product was extracted with ether. From the washed and dried ethereal solution, the crude 16-methyltestosterone was separated by concentration and chilling. The product 1.0 g. (89.5%) melted at 175–182°. Several recrystallizations from acetone gave prisms melting at 182–184°; $[\alpha]^{27}D$ + 106 ± 2° (56.6 mg. made up to 5 ml. with chloroform, α_D + 1.20°, *l*, 1 dm.).

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.43; H, 9.99. Found: C, 79.50; H, 9.93.

Hydrolysis of 16-methyltestosterone acetate in this manner gave the same product as described above. In one experiment, after one hour of hydrolysis, a considerable portion of the benzoate was recovered unchanged. A comparable hydrolysis of testosterone benzoate under these conditions went to completion.

A sample of the 16-methyltestosterone was converted to the propionate (XI) by treatment with propionic anhydride at steam-bath temperature for two hours. After several recrystallizations from methanol, the propionate melted at 138–140.5°.

Anal. Calcd. for $C_{23}H_{34}O_3$: C, 77.04; H, 9.57. Found: C, 77.26; H, 9.71.

3(β),17-Diacetoxy-16-methyl-5-androstene (VI).—In a manner similar to that described for the preparation of the acetate-benzoate (V), 16-methylenedehydroisoandrosterone acetate was converted to the diacetate (VI). In this instance, after removal of solvent from the reduction solution, the residue gave upon acetylation with acetic anhydride–acetic acid 45.5% of crude crystalline material, from ether–petroleum ether (b. p. 35–60°), melting at 165–175°. Several recrystallizations from the same solvent mixture yielded glistening white plates which melted at 175–177.5°; $[\alpha]^{27}D$ − 39.9 ± 1° (36.3 mg. made up to 5 ml. with chloroform, α_D − 0.29°, *l*, 1 dm.).

Anal. Calcd. for $C_{24}H_{36}O_4$: C, 74.18; H, 9.34. Found: C, 74.00; H, 9.24.

3(β)-Hydroxy-17-acetoxy-16-methyl-5-androstene (VIII).—To a hot solution of 9.7 g. of the diacetate (VI) in 450 ml. of methanol, there was added a solution of 1.8 g. of potassium hydroxide in 18 ml. of water and 50 ml. of methanol. After being refluxed for twenty-five minutes, the mixture was rapidly concentrated *in vacuo* with little heat to about 100 ml. The cold mixture was filtered and the solid washed sparingly with cold methanol. There resulted 7.0 g. (80.9%) of white crystalline material melting at 156–164°. Several recrystallizations from methanol gave glistening plates, m. p. 164.5–168.5°, which lose solvent of crystallization upon careful drying *in vacuo*. $[\alpha]^{27}D$ − 36.7 ± 1° (38.1 mg. made up to 5 ml. with chloroform, α_D − 0.28°, *l*, 1 dm.).

Anal. Calcd. for $C_{22}H_{34}O_3$: C, 76.25; H, 9.90. Found: C, 75.79; H, 9.77.

16-Methyltestosterone Acetate (X).—A solution of 4.5 g. of the monoacetate in 40 ml. of toluene containing 4.0 g. of aluminum isopropoxide and 15 ml. of cyclohexanone was refluxed for two hours. After cooling, the mixture was diluted with 10% hydrochloric acid and extracted with ether. The ethereal solution was washed with water, 10% sodium hydroxide solution, water and steam distilled. The chilled residue was taken up in ether and washed with 2% sodium hydroxide and water. The product was crystallized from the dried, concentrated ethereal solution. After chilling, it was filtered and washed with cold ether; 3.9 g. (87%), m. p. 150–160°. After a number of crystallizations from ether–petroleum ether (b. p. 35–60°), the melting point was still not sharp; however, this material gave a good yield of 16-methyltestosterone (80%). This range *may* be due to minor contamination with isomeric material which is difficult to separate.

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.71; H, 9.35. Found: C, 76.77; H, 9.55.

