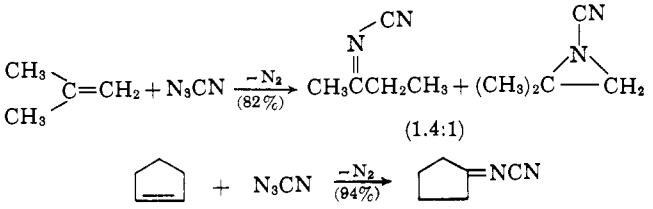
to avoid separating cyanogen azide from solution through evaporating low-boiling solvents, cooling saturated solutions, or freezing the solvent.

Cyanogen azide behaves principally as a highly reactive organic azide. It is reduced by hydrogen sulfide to cyanamide in 80% yield, and with triphenylphosphine **1** forms N-cyanotriphenylphosphinimide **2**, m.p. 193–195°, in 88% yield.

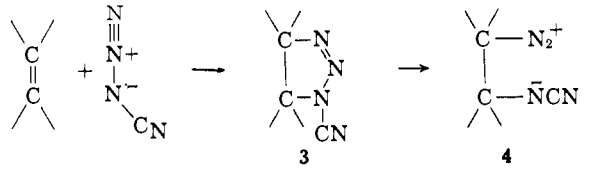
$$N_3CN + H_2S \longrightarrow H_2NCN + S + N_2$$

$$N_3CN + (C_6H_5)_3P \longrightarrow (C_6H_5)_3P{=}NCN + N_2$$

Cyanogen azide reacts rapidly with olefins at 0–35° to form alkylidene cyanamides and/or N-cyanoaziridines. The following examples illustrate the reaction.

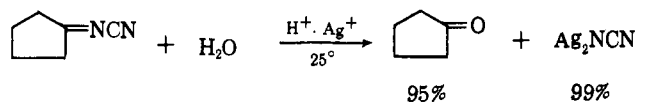


In all cases, the cyano-bearing nitrogen is found on the most highly substituted carbon of the olefin, and mechanism studies, including reaction kinetics, indicate that the rate-determining step is concerted addition of the polarized, electron-deficient azide group to the double bond to form an unstable triazoline **3**. The products and product ratios can be interpreted in terms of carbonium ion intermediates believed to arise *via* the zwitterion **4**. The reaction is potentially of con-



siderable mechanistic interest since it resembles the Tiffeneau–Demjanov reaction and may present the opportunity to study the behavior of aliphatic diazonium ions in aprotic media.

The alkylidene cyanamides are rapidly hydrolyzed by aqueous acid at room temperature to ketones and cyanamide, and the reaction is facilitated by silver ion, *e.g.*



This new ketone synthesis occurs without further rearrangement and is general.

Complete details on the chemistry of cyanogen azide will be published later.

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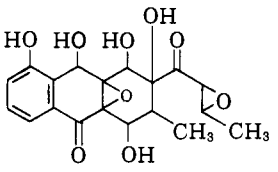
The Structure of Cervicarcin

Sir:

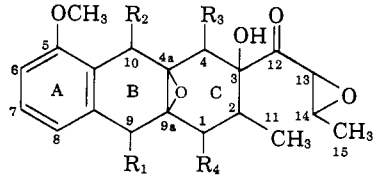
Cervicarcin[1] is an antitumor antibiotic[2] produced by *Streptomyces ogaensis*.[3] We wish to present evidence which enables the assignment of structure I to cervicarcin.



I

Cervicarcin, $C_{19}H_{20}O_9$, m.p. 205°, $[\alpha]^{26}D$ −59.7° (*c* 1.4, ethanol), is monophenolic (pK_a' 9.0 in 60% ethanol) and converted with diazomethane into methylcervicarcin (II), $C_{20}H_{22}O_9 \cdot 0.5H_2O$, m.p. 227°, ν^{KBr} 1720 and 1693 cm.$^{-1}$. The ultraviolet spectrum of cervicarcin, λ_{max}^{EtOH} 227, 264, and 323 mμ (ε 14,700, 7860, and 3700), was superimposable with that of 5-hydroxytetralone.[4] II was acetylated with acetic anhydride and sodium acetate to furnish a triacetate (III), $C_{26}H_{28}O_{12}$, m.p. 256°. The n.m.r. spectrum ($CDCl_3$)[5] showed the presence of three acetyl groups at δ 1.65, 2.04, and 2.11, and one hydroxyl at δ 3.61, indicating that four hydroxyls must be present in the molecule.

