then allowed to cool. Crystallization from methyl Cellosolve, xylene and then acetic acid gave 1.86 g. (58%) of feathery yellow needles, m.p. 340–342°.

The mixed melting points of (a), (b) and (c) showed these compounds to be identical.

Anal. Calcd. for $C_{12}H_6N_2O_4Se$: C, 44.9; H, 1.87; N, 8.72. Found: C, 44.9; H, 1.84; N, 8.58.

2-Acetyldibenzoselenophene.—Dibenzoselenophene was acetylated by Buu-Hoi's directions.[13] The crude oily solid was dissolved in benzene and chromatographed through alumina; the developing solvent was benzene–heptane. The starting product came through first, followed by the monoacetylated compounds. The polyacetylated derivatives had to be eluted from the column with acetone. The middle fraction was dissolved in benzene and chromatographed as before. The 4-acetyl derivative came through first followed by the 2-isomer. Crystallization of the second fraction from methanol gave an approximately 10% yield of colorless needles, m.p. 116–117°.

Anal. Calcd. for $C_{14}H_{10}OSe$: C, 61.5; H, 3.66. Found: C, 61.7; H, 3.73.

4-Acetyldibenzoselenophene.—The crude acetyl derivative obtained from chromatography was crystallized out of methanol to give an approximately 10% yield of colorless crystals, m.p. 143–145°.

Anal. Calcd. for $C_{14}H_{10}OSe$: C, 61.54; H, 3.66. Found: C, 61.5; H, 3.50.

2(?),6-Diacetyldibenzoselenophene.—The polyacetylated fraction obtained through chromatography was fractionally crystallized from benzene. A small amount of colorless needles was obtained, m.p. 213–215°, lit.[13] m.p. 213°

2,8-Diacetyldibenzoselenophene.—Crystallization of the polyacetylated fraction from xylene, alcohol and then nitrobenzene gave a small amount of colorless needles, m.p. 244–245°.

Anal. Calcd. for $C_{16}H_{12}O_2Se$: C, 61.0; H, 3.81. Found: C, 60.9; H, 3.70.

2-Azido-9-methylcarbazole.—The general preparation of the azido compounds, physical properties of which are given in Table I, is essentially as described for the carbazole derivative.

TABLE I

AZIDO DERIVATIVES

Compound	M.p., °C.	Yield, %	Nitrogen, % Calcd.	Found
2-Azidodibenzothiophene	117–118	94	18.7	18.5[a]
3-Azidodibenzothiophene	107–108	90	18.7	18.6
2-Azidodibenzoselenophene	96–97	92	15.4	15.3
3-Azidodibenzoselenophene	85–86	89	15.4	15.4
3-Azido-9-methylcarbazole	81–82	79	25.2	25.1
2-Azido-9-methylcarbazole	109–110	93	25.2	24.9[b]

[a] *Anal.* Calcd. for $C_{12}H_7N_3S$: C, 64.0; H, 3.11. Found: C, 63.9; H, 3.22. [b] *Anal.* Calcd. for $C_{13}H_{10}N_4$: C, 70.3; H, 4.50. Found: C, 70.3; H, 4.58.

To a finely divided stirred suspension of 2.0 g. (0.01 mole) of 2-amino-9-methylcarbazole in 7 ml. of water and 2.5 ml. (0.03 mole) of concentrated hydrochloric acid was added dropwise 0.83 g. (0.012 mole) of sodium nitrite in 5 ml. of water. The mixture was filtered and the filtrate cooled to 0–10°; red needles of the diazonium chloride precipitated out. To this cold stirred mixture a solution of 0.72 g. (0.011 mole) of sodium azide in 7 ml. of water was added dropwise and the foamy mixture allowed to stand for one hour. Filtration and crystallization from aqueous ethanol gave 2.06 g. (93%) of gleaming crystals, m.p. 109–110°.

