Reaction Between 2,2'-Anhydro-1-β-D-arabinofuranosyluracil and Thiolate Ions

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2,2'-Anhydro-1-β-D-arabinofuranosyluracil [2,2'-anhydrouridine] (1a) reacts with the conjugate bases of thiophenol, toluene-4-thiol, ethanethiol, propane-1-thiol, 2-methylpropane-2-thiol and 4-methoxyphenylmethanethiol to give good to high yields of the corresponding 2'-deoxy-2'-mercaptouridine derivatives (2a; R^2 = Ph, 4-MeC$_6$H$_4$, Et, Pr, Bu^t, and 4-MeOC$_6$H$_4$CH$_2$, respectively).

THE reaction between 2,2'-anhydro-1-β-D-arabino-furanosyluracil (2,2'-anhydrouridine) (1a) and thiolate ions would appear to be an obvious route for the synthesis of derivatives of 2'-deoxy-2'-mercaptouridine (2a; R^2 = H). However, Brown et al. reported[1] that when 2,2'-anhydrouridine (1a) was heated with a large excess of sodium ethanethiolate in dimethylformamide and the product obtained was desulphurized with Raney nickel, 3'-deoxyuridine (3), rather than the expected 2'-isomer (4) was obtained. The latter workers[1] inferred that the reaction between 2,2'-anhydrouridine (1a) and sodium ethanethiolate led to the formation of 1-β-D-(3-ethylmercapto-3-deoxyxylofuranosyl)uracil (5) and not to (2a; R^2 = Et).

Brown et al.[1] rationalized their conclusions by suggesting that 2,2'-anhydrouridine (1a) is first converted, under the basic reaction conditions, into the isomeric epoxide (6) and that the latter compound then undergoes nucleophilic attack by ethanethiolate ion at C-3' to give (5). This hypothesis is by no means unreasonable and, indeed, we ourselves recently found[2] that when the 8-oxyadenosine-derived anhydronucleoside (7) was treated with sodium hydroxide in dimethyl sulphoxide solution at room temperature, it was readily converted into the isomeric epoxide (8). Furthermore, 2',3'-anhydro-ribonucleosides (e.g. 2',3'-anhydroadenosine) are known[3] to undergo nucleophilic attack predominantly on C-3'. In support of the conclusions of Brown et al., Furukawa and his co-workers reported[4] that (5) was obtained in high yield when 3',5'-di-O-acetyl-2,2'-anhydrouridine (1b) was treated with an excess of sodium ethanethiolate in dimethylformamide. The latter workers assigned[4] structure (5) to the product obtained mainly on the basis of its ^{1}H n.m.r. spectrum which they reported to be ' in good agreement ' with the spectrum of a putative authentic sample of (5) prepared by Kowollik and Langen[5] from 2',5'-di-O-trityl-3'-O-mesyluridine. Although the acetyl groups were apparently lost during the course of the reaction between (1b) and sodium ethanethiolate, Furukawa et al. suggested[4] that the formation of (5) rather than of (2a; R^2 = Et) may have been due to the participation of the 3'-acetoxy-group.

If the conclusions of previous workers[1,4] are correct, there would appear to be a better chance of obtaining a 2'-deoxy-2'-mercaptouridine derivative (2a) from 2,2'-

(1) a; R = H
    b; R = Ac

(2) a; R^1 = H
    b; R^1 = Ac

(3)

(4)

(5)

(6)

(7)