Summary

1. Dehydroisoandrosterone has been subjected to the Mannich reaction to yield the expected 16-aminomethyl derivatives.

2. 16-Dimethylaminomethyldehydroisoandrosterone was converted into 16-methylenedehydroisoandrosterone acetate on treatment with acetic acid–acetic anhydride.

3. By reduction of 16-methylenedehydroisoandrosterone acetate followed by esterification, partial saponification, oxidation, and hydrolysis, a 16-methyltestosterone was prepared. This testosterone showed androgenic activity.

CHICAGO, ILLINOIS RECEIVED MAY 13, 1948

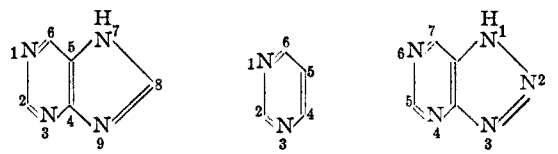
[CONTRIBUTION FROM THE SLOAN-KETTERING INSTITUTE FOR CANCER RESEARCH]

Ultraviolet Absorption Spectra of Purines, Pyrimidines and Triazolopyrimidines[1]

BY LIEBE F. CAVALIERI, AARON BENDICH, JOHN F. TINKER AND GEORGE BOSWORTH BROWN[2]

Introduction

The ultraviolet absorption spectra of purines and pyrimidines have received considerable attention in the past[3,4] but the specific chromophore or chromophores responsible for the absorption have not been definitely assigned. The purpose of the present investigation was to correlate the spectra of various substituted purines, pyrimidines and triazolopyrimidines and ascertain which functional groups are the chromophores.



Purine Pyrimidine Triazolopyrimidine

The purity of the compounds studied here is not readily determined by ordinary means and it was necessary to resort to another technique to determine their homogeneity. The counter-current distribution procedure has been applied successfully to this class of compounds[5] and the detection and separation of small amounts of related sub-

(1) The material in this paper was presented before the 113th Meeting of the American Chemical Society, Chicago, Ill., April, 1948.

(2) The authors gratefully acknowledge the assistance of the Office of Naval Research, the James Foundation of New York, Inc., and the Lord and Taylor Fund, New York.

(3) (a) Heyroth and Loofbourow, THIS JOURNAL, **56**, 1728 (1934); (b) Stimson and Reuter, *ibid.*, **65**, 154 (1943).

(4) Loofbourow and Stimson, *J. Chem. Soc.*, 844 (1940).

(5) Tinker and Brown, *J. Biol. Chem.*, **178**, 585 (1948).

stances was readily possible. The compounds examined, with the exception of hypoxanthine, were found by this method to be homogeneous within the limits of experimental error.

Results

The spectra of various pyrimidines are given in Fig. 1. 4,5,6-Triaminopyrimidine (Curve 1C), 4,5,6-triamino-2-hydroxypyrimidine (Curve 3C),

