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Syntheses and Properties of 3-Hydroxy-4,6-dimethylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-dione (9-Hydroxy-9-deazatheophylline) Derivatives

Fumio Yoneda,*[a] Miyuki Motokura,[a] Mutsuko Kamishimoto,[a] Tomohisa Nagamatsu,[a] Masaki Otagiri,[a] Kaneto Uekama,[a] and Masayuki Takamoto[b]

Faculty of Pharmaceutical Sciences, Kumamoto University,[a] Oe-honmachi, Kumamoto 862, Japan and Central Research Division, Takeda Chemical Industries, Ltd.,[b] Jusohonmachi, Yodogawa-ku, Osaka 532, Japan

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Treatment of 1,3,6-trimethyl-5-nitrouracil with aryl aldehydes in the presence of piperidine results in condensation to the 5-nitro-6-styryluracil derivatives, followed by intramolecular cyclization including piperidine-catalyzed oxidation-reduction to give rise to the corresponding 3-hydroxy-4,6-dimethylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-dione (9-hydroxy-9-deazatheophylline) derivatives in a single step. Some properties of these compounds and an X-ray crystal structure determination of 8-(*p*-chlorophenyl)-9-methoxy-7-methyl-9-deazatheophylline are described.

Keywords——1,3,6-trimethyl-5-nitrouracil; pyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-dione; 9-deazatheophylline; ESR spectra; 9-hydroxy-9-deazatheophylline radical; X-ray analysis

The pyrrolo[3,2-*d*]pyrimidine (9-deazapurine) ring system is of interest because of its close structural similarity to naturally-occurring and physiologically active purine as well as to other biologically important heterocycles, *e.g.*, pyrrolo[2,3-*d*]pyrimidine, pyrazolo[4,5-*d*]-pyrimidine, and indole.[1] It is known that conventional reductions of 1,3-dimethyl-5-nitro-6-styryluracils (IV) give 2-aryl-4,6-dimethylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-diones (VI).[2] Senda and coworkers reported that the irradiation of IV in isopropanol gave the same products.[3] The present paper describes a new and convenient synthesis of 3-hydroxy-4,6-dimethylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)dione (referred to hereafter as 9-hydroxy-9-deazatheophylline) derivatives which belong to an unexplored class of pyrrolo[3,2-*d*]pyrimidines.[4] In addition, we report some properties of these compounds and an X-ray crystal structure determination of one of their dimethyl derivatives.[5]

Syntheses of 9-Hydroxy-9-deazatheophylline Derivatives

The new synthesis of 9-hydroxy-9-deazatheophylline derivatives consists of the treatment of 1,3,6-trimethyl-5-nitrouracil (I)[6] with aryl aldehydes in the presence of piperidine. For example, refluxing a mixture of I and benzaldehyde in dimethylformamide in the presence of piperidine for 2 h gave 9-hydroxy-8-phenyl-9-deazatheophylline (IIa) in 48% yield. Similarly, heating I with othe aryl aldehydes under the same conditions led to the formation of the corresponding 9-hydroxy-9-deazatheophyllines (IIb—e) (Table I).

The structures of IIa—e were assigned on the basis of elemental analyses, molecular weights as determined by mass spectrometry and the presence of a hydroxy proton at about 8.3 ppm (DMSO-d_6) as well as the absence of the C–9 proton in the nuclear magnetic resonance (NMR) spectra. Furthermore, several attempted reductions of II failed, and the starting materials were recovered. This fact excluded the possibility for II to possess the 7-hydroxy-9-deazatheophylline-type structure (V). Finally, the structures of II were determined by X-ray analysis of one of their dimethyl derivatives (III), as will be described below.

The treatment of 1,3-dimethyl-5-nitro-6-styryluracils (IV)[2] with piperidine in dimethyl-