(8)
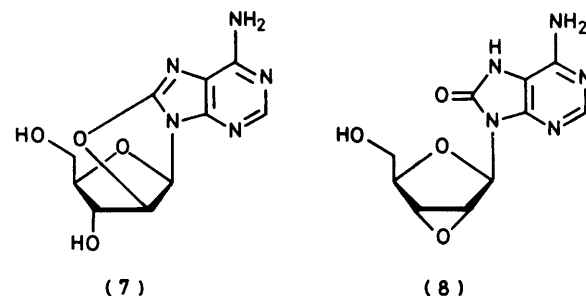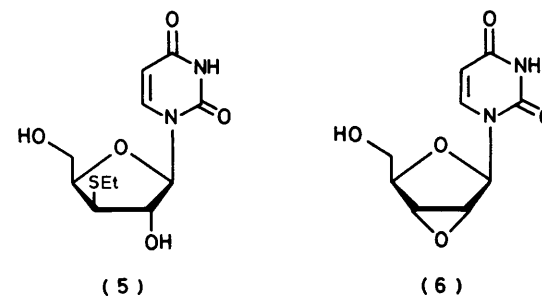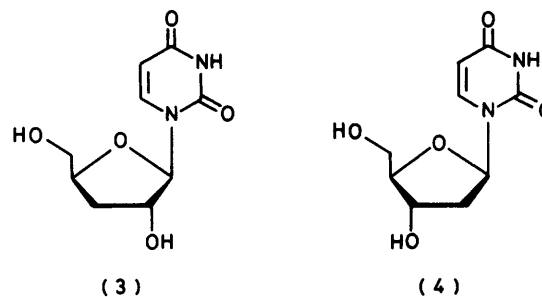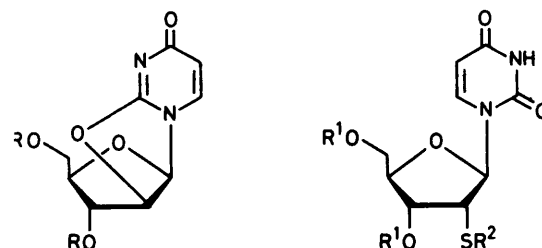
anhydrouridine (1a) by allowing it to react with a less basic sulphur nucleophile than ethanethiolate ion. Some support for this hypothesis came from the findings [6] that, although the reaction between (1b) and thioacetate (or thiobenzoate) ion gave uracil as the main product, the reaction between (1b) and thioacetic acid itself in dioxan solution at 110 °C gave 2',3',5'-tri-*O*-acetyl-2'-deoxy-2'-mercaptouridine (2b; $R^2 = Ac$) in satisfactory yield. We nevertheless felt that the overall

would be expected for the resonance of a proton attached to a sulphur- rather than an oxygen-substituted carbon atom, to collapse to a doublet but has no noticeable effect on any other signal in the spectrum. The multiplicity of the signal at δ 3.87 is not affected by the addition of deuterium oxide to the $(CD_3)_2SO$ solution. Although the configuration at C-2' has not been established unequivocally, it is reasonable to assume that attack by a weakly basic soft nucleophile at C-2' of the

TABLE 1

Reactions between 2,2'-anhydro-1-β-D-arabinofuranosyluracil (1a) and thiolate ions

Expt. no.	Thiol	Solvent [a]	Base [b]	Temp. (°C)	t/h	Isolated yield (%)	M.p. [d] (°C)
1	PhSH	A	C	100	6	90	199—200
2	4-MeC$_6$H$_4$SH	B	C	c	3	87	212
3	EtSH	A	D	60	12	93	183.5
4	PrSH	A	D	100	5	69	185.5
5	Bu^{t}SH	A	D	100	16	94	227
6	4-MeOC$_6$H$_4$CH$_2$SH	A	D	120	0.33	80	151

[a] Reactions were carried out in dimethylformamide (solvent A) or methanol (solvent B). [b] The base used was triethylamine (base C) or N^1,N^1,N^3,N^3-tetramethylguanidine (base D). [c] This reaction was carried out under reflux. [d] Satisfactory microanalytical data (Experimental section) were obtained for all the compounds in this table.

picture which emerged from literature reports regarding the chemistry of the reactions between 2,2'-anhydrouridine (1a) and thiolate ions was far from clear and merited further investigation. In order to minimize the possibility of 2',3'-anhydrouridine (6) being formed as an intermediate, we first examined the reactions between 2,2'-anhydrouridine (1a) and relatively weakly basic arenethiolate ions.*

anhydro-nucleoside (1a) would result in an inversion of configuration at that centre. It is noteworthy that the ^{13}C n.m.r. spectrum of (2a; $R^2 = Ph$) [Table 2, entry no. 1] includes a relatively high-field signal at δ 54.7 which may be assigned to the resonance of C-2'.

