26. Antibiotic X-5108. VI. Relative Configuration of the Tetrahydrofuran Moiety of Goldinamine[1][2])

Preliminary communication

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Zusammenfassung. Die relative Konfiguration des 3,4-dihydroxy-2,5-disubstituierten Tetrahydrofuranringes, ein Strukturelement des Antibiotikum X-5108 und Mocimycin, wurde durch NMR.-Spektroskopie unter Zuhilfenahme von Modellverbindungen bestimmt. Alle vier Substituenten liegen auf derselben Ringseite.

We have recently established structures **1** and **2** for antibiotic X-5108 (goldinodox[3]) and mocimycin [1–3]. It was shown that both compounds possess the same stereochemistry and differ in structure only by an N-methyl substituent [1]. The absolute stereochemistry of the goldinonic acid moiety [2] as well as the configuration of all double bonds in **1** and **2** was elucidated and a 1,2-*threo* relationship in the 5′ side chain of **1** and **2** was established [3]. This paper presents evidence for the assignment of the relative configuration of the 2,5-disubstituted 3,4-dihydroxytetrahydrofuran ring.

Coupling constants must be applied with caution to configurational assignments in 5-membered rings due to uncertainties of the preferred conformation of such cyclic systems in solution [4–5]. To stabilize the conformation of the tetrahydrofuran ring and thereby facilitate configurational assignments based on NMR. data, the vicinal diol of the tetrahydrofuran ring in the goldinamine moiety was made part of a bicyclic system. An empirical study of models **4–7** and related compounds [6–7] revealed coupling constants of 3–6.5 Hz for vicinal *cis* relationships, whereas *J*-values of no larger than 1 Hz were found for vicinal *trans* configurations. Specifically, $J_{3,4}$(*trans*) = 0 and 0.5 Hz was observed in **5** and **7**, respectively, compounds **4** and **6** exhibited $J_{3,4}$(*cis*) = 3.5 Hz, whereas $J_{2,3}$ *cis* = 6 Hz was revealed in **4–7**. To apply these findings to antibiotic X-5108 and mocimycin, N-(2,4-dinitrophenyl) goldinamine 4-bromobenzyl ether [3], derived from antibiotic X-5108, was acetalized to give the 3′,4′-O-isopropylidene derivative **3**, $\delta^{CDCl_3}_{TMS}$ at 220 MHz 3.56 (H-5′, $d \times d$, $J_{1,5'}$ = 6, $J_{4',5'}$ = 3.5 Hz), 3.98 (H-2′, $d \times d$, $J_{2',7''}$ = 8, $J_{2',3'}$ = 4 Hz), 4.62 (H-3′, $d \times d$, $J_{2',3'} = 4$, $J_{3',4'} = 6$ Hz) and 4.72 (H-4′, $d \times d$, $J_{3',4'} = 6$, $J_{4',5'} = 3.5$ Hz). The coupling constants $J_{2',3'}$ and $J_{4',5'}$ of **3** are comparable in magnitude with $J_{3,4}$ = 3.5-4 Hz of **4** and **6**, whereas $J_{3',4'}$ of **3** is identical with $J_{2,3}$ = 6 Hz observed in **4–7**, permitting the assignment of *cis* relationships between vicinal substituents of the tetrahydrofuran rings in **1** and **2**.

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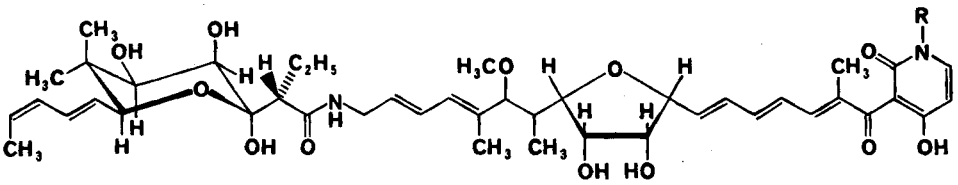
[1]) This paper was part of a presentation given at the Gordon Research Conference on Natural Products, New Hampton, N. H., July 31–Aug. 3, 1973.

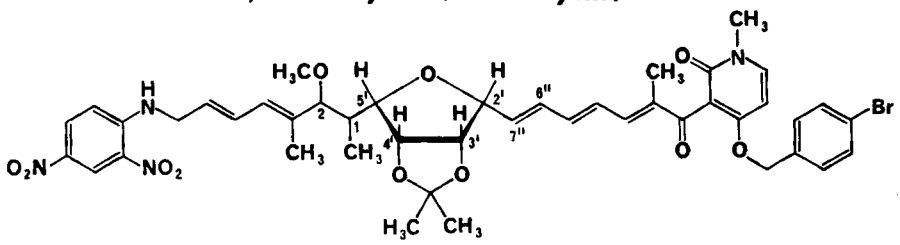
[2]) Paper V of this series, see [1].

[3]) Proposed nonproprietary name.



1: R = CH_3, Antibiotic X-5108 (Goldinodox)

2: R = H, Mocimycin (Delvomycin)



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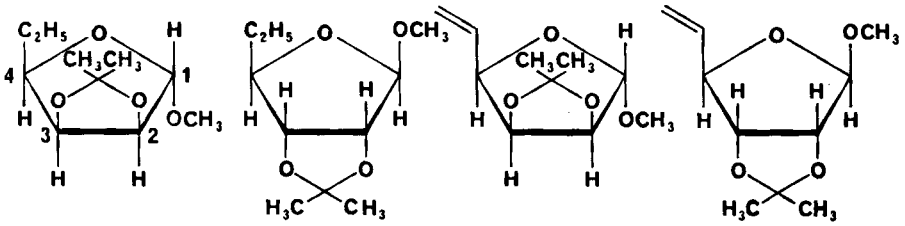

4 **5** **6** **7**

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