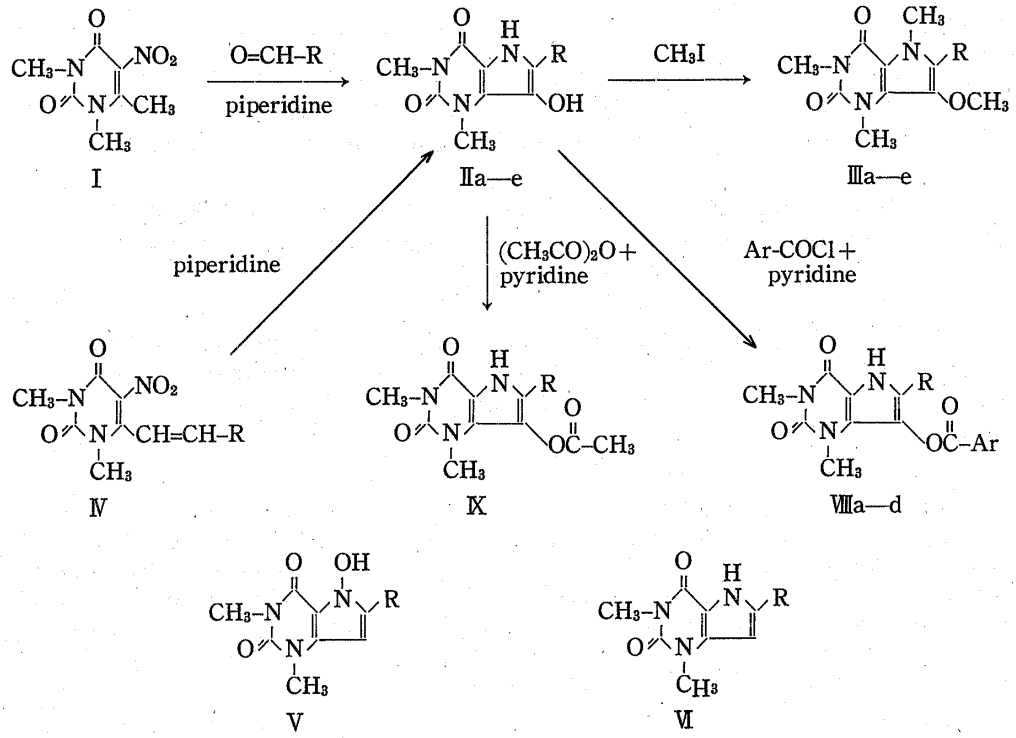
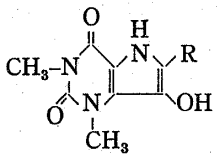


Chart 1

TABLE I. 9-Hydroxy-9-deazatheophyllines



Compd. No.	R	Yield (%)	mp[a] (C°)	Appearance	Formula	Analysis (%) Calcd (Found) C	H	N
IIa	C_6H_5	48	316	Yellow powder	$C_{14}H_{13}N_3O_3$	61.98 (61.77	4.83 4.90	15.49 15.23)
IIb	4-Cl-C_6H_4	52	333	Yellow powder	$C_{14}H_{12}ClN_3O_3$	55.00 (54.98	3.96 3.88	13.75 13.49)
IIc	4-F-C_6H_4	52	207	Yellow powder	$C_{14}H_{12}FN_3O_3$	58.13 (58.06	4.18 4.12	14.53 14.64)
IId	4-CH_3-C_6H_4	43	316	Yellow powder	$C_{15}H_{15}N_3O_3$	63.15 (63.10	5.30 5.33	14.73 14.78)
IIe	4-CH_3O-C_6H_4	47	221	Yellow powder	$C_{15}H_{15}N_3O_4$	59.79 (59.90	5.02 4.86	13.95 14.02)

a) All compounds were recrystallized from ethanol.

formamide under the same conditions also gave II, although in slightly lower yields (for example, 37% for IIa).

Therefore, we rationalize the conversion of I to II in terms of the initial formation of the 5-nitro-6-styryluracils (IV). Intramolecular oxidation-reduction of IV catalyzed by piperidine would give 5-nitrosouracil intermediates (VII) of the heterohexatriene type. Subsequent electrocyclization[7] of VII to the 7,9-dihydroxy-9-deazatheophyllines followed by thermal deoxygenation would lead to the final products (II) (Chart 2).

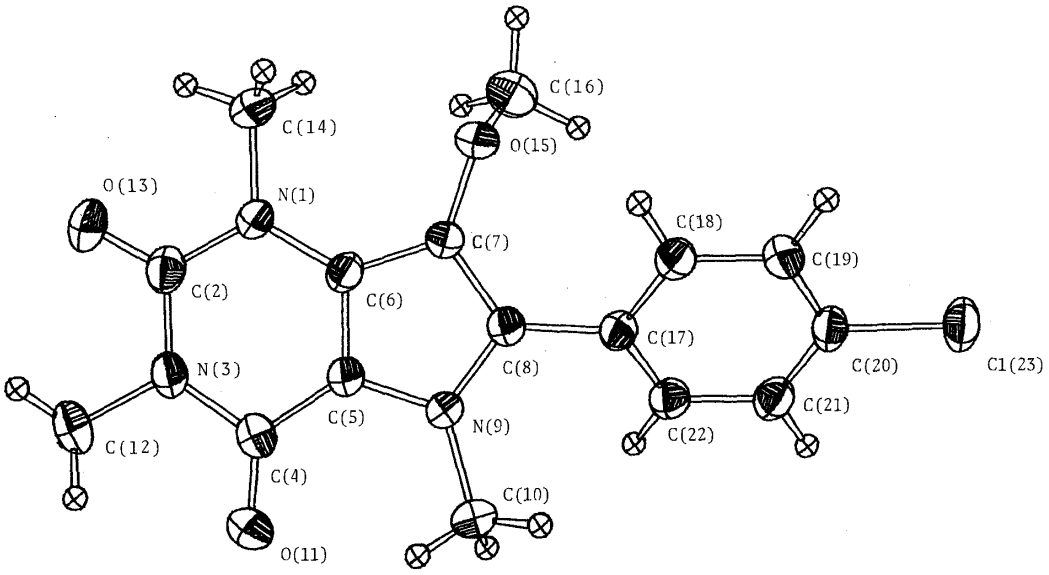
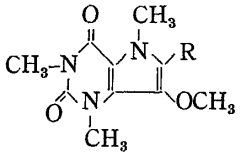