Ultraviolet Absorption Spectra.—All ultraviolet absorption spectra were determined with a Beckman model DU quartz spectrophotometer in 95% ethanol unless otherwise stated. Infrared absorption spectra were measured with a Perkin–Elmer model 21 infrared spectrophotometer.

Acknowledgment.—The author is indebted to Dr. Francis E. Ray for his encouragement and interest in this work and to Miss Mary Louise Van Natta of the Chemistry Department of the University of Florida for determining the infrared spectra.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, THE ARMOUR LABORATORIES]

Synthesis of Compounds Related to Thymine. I. 5-Mercaptouracil and Some S-Substituted Derivatives

BY THOMAS J. BARDOS, ROSS R. HERR AND TAKASHI ENKOJI

RECEIVED AUGUST 27, 1954

5-Mercaptouracil, 5-uracilyl disulfide and uracil-5-isothiouronium chloride have been synthesized from 5-aminouracil by way of the diazonium salt. These compounds are competitive antagonists of thymine.

Structural analogs of thymine are of biochemical and possibly of chemotherapeutic interest as potential inhibitors (anti-metabolites) of desoxyribonucleic acid synthesis. Several simple analogs are known, including those in which one or both of the oxygens in the thymine molecule are replaced by sulfur (thiothymines),[1,2] or in which the 5-methyl group is replaced by a halogen,[3–5] nitro,[4,6] amino[7] or hydroxyl[8] group.

Most of these compounds inhibit the growth of microörganisms under certain conditions. The inhibitory effect of some, however, can be reversed by metabolites other than thymine (*e.g.*, uracil, folic acid).[9,10] Others, such as 5-bromouracil, can be incorporated into the desoxyribonucleic acids in place of thymine.[11] These latter compounds therefore may act as thymine substitutes rather than inhibitors, depending on the composition of the growth media.[10,11]

In the search for thymine antagonists that would competitively block the utilization of thymine in the presence as well as in the absence of folic acid, and which would not replace thymine as a substitute metabolite, we have synthesized a group

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(2) G. B. Elion and G. H. Hitchings, THIS JOURNAL, **69**, 2138 (1947).

(3) T. B. Johnson, *Am. Chem. J.*, **40**, 27 (1908).

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(5) T. B. Johnson and C. O. Johns, *J. Biol. Chem.*, **1**, 310 (1906).

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(7) E. Fisher, *Ann.*, **239**, 193 (1887).

(8) R. Behrend, *ibid.*, **229**, 39 (1885).

(9) F. B. Strandskov and O. Wyss, *J. Bact.*, **50**, 237 (1947).

(10) G. H. Hitchings, G. B. Elion and E. A. Falco, *J. Biol. Chem.*, **185**, 547 (1950).

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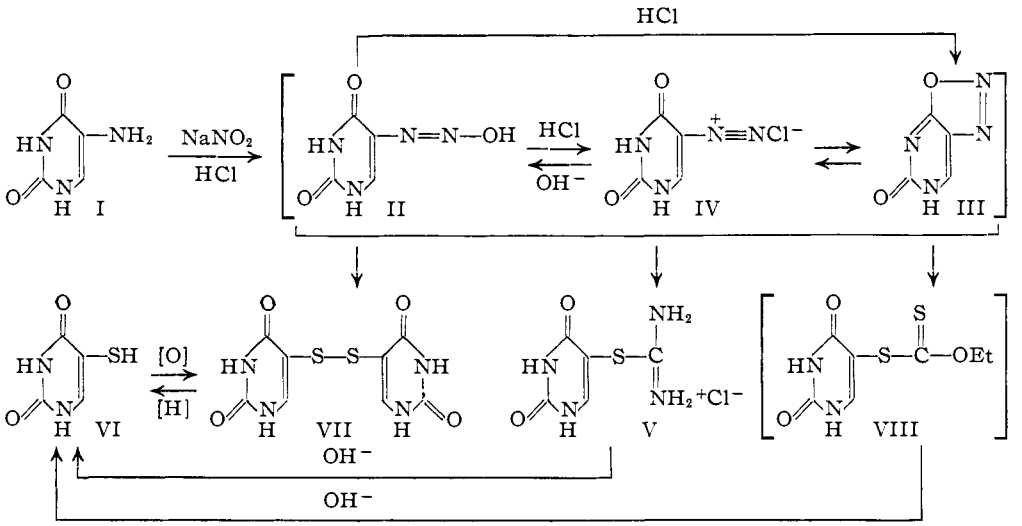
of new compounds. Structurally, these compounds are derived from thymine by replacement of the 5-methyl group by a sulfhydryl or a substituted sulfhydryl group. In this paper, the syntheses of these compounds are described.

