1016. *Pteridine Studies. Part XV.*[1] *The Reduction of 2-Hydroxypteridine.*

By ADRIEN ALBERT and SADAO MATSUURA.

The first example of a reduction in the pyrimidine ring of a pteridine is reported, *viz.*, 2-hydroxypteridine, which gives 3,4-dihydro-2-hydroxypteridine with a variety of reducing agents.

In a new type of 7,8-dihydropteridine synthesis, aminoacetal was condensed with 2,4-dichloro-5-nitropyrimidine to give (eventually) 7,8-dihydro-2-hydroxypteridine. This was reduced to 5,6,7,8-tetrahydro-2-hydroxypteridine.

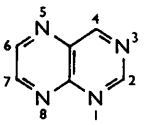
5,6,7,8-TETRAHYDROPTERIDINE is the sole product of the reduction [2] of pteridine (I) and hitherto it has been assumed that substituted pteridines, also, are reduced first in the pyrazine ring.[3] However, the principal product of the reduction of 2-hydroxypteridine is the 3,4-dihydro-derivative.

2-Hydroxypteridine resisted reduction in neutral or acidic solution over Raney nickel and Adams platinum catalysts, respectively. However, it was readily reduced to a

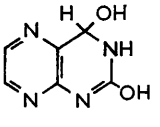
[1] Part XIV, Brown and Jacobsen, *J.*, 1961, 4413.
[2] Taylor and Sherman, *J. Amer. Chem. Soc.*, 1959, **81**, 2464.
[3] O'Dell, Vandenbelt, Bloom, and Pfiffner, *J. Amer. Chem. Soc.*, 1947, **69**, 250; Pohland, Flynn, Jones, and Shive, *ibid.*, 1951, **73**, 3247; Cosulich, Roth, Smith, Hultquist, and Parker, *ibid.*, 1952, **74**, 3252.

dihydro-2-hydroxypteridine in alkaline solution with potassium borohydride, sodium dithionite, or hydrogen (over palladium or nickel). That the anion should be the easily reduced species suggests that reduction takes place at the 3,4-double bond, because this position is masked by covalent hydration to give compound (II) as the stable neutral molecule.[4] However, the anion of 2-hydroxypteridine has a free 3,4-double-bond.[5]

Marked differences exist between the ionization constants and spectra of the reduction product and 7,8-dihydro-2-hydroxypteridine, and different R_F values were found on paper chromatography.



(I)



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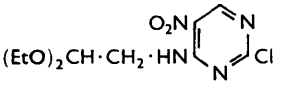

(III)

The constitution of the reduction product was established by reduction of 2-hydroxypteridine in deuterium oxide with a hydrogen-free reagent (sodium dithionite). The product was equilibrated with light water by recrystallization and then found to contain only one deuterium atom per molecule (by combustion and infrared measurement of the $D_2O : H_2O$ ratio). This single, unexchangeable deuterium atom in the reduced product must be located on a carbon atom;[6] thus 6,7- and 5,8-hydrogenation, which require 2 and 0 unexchangeable deuterium atoms respectively, were excluded. The constitution was finally shown to be 3,4-dihydro-2-hydroxypteridine by stepwise oxidation of the monodeuterated product to (*a*) 2-hydroxypteridine (with retention of half of the deuterium) and to 2,4-dihydroxypteridine (with complete loss of deuterium). There is, of course, no real distinction between 3,4-dihydro- and 1,4-dihydro-2-hydroxypteridine because the " hydroxy-group " in such substances is largely in the amide form where the hydrogen is sited on a nitrogen atom in the pyrimidine ring.[4,7]

2-Hydroxy-6-methylpteridine, upon reduction, gave a dihydro-derivative so similar in physical properties to that obtained by reducing 2-hydroxypteridine (see Table) that it is assigned the structure 3,4-dihydro-2-hydroxy-6-methylpteridine.