Fig. 2. Structure of the Molecule of IIIb and Numbering of Atoms

Treatment of II with excess methyl iodide in dimethylformamide under reflux in the presence of potassium carbonate gave the corresponding 9-methoxy-7-methyl-9-deazatheophyllines (IIIa—e) (Table II). The structures of III were confirmed by satisfactory analytical data as well as their several spectra, in particular the presence of characteristic proton signals of N_7–CH_3 and C_9–OCH_3 at about 3.6 and 3.8 ppm in the NMR (trifluoroacetic acid).

Table II. 9-Methoxy-7-methyl-9-deazatheophyllines



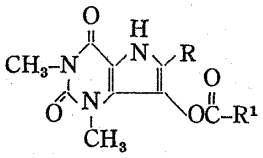
Compd. No.	R	Yield (%)	mp[a] (°C)	Appearance	Formula	Analysis (%) Calcd (Found) C	H	N
IIIa	C_6H_5	78	175	Pale yellow needles	$C_{16}H_{17}N_3O_3$	64.20	5.72	14.04
						(64.17	5.70	13.89)
IIIb	4-Cl-C_6H_4	84	221	Pale yellow needles	$C_{16}H_{16}ClN_3O_3$	57.57	4.83	12.59
						(57.46	4.83	12.40)
IIIc	4-F-C_6H_4	42	191	Brown needles	$C_{16}H_{16}FN_3O_3$	60.56	5.08	13.24
						(60.61	5.04	13.45)
IIId	4-$CH_3C_6H_4$	69	217	Yellow needles	$C_{17}H_{19}N_3O_3$	65.16	6.11	13.41
						(65.22	6.26	13.53)
IIIe	4-CH_3O-C_6H_4	62	224	Brown needles	$C_{17}H_{19}N_3O_4$	61.99	5.82	12.76
						(62.08	5.84	12.80)

a) All compounds were recrystallized from ethanol.

When IIa and IIb were treated with benzoyl chlorides in the presence of pyridine, the corresponding 9-benzoxy-9-deazatheophyllines (VIIIa—d) were obtained in good yields (Table III). Also, the treatment of IIa with a mixture of acetic anhydride and pyridine gave the corresponding 9-acetoxy-9-deazatheophylline (IX) (Table III). The structures of these 9-acyloxy derivatives (VIII and IX) were confirmed by the disappearance of the characteristic

9-hydroxy proton signal at around 8.3 ppm in the NMR and by the presence of the carbonyl absorptions at around 1760 cm^{-1} and of the amino absorptions at arround 3200 cm^{-1} in the infrared (IR) spectra (in Nujol).

TABLE III. 9-Acyloxy-8-aryl-9-deazatheophyllines



Compd. No.	R	R^1	Yield (%)	mp[a] (°C)	Appearance	Appearance	Analysis (%) Calcd (Found) C	H	N
VIIIa	C_6H_5	C_6H_5	62	336	Colorless needles	$C_{21}H_{17}N_3O_3$	67.19	4.57	11.20
							(67.25	4.54	11.08)
VIIIb	C_6H_5	4-Cl-C_6H_4	84	340	Colorless powder	$C_{21}H_{16}ClN_3O_4$	61.54	3.94	10.25
							(61.66	4.01	10.27)
VIIIc	4-Cl-C_6H_4	C_6H_5	79	>350	Colorless needles	$C_{21}H_{16}ClN_3O_4$	61.54	3.94	10.25
							(61.50	3.90	10.28)
VIIId	4-Cl-C_6H_4	4-Cl-C_6H_4	70	>350	Colorless needles	$C_{21}H_{15}Cl_2N_3O_4$	56.77	3.40	9.46
							(56.83	3.41	9.50)
XI	C_6H_5	CH_3	89	313	Colorless needles	$C_{16}H_{15}N_3O_4$	61.33	4.83	13.41
							(61.37	4.88	13.59)

a) All compounds were recrystallized from ethanol.