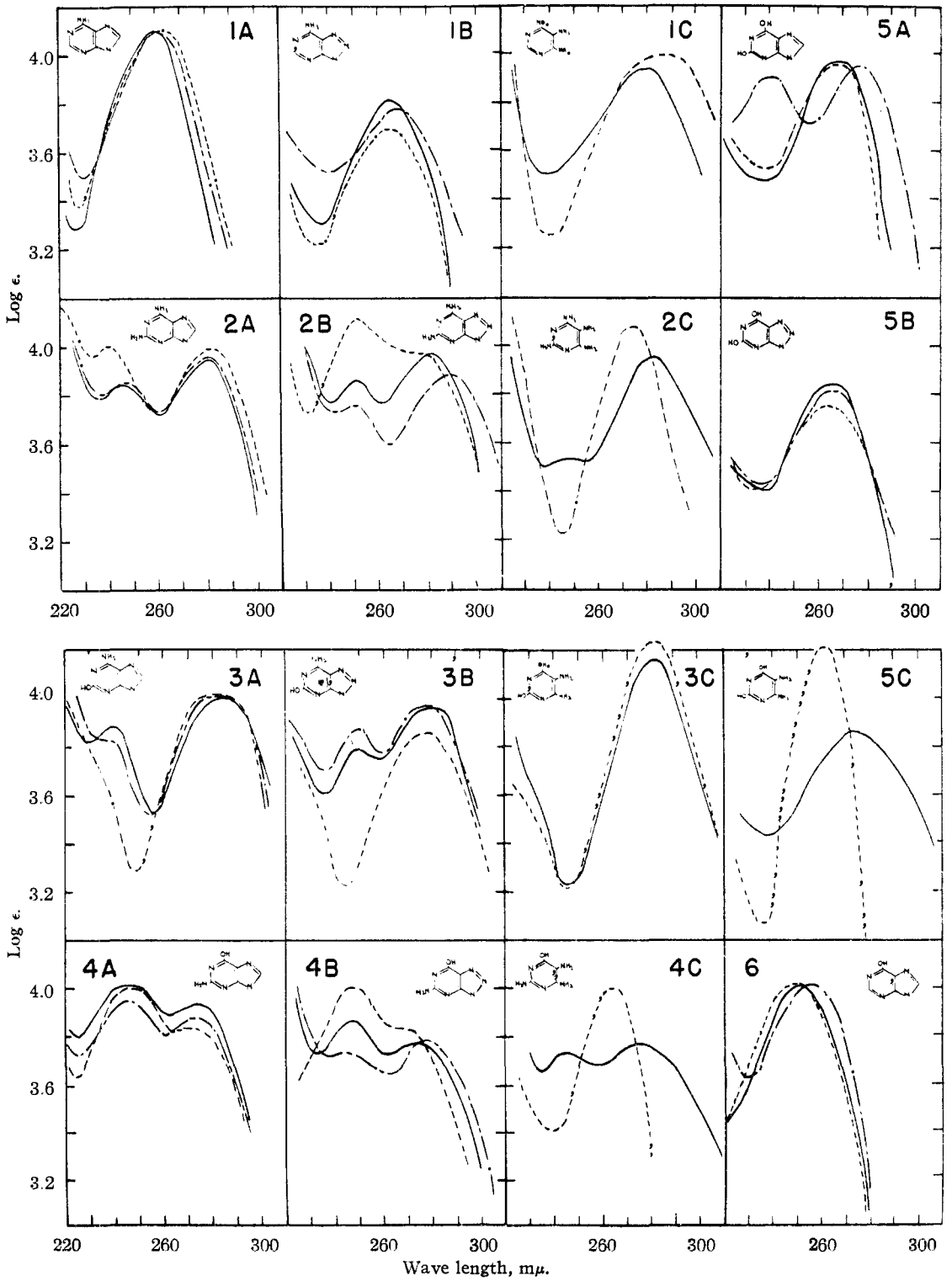


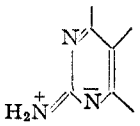
Fig. 1.—Absorption spectra curves: ----, *p*H 2; — *p*H 6; —·— *p*H 9.

4,5-diamino-2,5-dihydroxypyrimidine (Curve 5C) and 4,5-diamino-6-hydroxypyrimidine (Table I) exhibit only one maximum in the region of 278 ± 5 mμ. Pyrimidine and 6-amino-2-hydroxypyrimidine[6] (cytosine) also exhibit only one band.[7] On the other hand, 2,4,5,6-tetraminopyrimidine (Curve 2C) and 2,4,5-triamino-6-hydroxypyrimidine (Curve 4C) possess two maxima. Stimson and Reuter[7] report that 2-aminopyrimidine and 2-amino-6-hydroxypyrimidine (isocytosine) possess two bands which appear at 225, 290 and 265, 285, respectively. Thus the data indicate that the appearance of a second band toward the far ultraviolet region coincides with the presence of the 2-amino group.

In the purine series, adenine (Curve 1A) hypoxanthine (Curve 6) and xanthine (Curve 5A, at *p*H 2 and 6) exhibit one maximum, while 2,6-diaminopurine (Curve 2A), isoguanine (Curve 3A) and guanine (Curve 4A) exhibit two bands (Fig. 1). The presence of either a 2-amino or 2-hydroxyl group coincides therefore with the appearance of the second maximum in the far ultraviolet. The spectra of the related triazolopyrimidines (Curves 1B-5B) bear a remarkable similarity to those of the corresponding purines.