Although there is no recorded method for producing 7,8-dihydropteridines lacking a substituent in the 6-position, 7,8-dihydro-2-hydroxypteridine was obtained by condensing aminoacetal with 2,4-dichloro-5-nitropyrimidine to give 2-chloro-4-(2,2-diethoxyethylamino)-5-nitropyrimidine (III) which was then hydrolysed to the 2-hydroxy-analogue. Reduction of the nitro-group in the latter did not give a useful intermediate unless the acetal group was first hydrolysed by acid. 5-Amino-2-hydroxy-4-methylformamidopyrimidine, formed in this way, cyclized spontaneously to 7,8-dihydro-2-hydroxypteridine in good yield.

7,8-Dihydro-2-hydroxy-6-methylpteridine was obtained by Boon and Jones's method[8] in which aminoacetone (improved preparation given in the Experimental section) was condensed with 2,4-dichloro-5-nitropyrimidine to give 4-acetonylamino-2-hydroxy-5-nitropyrimidine which gave the desired substance on reduction. Oxidation of the product with potassium permanganate furnished 2-hydroxy-6-methylpteridine (mentioned above).

Reduction of 7,8-dihydro-2-hydroxypteridine gave 5,6,7,8-tetrahydro-2-hydroxypteridine whose constitution follows from the resemblance of the ultraviolet spectra to those of 4,5-diamino-2-hydroxypteridine. The resemblance is striking when the three ionic species are compared (Fig. 1), and the displacement of the pteridine spectra to slightly

[4] Brown and Mason, *J.*, 1956, 3443.
[5] Perrin and Inoue, *Proc. Chem. Soc.*, 1960, 342.
[6] Linderstrøm-Lang, Symposium on Peptide Chemistry, *Chem. Soc. Special Publ. No.* 2, 1955, 1.
[7] Albert and Phillips, *J.*, 1956, 1294.
[8] Boon and Jones, *J.*, 1951, 591.

TABLE. Physical properties of pteridines.

Pteridine	Species (charge)	Ionization in water at 20° pK_a	Spread (±)	Concn.[c] (M)	Spectroscopy in water $\lambda_{max.}$ (mμ)	log ε	pH
2-Hydroxy-[a]	0	—	—	—	230, 307	3·88, 3·83	7
2-Hydroxy-6-methyl-	0	—	—	—	235, 315	4·05, 3·93	7
	−	11·0	0·02	0·02	261, 377	3·87, 3·77	13
	+	−0·2	—	10^{-4}	240, 310	3·96, 3·84	−2
3,4-Dihydro-2-hydroxy-	0	—	—	—	248, 317	3·72, 3·89	7
	−	12·6	[b]	10^{-4}	281, 343	3·98, 3·84	14
	+	0	—	10^{-4}	254, 337	3·78, 3·85	−2
3,4-Dihydro-2-hydroxy-6-methyl-	0	—	—	—	248, 321	3·83, 3·92	7
	−	13·05	0·04	10^{-4}	281, 352	4·01, 3·84	14·2
	+	0·20	0·06	10^{-4}	257, 347	3·86, 3·88	−2
7,8-Dihydro-2-hydroxy-	0	—	—	—	223, 290	4·35, 3·88	7
	−	[b]	—	—	308	3·95	14
	+	3·50	0·02	0·02	225, *282*, 290, *310*	3·68, *3·75*, 3·79, *3·75*	1
7,8-Dihydro-2-hydroxy-6-methyl	0	—	—	—	220, 287	4·46, 3·99	7
	−	11·85	0·02	10^{-4}	309	4·08	14
	+	3·42	0·06	0·02	<225, 279, *287, 310*	>3·7, 4·06, *4·04, 3·82*	2
7,8-Dihydro-2-hydroxy-4,6-dimethyl-	0	—	—	—	222, 289	4·39, 4·04	7
	−	12·50	0·04	10^{-4}	223, 304	4·37, 4·10	14
	+	3·99	0·02	0·01	<225, 283+ 288, *312*	>3·7, 4·07+ 4·07, *3·90*	2
5,6,7,8-Tetrahydro-2-hydroxy-	0	—	—	—	232, 306	4·09, 3·70	7
	−	12·5	—	—	315	3·79	14
	+	4·35	0·05	0·02	229, 327	4·00, 3·69	1

[a] Albert, Brown, and Cheeseman, *J.*, 1951, 474. [b] Instability to alkali prevented determination. [c] The concn. 0·01—0·02M refers to potentiometric, and the 10^{-4}M, to spectrometric, determinations. [d] In 1 and 4 cm. cells; shoulders in italics.

