



FIG. S3. Absolute configuration of constituent amino acids of signermycin B was determined using the advanced Marfey method. Signermycin B was recrystallized from the solvent system of MeOH–H₂O to obtain colorless platelets. A single platelet crystal was analyzed by x-ray crystallography to elucidate the relative stereochemistry. To clarify the absolute stereostructure, signermycin B was degraded to afford alanine by periodate oxidation at room temperature for 18 h, followed by acid hydrolysis with 6 M HCl at 105°C for 15 h. The absolute stereochemistry of the isolated alanine was determined to be S by the advanced Marfey method (20). The absolute stereostructure of signermycin B was elucidated in Fig. 2.