Discussion

Since the pyrimidines bearing a hydrogen or an hydroxyl in the 2 position exhibit a single maximum at 278 ± 5 mμ, it is reasonable to assume that the same type of chromophore is involved in each case. Further, the appearance of a single band suggests that the chromophore is relatively simple. The $-\overset{|}{C}=N-$ group in the 6,1-position fulfils these conditions. Undoubtedly interaction of this group with the $-\overset{|}{C}=\overset{|}{C}-$ in the 4,5-position occurs, but this is minimal since the 3-nitrogen attracts the π electrons of $-\overset{|}{C}=\overset{|}{C}-$, thereby decreasing their tendency to enter into a resonating system. When an amino group is present in the 2-position, the situation is altered. The form

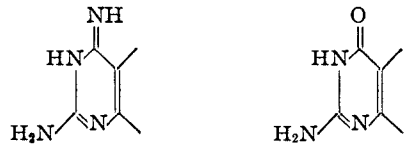


tends to decrease the inductive effect of the 3-nitrogen on the π electrons in the $-\overset{|}{C}=\overset{|}{C}-$ at the 4,5-position. These π electrons then have a greater tendency to interact with the $-\overset{|}{C}=N-$ in the 6,1-position and the resonator $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=N-$ makes a greater contribution to the actual state of the molecule. In many cases, such α,β-unsaturated systems exhibit two bands.

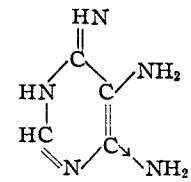
(6) The numbering of this compound according to *Chem. Abs.* is 4-amino-2-hydroxypyrimidine; however, in order to better correlate the purines and pyrimidines and to avoid confusion with previous literature, the older system is used throughout this paper.

(7) Stimson and Reuter, THIS JOURNAL, **67**, 2191 (1945).

It must be pointed out that in the cases in which an amino or an hydroxyl group is present in the 6-position, the same type of resonating system may result.



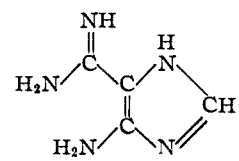
The fact that both 6-aminopyrimidine and 6-hydroxypyrimidine exhibit two bands[8] although neither compound contains a 2-amino group, while 4,5-diamino-6-hydroxypyrimidine and 4,5,6-triaminopyrimidine exhibit one band, would appear to be contradictory. The difference between these pairs of compounds may be interpreted as an effect of the 4-amino group, which, in the latter two compounds, tends to oppose the participation of the π electrons of the $-\overset{|}{C}=\overset{|}{C}-$ in the $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=N-$ through an inductive mechanism. This inductive



effect cannot be present in either 6-hydroxypyrimidine or 6-aminopyrimidine. Thus when a 4-amino group is present the compensating effect of a 2-amino group is necessary to bring about the appearance of two bands.

In the purine series, adenine, hypoxanthine and xanthine (at *p*H 6) exhibit only one band. It will be seen (Fig. 1) that the parent pyrimidines also possess only one band. Guanine, isoguanine and 2,6-diaminopurine exhibit two maxima and the parent pyrimidines, except 4,5,6-triamino-2-hydroxypyrimidine (which has, however, a shoulder at 235 mμ), also possess two maxima. These data suggest that the ultraviolet spectra of purines are due principally to the pyrimidine moiety of the molecule. Further evidence to support this interpretation is found in the spectra of the triazolopyrimidines which exhibit a high degree of similarity to those of the corresponding purines. Thus the change from an imidazole to a triazole ring has little effect on the spectroscopic properties of the molecule as a whole.

It can further be postulated that the chromophore in the pyrimidine ring resides principally in the $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=N-$ system. 4(5)-Amino-5(4)-



(8) Williams, Ruehle and Finkelstein, *ibid.*, **59**, 526 (1937).