The n.m.r. spectra of cervicarcin were measured in pyridine and acetone solutions. In the latter solution absorptions of protons at 1, 4, and 10 positions are further split into AB types[6] as compared with those in pyridine, which disappeared upon adding a trace of acid, and which shifted to lower field upon acetylation,[7] indicating that those protons are attached to carbons bearing hydroxyl groups. Spin-decoupling experiments established relationships between ten hydrogens in cervicarcin; upon double irradiation at 14-H and at 2-H, multiplicity changes of 15-CH_3 (d → s) and 13-H (d → s), and of 11-CH_3 (d → s) and 1-H (d → s), respectively, were observed. The n.m.r. data afforded strong evidence for the proposed structure which was supported by the following additional chemical evidence.



II, R_1 = O, R_2 = R_3 = R_4 = OH
III, R_1 = O, R_2 = R_3 = R_4 = $OCOCH_3$
IV, R_1 = R_2 = R_3 = R_4 = OH
V, R_1 = R_2 = O, R_3 = R_4 = OH

(1) (a) K. Ohkuma, J. Nagatsu, C. Itakura, S. Suzuki, and Y. Sumiki, *J. Antibiotics, (Tokyo), Ser. A*, **15**, 152 (1962); (b) K. Ohkuma, S. Suzuki, C. Itakura, T. Sega, and Y. Sumiki, *ibid.*, **15**, 247 (1962).

(2) C. Itakura, T. Sega, S. Suzuki, and Y. Sumuki, *ibid.*, **16**, 231 (1963).

(3) J. Nagatsu, T. Sega, S. Suzuki, and Y. Sumiki, *ibid.*, **16**, 203 (1963).

(4) The sample of 5-hydroxytetralone was kindly supplied by Dr. Y. Ohkura, Faculty of Medicine, Kyushu University.

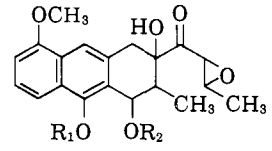
(5) N.m.r. spectra were measured at 60 Mc.; shifts are expressed as δ-values (p.p.m.) from tetramethylsilane as internal standard; coupling constants (*J*) are expressed in c.p.s.

(6) O. L. Chapman, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

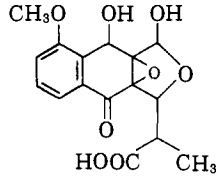
(7) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 55.

The α,β-epoxy ketone side chain was confirmed by: (1) periodate oxidation of methylcervicarcin glycol, $C_{20}H_{24}O_{10}$, m.p. 265°, obtained by acid treatment of II, which afforded acetaldehyde quantitatively; (2) heating of II with potassium iodide in acetic acid[8] produced deoxymethylcervicarcin, $C_{20}H_{22}O_8 \cdot H_2O$, m.p. 144°, which gave crotonic acid after periodate oxidation.

Potassium permanganate oxidation of II afforded 3-methoxyphthalic anhydride.[9] *meta* Relationship of the phenolic hydroxyl to aryl ketone was indicated by the fact that the pK_a value of cervicarcin is closer to that of *m*-hydroxyacetophenone (9.19)[10] than to that of the *ortho* analog (10.82).[11] Catalytic hydrogenation of III with platinum oxide in ethyl acetate produced a dihydro derivative (IV), $C_{26}H_{30}O_{12} \cdot 0.5H_2O$, m.p. 193°, λ_{max}^{EtOH} 282 and 274 mμ (ε 2400 and 2300), n.m.r. ($CDCl_3$) new singlets at δ 5.15 (1H) and 4.95 (OH) indicating there is no hydrogen on C-9a. Oxidation of II with chromium trioxide–pyridine[12] gave a triketo derivative (V), $C_{20}H_{20}O_9$, m.p. 128°. The ultraviolet spectrum, λ_{max}^{EtOH} 237 and 349 mμ (ε 12,500 and 4600), corresponded to that of β-hydrojuglone.[13] The proton at C-10 appeared at δ 6.42 as a singlet, suggesting the absence of a hydrogen on C-4a. II could be hydrogenolized with 30% palladium on carbon to a naphthalenic compound (VI), the structure of which was established on the basis of the following evidence: $C_{20}H_{22}O_6 \cdot H_2O$, m.p. 226°, ν^{KBr} 1720, 1595, and 1495 cm.$^{-1}$, λ_{max}^{EtOH} 235, 290, 303, 318, and 333 mμ (ε 73,800, 5530, 7080, 6410, and 5830). The diacetate (VII), $C_{24}H_{26}O_8$, had m.p. 240°, n.m.r. ($CDCl_3$) δ 0.99 (3H, d, J = 7), 1.45 (3H, d, J = 5), 2.18 (3H, s), 2.43 (3H, s), 2.69 (2H, s), 2.7 (1 H, m), 3.09 (1 H, m), 3.65 (1H, d, J = 2.5), 3.73 (1 H, s), 3.90 (3H, s), 6 54 (1 H, d, J = 2), and 6.6–7.9 (4H, m). Formation of VI supported a six-membered B-ring structure in cervicarcin and suggested the possibility that an epoxide might be situated at the B,C-ring juncture.



