

The structure of carbomycin has been elucidated by WOODWARD et al.⁸

From these findings, the structure of maridomycin II was determined to be II. Its absolute configuration, except for the C₉-hydroxyl group, was also clarified. Further treatment of XXVI with KI in AcOH yielded dehydrode-epoxymaridomycin II which was identical with carbomycin B⁷ in all respects.

⁸ R. B. WOODWARD, *Angew. Chem.* 69, 50 (1957). – M. E. KUEHNE and B. W. BENSON, *J. Am. chem. Soc.* 87, 4660 (1965). – R. B. WOODWARD, L. S. WEILER and P. C. DUTTA, *J. Am. chem. Soc.* 87, 4662 (1965).

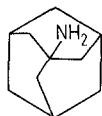
Zusammenfassung. Das aus *Streptomyces hygroscopicus* isolierte neue Makrolid Maridomycin II lässt sich mit Säure Mycarbose und Mycaminose spalten. Auf Grund der Oxidation ins Carbomycin sowie der spektroskopischen Daten wurde die Struktur als II erklärt.

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The Dissociation Constant of the 1-Aminoadamantane Cation

The p*K* value of 1-aminoadamantane (I) has not previously been reported. This omission is surprising in view of the unusual, diamond-like structure of this base and of the widespread interest in 1-aminoadamantane and its derivatives as antiviral and antitumour agents. From measurements of the enthalpy of sublimation, BRATTON and SZILARD¹ concluded that the structure of adamantane leads to a low strain energy, and this appears to be supported by the similarity of p*K*_a values for adamantane-1-carboxylic acid (6.81²) and cyclohexanecarboxylic acid (6.40³), measured in aqueous 50% ethanol at 25°.



(I)

On this basis, 1-aminoadamantane should be similar in strength to the corresponding alkyl analogues⁴, 2-amino-2-methylpropane (p*K*_a = 10.68⁵ at 25°) and 3-amino-3-ethylpentane (p*K*_a = 10.59⁵).

Solutions 0.005 *M* in 1-aminoadamantane hydrochloride (Fluka *purum*, recrystallized from ethanol/ethyl

ether) were titrated potentiometrically with 1 *M* carbonate-free potassium hydroxide under nitrogen, using the procedure of ALBERT and SERJEANT⁶. The ionic strengths of the solutions were varied from 0.005 to 0.105 by adding potassium nitrate. Free hydroxyl ion concentrations were calculated from the measured pH values, using the ionic product of water and DAVIES' equation⁷ to approximate the required activity coefficients at the specified ionic strengths. At each temperature and ionic strength, 9 points were taken covering the range from 1/10 to 9/10 neutralization, and the p*K*'_a values calculated for these points were averaged. (The maximum range in any set was within ±0.05 pH unit.) The resulting 'practical' p*K*_a values for 20° and 37° are given in the Table.

Extrapolation to zero ionic strength afforded thermodynamic p*K*_a values of 10.71 ± 0.01 at 20° and 10.14 ± 0.02 at 37°. For intermediate temperatures, values were 10.58 at 25°, 10.39 at 30° and 10.25 at 35°. A linear plot gave $-d(pK_a)/dT = 0.034$, in good agreement with a predicted⁸ value of 0.032.

The near-identity of p*K*_a values of 1-adamantane and 3-amino-3-ethylpentane supports the conclusion that there is little strain in this alicyclic molecule. Similar agreement is found for quinuclidine (10.58⁹ or 10.95¹⁰ at 25°) and its analogue, triethylamine (10.67¹¹ or 10.75¹² at 25°).

Zusammenfassung. Der p*K*_a-Wert des 1-Aminoadamantans zwischen 20° und 37° wurde durch potentiometrische Messungen bestimmt.

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p*K*'_a values

I =	0.005	0.010	0.015	0.030	0.055	0.105
20°	10.74	10.77	10.79	10.80	10.84	10.92
37°	10.12	10.21	10.23	10.26	10.30	10.34

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³ S. SIEGEL and J. M. KOMARMY, *J. Am. chem. Soc.* 82, 2547 (1960).

⁴ J. CLARK and D. D. PERRIN, *Q. Rev. chem. Soc.* 18, 295 (1964).

⁵ G. GIRAULT-VEXLEARSCHI, *Bull. Soc. chim. Fr.* 1956, 589.

⁶ A. ALBERT and E. P. SERJEANT, *The Determination of Ionization Constants*, 2nd edn (Chapman and Hall, London 1971).

⁷ C. W. DAVIES, *J. chem. Soc.* 1938, 2093.

⁸ D. D. PERRIN, *Austr. J. Chem.* 17, 484 (1964).

⁹ B. M. WEPSTER, *Recl. Trav. chim. Pays-Bas Belg.* 71, 1171 (1952).

¹⁰ C. A. GROB, A. KAISER and E. RENK, *Chem. Ind.* 1957, 598.

¹¹ W. S. FYFE, *J. chem. Soc.* 1955, 1347.

¹² W. C. SOMERVILLE, *J. phys. Chem.* 35, 2412 (1931).