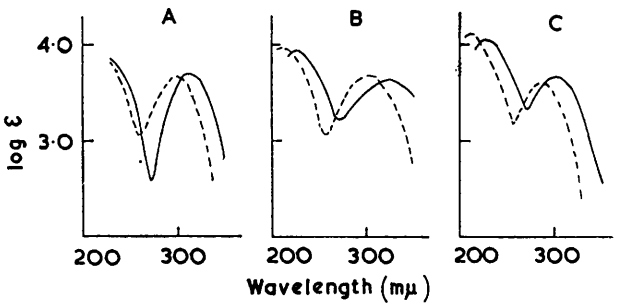

FIG. 1. Ultraviolet spectra of (A) anions at pH 14, (B) cations at pH 1, and (C) neutral molecules at pH 7, of (——) 5,6,7,8-tetrahydro-2-hydroxypteridine, and of (– – – –) 4,5-diamino-2-hydroxypyrimidine.

longer wavelengths is typical.[2] This tetrahydropteridine was identical in R_F and ultraviolet spectra with material isolated chromatographically, in trace amounts insufficient for analysis, from the reduction of 2-hydroxypteridine with potassium borohydride and with hydrogen and nickel.

In unsuccessful attempts to synthesize 2-hydroxy-3,4-dihydropteridine, methyl 3-aminopyrazine-2-carboxylate was reduced to 2-amino-3-hydroxymethylpyrazine. Several attempts to reduce 2-amino-3-cyanopyrazine and 2-amino-3-formylpyrazine oxime to 2-amino-3-aminomethylpyrazine gave only resins. In an attempt to produce 5,6-dihydro-2-hydroxypteridine, glyoxal monoacetal was condensed with 4,5-diamino-2-hydroxypyrimidine to give (after reduction) 4-amino-5-(2,2-diethoxyethylamino)-2-hydroxypyrimidine. 2-Hydroxypteridine and aqueous sodium metabisulphite gave sodium 3,4-dihydro-2-hydroxypteridine-4-sulphonate [the orientation follows from the site of addition of water in 2-hydroxypteridine (II)].

Experimental

Elementary analyses were carried out by the Analytical Section of this Department under Dr. J. E. Fildes. Yields are based on the stage in purification when the substance first gave a single spot in paper chromatography (in both 3% aqueous ammonium chloride and butanol–5N-acetic acid, 7 : 3 v/v), but further purification was carried out before analysis. Ultraviolet spectra were measured on a Perkin–Elmer " Spectracord " instrument and checked on a Hilger " Uvispek " manual instrument. Ionization constants were determined as before.

3,4-*Dihydro-2-hydroxypteridine.*—(*a*) 2-Hydroxypteridine monohydrate [9] (1·0 g., 0·006 mole) in 0·1N-sodium hydroxide (100 ml.) was hydrogenated at room temperature and pressure over 10% palladium–carbon (0·5 g.) until saturated (20 min.; 1·6 atoms per mole absorbed). The filtrate, adjusted to pH 6, deposited 3,4-*dihydro-2-hydroxypteridine* which from water (soluble in 120 parts at 100°, and in 1300 parts at 20°) gave crystals (67%) which darkened at 250° without melting (Found, for material dried at 20°/20 mm.: C, 47·9; H, 4·1; N, 37·2. $C_6H_6N_4O$ requires C, 48·0; H, 4·0; N, 37·3%). It is soluble in cold N (but not 0·1N)-sodium hydroxide, and insoluble in cold dilute mineral acids. Hydrogenation of 2-hydroxypteridine over Raney nickel, in methanol containing one equivalent of sodium hydroxide, gave the same substance (42%).