TABLE I
SPECTRAL DATA

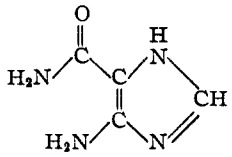
Curve	Compound	Concn. moles/lit. × 10^5	pH[a]	Max. mμ	Log ε	Max. mμ	Log ε	Distribution constant[b]
			Purines					
1A	Adenine[2]	7.03	1.99			264	4.098	2.20
			6.47			261	4.098	
			8.99			262	4.094	
2A	(2,6-Diaminopurine)$_2$ $H_2SO_4 \cdot H_2O$	2.14	1.97	241	4.001	282	3.997	1.21
			6.49	247	3.845	280	3.945	
			9.02	248	3.885	280	3.956	
3A	(Isoguanine)$_2$ $H_2SO_4 \cdot H_2O$	2.20	1.97			282	4.125	0.28
			6.48	238	3.868	286	4.017	
			8.96			282	4.095	
4A	(Guanine)$_2 \cdot H_2SO_4 \cdot 2H_2O$[3]	3.59	1.93	247	4.020			.45
			5.99	246	4.033	275	3.934	
			8.80	245	3.941	275	3.977	
5A	Xanthine[3,13]	7.37	2.01			266	3.963	.46
			6.58			268	3.965	
			9.02	240	3.908	277	3.948	
6	Hypoxanthine[3]	10.59	1.99			250	4.023	.54
			6.44			251	4.013	
			8.82			257	4.023	
			Triazolopyrimidines					
1B	7-Amino-1-v-triazolo[d]pyrimidine[16]	14.25	2.01			265	3.691	1.05
			6.53			265	3.820	
			8.83			265	3.776	
2B	(5,7-Diamino-1-v-triazolo[d]pyrimidine)$_2$· H_2SO_4	5.15	1.97	252	4.119			1.03
			6.49	251	3.860	282	3.974	
			8.19	250	3.756	289	3.882	
3B	7-Amino-5-hydroxy-1-v-triazolo[d]-pyrimidine·HCl	5.54	2.08			277	3.368	0.21
			6.68	250	3.799	277	3.956	
			8.56	250	3.872	277	3.972	
4B	5-Amino-7-hydroxy-1-v-triazolo[d]-pyrimidine·HCl[16]	8.64	1.98	247	4.012			.32
			6.59	247	3.859	274	3.772	
			8.43	247	3.738	274	3.778	
5B	5,7-Dihydroxy-1-v-triazolo[d]-pyrimidine	9.54	1.97			265	3.752	.24
			6.54			265	3.842	
			8.45			265	3.812	
			0.1 *N* NaOH	234	3.669	285	3.770	
			Pyrimidines					
1C	4,5,6-Triaminopyrimidine	13.36	1.97			287	4.008	.45
		5.34	6.50			279	3.938	
2C	2,4,5,6-Tetraminopyrimidine·H_2SO_4	6.77	2.20			273	4.064	.040[c]
		5.88	6.29	250	3.534	283	3.944	.026[d]
3C	4,5,6-Triamino-2-hydroxypyrimidine· H_2SO_4	2.99	1.97			280	4.231	.14
			6.46			280	4.156	
4C	(2,4,5-Triamino-6-hydroxypyrimidine)· H_2SO_4	6.83	1.95			264	3.994	.023[c]
		5.72	6.29	245	3.728	275	3.768	.025[d]
5C	(4,5-Diamino-2,6-dihydroxypyrimidine)$_2$· H_2SO_4	3.88	2.03			260	4.216	.043[c]
		3.85	6.28			273	3.865	.045[d]
	4,5-Diamino-6-hydroxypyrimidine·HCl[16]	9.30	2.26			257	3.824	.24
		9.47	6.30			279	4.000	

[a] The *p*H of each solution was determined with a Beckman *p*H meter. [b] Determined in *n*-butanol–1 *M* potassium phosphate buffer, *p*H 6.5. [c] These values are probably in error due to the instability of the compounds at a neutral *p*H. [d] Determined in *n*-butanol–1 *M* potassium phosphate buffer, *p*H 1.99.

imidazolecarboxamidine[9] possesses a single intense maximum at 287 mμ. It will be noted that this compound is the adenine molecule with the 2-carbon atom removed. The shift of the band from 261 mμ in adenine to 287 mμ in the imidazole derivative is doubtless associated with the greater resonance possible in the 5(4)-carboxamidine portion of the latter. Another example of this effect