Not unexpectedly, the reaction between 2,2'-anhydrouridine (1a) and toluene-4-thiolate ion in methanol followed the same course and gave (2a; $R^2 = 4$-MeC$_6$H$_4$)

TABLE 2

N.m.r. spectroscopic data [a] relating to 2'-deoxy-2'-mercaptouridine derivatives (2a)

Entry no.	Compound	H-1'	H-2'	H-3'	C-2'
1	(2a; $R^2 = Ph$)	6.20 (d, *J* 9.2 Hz)	3.87 (dd, *J* 5.0, 9.2 Hz)	4.35 (m)	54.7
2	(2a; $R^2 = 4$-MeC$_6$H$_4$)	6.17 (d, *J* 9.2 Hz)	3.77 (dd, *J* 5.5, 9.2 Hz)	4.31 (m)	
3	(2a; $R^2 = Et$)	6.02 (d, *J* 8.7 Hz)	3.43 (dd, *J* 5.0, 8.7 Hz)	4.18 (m)	51.7
4	(2a; $R^2 = Pr$)	6.02 (d, *J* 8.7 Hz)	3.40 (dd, *J* 5.5, 8.7 Hz)	4.17 (m)	51.8
5	(2a; $R^2 = Bu^t$)	5.89 (d, *J* 9.6 Hz)	3.37 (dd, *J* 4.6, 9.6 Hz)	4.07 (m)	49.9
6	(2a; $R^2 = 4$-MeOC$_6$H$_4$CH$_2$)	6.05 (d, *J* 9.2 Hz)	3.33 (dd, *J* 5.5, 9.2 Hz)	4.17 (m)	51.3

[a] ^{1}H and ^{13}C N.m.r. spectra were measured at 250 and 22.63 MHz, respectively, in anhydrous $(CD_3)_2SO$ solution. Chemical shifts are expressed in p.p.m. on a δ scale.

When 2,2'-anhydrouridine (1a) was heated with *ca.* 5 mol equiv. each of thiophenol and triethylamine in dimethylformamide solution for 6 h at 100 °C [Table 1, experiment no. 1], 2'-deoxy-2-phenylthiouridine (2a; $R^2 = Ph$) was obtained as the sole nucleoside product. The latter compound (2a; $R^2 = Ph$) was isolated as a crystalline solid in 90% yield and characterized on the basis of its elemental analysis and ^{1}H n.m.r. spectrum [Table 2, entry no. 1 and Experimental section]. There can be no doubt whatsoever that the phenylthio-group is attached to C-2': double-irradiation at δ 6.20 (corresponding to the chemical shift of the anomeric proton) causes the double-doublet at δ 3.87 (assigned to the resonance of H-2'), which is at relatively high field as

which was isolated as a crystalline solid in very good yield [Table 1, experiment no. 2; Table 2, entry no. 2 and Experimental section]. However, in the light of the previous reports [1,4], we were particularly interested to find that when 2,2'-anhydrouridine (1a) was allowed to react with *ca.* 5 mol equiv. each of ethanethiol and N^1,N^1,N^3,N^3-tetramethylguanidine in dimethylformamide for 12 h at 60 °C, 2'-deoxy-2'-ethylthiouridine (2a; $R^2 = Et$) was obtained as the sole nucleoside product and was isolated as a crystalline compound in 93% yield [Table 1, experiment no. 3]. The structure of (2a; $R^2 = Et$) is based firmly on its elemental analysis and on its u.v. ($\lambda_{max.}$ 261 nm) and n.m.r. (^{1}H and ^{13}C) spectra [Table 2, entry no. 3]. It is clear from the ^{1}H n.m.r. spectrum of (2a; $R^2 = Et$) that the ethylthio-group is attached to C-2': the double-doublet at δ 3.43 (*J* 5.0, 8.7 Hz), assigned to the resonance of 2'-H and the doublet at δ 6.02 (*J* 8.7 Hz), assigned to the