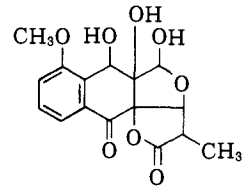
VI, $R_1 = R_2 = H$
VII, $R_1 = R_2 = OCOCH_3$
VIII, $R_1 = CH_3$, $R_2 = H$



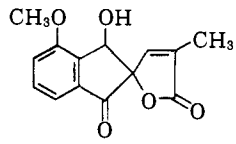
IX

II consumed two moles of sodium periodate with formation of two acids, one being cervic acid (IX), $C_{16}H_{16}O_8$, m.p. 180°, pK_a' 4.50, ν^{KBr} 1740 and 1692 cm.$^{-1}$, n.m.r. (pyridine) δ 1.80 (3H, d, J = 7.2), 3.49 (1 H, m, J = 7.2), 3.74 (3H, s), 5.52 (1 H, d, J = 7.2); (acetone) δ 3.96 (3H, s), 4.75 (1 H, d, J = 7.2), 5.54 (1 H, s), 6.73 (1 H, s), and 7.7–7.2 (3H, m). The pK_a value was consistent with β-hydroxycarboxylic acid structures[14] indicating that the carboxyl group, derived from C-3, originally the α-carbon in an α,β-dihydroxy ketone system which underwent oxidative cleavage, must be attached to C-2, the only carbon without oxygen. The structure of the C-ring is thus established.

There are two possible ways for rings B and C to be fused and this problem was solved by the following evidence. When IX was refluxed at pH 3, the epoxide was opened, giving cervilactone (X), $C_{16}H_{16}O_8$, m.p. 220°, ν^{KBr} 1780 and 1718 cm.$^{-1}$.[15] Periodate oxidation



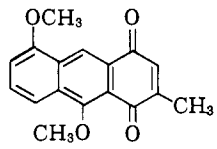
X



XI

converted X through decarboxylation followed by intramolecular aldol condensation and deformylation into XI, $C_{14}H_{12}O_5$, m.p. 141°, ν^{KBr} 1765 and 1735 cm.$^{-1}$, λ_{max}^{EtOH} 230, 260 (sh), and 315 mμ (ε 64,200, 19,100, and 5700), n.m.r. ($CDCl_3$) δ 1.95 (3 H, s, slightly coupled with the proton at 6.91),[16] 3.30 (OH), 3.94 (3 H, s), 5.61 (1 H, s), 6.91 (1 H, s),[17] and 7.1–7.6 (3H, m).

The evidence that the C-ring is six-membered was obtained from the transformation of VIII, m.p. 209°, by oxidation with chromium trioxide–pyridine into 2-methyl-5,9-dimethoxyanthra-1,4-quinone (XII), $C_{17}H_{14}O_4$, m.p. 238°. The ultraviolet spectrum was



XII

clearly related to the chromophore of anthra-1,4-quinone.[18] The n.m.r. spectrum ($CDCl_3$) showed methyl protons at δ 2.09 (3H, d, J = 1), methoxyls at δ 3.95 (6 H, s), and aromatic protons at δ 6.7–7.3 (5 H, m).

Thus the structure of cervicarcin, aside from its stereochemistry, was established as I, which also satisfies biogenetic considerations.

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