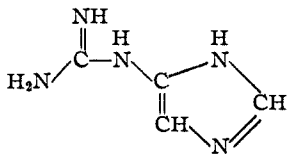
(9) The properties and preparation of this compound are described in a forthcoming publication.

is seen in the spectrum of 4(5)-amino-5(4)-imidazolecarboxamide[10] which exhibits a maximum at 269 mμ. The parent compound, hypoxanthine, has a band at 251 mμ. Thus the intact pyrimidine



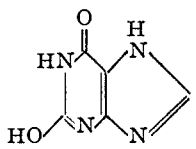
ring is not required for the absorption of ultraviolet light and it may be concluded that the —C=N— group in the 2,3-position is of secondary importance in the spectroscopic properties of the molecule. The —C=C—C=N— or —C=C—C=O groupings in the 4(5)-amino-5(4)-imidazolecarboxamidine and 4(5)-amino-5(4)-imidazolecarboxamide would not be expected to show two bands because the 4(5)-amino group in each case has a strong attraction for the π electrons of the —C=C— group and interaction between this group and the C=O or C=N is minimized.

Further evidence in support of the hypothesis that the —C=C—C=N is the major chromophore is afforded by the spectrum of 4(5)-guanidinoimidazole[11] in which the —C=C— and the —C=N— are insulated by an —NH— group. This compound



shows only general absorption. The fact that this imidazole derivative, as well as imidazole itself,[11] shows no selective absorption also confirms the conclusion that the spectra of the purines is due principally to the pyrimidine moiety.

The behavior of xanthine at an alkaline *p*H (Curve 5A) presents an interesting case. At *p*H 8.45 a second maximum at 240 mμ appears[12]; this implies that a form of the type



predominates. Evidence that the appearance of the second peak at 240 mμ parallels the enolization of the 2-carbonyl group is found in the spectra of 1-methylxanthine and 3-methylxanthine.[13] 3-Methylxanthine, which cannot enolize to a form of the type shown, shows one band at 275 mμ, while 1-methylxanthine, the structure of which necessitates a 6-carbonyl, but permits enolization of the 2-carbonyl, shows spectra in neutral and alkaline solutions similar to those of xanthine. This enolization results in a decrease of the electronegativity of the 3-nitrogen (by virtue of the loss of a hydrogen atom) with the result that the —C=C— interacts to a greater extent with the >C=O group; hence the second band.

The previous discussion has revolved about the —C=C—C=N— system as the principal chromophore. This is doubtless oversimplified since it is clear that the interaction of the —C=C—C=N— with the rest of the molecule is involved and the actual chromophore is the resultant of all of these electrical effects. It is felt, however, that a working hypothesis has been established.

TABLE II

Pyrimidines	Formula	Calculated	Found	Reference
4,5,6-Triamino-	$C_4H_7N_5$	N, 55.97	55.91	14
2,4,5,6-Tetramino-	$C_4H_8N_6 \cdot H_2SO_4$[a,b]	S, 13.45	13.06	17
2,4,5-Triamino-6-hydroxy-	$C_4H_7ON_5 \cdot H_2SO_4$[b]	S, 13.40	13.41	19
4,5,6-Triamino-2-hydroxy-	$C_4H_7ON_5 \cdot H_2SO_4$	N, 29.28	29.21	18
4,5-Diamino-2,6-dihydroxy-	$(C_4H_6O_2N_4)_2 \cdot H_2SO_4$[b]	S, 8.39	8.31	17
4,5-Diamino-6-hydroxy-	$C_4H_6ON_4 \cdot HCl$	N, 34.49	34.35	16
7-Amino-1-v-triazolo-[d]-Purines	$C_4H_4N_6$	N, 61.76	61.57	16
Adenine	$C_5H_5N_5$	N, 51.83	51.60	15
Guanine	$(C_5H_5ON_5)_2 \cdot H_2SO_4 \cdot 2H_2O$	N, 32.1	31.90	14
Isoguanine	$(C_5H_5ON_5)_2 \cdot H_2SO_4 \cdot H_2O$	N, 33.50	33.40	18
Xanthine	$C_5H_4O_2N_4$	N, 36.84	36.60	14
2,6-Diamino-purine	$(C_5H_6N_6)_2 \cdot H_2SO_4 \cdot H_2O$	S, 7.70	7.67	18