* The reported pK_a values [A. Albert and E. P. Serjeant, ' Ionization Constants of Acids and Bases' Methuen, London, 1962, p. 135] of thiophenol and ethanethiol are 6.5 and 10.5, respectively.

resonance of the anomeric proton, have a common coupling constant. Furthermore double-irradiation at δ 6.02 causes the signal at δ 3.43 to collapse to a doublet ($J \sim 5$ Hz) and has no detectable effect on the rest of the spectrum. Addition of deuterium oxide to the $(CD_3)_2SO$ solution causes the multiplet at δ 4.18, assigned to the resonance of H-3', to collapse to a double-doublet (J 1.8, 5.0 Hz) thereby indicating that H-2' also has a common coupling constant with H-3'. The ^{13}C n.m.r. spectrum of (2a; $R^2 = $ Et) [Table 2, entry no. 3 and Experimental section] includes a signal at δ 51.7, which may be assigned to the resonance of C-2'. The ^1H n.m.r. spectrum of the 2'-ethylthio-derivative (2a; $R^2 = $ Et) corresponds very closely indeed to that reported [6] by Imazawa et al. for 2'-deoxy-2'-methylthiouridine (2a; $R^2 = $ Me). The latter compound was prepared [6] by treating 2',3',5'-tri-O-acetyl-2'-deoxy-2'-mercaptouridine (2a; $R^2 = $ Ac) with sodium hydroxide and then methylating the product. The ^1H n.m.r. spectrum of (2a; $R^2 = $ Et) appears to differ markedly from that reported for the putative 3'-ethylthio-derivative (5) which was prepared [5] (see above) from 3',5'-di-O-acetyl-2,2'-anhydrouridine (1b).

2'-Alkylthio-2'-deoxyuridine derivatives (2a; $R^2 = $ Pr, But, and 4-MeOC$_6$H$_4$CH$_2$) were also obtained in satisfactory to very high yields by heating 2,2'-anhydrouridine (1a) with excesses of propane-1-thiol, 2-methylpropane-2-thiol and 4-methoxyphenylmethane-thiol, respectively, and an excess of N^1,N^1,N^3,N^3-tetramethylguanidine in dimethylformamide solution [Table 1, experiments nos. 4—6]. The products were again characterized on the basis of their elemental composition and spectroscopic [especially ^1H n.m.r.; see Table 2, entries nos. 4—6] properties. The last two compounds (2a; $R^2 = $ But and 4-MeOC$_6$H$_4$CH$_2$) may be regarded as protected derivatives [7] and hence potential precursors of the parent 2'-deoxy-2'-mercaptouridine (2a; $R^2 = $ H).

We are unable at the present time to explain the apparent discrepancy between our own results and those previously reported by Brown and Furukawa and their co-workers.[1,4] However, it would be very surprising if this discrepancy were due solely to a difference between the nucleophilic properties of the sodium and the $N^1,N^1,-N^3,N^3$-tetramethylguanidinium salts of ethanethiol.

EXPERIMENTAL

^1H N.m.r. spectra were measured at 250 MHz with a Bruker WH 250 spectrometer; tetramethylsilane was used as an internal standard. ^{13}C N.m.r. spectra were measured at 22.63 MHz with a Bruker HFX 90 spectrometer. U.v. absorption spectra were measured with a Cary 17 recording spectrophotometer. Merck silica gel 60 F$_{254}$ plates were used for t.l.c.; Merck silica gel H was used for short column chromatography. Dimethylformamide and triethylamine were dried by heating with calcium hydride and were then redistilled.

2'-Deoxy-2'-phenylthiouridine (2a; $R^2 = $ Ph).—2,2'-Anhydrouridine [8] (2.26 g, 10.0 mmol), thiophenol (5.1 ml, 49.7 mmol), triethylamine (7.0 ml, 50.2 mmol), and dimethylformamide (50 ml) were heated together at 100 °C.