In these syntheses, 5-aminouracil (I) was the starting material. 5-Aminouracil reacts like an aromatic amine when diazotized. Angeli[12] has isolated from the diazotization mixture a relatively stable "diazouracil" (II) first prepared by Behrend and Ernert[13] by the decarboxylation of diazoorotic acid. Johnson, *et al.*,[14] later obtained the anhydride form III under more acidic conditions. The diazonium chloride (IV) has not been isolated but is assumed to be present in the aqueous acidic diazotization mixture in equilibrium with the precipitated diazouracil anhydride (III).



It is probably the diazonium chloride form IV that reacts with the readily polarizable thiourea, a strong nucleophilic reagent[15] to give uracil-5-isothiouronium chloride (V). This compound, easily soluble in water, can be crystallized from aqueous alcohol in the presence of hydrochloric acid. It melts at 264–266° with decomposition and characteristic effervescence. The disulfide VII of 5-mercaptouracil is obtained as a secondary product in the thiourea reaction, and is also the product of the alkaline hydrolysis of uracil-5-isothiouronium chloride under conditions of air oxidation. 5-Mercaptouracil (VI) can be obtained from the isothiouronium salt if the alkaline hydrolysis is carried out rapidly, or under nitrogen atmosphere. It can also be obtained from the disulfide VII by reduction. On the other hand, prolonged exposure of 5-mercaptouracil to air in boiling water or in alkaline solution leads to the formation of the disulfide.

If the solution of diazotized 5-aminouracil is added to an alkaline solution of sodium disulfide, the product is 5-uracilyl disulfide (VII). The conditions of this reaction are similar to those used in the preparation of dithiosalicylic acid[16] and the yield is good.

The well-known xanthate synthesis of thiols[17] is also applicable to these compounds. Addition of the diazotization mixture to a solution of potassium ethyl xanthate presumably gives 5-uracilyl xanthate (VIII) from which 5-mercaptouracil is obtained by alkaline hydrolysis. In this hydrolysis, a small amount of a reducing agent, such as glucose, is added to prevent oxidation to the disulfide.

Both the mercaptouracil (VI) and the disulfide (VII) are soluble in alkali and are precipitated by acid. They have no definite melting point but decompose slowly above 300°. Their ultraviolet spectra are similar, both showing an acid–base shift of about 18 mμ in their absorption maxima. The infrared absorption spectrum[18] of the thiol shows an S–H absorption band at 4.1 μ and another at 11.0 μ, neither of which are present in the spectrum of the disulfide. In other respects, the spectra of the two compounds are similar.

Polarographic measurements[19] on 5-mercaptouracil show an anodic oxidation wave at 0.5 volt *vs.* S.C.E. The disulfide gives a cathodic wave at the same potential. In these measurements the compounds were approximately 10^{-3} M in 0.1 M ammonia plus 0.1 M ammonium chloride, with the oxygen removed by nitrogen.

In potentiometric titrations, 5-mercaptouracil behaves like a relatively strong monobasic acid with a pK_a of 5.5, while the disulfide has two indistinguishable weak acidic groups and an apparent pK_a of 8.0.