Electron Spin Resonance (ESR) Spectra of 9-Hydroxy-9-deazatheophyllines (II)

During the above investigation, it was found that II does not show any proton signals in trifluoroacetic acid in the NMR. We thought this phenomenon might be ascribable to the formation of a radical from II in strong acids. In fact, II exhibited ESR signals in trifluoroacetic acid. Figure 1 shows the ESR spectrum of IIa under anaerobic conditions at room temperature as a typical example of 9-hydroxy-9-deazatheophyllines (II); a broad signal was observed without hyperfine structure. A single broad signal was also observed under aerobic conditions. All other compounds also showed broad signals under the same conditions (Table IV). All the g values are about the same in the range of 2.0031 to 2.0037. However, the line widths depend significantly on the substituents on the benzene ring. It is evident from these line widths that there is a large spin density on the nitrogen or oxygen atom. Further it is noteworthy that the line widths of the ESR line for IIa under anaerobic conditions is smaller than that under aerobic conditions. The narrow line width obtained by degassing of samples may be attributed to the increment of radical concentration. That is, the spin density of the radical obtained under anaerobic conditions may be more localized on nitrogen or oxygen atom than under aerobic conditions. However, it seems more likely that an un-

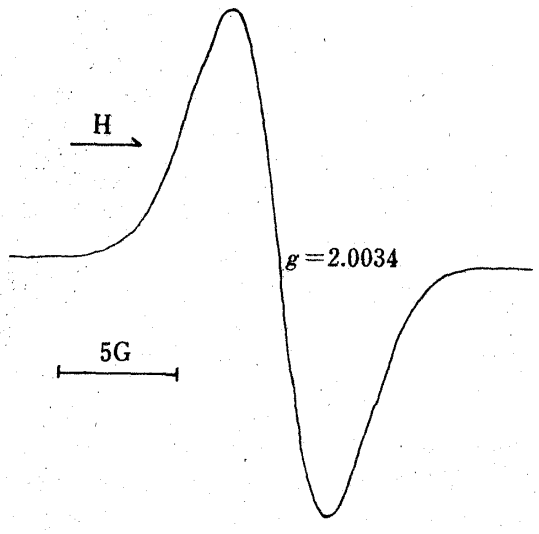


Fig. 1. ESR Spectra of a Radical formed from IIa in Trifluoroacetic Acid

paired electron of oxygen may alter the environment of the radical. Recently, Kurreck *et al.* have found that flavin and thiaflavin radical cations are formed in trifluoroacetic acid at 265 K.[8] However, it is rather difficult to identify the radical species from these limited data, and determination of whether the ESR spectra observed in this study are due to a cation radical or a neutral radical will have to await detailed ESR studies.

Table IV. ESR Data of 8-Aryl-9-hydroxy-9-deazatheophyllines (II)

Compd. No.	*g* value	Line width (gauss)
IIa	2.0037	5.50
IIa (Degassed)	2.0034	4.20
IIb	2.0036	6.00
IId	2.0033	7.00
IIe	2.0031	5.00

X-Ray Analysis of 8-(*p*-Chlorophenyl)-9-methoxy-7-methyl-9-deazatheophylline (IIIb)

Crystal data are given in Table V and individual atomic parameters are listed in Tables VI, VII and VIII. The structure IIIb is unambiguously established. Figure 2 shows the molecular conformation together with the numbering of atoms. The 9-deazatheophylline ring is almost planar. The standard deviation of the 9-atoms from the least-squares plane defined by them is 0.025 Å. C(7) and N(3) are 0.037 and 0.035 Å out of the plane, respectively, but other atoms are within 0.03 Å. The 9-deazatheophylline and the benzene rings are not coplanar or orthogonal. The angle between their least-squares planes is 39.0°. This situation

