Supporting Information: Independent Generation and Study of 5,6-Dihydro-2'-deoxyuridin-6-yl. A Member of the Major Family of Reactive Intermediates Formed in DNA from the Effects of γ -Radiolysis.

K. Nolan Carter and Marc M. Greenberg*
Department of Chemistry
Johns Hopkins University
3400 N. Charles St., Baltimore, MD 2128

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5'-Benzoyl-5,6-dihydro-2'-deoxyuridine (10a). To a solution of 5,6-dihydro-2'-deoxyuridine (100 mg, 0.43 mmol) and Et₃N (57 mg, 0.56 mmol) in DMF (4.0 mL) at -40 °C was added benzoyl cyanide (57mg, 0.43 mmol). The reaction was stirred overnight and allowed to warm to ambient temperature. The reaction was quenched with H₂O and diluted with EtOAc. The crude reaction mixture was washed with H₂O, brine, dried over Na₂SO₄ and concentrated. The crude product was purified via silica gel flash chromatography (5% MeOH/CHCl₃) to afford **10a** (24 mg, 16 %) as a white foam; ¹H NMR (MeOH-d₄) δ 8.04-8.01 (m, 2 H), 7.63-7.56 (m, 2 H), 7.49-7.44 (m, 2 H), 6.34 (t, *J* = 7.5 Hz, 1 H), 4.54-4.43 (m, 3 H), 4.12 (dd, *J* = 8.4 Hz, 4.2 Hz, 1 H), 3.52-3.45 (m, 1 H), 3.33-3.25 (m, 1 H), 2.61-2.53 (m, 2 H), 2.39 (s, 1 H), 2.20-2.15 (m, 2 H); ¹³C NMR (MeOH-d₄) δ 172.3, 167.3, 154.4, 134.1, 130.8, 130.2, 129.4, 84.9, 84.1, 72.0, 65.2, 36.9, 36.5, 31.4; IR (Film) 3230, 1716, 1487, 1450, 1276, 1217, 1088, 1025, 712 cm⁻¹; HRMS (FAB) calcd 335.1244 (M+H) 335.1243 found.

5-Benzoyl-2-deoxyribonolactone (13). To a solution of 2-deoxyribonolactone (230 mg, 1.74 mmol) and Et₃N (229mg, 2.26 mmol) in DMF (15 mL) at -40 °C was added benzoyl cyanide (274 mg, 2.09 mmol). The reaction was stirred overnight and allowed to warm to ambient temperature. The reaction was quenched with H₂O and diluted with EtOAc. The crude reaction mixture was washed with H₂O, brine, dried over Na₂SO₄ and concentrated. The crude product was purified via silica gel flash chromatography (2:1-1:1 Hexanes/EtOAc) to afford **13** (127 mg, 31 %) as a clear oil; ¹H NMR (CDCl₃) δ 7.99-7.96 (m, 2 H), 7.62-7.57 (m, 1 H), 7.48-7.45 (m, 2 H), 4.70-4.68 (m, 1 H), 4.61-4.55 (m, 3 H), 3.08 (s, *J* = 3 Hz, 1 H), 2.95 (dd, *J* = 18, 6.9 Hz, 1 H), 2.62 (dd, *J* = 18 Hz, 3.9 Hz, 1 H); ¹³C NMR (CDCl₃) δ 176.0, 167.4, 134.8, 130.7, 129.9, 129.7, 85.9, 70.0, 64.6, 38.9; IR (Film) 3461, 2950, 1601, 1451, 1781, 1720, 1176, 1164, 1026, 944 cm⁻¹; HRMS (FAB) calcd 254.1035 (M+H) 254.1028 found.