Finally, 5-mercaptouracil, but not the disulfide, gives a strong red color reaction with sodium nitroprusside.[20]

(12) A. Angeli, *Gazz. Chim. Ital.*, [2] **24**, 368 (1894).

(13) R. Behrend and P. Ernert, *Ann.*, **258**, 358 (1890).

(14) T. B. Johnson, O. Baudisch and A. Hoffmann, *Ber.*, **64B**, 2629 (1931).

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(16) C. F. H. Allen and D. D. MacKay, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 580.

(17) D. S. Tarbell and D. K. Fukushima, *Org. Syntheses*, **27**, 81 (1947).

(18) We are grateful to Dr. A. S. Hussey of Northwestern University for obtaining the infrared spectra of these compounds. The spectra were determined in a Baird Spectrophotometer, with the sample in a compressed potassium bromide disk.

(19) We wish to thank Dr. H. Fiess at Northwestern University for carrying out the polarographic experiments on these compounds.

(20) H. Meyer, "Analyse und Konstitutionermittlung Organischer Verbindungen," V. Auflage, J. Springer Verlag, Berlin, 1931, p. 631.

Both 5-mercaptouracil and the disulfide inhibit the growth of *L. leichmannii* at a concentration of one microgram per milliliter.[21] This inhibition can be reversed competitively with thymine or with thymidine. It is not reversed by folic acid. Uracil-5-isothiouronium chloride shows a similar inhibitory effect but is only about one-half as active (on a weight basis). The microbiological experiments will be published elsewhere in detail.

Acknowledgment.—We wish to thank Dr. J. P. Dailey for the many helpful discussions we have had during the course of this work.

Experimental[22]

Reaction of Diazotized 5-Aminouracil with Thiourea.—A solution of 12.0 g. (0.2 mole) of thiourea in 100 cc. of 0.5 *N* hydrochloric acid and 100 cc. of 95% ethanol was cooled to 0° and added while stirring to a cold suspension of diazonium salt prepared from 12.7 g. (0.1 mole) of 5-aminouracil, 200 cc. of 1 *N* hydrochloric acid and 7 g. (0.1 mole) of sodium nitrite in 100 cc. of water. After addition, stirring was continued at 0–5° for 30 minutes. The mixture was then adjusted to *p*H 3–4 with 20% sodium hydroxide, allowed to warm to room temperature, and refluxed for four hours. Filtration of the hot mixture removed 5.7 g. of dark red solid which was discarded. The clear filtrate was acidified to *p*H 1 with concentrated hydrochloric acid, cooled, and the deep yellow precipitate separated by filtration. The filtrate was concentrated to 150 cc., cooled and filtered to obtain more of the deep yellow solid. This material was the crude disulfide VII. The two fractions were combined and purified by dissolving in 40 cc. of 3% sodium carbonate, treating with charcoal and filtering. Acidification of the solution precipitated the disulfide which was filtered and dried to give 0.3 g. of yellow solid. Recrystallization from boiling water gave almost colorless 5-uracilyl disulfide.

Anal. Calcd. for $C_8H_6N_4O_4S_2$: C, 33.5; H, 2.11; N, 19.6; S, 22.4. Found: C, 33.2; H, 2.52; N, 19.4; S, 22.3.

The filtrate from the reaction mixture, after removal of the disulfide, was evaporated to dryness and the residue treated three times with 25-cc. portions of 95% ethanol acidified to *p*H 1 with concentrated hydrochloric acid. The insoluble material was then triturated twice with a mixture of 10 cc. of 1 *N* hydrochloric acid and 10 cc. of 95% ethanol. The solid remaining was washed with 25 cc. of absolute ethanol and dried. About 14 g. of residue remained, m.p. 257–259°. This crude uracil-5-isothiouronium chloride (V) was dissolved in 150 cc. of water, a few drops of concentrated hydrochloric acid were added (to *p*H 1) and the solution was filtered. The filtrate was concentrated to about 65 cc., at which point a solid began to separate. Addition of 80 cc. of absolute ethanol and cooling gave 5.0 g. (23%) of crystalline isothiouronium salt, m.p. 262–264°. A sample for analysis melted at 264–266°, with decomposition and effervescence.

