be attached at the carbon atom which becomes the methyl group of D-2-aminopropanol after desulfurization and hydrolysis. Such a hypothesis, in view of the molecular formula of sparsomycin, suggests that a $C_2H_5S_2O$ moiety is attached through a sulfur atom with the carbon–sulfur bond being cleaved by Raney nickel.

The nmr spectrum of sparsomycin indicates the presence of three methylene groups. One of these groups generates a doublet of doublets (δ 3.85 and 4.02) which must arise from a methylene having no adjacent hydrogen. A second methylene group is represented by a complex AB pattern (of an ABX system) and must be the methylene of the hydroxymethyl group as the signal shifts downfield on acylation. Another AB complex centered at δ 3.14 necessarily arises from the methylene group attached to sulfur which methylene group becomes the methyl group of D-2-aminopropanol. The value of the chemical shift is such that the sulfur atom must be oxidized either to sulfoxide or sulfone.[5] Of the nmr signals representing methyl groups, the one with a chemical shift of δ 2.30 must be a CH_3S group as the chemical shift is appropriate for such a system,[5] and this methyl group appears substantially downfield after treatment of sparsomycin with sodium periodate or hydrogen peroxide. There, then, remains a methylene group which must separate the two sulfur atoms. The AB pattern already mentioned no doubt arises from such a group. A combination of the above groups leads to the view that the moiety CH_3SCH_2SO is present in sparsomycin and is removed by Raney nickel treatment. Evolution of 2 mol of methane is to be expected from this fragment.

The combination of the above data points to I as the structure of sparsomycin.

Acknowledgments. We wish to express our gratitude to Dr. Marvin Grostic for his invaluable assistance with the mass spectra.

(4) T. B. Johnson and F. W. Heyl, *Am. Chem. J.*, **38**, 659 (1907).

(5) F. A. Bovey, "Nmr Data Tables for Organic Compounds," Vol. 1, Interscience Publishers, New York, N. Y., 1967, pp 152, 217–219.

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Isotopic Exchange Induced by Excitation of the Iodine–Iodobenzene Charge-Transfer Complex

Sir:

The photochemical isotopic exchange between radioactive iodine and iodoaromatic compounds has been the subject of several investigations.[1-3] The experimental observations were discussed in terms of two possible mechanisms, involving initiation *via* photodissociation of either iodine ($I_2 \xrightarrow{h\nu} 2I$ followed by $I + I^*I \rightarrow I^* + I_2$ and $PhI + I^* \rightarrow PhI^* + I$) or the iodoaromatics ($PhI \xrightarrow{h\nu} Ph + I$ followed by $Ph + I^* \rightarrow PhI^*$ or $Ph + I^*I \rightarrow PhI^* + I$).[4] However, no attempts have been made to carry out critical tests of such schemes. It is the purpose of the present communication to report experimental evidence indicating that, in iodine–iodobenzene methylcyclohexane solutions, the photochemical exchange is not induced by excitation of either I_2 or PhI, but rather by light absorption within the charge transfer (CT) band of the $PhI \cdot I_2$ complex. The results bear not only on the mechanism of isotopic exchange in iodoaromatic systems, but also on the chemical consequences of light absorption within CT bands, a problem which, in spite of the extensive

(1) R. M. Noyes, *J. Amer. Chem. Soc.*, **70**, 2614 (1948).
(2) R. M. Noyes and D. J. Sibbett, *ibid.*, **75**, 767 (1953).
(3) M. Anbar and R. Rein, *Chem. Ind.* (London), 1524 (1963).
(4) R. K. Sharma and N. Kharasch, *Angew. Chem. Intern. Ed. Engl.*, **7**, 36 (1968).