Photoreduction product (9b). NaBH₄ (15.5 mg, 0.41 mmol) was added to a solution of **8** (114 mg, 0.20 mmol) in MeOH (2.0 mL) at 0 °C. The reaction was stirred 2h then diluted with Et₂O. The reaction mixture was washed with H₂O, brine, dried over Na₂SO₄ and concentrated *in vacuo*. The crude reaction mixture was purified via silica gel flash chromatography (2:1-1:1 Hexanes/EtOAc) to afford the alcohol (82 mg, 71%) as a white foam; ¹H NMR (CDCl₃) δ 6.56 (s, 1H), 5.92 (t, *J* = 6.9 Hz), 5.47 (s, 1 H), 4.50-4.47 (m, 1 H), 4.22 (d, *J* = 3.3 Hz, 1H), 4.22-3.84 (m, 3 H), 3.69-3.67 (m, 1 H), 2.86-2.80 (m, 1 H), 2.34-2.21 (m, 3 H), 1.09-0.91 (m, 37 H); ¹³C NMR (CDCl₃) δ 166.4, 152.2, 80.6, 79.5, 78.1, 65.8, 57.2, 46.3, 37.1, 31.1, 30.1, 19.7, 13.1, 13.0, 12.9, 12.8, 12.6, 12.5, 12.4, 9.0, 8.8, 8.7, 8.0; IR (Film) 3390, 3182, 2945, 2868, 2360, 1744, 1688, 1633, 1453, 1367, 1328, 1279, 1081, 1039, 963, 919, 885 cm⁻¹; HRMS (FAB) calcd 581.3075 (M+H) 581.3078 found.

Et₃N•3HF (101 mg, 0.63 mmol) was added to a solution of protected photoreduction product (70 mg, 0.12 mmol). The reaction was stirred overnight and concentrated *in vacuo*. The crude reaction mixture was purified via silica gel flash chromatography (5-10% MeOH/CHCl₃) to afford **9b** (33mg, 83%) as a white foam; ¹H NMR (MeOH-d₄) δ 5.77 (dd, *J* = 9.5, 9.3 Hz, 1 H), 4.31-4.29 (m, 1 H) 4.17-4.12 (m, 2 H), 3.80-3.65 (m, 2 H), 2.73-2.63 (m, 2 H), 2.44-2.41 (m, 1 H)

1.93-1.86 (m, 2 H) 0.92 (s, 9 H); ^{13}C NMR (MeOH- d_4) δ 168.6, 153.0, 81.9, 81.7, 79.8, 66.6, 57.4, 47.2, 36.3, 31.3, 29.6, 18.7; IR (Film) 3368, 2359, 1735, 1670, 1073, 726 cm^{-1} ; HRMS (FAB) calcd 317.1725 (M+H) 317.1712 found.

Response factors for **4a**, **10a**, and **11-13** were calculated versus the 5'-benzoate ester of thymidine. For **2b**, **10b**, and 2'-deoxyuridine (dU), response factors were calculated versus thymidine. Response factors were calculated using the following formula: $([X]/[S])=R_f (A(X)/A(S))$ where [X] is the concentration of the compound of interest, and [S] is the concentration of internal standard. A(S) and A(X) are the areas under the peaks corresponding to the compound of interest and the internal standard, respectively (Table 1).

Supporting Information Table 1. Response Factors and Retention Times

Compound	Retention Time (min)				Response Factor
	Gradient A	Gradient B	Gradient C	Gradient D	
2a	50.1	53.4	60.9	-	1.6
2b	-	-	-	18.7	1.7
10a	34.8	37.1	41.7	-	1.4
10b	-	-	-	16.6	1.6
11	32.1	34.4	38.1	-	1.6
12	35.6	37.9	42.3	-	1.3
13	-	-	46.1	-	1.4
dU	-	-	-	9.4	1.2

Supporting Information Figure 1. Energy minimized structures of: A. *anti*-7 (6*R*); B. *anti*-8 (6*S*).

Supporting Information Table 2. Calculated ΔH_f (kcal/mol) of energy minimized *syn* and *anti* conformational isomers.

	ΔH_f (kcal/mol)	
	<i>anti</i>	<i>syn</i>
6	-495	-495
7 (6R)	-520	-510
8 (6S)	-521	-513
-459	-462