

9 H), 2.07 (s, 9 H), 3.73 (br s, 2 H), 4.15 (q, 1 H,  $J = 2$  Hz), 4.62 (q, 1 H,  $J = 2$  Hz); GC-MS  $m/z$  304 ( $M^+$ ), 247 (base).

**Spiro[2,3-dihydro-5-(*tert*-butyldimethylsiloxy)-4,6,7-trimethylbenzofuran-2,1'-cyclopropane]**. Cyclopropanation of 11 was conducted according to the method of Furukawa et al.<sup>16</sup> A 1.29-g sample of 11 (4.24 mmol) was dissolved in 6 mL of dry diethyl ether. To this solution, under argon, was added a 1 M solution of diethylzinc in hexanes (3.3 mL, 3.30 mmol) and diiodomethane (0.42 mL, 5.3 mmol). The reaction mixture was refluxed under argon for 4 h, held at ambient temperature for 8 h, and then quenched with water (10 mL). Following extraction of the mixture with diethyl ether (4 × 15 mL), the combined organic solutions were washed with brine and dried ( $Na_2SO_4$ ). Filtration and concentration afforded the desired product (93% yield) as an off-white solid. Spectral data:  $^1H$ -NMR (90 MHz)  $\delta$  0.10 (s, 6 H), 0.65 (br s, 2 H), 1.13 (br s, 2 H), 2.08 (br s, 9 H), 3.27 (br s, 2 H); GC-MS  $m/z$  318 ( $M^+$ ), 261; HRMS  $m/z$  calcd 318.20151, found 318.20118.

**Spiro[2,3-dihydro-5-hydroxy-4,6,7-trimethylbenzofuran-2,1'-cyclopropane]** (5). A 196-mg sample of spiro[2,3-dihydro-5-(*tert*-butyldimethylsiloxy)-4,6,7-trimethylbenzofuran-2,1'-cyclopropane] (0.62 mol) was stirred with tetrabutylammonium fluoride (489 mg, 1.55 mmol) in 11 mL of dry THF. After 1.5 h the solution was diluted with water (20 mL) and washed with diethyl ether (5 × 10 mL). The pooled extracts were washed with brine (20 mL), dried ( $Na_2SO_4$ ), and concentrated to afford 115 mg (92% yield) of crude phenol 4. Sublimation (95 °C (0.25

mmHg)) provided 4 as a white microcrystalline solid, mp 179–182 °C. Spectral data:  $^1H$ -NMR (DMSO- $d_6$ )  $\delta$  0.70 (m, 2 H), 1.2 (m, 2 H), 1.93 (s, 3 H), 2.03 (s, 6 H), 3.15 (s, 2 H), 7.50 (s, 1 H);  $^{13}C$ -NMR (DMSO- $d_6$ )  $\delta$  12.07, 12.43, 13.30, 35.94, 66.25, 114.30, 118.85, 122.28, 122.77, 146.22, 150.72; GC-MS  $m/z$  204 ( $M^+$ ), 189 (base), 176; HRMS  $m/z$  calcd 204.11503, found 204.11468. Anal. Calcd for  $C_{13}H_{16}O_2$ : C, 76.44; H, 7.90. Found: C, 76.26; H, 8.00.

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**Supplementary Material Available:**  $^1H$ -NMR spectra of 2-allyl-1,4-diacetoxy-3,5,6-trimethylbenzene, 2',5'-diacetoxy-3',4',6'-trimethylphenylacetaldehyde, 2',5'-diacetoxy-3',4',6'-trimethylphenylacetic acid (9), 5-(*tert*-butyldimethylsiloxy)-2-methylene-4,6,7-trimethyl-(3*H*)-benzofuranone, 5-(*tert*-butyldimethylsiloxy)-2-methylene-4,6,7-trimethyl-(3*H*)-benzofuran (11), and spiro[2,3-dihydro-5-(*tert*-butyldimethylsiloxy)-4,6,7-trimethylbenzofuran-2,1'-cyclopropane] (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

## Additions and Corrections

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**Dale L. Boger,\* Royce F. Menezes, and Qun Dang.** Synthesis of Desacetamidopyrimidoblastic Acid and Deglyco Desacetamidobleomycin  $A_2$ .

Page 4336. Text was inadvertently published in the Acknowledgment section. The last paragraph and Acknowledgment should read as follows.

A preliminary study of the ability of the Fe(II) complex of 4 to cleave duplex DNA was conducted through examination of single-strand and double-strand cleavage of supercoiled  $\phi$ X174 RFI DNA (Form I) to produce relaxed (Form II) and linear (Form III) DNA, respectively. Like Fe(II)-bleomycin  $A_2$ <sup>17</sup> and deglycobleomycin  $A_2$ <sup>17</sup>, Fe(II)-4 produced both single- and double-strand cleavage of  $\phi$ X174 RFI DNA, Figure 2. The direct comparison of the efficiency of DNA cleavage by Fe(II)-4 and Fe(II)-deglycobleomycin  $A_2$  permits the assessment of the relative importance and functional role of the pyrimidoblastic acid C2 acetamido side chain. Although the side chain has been shown not to be intimately involved in the metal chelation, it has been suggested to contribute to the efficiency of DNA cleavage by constituting one side or component of the oxygen binding pocket thereby sterically shielding or protecting the activated and reactive iron-oxo intermediate.<sup>1</sup> Consistent with this latter suggestion, Fe(II)-de-

glycobleomycin  $A_2$  proved to be 3–5× more effective than Fe(II)-4 in its efficiency for producing the cleavage of supercoiled  $\phi$ X174 RFI DNA, Figure 3 [relative efficiency: bleomycin  $A_2$  (1), deglycobleomycin  $A_2$  (0.5–0.2), 4 (0.2–0.05)]. Under the conditions of the assay, both Fe(II)-deglycobleomycin  $A_2$  and Fe(II)-4 produced little or no cleavage at 0.2  $\mu$ M, significant cleavage at 1  $\mu$ M, and complete cleavage at 5  $\mu$ M. Both agents proved to be slightly less efficient than Fe(II)-bleomycin  $A_2$  which produced significant cleavage of the supercoiled DNA at concentrations as low as 0.2  $\mu$ M with complete cleavage of the DNA at 1  $\mu$ M. Consistent in each of multiple assays, Fe(II)-deglycobleomycin  $A_2$  proved at least as effective in producing linear DNA resulting from double-stranded DNA cleavage as Fe(II)-bleomycin  $A_2$  itself which in turn generally proved more effective than Fe(II)-4. Detailed studies of the DNA cleavage properties of Fe(II)-4 including additional comparison of its duplex DNA cleavage efficiency and selectivity with that of bleomycin  $A_2$ , deglycobleomycin  $A_2$ , and structurally related analogs are in progress and will be reported in due course.

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