**Table I.** Partial $^1H$ NMR Spectra of Sibiromycin and Related Compounds[a]

| assignment | sibiromycin (**1**·$NaHSO_3$) | | anhydrosibiromycin[b] (**6**) | anthramycin[c] (**3**·$NaHSO_3$) | sibiromycin aglycone | |
|---|---|---|---|---|---|---|
| | | | | | (**2**·$NaHSO_3$)[c] | 2-imine |
| | δ | 2D-connectivity | δ | δ | δ | δ |
| 1α | 2.85–3.05 (m) | 3, 11a | 7.14 (d) | 3.0 (m) | d | 3.31 (dd) |
| 1β | | | | 3.2 (m) | d | 3.18 (dd) |
| 3 | 6.90 (s) | 1, 14 | 8.18 (d) | 7.38 (s) | 6.90 (s) | 6.90 (s) |
| 6 | 6.76 (s) | | 7.94 (s) | 6.97 (d) | 6.53 | 6.85 (s) |
| 11 | 3.91 (d) | 11a | 8.28 (s) | 4.00 (d) | 3.87 (d) | 7.82 (d) |
| 11a | 4.11 (dt) | 1, 11 | | 4.28 (dt) | 4.3 (m) | 4.3–4.4 (m) |
| 12 | 6.31 (d) | 13, 14 | 6.37 (d) | 7.31 (d) | 6.30 (d) | 6.33 (d) |
| 13 | 5.41 (dq) | 12, 14 | 6.21 (dq) | 5.79 (d) | 5.6 (dq) | 5.67 (dq) |

[a] Chemical shifts (δ) are reported in ppm, relative to $(CH_3)_4Si$. Two-dimensional connectivities were determined with a COSY program. The spectrum of **1** was obtained in DMSO-$d_6$. [b] *Reference* 7b. [c] The anthramycin and sibiromycin aglycone bisulfite adducts were obtained by adding 4 equiv of $Na_2S_2O_5$ in $D_2O$ to DMSO-$d_6$ solutions of these compounds. [d] Signal obscured.

were shown to be consistent with the connectivities determined by 2D homonuclear correlation NMR spectroscopy (Table I), providing further support for the proposed dihydropyrrole structure.

The revised structure **1** for sibiromycin has been confirmed by total synthesis of sibiromycin aglycone (**2**).[12] Comparison of the $^1H$ and $^{13}C$ NMR spectra of **1** and **2** indicated a correspondence in the chemical shifts and multiplicities for the atoms shared in common.[13] We suggest that the error in the original structure assignment of sibiromycin[14] can be attributed to a facile oxidative aromatization of the dihydropyrrole moiety under acidic conditions, such as those used to dehydrate the carbinolamine during the original structure determination.[4]

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**Supplementary Material Available:** Table of $^1H$ and $^{13}C$ NMR spectral data of sibiromycin and related compounds (2 pages). Ordering information is given on any current masthead page.

(11) The chemical shift values for C-11 H of the carbinolamine form of anthramycin methyl ether[10] and our synthetic sibiromycin aglycone[12] were δ 4.78 and 4.71, respectively. In DMSO-$d_6$ the NMR spectrum of the sibiromycin sample (NSC 291320 ND) used in this study consisted only of signals corresponding to a derivative hydrated at C-11. Under the same conditions anthramycin and sibiromycin aglycone exhibited spectra for the imine form only, with carbinolamine signals appearing on addition of $D_2O$. These data, along with the differences in chemical shift of the C-11 H signals, indicated that the sibiromycin sample had been converted to the more stable bisulfite adduct, probably during isolation (see ref 4a).

(12) Hoover, J. R. E.; Leber, J. D.; Holden, K. G.; Hecht, S. M., in preparation.

(13) Complete $^1H$ and $^{13}C$ NMR spectra for **1**, **2**, **3**, and **6** are included as Supplementary Material.

(14) In trifluoroacetic acid (25 °C) anthramycin was dehydrated and aromatized to afford **8** in approximately 50% yield (Malhotra, R. K.; Ostrander, J. M.; Hurley, L. H.; McInnes, A. G.; Smith, D. G.; Walter, J. A.; Wright, J. L. C. *J. Nat. Prod.* **1981**, *44*, 38). The aromatization was assumed to occur through disproportionation, although coformation of a reduced product **9** was not explored. Upon reinvestigation of this reaction, we obtained both **8** and **9** ($m/z$ 309.1352); however, the latter was present to a lesser extent than **8**. In addition, we have observed that sibiromycin and anthramycin were dehydrated and aromatized, without disproportionation, when dilute solutions of the antibiotics in DMSO-$d_6$ (NMR sample) were acidified without prior removal of dissolved air. Aromatization did not occur when the solutions were degassed and purged with argon.

# *Additions and Corrections*

**Rates and Mechanisms of Hydrolysis of Esters of Phosphorous Acid** [*J. Am. Chem. Soc.* **1988**, *110*, 181–185]. F. H. WESTHEIMER,* SHAW HUANG, and FRANK COVITZ

Page 182: The names appearing in lines 9 and 12 of Table I should read "dimethyl hydrogenophosphonate" (instead of "dimethyl hydrogen phosphate"), and "diethyl hydrogenphosphonate" (instead of "diethyl hydrogen phosphate"), respectively. The name appearing on line 3 of Table II should read "trimethyl phosphite" (instead of "trimethyl phosphate").