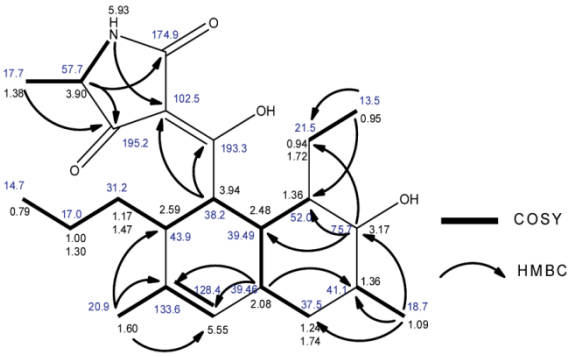

FIG. S2. Two-dimensional NMR analysis of signermycin B. Analysis of the ^{1}H-^{1}H correlation spectroscopy of signermycin B revealed the five partial structures drawn with bold lines: from methyl proton at δ 0.79 (H14) to 1.00, 1.30 (H13), 1.17, 1.47 (H12), 2.59 (H11), 3.94 (H2), 2.48 (H3) (the proton of which branched to 1.36 (H4) and to 2.08 (H8), and 1.24), 1.74 (H7); from δ 0.95 (H16) to 0.94, 1.72 (H15); from δ 1.09 (H17) to 1.36 (H6); from δ 1.38 (H6') to 3.90 (H5'), and 5.93 (H1'); and long-range coupling from δ 1.60 (H18) to 5.55 (H9). The connectivities of these partial structures were determined by heteronuclear multiple bond correlation (HMBC). The long-range ^{1}H-^{13}C couplings from δ1.60 to δ133.6 (C10), 43.9 (C11), and 128.4 (C9), from the methine proton at δ 2.08 to δ 128.4, 133.6, and 41.1, from the methyl proton at δ1.09 to δ 37.5 (C7), 41.1, and 75.7 (C5), from the oxymethine at δ 3.17 (H5) to δ 52.0 (C4), 21.5 (C15), and 39.5 (C3), and from the methyl proton at δ0.95 to δ21.5 (C16), and 52.0 revealed the decalin ring structure. The tetramic acid moiety described above was further determined by HMBC, from the methyl proton at δ 1.38 to δ 57.7 (C6') and 195.2 (C5'), from the nitrogen-bearing methine proton at δ 3.90 (δ 57.7, C5') to δ174.9 (C2'), and 195.2, and from the NH proton at δ5.93 to δ102.5 (C3'). Finally, the long-range connections from the methine proton at δ 3.94 to δ193.3 (C1) and 102.5 revealed the connectivity of a tetramic acid moiety and attached to C2 of the decalin ring. The planar structure of signermycin B was elucidated as shown in Fig. 1.