(*b*) Potassium borohydride (0·33 g.; 8H) was added to 2-hydroxypteridine monohydrate (1 g.) in 0·1N-sodium hydroxide (100 ml.) at 20°. Next day, the suspension was adjusted to pH 7 (H_3PO_4), and left at 20° for 1 day. The deposit, recrystallized from water (80 ml.), gave 3,4-dihydro-2-hydroxypteridine (55%) (Found: C, 48·1; H, 4·1; N, 36·9%).

(*c*) To 2-hydroxypteridine monohydrate (1 g.), dissolved in boiling N-sodium carbonate (30 ml.), was added sodium dithionite (4·8 g., 0·024 mole = 8H). The solution became deep orange and deposited white crystals. The suspension (pH 9) was refrigerated overnight and filtered. The crystals were extracted with boiling water (2 × 20 ml.) under carbon dioxide, and the second extract, concentrated to 5 ml., was added to the first. Chilling produced 3,4-dihydro-2-hydroxypteridine (25%) (Found: C, 47·9; H, 4·05; N, 37·1%).

Deuterium Studies.—2-Hydroxypteridine monohydrate (1 g.) was reduced with sodium dithionite as above but in heavy water (100% D_2O), then recrystallized several times from light water. Combustion of the 4-deutero-3-hydro-2-hydroxypteridine (15·243 mg.) gave 1·03 atoms of deuterium per mole, calculated from the D_2O content of the combustion sample (diluted to 100 mg. with light water) as estimated by infrared spectrophotometry (in a 0·1 mm. quartz cell, interpolating the optical density on a linear graph constructed from densities of 0·1 to 2·0% D_2O in H_2O w/w at 2500 cm.$^{-1}$).[10] When the reduction was carried out in 75% and 50% D_2O, only 0·41 and 0·24 atom per mole respectively were found, and hence a large isotope effect is operative.

0·4N-Potassium permanganate (5 ml.) was added dropwise to a stirred suspension of 3,4-dihydro-2-hydroxypteridine (0·15 g.) in 0·02N-potassium hydroxide (150 ml.) at 0°. After 10 min., the mixture was adjusted to pH 6, filtered from manganese dioxide, and evaporated to dryness. Recrystallization of the residue from water gave 2-hydroxypteridine (80%) (Found: C, 43·6; H, 3·8; N, 33·6. Calc. for $C_6H_4N_4O,H_2O$: C, 43·4; H, 3·65; N, 33·7%). This was further oxidized with potassium permanganate as before, and heated for 10 min. at 100° and pH 6 to complete the reaction. The filtrate, treated as before, gave 2,4-dihydroxypteridine (60%), indistinguishable in physical properties from a synthetic sample.[9] When these oxidations were carried out on 4-deutero-3-hydro-2-hydroxypteridine, the 2-hydroxypteridine retained slightly more than half of the deuterium whereas the 2,4-dihydroxypteridine was completely free from deuterium.

Hitherto the combustion of deuterated substances has been carried out in filled tubes.[11] Pteridines, however, burn best in an empty tube at a high temperature. Hence we burned the sample (0·1 to 0·2 mmole) in a Belcher–Ingram " rapid empty-tube " combustion apparatus attached to a vacuum line (a scale drawing is given in Fig. 2; all joints B14). Trap B (27 mm. diam.) was cooled with a carbon dioxide–ethanol bath, and sodium carbonate (5 mg.) was placed in trap C. After complete combustion, additional water was added to the combustion tube to

[9] Albert, Brown, and Cheeseman, *J.*, 1951, 474.

[10] Jones and MacKenzie, *Talanta*, 1960, **3**, 356; Thornton and Condon, *Analyt. Chem.*, 1950, **22**, 690.