Anal. Calcd. for $C_6H_7ClN_4O_2S$: C, 26.5; H, 3.11; Cl, 15.6; N, 24.7; S, 14.1. Found: C, 26.9; H, 3.33; Cl, 15.8; N, 24.9; S, 14.3.

Hydrolysis of Uracil-5-isothiouronium Chloride.—A solution of 1.5 g. (0.00675 mole) of uracil-5-isothiouronium chloride in 50 cc. of water was stirred under a nitrogen atmosphere, and 15 cc. (0.015 mole) of 1 *N* sodium hydroxide was added. A precipitate formed which then redissolved. The solution was stirred at room temperature for 30 minutes, and was then acidified with concentrated hydrochloric acid and chilled in an ice-bath. Crystals formed on scratching, and the mixture was stirred in the ice-bath for about 30 minutes. The product was collected by filtration, washed with water, and dried in a vacuum desiccator over sodium hydroxide to give 0.550 g. (57%) of bright yellow 5-mercaptouracil. This material gave a strong red color in the nitroprusside reaction.

Anal. Calcd. for $C_4H_4N_2O_2S$: C, 33.3; H, 2.80; N, 19.4; S, 22.2. Found: C, 33.6; H, 2.93; N, 19.7; S, 21.8.

Reaction of Diazotized 5-Aminouracil with Sodium Disulfide.—A solution of 19.1 g. (0.15 mole) of 5-aminouracil in 150 cc. of 50% aqueous ethanol and 30 cc. of concentrated hydrochloric acid was cooled to −5° and diazotized by the addition of a solution of 10.4 g. (0.15 mole) of sodium nitrite in 45 cc. of water. The mixture was stirred for 15 minutes.

An alkaline solution of sodium disulfide was prepared by dissolving 39 g. (0.16 mole) of crystallized sodium sulfide ($Na_2S \cdot 9H_2O$) and 5.1 g. (0.16 mole) of sulfur in 45 cc. of hot water, and then adding 150 cc. of 1 *N* sodium hydroxide solution.

After cooling the disulfide solution to 0°, the cold diazonium salt mixture was added gradually while stirring. When the addition was complete, the mixture was allowed to warm to room temperature. A few milliliters of ether were added to moderate the foaming, and stirring was continued until the evolution of nitrogen ceased. The solution was then acidified with 27 cc. of concentrated hydrochloric acid. A light tan flocculent precipitate separated, which was filtered with suction and washed with water. This crude product was heated to boiling with 400 cc. of 3% sodium carbonate and filtered. The clear filtrate was cooled and acidified with concentrated hydrochloric acid. The precipitate was filtered, washed with water and dried to give 8.3 g. (39%) of almost white solid, 5-uracilyl disulfide (VII). This can be further purified by recrystallization from a large quantity of water.

Alternatively, the crude product may be purified by extraction with water in a Soxhlet extractor. On cooling the extract, 5-uracilyl disulfide crystallizes in clusters of needles. This procedure gives a purer product but is considerably longer than the sodium carbonate extraction.

Reduction of 5-Uracilyl Disulfide. (a).—To a stirred suspension of 9.0 g. (0.031 mole) of 5-uracilyl disulfide in 300 ml. of glacial acetic acid was added 13.5 g. of zinc dust. The mixture was refluxed for three hours, during which time it turned yellow-green in color. An additional 7 g. of zinc dust was then added, and the stirring and refluxing continued for another three hours. At the end of this time the mixture was cooled and filtered. The collected solid was dissolved in warm 5% sodium hydroxide solution and filtered. On acidification of the filtrate with concentrated hydrochloric acid, a bright yellow precipitate separated which became granular on cooling in an ice-bath. This solid was collected by filtration, washed with water and dried in a vacuum desiccator over sodium hydroxide, to give 5.7 g. (63%) of 5-mercaptouracil. This product gave a strong red color in the nitroprusside reaction for thiophenols.