[a] The sulfate was obtained by recrystallizing the bisulfite from 2 *N* sulfuric acid. [b] An interesting feature of these compounds is their great instability in an aqueous medium at a neutral *p*H. After a period of fifteen minutes marked changes occurred in these solutions, and after two hours they were completely transparent to ultraviolet light. It was impossible to obtain satisfactory spectra in alkaline solution. 4,5,6-Triaminopyrimidine and 4,5,6-triamino-2-hydroxypyrimidine are somewhat more stable under these conditions.

(10) (a) Shive, Ackermann, Gordon, Getzendanner and Eakin, THIS JOURNAL, **69**, 725 (1947); (b) Stetten and Fox, *J. Biol. Chem.*, **161**, 333 (1945).

(11) Hunter, *Biochem. J.*, **30**, 1183 (1936).

(12) In the case of the triazolo analog of xanthine a higher *p*H (0.1 *N* sodium hydroxide) is required for the appearance of a second band (Table I).

(13)(a) Gulland, Holiday and Macral, *J. Chem. Soc.*, 1639 (1943); (b) Gulland and Holiday, *Nature*, **132**, 728 (1933).

(14) Brown, Roll, Plentl and Cavalieri, *J. Biol. Chem.*, **172**, 469 (1948).

(15) Traube, *Ann.*, **331**, 64 (1904).

(16) Roblin, Lampers, English, Cole and Vaughn, THIS JOURNAL, **67**, 290 (1945).

(17) Cain, Mallette and Taylor, *ibid.*, **68**, 1996 (1946); Mallette, Taylor and Cain, *ibid.*, **69**, 1814 (1947).

(18) Bendich, Tinker and Brown, *ibid.*, **70**, 3109 (1948).

(19) Plentl and Schoenheimer, *J. Biol. Chem.*, **153**, 205 (1944).

Experimental

Methods.—The spectra reported were determined with a Beckman spectrophotometer, Model DU. Measurements were made at 1 mμ intervals throughout the critical ranges. The appropriate amounts of purines and triazolopyrimidines were dissolved in 100 cc. of water and diluted 1 to 10 with 0.1 *M* phosphate buffer. In the case of the pyrimidines the spectral determinations at *p*H 6 were made in the following manner: solutions were first prepared at *p*H 2 and then diluted 1 to 10 with phosphate buffer of *p*H 6.53 and the spectrum determined immediately.

Materials.—The purity of each compound (Tables I and II) was determined by the counter-current distribution method and each was shown to be homogeneous within experimental error (0.5 to 2.0%). All compounds were synthesized in this Laboratory with the exception of hypoxanthine which was a commercial sample and which was shown to contain about 3–4% adenine.

5,7-Diamino-1-*v*-triazolo[*d*]pyrimidine sulfate.—2,4,5,6-Tetraminopyrimidine sulfate (9 g.) was dissolved in 1500 cc. of boiling water. The solution was decolorized, filtered and cooled to about 15°. Sodium nitrite (2.8 g.) in 5 cc. of water was added. After fifteen minutes the product was collected by filtration. It was recrystallized from hot 2 *N* sulfuric acid. The resulting triazolopyrimidine sulfate was taken up in dilute ammonia, decolorized and filtered. To the clear solution was added 12 cc. of 18 *N* sulfuric acid and the sulfate precipitated. The mixture was heated until all the solid had gone into solution and the solution was again decolorized, filtered and cooled, yielding 2.2 g. of product. Another recrystallization from 2 *N* sulfuric acid gave a sample which was homogeneous when investigated by counter-current distribution.[5]

Anal. Calcd. for $(C_4H_5N_7)_2H_2SO_4$: S, 7.99. Found: S, 7.87.

