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Addendum: Cryptic phosphorylation in nucleoside natural product biosynthesis

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After publication, we identified errors in the stereochemical assignments of two compounds in the original published work and, through this addendum, correct these assignments. Upon further characterization studies of 5′-amino-6′-hydroxy-octosyl acid (AHOA), we are revising its stereochemistry, and that of AHOAP (**16**), at the 4′, 5′, 6′, and 7′ positions (Supplementary Fig. 17a,b). In our recent characterization of AHOA by two-dimensional Nuclear Overhauser Spectroscopy (NOESY) experiments, the data revealed a strong correlation between proton signals at δ 4.42 and 3.95 ppm (red dashed circle in Supplementary Fig. 17c). Originally, these two signals were assigned as H2′ and H6′, respectively. However, they are positioned on opposite sides of the molecule and too spatially separated (~5.9 Å) to yield a strong NOESY correlation. Consequently, we revisited the original ^{1}H NMR assignment and noticed an alternative interpretation of the original ^{1}H-^{1}H COSY data (compare Supplementary Fig. 17e,f). This alternative assignment was also consistent with the newly determined HMBC spectrum of AHOA (Supplementary Fig. 17g), in which the observed H1′-C2′ and H7′-C8′ correlations are consistent with the alternative assignment and inconsistent with the original assignment. With this alternative assignment, analysis of *J*-coupling constants suggested a revised stereochemistry of AHOA (Supplementary Figure 17b). This structure is fully consistent with the NOESY data (Supplementary Fig. 17d), and all the NOESY correlations are between protons with distances within 2.6 Å. Furthermore, the revised structure eliminates the requirement for the epimerization originally proposed to occur during the transformation of HKOAP to AHAP via AHOAP. The structures of AHOA and AHOAP in Figs. 1, 3, and 5, Extended Data Fig. 10, Supplementary Fig. 9 and the Supplementary Note and the corresponding text have now been corrected. Supplementary Fig. 17 has been added to the Supplementary Information, and the new NOESY and HMBC spectra have also been added to the Supplementary Note.

Supplementary Material

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