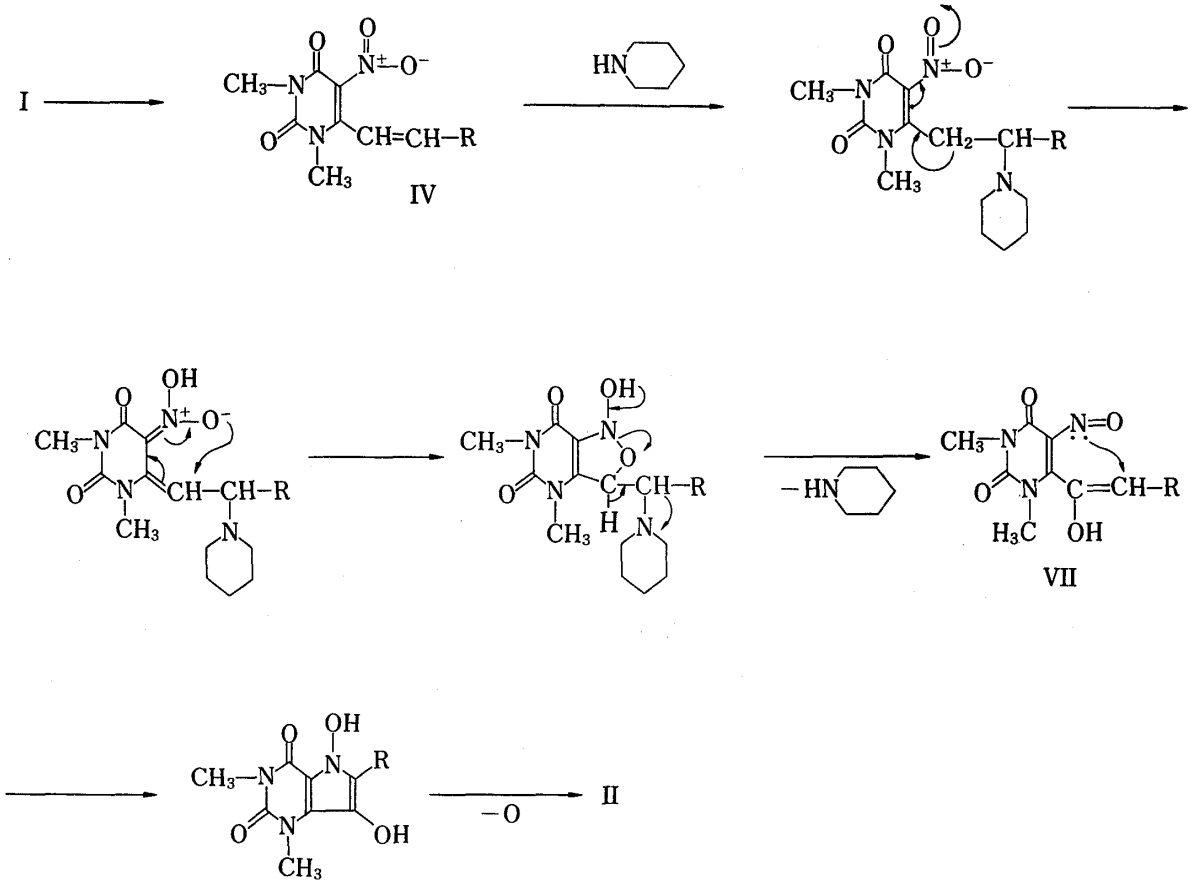


Chart 2

probably results from the substitution at the C(7) position by the methoxy group. The benzene ring is so oriented that the methyl C(16) takes the position of least steric interaction. The bond lengths and angles are listed in Tables IX and X, respectively. They are in good agreement with those of compounds of similar structures.

TABLE V. Crystal Data

Formula	$C_{16}H_{16}ClN_3O_3$
Formula weight	333.8
Crystal system	Triclinic
Cell dimensions	$a = 9.585(2)$ Å
	$b = 10.934(2)$ Å
	$c = 7.189(2)$ Å
	$\alpha = 94.79(4)°$
	$\beta = 100.17(2)°$
	$\gamma = 87.22(2)°$
Cell volume	738.6(3) Å^3
Space group	$P\bar{1}$
Calculated density	1.50 g/cm^3
Number of formula units in the unit cell	$Z=2$

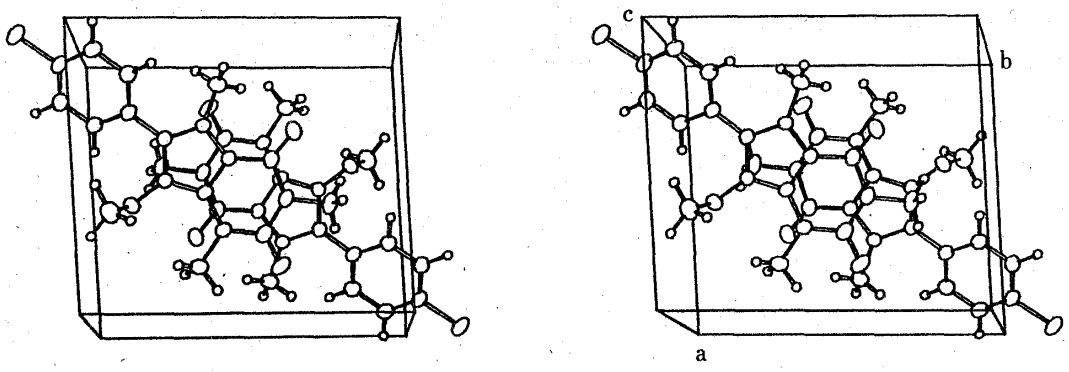


Fig. 3. Stereodrawing of the Molecular Arrangement in the Unit Cell Seen Normal to the a-b Plane

Figure 3 shows the molecular arrangement in the unit cell. The plane of the 9-deazatheophylline is almost parallel to the a-b plane, and lies right above or below that of the molecule which is spatially related by the center of symmetry. Thus, the molecules are stacked in the crystal lattice in the direction of the c axis.

Experimental

Melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. NMR spectra were recorded on a Hitachi R-24B 60 MHz spectrometer with tetramethylsilane as an internal standard. IR spectra were obtained from Nujol mulls with a JASCO RI-A1 spectrometer.

2-Aryl-3-hydroxy-4,6-dimethylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-diones (8-Aryl-9-hydroxy-9-deazatheophyllines) (II). General Procedure——A mixture of 1,3,6-trimethyl-5-nitrouracil (I) (0.5 g, 0.0025 mol), an aryl aldehyde (0.0075 mol), and piperidine (0.32 g, 0.0037 mol) in dimethylformamide (DMF) (5 ml) was refluxed at 170°C (oil bath temperature) for 2 h. The reaction mixture was evaporated *in vacuo*, and the residue was treated with a small amount of ethanol to cause the separation of crystals, which were filtered off and dried. Recrystallization from ethanol gave the corresponding 8-aryl-9-hydroxy-9-deazatheophylline as a microcrystalline powder (Table I).