[11] Trenner, Arison, and Walker, *Analyt. Chem.*, 1956, **28**, 530.

make 100 mg. in all. By continuing to pass dry oxygen, all the water was collected in B. The tap A was then closed and the apparatus was evacuated to 0·01 mm. The water in B was transferred to C by moving the cooling bath to C. After neutralization, the water was similarly transferred to trap D, which ends in a capillary tube to facilitate transfer to the photometric cell.

Reduction of 2-*Hydroxy*-6-*methylpteridine*.—2-Hydroxy-6-methylpteridine (0·36 g., see below), reduced with potassium borohydride as was 2-hydroxypteridine (see above), gave 3,4-*dihydro*-2-*hydroxy*-6-*methylpteridine* (30%) which, recrystallized from water, darkened at 265° without melting (Found: C, 51·3; H, 4·95; N, 34·0. $C_7H_8N_4O$ requires C, 51·2; H, 5·0; N, 34·1%).

7,8-*Dihydro*-2-*hydroxypteridine*.—Aminoacetal (13·5 g., 0·1 mole) in water (100 ml.) was adjusted to pH 7·5 with acetic acid. Sodium hydrogen carbonate (12 g.) was dissolved in this solution which was added dropwise to a stirred solution of 2,4-dichloro-5-nitropyrimidine [12] (20 g., 0·1 mole) in chloroform (100 ml.). After 3 hours' stirring, the chloroform layer was separated and distilled with N-sodium hydroxide (500 ml.) on a steam bath while nitrogen was bubbled through it for 20 min. The 2-chloro-4-(2,2-diethoxyethylamino)-5-nitropyrimidine

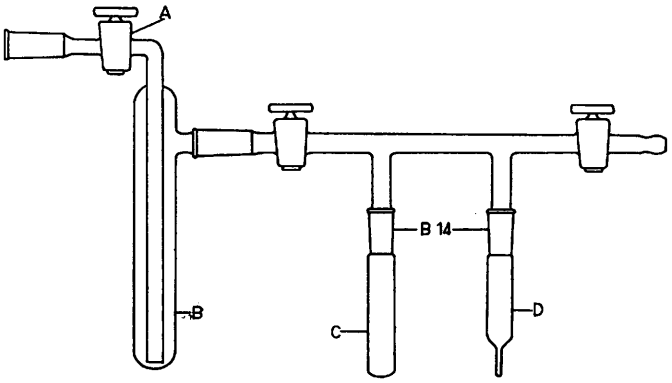

FIG. 2. Apparatus for receiving, purifying, and diluting deuterium oxide after combustion of deuterium-containing substances.

(III) first formed is thus hydrolysed to 4-(2,2-*diethoxyethylamino*)-2-*hydroxy*-5-*nitropyrimidine* which was isolated in 53% yield by extracting the solution with benzene (3 × 30 ml., set aside), adjusting the aqueous layer to pH 6 (acetic acid), and recrystallizing the precipitate from ethanol to give leaflets, m. p. 157° (Found: C, 44·15; H, 5·9. $C_{10}H_{16}N_4O_5$ requires C, 44·1; H, 5·9%). The benzene layer yielded 2,4-*bis*-2′-*diethoxyethylamino*-5-*nitropyrimidine*, m. p. 99—100° (Found: C, 49·8; H, 7·3. $C_{16}H_{29}N_5O_6$ requires C, 49·6; H, 7·55%).

4-(2,2-Diethoxyethylamino)-2-hydroxy-5-nitropyrimidine (2·53 g.) in ethanol (300 ml.) was hydrogenated (6H) over Raney nickel at room temperature and pressure. The filtrate was taken to dryness under nitrogen and the residue recrystallized from ethanol–ethyl acetate (1 : 9), giving 5-*amino*-4-(2,2-*diethoxyethylamino*)-2-*hydroxypyrimidine* (53%), m. p. 174—175° (Found, for substance dried at 20°/0·1 mm.: C, 47·0; H, 7·9; N, 22·1. $C_{10}H_{18}N_4O_3$,0·75H_2O requires C, 46·95; H, 7·7; N, 21·95%). Attempted cyclization gave a complex mixture and hence the following pathway was preferred.

