The Structure of an Antibiotic, B-58941

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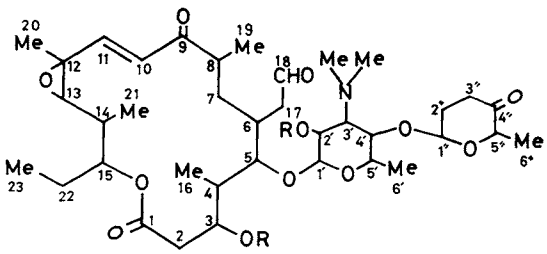
Streptomyces fradiae var. acinicolor B-58941 produced a basic macrolide[1] (I), $C_{37}H_{59}O_{12}N$, *m/e* 709 (M^+), mp 229°C, $[\alpha]_D^{22}$ −88.4° (*c* 1, $CHCl_3$), UV: 240 mμ (log ε: 4.21), IR: 2705, 1738, 1730, 1715, 1682, 1615 cm^{-1}, NMR*1: 9.71 (1H, COH), 6.54 (1H, d, 16Hz), 6.34 (1H, d, 16Hz), 2.52 (6H, $-NMe_2$), 1.40 (3H, –C–Me), 1.3—1.0 (15H, 5 *s*-Me), 0.87 (3H, t), similar to acumycin[2] and cirramycin B.[3]

I gave the diacetate (II), $C_{41}H_{63}O_{14}N$, mp 121°C, which lacked a free OH, and a monothiosemicarbazone which showed a new signal at 7.52 ppm (1H, t, $-N{=}CH{-}CH_2-$) in its NMR spectrum.

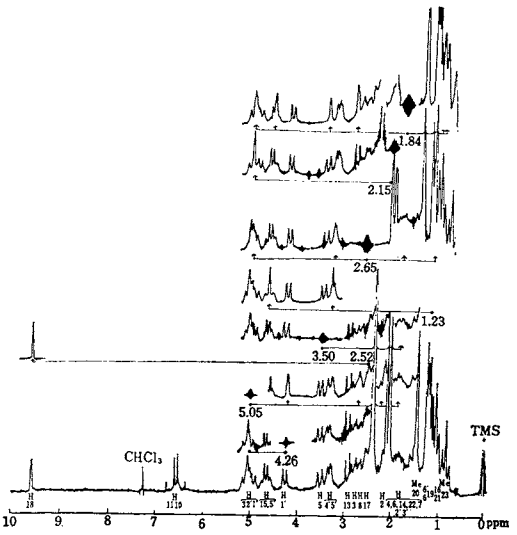
The mild hydrolysis of I afforded a neutral sugar (III), $C_6H_{10}O_3$, *m/e* 130 (M^+), UV: 280 mμ (log ε: 1.27), IR: 3420, 1720 cm^{-1}, NMR: 5.7—5.0 (1H, O–CH), 4.6—3.8 (1H, Me–CH), 2.3—1.8 (4H), 1.5—1.1 (3H, *s*-Me), positive to Fehling's reagent and iodoform reaction, and a basic substance (IV, B-58941-B), $C_{31}H_{51}O_{10}N$, mp 123°C, UV: 240 mμ (log ε: 4.11), IR: 2725, 1740—1710, 1687, 1620 cm^{-1}, which appeared to be very similar to cirramycin A_1 (CMA_1) in its physicochemical and biochemical properties. The periodate oxidation of III yielded one mole each of acetaldehyde and succinaldehydic acid. III was concluded to be 2,3,6-trideoxyhexopyranos-4-ulose.

From the hydrolysate of IV mycaminose[5] (V), $C_8H_{17}O_4N$, was obtained. The catalytic reduction of I gave a tetrahydro product which lacked an absorption maximum at 240 mμ and showed the presence of a new signal due to *s*-Me and the loss of the *t*-Me. The treatment of IV with KI-AcOH afforded a compound, UV: 281 mμ (log ε: 4.09), which showed a new signal at 1.78 ppm (3H, (s), C=C–Me).

The structure of CMA_1 has been proposed by Kawaguchi *et al.*,[4] but the position of the attachment of the macrolactone moiety ot V has not been established. The author has undertaken NMR spin-decoupling studies of II. As Fig. 1 shows, all the protons in II were unambiguously assigned, and the structure of IV was shown to be in good agreement with that of CMA_1. The signal due to H_3, which was coupled to H_2 and H_4, showed a downfield shift upon acetylation, whereas the signal due to H_5 (doublet-like) did not shift. This certainly establishes that the anomeric hydroxyl of V is combined with the C_5–OH of II. Since the anomeric H'_1 is coupled to H'_2, which shifts downfield upon acetylation, III should be bonding at the C'_4–OH of V. In conclusion, the structure I may be proposed for B-58941.



I R=H II R=Ac



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*1 Measured in $CDCl_3$, δ (ppm), 100 Mc.

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