Alternative Synthesis of 3-Hydroxy-4,6-dimethyl-2-phenylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-dione (8-Phenyl-9-hydroxy-9-deazatheophylline) (IIa)——A mixture of 1,3-dimethyl-5-nitro-6-styryluracil (IV) (0.5 g, 0.0017 mol) and piperidine (0.22 g, 0.0026 mol) in DMF (5 ml) was refluxed at 170°C (oil bath temperature) for 3 h. The reaction mixture was evaporated *in vacuo* and the residue was recrystallized from DMF to give IIa as a yellow powder, mp 316°C, in 37% yield.

2-Aryl-3-methoxy-1,4,6-trimethylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-diones (8-Aryl-9-methoxy-7-methyl-9-deazatheophyllines) (III). General Procedure——A mixture of an 8-aryl-9-hydroxy-9-deazatheophylline (II) (0.002 mol), methyl iodide (0.71 g, 0.005 mol), and potassium carbonate (0.51 g, 0.0037 mol) in DMF (25 ml) was refluxed at 170°C (oil bath temperature) for 3 h. The reaction mixture was evaporated *in vacuo* and the residue was diluted with water to separate crystals, which were filtered off, washed with water and dried. Recrystallization from ethanol gave the corresponding 8-aryl-9-methoxy-7-methyl-9-deazatheophylline as needles (Table II).

2-Aryl-3-benzoxy-4,6-dimethylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-diones (8-Aryl-9-benzoxy-9-deazatheophyllines (VIII). General Procedure——A mixture of an 8-aryl-9-hydroxy-9-deazatheophylline (II) (0.0024 mol) and a benzoyl chloride (0.006 mol) in pyridine (10 ml) was heated under stirring at 100°C for 4 h, then cooled. The crystals which separated were filtered off, washed with water and dried. Recrystallization from ethanol gave the corresponding 8-aryl-9-benzoxy-9-deazatheophylline (Table III).

3-Acetoxy-4,6-dimethyl-2-phenylpyrrolo[3,2-*d*]pyrimidine-5,7(4*H*,6*H*)-dione (9-Acetoxy-8-phenyl-9-deazatheophylline) (IX)——A mixture of acetic anhydride (5 ml), pyridine (5 ml) and IIa (0.6 g, 0.0024 mol) was heated at 90°C for 5 h. The reaction mixture was evaporated *in vacuo* and the residue was recrystallized from ethanol to give colorless needles (0.67 g, 89%).

ESR Measurements——The ESR measurements were made with a Varian E-4 X-band ESR spectrometer. The sample was dissolved in trifluoroacetic acid and transferred into ESR tubes. The ESR spectra of trifluoroacetic acid solution were measured at room temperature after degassing or without degassing.

X-Ray Determination of 8-(*p*-Chlorophenyl)-9-methoxy-7-methyl-9-deazatheophylline (IIIb) Crystallographic Measurement——The crystal used in this study was a colorless plate with dimensions of $0.5 \times 0.3 \times 0.1$ mm obtained from acetone solution. All the measurements were performed on a Rigaku AFC-5 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The cell parameters were determined by least-squares fitting of 25 reflections in the range of $28° < 2\theta < 37°$. The intensities of reflections with 2θ values up to 50° were collected by the ω scan technique ($2\theta \leqq 30°$) or 2θ-ω scan technique ($30° < 2\theta \leqq 50°$) with a scan rate of 4°/min. The background was measured at each end of the scan range for 5 s, and the reflections were measured repeatedly (up to three times) until the structure factor became ten times greater than its standard deviation. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption.

Table VI. Atomic Coordinates for Nonhydrogen Atoms with Their Standard Deviations in Parentheses

Atom	*x/a*	*y/b*	*z/c*
N (1)	0.3084(3)	0.5654(2)	0.2217(4)
C (2)	0.2936(3)	0.4408(3)	0.2139(4)
N (3)	0.4183(3)	0.3678(2)	0.2386(4)
C (4)	0.5581(3)	0.4078(3)	0.2582(4)
C (5)	0.5626(3)	0.5384(3)	0.2593(4)
C (6)	0.4425(3)	0.6148(3)	0.2476(4)
C (7)	0.4865(3)	0.7360(3)	0.2631(4)
C (8)	0.6339(3)	0.7315(3)	0.2798(4)
N (9)	0.6800(2)	0.6102(2)	0.2791(4)
C (10)	0.8277(3)	0.5627(3)	0.3232(5)
O (11)	0.6585(2)	0.3340(2)	0.2723(4)
C (12)	0.4008(4)	0.2346(3)	0.2394(5)
O (13)	0.1774(2)	0.3950(2)	0.1865(4)
C (14)	0.1789(3)	0.6437(3)	0.1962(7)
O (15)	0.4024(2)	0.8411(2)	0.2756(3)
C (16)	0.3583(4)	0.8987(3)	0.1020(6)
C (17)	0.7280(3)	0.8363(3)	0.2894(4)
C (18)	0.6976(3)	0.9475(3)	0.3872(4)
C (19)	0.7791(3)	1.0497(3)	0.3883(4)
C (20)	0.8930(3)	1.0392(3)	0.2926(4)
C (21)	0.9271(3)	0.9300(3)	0.1971(4)
C (22)	0.8432(3)	0.8285(3)	0.1933(4)
Cl (23)	0.9925(1)	1.1676(1)	0.2862(1)