4-2′-Diethoxyethylamino-2-hydroxy-5-nitropyrimidine (14 g.) was refluxed with N-hydrochloric acid (100 ml.) for 20 min. and adjusted to pH 4 with sodium hydrogen carbonate. 2-*Hydroxy*-4-*methylformamido*-5-*nitropyrimidine* (82%) was filtered off and recrystallized from water. It darkened at 220° without melting (Found: C, 36·5; H, 3·15. $C_6H_6N_4O_4$ requires C, 36·4; H, 3·05%). This substance (2 g.) was hydrogenated over Raney nickel in cold methanol. The catalyst was filtered off and extracted with boiling water (80 ml.), which deposited 7,8-*dihydro*-2-*hydroxypteridine* (23%) which, recrystallized from water, decomposed at 190° without melting (Found, for material dried at 135°/0·1 mm.: C, 47·0; H, 4·1; N, 36·6.

[12] Whittaker, *J.*, 1951, 1565.

$C_6H_6N_4O,0{\cdot}25H_2O$ requires C, 46·6; H, 4·25; N, 36·2%). Further, rather impure, material was obtained from the methanolic filtrate.

Reduction of 7,8-*Dihydro*-2-*hydroxypteridine*.—This substance (0·23 g.) was hydrogenated (2H) in 0·05N-acetic acid (50 ml.) over Adams platinum catalyst at 20°. The filtrate was neutralized, and taken to dryness in a vacuum, and the product recrystallized from alcohol to give 5,6,7,8-*tetrahydro*-2-*hydroxypteridine* (70%), decomp. 220° (Found, for material dried at 105°/0·1 mm.: C, 47·5; H, 5·9; N, 36·4. $C_6H_8N_4O$ requires C, 47·35; H, 5·3; N, 36·8%). It absorbed one mole of water from the air in 20 min. at 20°.

Aminoacetone (with Dr. F. REICH).—Bromoacetone (66 g.) was added to potassium phthalimide (92 g., 1 equiv.) in dimethylformamide (250 ml.) at 60—70° and kept at this temperature for 1 hr. Water (450 ml.) was added, and the mixture extracted with chloroform (3 × 150 ml.). The chloroform layer was washed with 0·5M-sodium hydroxide, then with water. Evaporation of the chloroform left phthalimidoacetone, m. p. 122°, which was hydrolysed with 7N-hydrochloric acid [13] to aminoacetone hydrochloride, m. p. 81°, in 74% yield based on the bromoacetone.

7,8-*Dihydro*-2-*hydroxy*-6-*methylpteridine*.—4-Acetonylamino-2-chloro-5-nitropyrimidine [8] (6·9 g., 0·03 mole) and sodium acetate trihydrate (6 g., 0·05 mole) were refluxed for 80 min. in acetic acid (100 ml.). The solid which separated on cooling recrystallized from water to give 4-*acetonylamino*-2-*hydroxy*-5-*nitropyrimidine* (36%), m. p. 186° (decomp.) (Found: C, 39·55; H, 3·9. $C_7H_8N_4O_4$ requires C, 39·6; H, 3·8%). This product (2·12 g.) was simultaneously reduced and cyclized by hydrogenation in 90% ethanol (500 ml.) at 50° over Raney nickel (5 g.). The suspension was refrigerated overnight. The catalyst was filtered off and extracted with boiling water (250 ml.) which deposited 7,8-*dihydro*-2-*hydroxy*-6-*methylpteridine* (53%), decomp. ~280° (Found, for material dried at 135°/0·1 mm.: C, 50·95; H, 4·8; N, 34·0. $C_7H_8N_4O$ requires C, 51·2; H, 4·9; N, 34·1%). 7,8-Dihydro-2-hydroxy-4,6-dimethylpteridine,[14] obtained similarly by reducing 4-acetonylamino-2-hydroxy-6-methyl-5-nitropyrimidine,[14] was recrystallized from 250 parts of boiling water (Found: C, 53·8; H, 5·8; N, 31·45. Calc. for $C_8H_{10}N_4O$: C, 53·9; H, 5·8; N, 31·4%).