After 6 h, the products were cooled and concentrated under reduced pressure. The residue was triturated with cyclohexane and then crystallized from ethanol to give 2'-deoxy-2'-phenylthiouridine (3.06 g, 90%) [Found: C, 53.1; H, 5.0; N, 8.3. $C_{15}H_{16}N_2O_5S$. 0.2 H_2O requires: C, 53.0; H, 4.9; N, 8.2%], m.p. 199—200 °C, $\lambda_{max.}$ (95% EtOH) 254 (ε 10 900), $\lambda_{min.}$ 240 nm (ε 5 200); δ_H [$(CD_3)_2SO$] 3.60 (2 H, m), 3.87 (1 H, dd, J 5.0, 9.2 Hz), 3.94 (1 H, m), 4.35 (1 H, m), 5.17 (1 H, m), 5.46 (1 H, d, J 7.8 Hz), 5.93 (1 H, d, J 5.0 Hz), 6.20 (1 H, d, J 9.2 Hz), 7.2—7.4 (5 H, m), 7.61 (1 H, d, J 8.3 Hz), 11.15br (1 H, s) [irradiation of the doublet at δ 6.20 caused the double-doublet at δ 3.87 to collapse to a doublet (J 5 Hz); addition of D_2O led to the disappearance of the signals at δ 5.17, 5.93 and 11.15 (assigned to the resonances of the 5'- and 3'-hydroxy and the 3-NH protons, respectively) and caused the multiplet at δ 4.35 (assigned to the resonance of H-3') to collapse to a doublet (J 5.0 Hz)]; δ_C [$(CD_3)_2SO$] 54.7, 61.6, 72.4, 86.8, 87.9, 102.4, 127.2, 129.0, 131.5, 133.3, 139.9, 150.5, and 162.6.

2'-Deoxy-2'-(4-tolylthio)uridine (2a; $R^2 = $ 4-MeC$_6$H$_4$).— 2,2'-Anhydrouridine (0.226 g, 1.0 mmol), toluene-4-thiol (0.62 g, 5.0 mmol), triethylamine (0.7 ml, 5.0 mmol) and methanol (5 ml) were heated together, under reflux. After 3 h, the products were cooled and concentrated under reduced pressure. The residue was triturated with cyclohexane and then crystallized from ethanol to give 2'-deoxy-2'-(4-tolylthio)uridine (0.305 g, 87%) [Found: C, 54.5; H, 5.25; N, 7.9. $C_{16}H_{18}N_2O_5S$ requires C, 54.8; H, 5.2; N, 8.0%), m.p. 212 °C, $\lambda_{max.}$ (95% EtOH) 255 (ε 12 300), $\lambda_{min.}$ 238 nm (ε 5 000); δ_H [$(CD_3)_2SO$] 2.22 (3 H, s), 3.57 (2 H, m), 3.77 (1 H, dd, J 5.5, 9.2 Hz), 3.91 (1 H, m), 4.31 (1 H, m), 5.14 (1 H, m) 5.44 (1 H, d, J 8.3 Hz), 5.89 (1 H, d, J 5.5 Hz), 6.17 (1 H, d, J 9.2 Hz), 7.04 (2 H, d, J 8.3 Hz), 7.23 (2 H, d, J 8.3 Hz), 7.56 (1 H, d, J 8.3 Hz), and 11.14br (1 H, s).