Table VII. Anisotropic Temperature Factors[a] ($Å^2 \times 10^3$) for Nonhydrogen Atoms with Their Standard Deviation in Parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N (1)	25(1)	29(1)	49(2)	−3(1)	10(1)	0(1)
C (2)	36(2)	33(2)	39(2)	−8(1)	10(1)	−2(1)
N (3)	37(1)	26(1)	40(1)	−7(1)	8(1)	4(1)
C (4)	37(2)	27(2)	40(2)	−3(1)	6(1)	2(1)
C (5)	27(1)	25(1)	40(2)	−2(1)	7(1)	1(1)
C (6)	25(1)	30(2)	33(2)	−4(1)	6(1)	1(1)
C (7)	26(1)	25(1)	32(2)	0(1)	7(1)	1(1)
C (8)	28(1)	26(1)	30(1)	−2(1)	6(1)	1(1)
N (9)	23(1)	26(1)	42(1)	−1(1)	6(1)	4(1)
C (10)	26(2)	38(2)	62(2)	3(1)	6(1)	8(2)
O (11)	40(1)	28(1)	90(2)	4(1)	8(1)	6(1)
C (12)	55(2)	26(2)	45(2)	−9(1)	7(2)	3(1)
O (13)	36(1)	42(1)	76(2)	−16(1)	11(1)	1(1)
C (14)	26(2)	38(2)	104(3)	1(1)	11(2)	2(2)
O (15)	30(1)	28(1)	45(1)	5(1)	9(1)	1(1)
C (16)	48(2)	42(2)	60(2)	6(2)	5(2)	16(2)
C (17)	26(1)	28(1)	30(2)	−3(1)	2(1)	3(1)
C (18)	29(2)	31(2)	35(2)	−2(1)	7(1)	0(1)
C (19)	34(2)	27(2)	38(2)	−3(1)	4(1)	0(1)
C (20)	30(2)	30(2)	36(2)	−9(1)	−2(1)	7(1)
C (21)	29(2)	38(2)	37(2)	−4(1)	7(1)	5(1)
C (22)	30(2)	32(2)	36(2)	−1(1)	9(1)	−1(1)
Cl (23)	42(1)	37(1)	53(1)	−17(1)	3(1)	6(1)

a) Anisotropic temperature factors are of the form: $T=\exp[-2\pi^2(U_{11}h^2a^{a)2}+U_{22}k^2b^{a)2}+U_{33}l^2c^{a)2}+2U_{12}hka^{a)}b^{a)}+2U_{13}hla^{a)}c^{a)}+2U_{23}klb^{a)}c^{a)})]$.

Table VIII. Atomic Coordinates and Isotropic Temperature Factors ($Å^2 \times 10^3$) for Hydrogen Atoms with Their Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	U
H (10)	0.889(4)	0.630(3)	0.405(5)	66(12)
H (10)′	0.867(4)	0.539(3)	0.200(5)	67(12)
H (10)″	0.828(4)	0.493(4)	0.413(6)	75(12)
H (12)	0.490(4)	0.199(4)	0.326(6)	73(12)
H (12)′	0.394(4)	0.197(4)	0.097(6)	76(13)
H (12)″	0.322(4)	0.223(4)	0.311(6)	80(13)
H (14)	0.092(4)	0.591(4)	0.147(6)	83(13)
H (14)′	0.175(4)	0.702(4)	0.090(6)	91(14)
H (14)″	0.166(5)	0.693(4)	0.323(6)	94(14)
H (16)	0.317(4)	0.834(3)	−0.006(5)	66(12)
H (16)′	0.276(4)	0.961(4)	0.110(6)	80(13)
H (16)″	0.447(4)	0.937(4)	0.067(6)	75(13)
H (18)	0.614(4)	0.957(3)	0.463(5)	52(10)
H (19)	0.752(4)	1.131(3)	0.461(5)	54(10)
H (21)	1.009(4)	0.923(3)	0.117(5)	56(11)
H (22)	0.864(4)	0.753(3)	0.102(5)	55(10)