5-Amino-7-hydroxy-1-*v*-triazolo[*d*]pyrimidine Hydrochloride.[15]—Ten grams of 2,4,5-triamino-6-hydroxypyrimidine sulfate was dissolved in 150 cc. of 18 *N* sulfuric acid. To the solution at 0° was added slowly 3 g. of sodium nitrite in 15 cc. of water. After two hours the solution was filtered and the residue discarded. The filtrate was brought to *p*H 5 with sodium hydroxide and the free triazolopyrimidine separated. The product was collected by filtration and dissolved in dilute aqueous ammonia. Acidification with glacial acetic acid produced a white precipitate (2.3 g.) which was recrystallized three times from 6 *N* hydrochloric acid.

Anal. Calcd. for $C_4H_4ON_6 \cdot HCl$: Cl, 18.80. Found: Cl, 18.75.

7-Amino-5-hydroxy-1-*v*-triazolo[*d*]pyrimidine Hydrochloride.—Ten grams of 4,5,6-triamino-2-hydroxypyrimidine sulfate was dissolved in 1500 cc. of boiling water, decolorized and filtered. The solution was cooled to room temperature and 3.4 g. of sodium nitrite in 10 cc. of water was added in several portions. The product was collected by filtration and reprecipitated from dilute aqueous ammonia by the addition of glacial acetic acid; yield 2 g. The base was recrystallized twice from 6 *N* hydrochloric acid.

Anal. Calcd. for $C_4H_4ON_6 \cdot HCl$: Cl, 18.80. Found: Cl, 18.95.

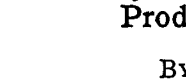
5,7-Dihydroxy-1-*v*-triazolo[*d*]pyrimidine.[16]—4,5-Diamino-2,6-dihydroxypyrimidine sulfate (1.7 g.) was dissolved in 375 cc. of boiling water and the solution decolorized. The solution was cooled to room temperature and 0.8 g. of sodium nitrite in 10 cc. of water was added. The mixture was allowed to stand overnight at room temperature and then evaporated to dryness under diminished pressure. The yellow residue was taken up in dilute ammonia, decolorized, reprecipitated with acetic acid, and recrystallized twice from water.

Anal. Calcd. for $C_4H_3O_2N_5$: N, 45.72. Found: N, 45.40.

The authors wish to thank Thelma Kaplan for assistance and Roscoe C. Funk, Jr., and Alice Angelos for analyses.

Summary

The ultraviolet absorption at various *p*H values of several pyrimidines, purines and triazolopyrimidines of known purity are presented. The variations of the spectra with certain substituents and the similarities of the spectra of the pyrimidines and the related purines and triazolopyrimidines are discussed. It is concluded that the ultraviolet absorption spectra of purines are due principally to the pyrimidine moiety and that the major chromophore in the pyrimidine ring is the



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Reaction of Paraffin Hydrocarbons with Phosphorus Trichloride and Oxygen to Produce Alkanephosphonyl Chlorides

BY J. O. CLAYTON AND W. L. JENSEN[1]

In an investigation of organic phosphorus compounds a new synthetic method was discovered for producing phosphonyl chlorides from aliphatic hydrocarbons. On mixing open chain or cyclic aliphatic hydrocarbons with phosphorus trichloride and bubbling the mixtures with oxygen alkane or cycloalkanephosphonyl chlorides were produced.

Petroleum white oil, consisting of hydrocarbons containing branched paraffin chains and saturated, alicyclic rings offered the advantage of providing a mixture of types so that reaction could be more readily detected should the reaction rates be low for certain hydrocarbon types. A mixture of white oil and phosphorus trichloride was bubbled with oxygen until the initial temperature rise subsided. The resulting material was hydrolyzed with water and washed several times with water. This reaction product was found to be acidic and to contain phosphorus.

Pure hydrocarbons were also investigated in order to determine the type of reaction product, the nature of the reactants and the yields. Liquid open chain aliphatic hydrocarbons, cyclohexane, toluene and higher benzene homologs reacted to give phosphorus containing products but benzene did not react. Olefins reacted readily but, in the case of the lower molecule weight straight chain

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