2'-Deoxy-2'-ethylthiouridine (2a; $R^2 = $ Et).—2,2'-Anhydrouridine (2.26 g, 10.0 mmol), ethanethiol (3.6 ml, 48.6 mmol), N^1,N^1,N^3,N^3-tetramethylguanidine (6.34 ml, 50.6 mmol) and dimethylformamide (50 ml) were heated together at 60 °C. After 12 h, the products were cooled, concentrated under reduced pressure, and then fractionated by short column chromatography [9] on silica gel (60 g). Concentration of the appropriate fractions, which were eluted with CHCl$_3$–EtOH (88 : 12, v/v) and crystallization of the residue from ethanol gave 2'-deoxy-2'-ethylthiouridine (2.7 g, 93%) [Found: C, 45.7; H, 5.6; N, 9.6. $C_{11}H_{16}$-N_2O_5S requires C, 45.8; H, 5.6; N, 9.7%), m.p. 183.5 °C, $\lambda_{max.}$ (95% EtOH) 261 (ε 9 300), $\lambda_{min.}$ 237 nm (ε 3 000); δ_H [$(CD_3)_2SO$] 1.10 (3 H, t, J 7.3 Hz), 2.43 (2 H, quart., J 7.3 Hz), 3.43 (1 H, dd, J 5.0, 8.7 Hz), 3.58 (2 H, m), 3.88 (1 H, m), 4.18 (1 H, m), 5.15 (1 H, m), 5.62 (1 H, d, J 5.5 Hz), 5.72 (1 H, d, J 7.8 Hz), 6.02 (1 H, d, J 8.7 Hz), 7.90 (1 H, d, J 8.3 Hz), and 11.39 (1 H, m) [irradiation of the doublet at δ 6.02 (assigned to the resonance of H-1') caused the double-doublet at δ 3.43 (assigned to the resonance of H-2') to collapse to a doublet ($J \sim 5$ Hz); addition of D_2O led to the disappearance of the signals at δ 5.15, 5.62, and 11.39 (assigned to the resonances of the 5'- and 3'-hydroxy and the 3-NH protons) and caused the multiplet at δ 4.18 (assigned to the resonance of H-3') to collapse to a double-doublet (J 1.8, 5.0 Hz)]; δ_C [$(CD_3)_2SO$] 15.0, 24.6, 51.7, 61.4, 72.0, 86.6, 87.5, 102.4, 140.4, 150.8, and 163.0.

2'-Deoxy-2'-(n-propylthio)uridine (2a; $R^2 = $ Pr).—2,2'-Anhydrouridine (2.26 g, 10.0 mmol), propane-1-thiol (4.5 ml,

49.7 mmol), N^1,N^1,N^3,N^3-tetramethylguanidine (6.34 ml, 50.6 mmol) and dimethylformamide (50 ml) were heated together at 100 °C. After 5 h, the products were cooled, concentrated under reduced pressure, and then purified by short-column chromatography on silica gel (60 g). Concentration of the appropriate fractions, which were eluted with CHCl$_3$–EtOH (4 : 1, v/v), and crystallization of the residue from ethanol gave 2'-deoxy-2'-(n-propylthio)-uridine (2.1 g, 69%) (Found: C, 47.65; H, 5.9; N, 9.3. C$_{12}$H$_{18}$N$_2$O$_5$S requires C, 47.7; H, 6.0; N, 9.3%), m.p. 185.5 °C, $\lambda_{max.}$ (95% EtOH) 261 (ε 9 500), $\lambda_{min.}$ 238 nm (ε 3 700); δ_H [(CD$_3$)$_2$SO] 0.86 (3 H, t, J 7.1 Hz), 1.44 (2 H, m), 2.42 (2 H, m), 3.40 (1 H, dd, J 5.5, 8.7 Hz), 3.57 (2 H, m), 3.88 (1 H, m), 4.17 (1 H, m), 5.14 (1 H, m), 5.62 (1 H, d, J 5.5 Hz), 5.72 (1 H, d, J 7.8 Hz), 6.02 (1 H, d, J 8.7 Hz), 7.90 (1 H, d, J 8.2 Hz), and 11.40 (1 H, m) [irradiation of the doublet at δ 6.02 caused the double-doublet at δ 3.40 to collapse to a doublet (J ∼ 5 Hz); addition of D$_2$O led to the disappearance of the signals at δ 5.14, 5.62, and 11.40 and caused the multiplet at 4.17 to collapse to a double-doublet (J 1.8, 5.5 Hz)]; δ_C [(CD$_3$)$_2$SO] 13.1, 22.7, 35.5, 51.8, 61.4, 72.0, 86.6, 87.6, 102.4, 140.4, 150.8, and 162.9.