Structure Determination——Of the 2589 independent reflections collected, 2172 satisfying the condition $F \geqq 3\sigma(F)$ were used for calculations. The structure was solved by the direct method using the MULTAN[9] series of programs, and refined by the unit weight block-diagonal least-squares method with the X-ray[10] system. The E-map prepared from the most probable set of phases revealed all 23 nonhydrogen atoms corresponding to the structure. At the first stage of the refinement all atoms except for the chlorine atom, which was twice to three times as large as other peaks on the E-map, were treated as carbon atoms with isotropic thermal vibrations. After several cycles of least-squares refinement, the six atoms with the smallest

temperature factors were considered to be oxygen or nitrogen. The bond distances also suggested that these assignments were reasonable. The structure was further refined by applying anisotropic temperature factors to all atoms, and all the 16 hydrogens were clearly located on the differential electron density map. They were included in the successive refinement with isotropic temperature factors, and a final R value of 0.044 for 2172 observed reflections was reached. The atomic scattering factors used were taken from those of Stewart *et al.*[11] for hydrogen and from the International Tables[12] for others.

TABLE IX. Bond Distances (Å) with Their Standard Deviations in Parentheses

N(1)-C(2)	1.371(4)	N(1)-C(6)	1.394(4)
N(1)-C(14)	1.466(4)	C(2)-N(3)	1.398(4)
C(2)-O(13)	1.222(4)	N(3)-C(4)	1.410(4)
N(3)-C(12)	1.475(4)	C(4)-C(5)	1.430(4)
C(4)-O(11)	1.221(4)	C(5)-C(6)	1.383(4)
C(5)-C(9)	1.384(4)	C(6)-C(7)	1.401(4)
C(7)-C(8)	1.396(4)	C(7)-O(15)	1.376(3)
C(8)-N(9)	1.377(4)	C(8)-C(17)	1.482(4)
N(9)-C(10)	1.474(4)	O(15)-C(16)	1.432(4)
C(17)-C(18)	1.397(4)	C(17)-C(22)	1.398(4)
C(18)-C(19)	1.392(4)	C(19)-C(20)	1.386(5)
C(20)-C(21)	1.381(4)	C(20)-Cl(23)	1.744(3)
C(21)-C(22)	1.398(4)		
C(10)-H(10)	1.04(4)	C(10)-H(10)′	1.03(4)
C(10)-H(10)″	1.04(4)	C(12)-H(12)	1.05(4)
C(12)-H(12)′	1.07(4)	C(12)-H(12)″	1.01(4)
C(14)-H(14)	1.03(4)	C(14)-H(14)′	1.03(5)
C(14)-H(14)″	1.05(4)	C(16)-H(16)	1.05(4)
C(16)-H(16)′	1.02(4)	C(16)-H(16)″	1.04(4)
C(18)-H(18)	1.04(4)	C(19)-H(19)	1.04(3)
C(21)-H(21)	1.05(4)	C(22)-H(22)	1.05(3)

TABLE X. Bond Angles (°) for Nonhydrogen Atoms with Their Standard Deviations in Parentheses

C(2)-N(1)-C(6)	120.6(2)	C(2)-N(1)-C(14)	117.8(2)
C(6)-N(1)-C(14)	121.5(2)	N(1)-C(2)-N(3)	116.9(3)
N(1)-C(2)-O(13)	122.0(3)	N(3)-C(2)-O(13)	121.1(3)
C(2)-N(3)-C(4)	126.8(2)	C(2)-N(3)-C(12)	116.3(3)
C(4)-N(3)-C(12)	116.9(2)	N(3)-C(4)-C(5)	112.1(2)
N(3)-C(4)-O(11)	120.6(3)	C(5)-C(4)-O(11)	127.3(3)
C(4)-C(5)-C(6)	123.0(3)	C(4)-C(5)-N(9)	128.4(2)
C(6)-C(5)-N(9)	108.6(2)	N(1)-C(6)-C(5)	120.4(2)
N(1)-C(6)-C(7)	132.0(3)	C(5)-C(6)-C(7)	107.6(2)
C(6)-C(7)-C(8)	107.4(2)	C(6)-C(7)-O(15)	126.7(2)
C(8)-C(7)-O(15)	125.7(2)	C(7)-C(8)-N(9)	108.3(2)
C(7)-C(8)-C(17)	127.4(2)	N(9)-C(8)-C(17)	124.3(2)
C(5)-N(9)-C(8)	108.2(2)	C(5)-N(9)-C(10)	124.1(2)
C(8)-N(9)-C(10)	127.0(2)	C(7)-O(15)-C(16)	115.5(2)
C(8)-C(17)-C(18)	119.9(3)	C(8)-C(17)-C(22)	121.1(2)
C(18)-C(17)-C(22)	118.9(3)	C(17)-C(18)-C(19)	121.0(3)
C(18)-C(19)-C(20)	118.9(2)	C(19)-C(20)-C(21)	121.5(2)
C(19)-C(20)-Cl(23)	119.4(2)	C(21)-C(20)-Cl(23)	119.1(2)
C(20)-C(21)-C(22)	119.4(3)	C(17)-C(22)-C(21)	120.4(3)

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