2-*Hydroxy*-6-*methylpteridine*.—0·1M-Potassium permanganate (20 ml.) was added dropwise with stirring to 7,8-dihydro-2-hydroxy-6-methylpteridine (0·52 g.) in 0·1N-potassium hydroxide (1·1 equiv.) at 0°. The manganese dioxide was filtered off and washed with hot water (10 ml.). The combined filtrate and washings were adjusted to pH 6 with acetic acid and refrigerated overnight. Recrystallization of the precipitate from water gave 2-*hydroxy*-6-*methylpteridine* (67%) decomp. 245° (Found: C, 46·95; H, 4·55; N, 31·3. $C_7H_6N_4O,H_2O$ requires C, 46·7; H, 4·5; N, 31·15%).

4-*Amino*-5-(2,2-*diethoxyethylamino*)-2-*hydroxypyrimidine*.—4,5-Diamino-2-hydroxypyrimidine [15] (0·63 g.) and glyoxal monoacetal [16] (0·85 g., 1 equiv.) in water (25 ml.) were heated for 10 min. on a steam bath. The mixture was taken to dryness under reduced pressure and the residue triturated with acetone (rejected). The solid was hydrogenated in ethanol (50 ml.) over Raney nickel. Concentration of the filtrate gave 4-*amino*-5-(2,2-*diethoxyethylamino*)-2-*hydroxypyrimidine* (10%), m. p. 198—200° (from ethanol) (Found: C, 49·15; H, 7·4; N, 22·7. $C_{10}H_{18}N_4O_3$ requires C, 49·6; H, 7·5; N, 23·1%).

2-*Amino*-3-*hydroxymethylpyrazine*.—To 2-amino-3-methoxycarbonylpyrazine [17] (1·53 g.) in tetrahydrofuran (200 ml.), lithium aluminium hydride (0·38 g.) was added, and the mixture was set aside at 20° for 2 hr. Water (3 ml.) was cautiously added, and the inorganic salts filtered off. The filtrate was taken to dryness and the residue, recrystallized from pentyl acetate, gave 2-*amino*-3-*hydroxymethylpyrazine* (46%), m. p. 118—119·5° (Found, for material dried at 65°/0·1 mm.: C, 47·65; H, 5·7; N, 33·1. $C_5H_7N_3O$ requires C, 48·0; H, 5·65; N, 33·6%). No reaction occurred with hydrobromic acid at 20°, urea at 170°, urethane at 190°, or cyanic acid in water.

Sodium metabisulphite (0·5 g.) was added to a solution of 2-hydroxypteridine monohydrate (0·16 g.) in 0·5N-sodium hydroxide (2 ml.; 1 equiv.). The precipitate obtained on refrigeration gave *sodium* 3,4(?)-*dihydro*-2-*hydroxypteridine*-4(?)-*sulphonate*, needles (from water) (90 mg.),

[13] Ellinger and Goldberg, *J.*, 1949, 263.
[14] Lister and Ramage, *J.*, 1953, 2234.
[15] Brown, *J. Appl. Chem.*, 1957, **7**, 109.
[16] Fischer and Baer, *Helv. Chim. Acta*, 1935, **18**, 514.
[17] Ellingson, Henry, and McDonald, *J. Amer. Chem. Soc.*, 1945, **67**, 1711.

m. p. 310° (decomp.) (Found: C, 27·85; H, 2·4; N, 21·45; S, 12·25. $C_6H_5N_4NaO_4S,0{\cdot}5H_2O$ requires C, 27·6; H, 2·3; N, 21·45; S, 12·3%).

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Department of Medical Chemistry, Institute of Advanced Studies,
Australian National University, Canberra. [*Received, June 6th*, 1961.]