2'-Deoxy-2'-(t-butylthio)uridine (2a; R² = Buᵗ).—2,2'-Anhydrouridine (2.26 g, 10 mmol), 2-methylpropane-2-thiol (2.8 ml, 24.8 mmol), N^1,N^1,N^3,N^3-tetramethylguanidine (6.34 ml, 50.6 mmol) and dimethylformamide (50 ml) were heated together at 100 °C. After 16 h, the products were cooled, concentrated under reduced pressure, and then purified by short-column chromatography on silica gel (60 g). Concentration of the appropriate fractions, which were eluted with CHCl$_3$–EtOH (9 : 1 v/v), and crystallization of the residue from ethanol gave 2'-deoxy-2'-(t-butylthio)uridine (2.98 g, 94%) (Found: C, 49.3; H, 6.3; N, 9.0. C$_{13}$H$_{20}$N$_2$O$_5$S requires C, 49.35; H, 6.4; N, 8.9%), m.p. 227 °C, $\lambda_{max.}$ (95% EtOH) 260 (ε 9 500), $\lambda_{min.}$ 238 nm (ε 3 700); δ_H [(CD$_3$)$_2$SO–D$_2$O] 1.20 (9 H, s), 3.37 (1 H, dd, J 4.6, 9.6 Hz), 3.62 (2 H, m), 3.94 (1 H, m), 4.07 (1 H, d, J 4.6 Hz), 5.75 (1 H, d, J 8.3 Hz), 5.89 (1 H, d, J 9.6 Hz), and 8.01 (d, J 8.3 Hz) [irradiation of the doublet at δ 5.89 caused the double-doublet at δ 3.37 to collapse to a doublet (J ∼ 5 Hz)]; δ_C [(CD$_3$)$_2$SO] 31.1, 42.8, 49.9, 61.8, 73.0, 86.5, 86.9, 102.4, 140.7, 150.9, and 162.9.

2'-Deoxy-2'-(4-methoxyphenylmethanethio)uridine (2a; R = 4-MeOC$_6$H$_4$CH$_2$).—2,2'-Anhydrouridine (1.6 g, 7.1 mmol), 4-methoxyphenylmethanethiol (2.46 ml, 17.7 mmol), N^1,N^1,N^3,N^3-tetramethylguanidine (4.5 ml, 35.9 mmol), and dimethylformamide (35 ml) were heated together at 120 °C. After 20 min, the products were cooled, concentrated under reduced pressure, and then purified by short-column chromatography on silica gel (40 g). Concentration of the appropriate fractions, which were eluted with CHCl$_3$–EtOH (91 : 9 v/v) and crystallization of the residue from ethanol–ethyl acetate (3 : 2 v/v) gave 2'-deoxy-2'-(4-methoxyphenylmethanethio)uridine (2.15 g, 80%) (Found: C, 53.9; H, 5.4; N, 7.5. C$_{17}$H$_{20}$N$_2$O$_6$S requires C, 53.7; H, 5.3; N, 7.4%), m.p. 151 °C, $\lambda_{max.}$ (95% EtOH) 263 (ε 9 200), $\lambda_{min.}$ 249 nm (ε 7 700); δ_H [(CD$_3$)$_2$SO] 3.33 (1 H, dd, J 5.5, 9.2 Hz), 3.56 (2 H, m), 3.65 (2 H, s), 3.72 (3 H, s), 3.89 (1 H, m), 4.17 (1 H, m), 5.12 (1 H, m), 5.57 (1 H, d, J 8.3 Hz), 5.65 (1 H, d, J 5.0 Hz), 6.05 (1 H, d, J 9.2 Hz), 6.81 (2 H, d, J 8.7 Hz), 7.14 (2 H, d, J 8.7 Hz), 7.71 (1 H, d, J 8.3 Hz), 11.35br (1 H, s); δ_C [(CD$_3$)$_2$SO] 33.5, 51.3, 54.5, 60.9, 71.4, 86.2, 87.0, 101.9, 113.3, 129.3, 139.6, 150.2, 157.8, and 162.4.

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