(b).—A small sample of the disulfide, 286 mg. (0.001 mole) was heated with 180 mg. (0.001 mole) of glucose and 8 cc. of 0.5 *N* sodium hydroxide solution for about 10 minutes on the steam-bath. The darkened but clear solution was then cooled and the uracil compound was precipitated with hydrochloric acid. The precipitate was filtered and washed with water. This product gave a positive color test with sodium nitroprusside.

Reaction of Diazotized 5-Aminouracil with Potassium Ethyl Xanthate Followed by Hydrolysis.—A cold solution of 12.7 g. (0.1 mole) of 5-aminouracil in 225 cc. of 1 *N* hydrochloric acid was diazotized with a solution of 7.0 g. (0.1 mole) of sodium nitrite in 50 cc. of water. The mixture was stirred for 15 minutes, then a solution of 20 g. of sodium acetate in 100 cc. of water was added. The diazotized mixture was added gradually while stirring to a solution of 22.4 g. (0.14 mole) of potassium ethyl xanthate in 100 cc. of water kept at 70–75° by heating on a steam-bath. A deep red precipitate formed during the addition. The mixture was heated at 90° on the steam-bath for one hour. Sixteen grams of solid potassium hydroxide and 2 g. of glucose were then added and the mixture refluxed for two hours. After filtering hot, the filtrate was boiled with 5 g. of charcoal and filtered again. The deep yellow filtrate was cooled and acidified with concentrated hydrochloric acid. A granular precipitate formed which was collected by filtration, washed with water and dried to give 3.24 g. (22%) of 5-mercaptouracil. This product gave a positive nitroprusside test for thiophenols. It was oxidized to the disulfide for analysis.

A small amount of the 5-mercaptouracil was dissolved in 5% sodium hydroxide, a few crystals of iodine were added

(21) The microbiological assays were carried out by Harry L. Gordon.

(22) Elemental analyses by Galbraith Laboratories, Knoxville, Tennessee.

and the solution refluxed for two hours. Acidification with concentrated hydrochloric acid precipitated the disulfide which was collected by filtration and recrystallized from water.

Anal. Calcd. for $C_8H_6N_4O_4S_2$: C, 33.5; H, 2.11; N, 19.6; S, 22.4. Found: C, 33.9; H, 2.54; N, 19.3; S, 21.5.

Ultraviolet Absorption Spectra.—One mg. per cc. stock solutions of the compounds were prepared; 5-mercaptouracil and 5-uracilyl disulfide were dissolved in 0.1 *N* sodium hydroxide, uracil-5-isothiouronium chloride was dissolved in water. These stock solutions were diluted 100-fold with 0.1 *N* hydrochloric acid and 0.1 *N* sodium hydroxide, respectively, to obtain the compounds in 10 γ/cc. final concentration, at *p*H 1 and 13. The corresponding solvent "blanks" were prepared the same way without the compounds. Beckman model DU spectrophotometer was used. The following absorption maxima and molar extinctions were obtained.

	*p*H 1		*p*H 13	
	λ_{max}	ϵ	λ_{max}	ϵ
5-Mercaptouracil	274	7,300	291	8,800
5-Uracilyl disulfide	272	15,000	290	19,000
Uracil-5-isothiouronium chloride	268	8,400	290	7,800

CHICAGO 9, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Some Pyrroles, Phenols and Pyridines Contained in a Gilsonite Distillate

BY JAMES M. SUGIHARA AND DAVID P. SORENSEN

RECEIVED SEPTEMBER 7, 1954

The pyrolysis of Gilsonite yielded a distillate, from which pyrroles and phenols were separated in the form of potassium salts. Pyridines then were extracted with aqueous phosphoric acid. Small amounts of each of these fractions were separated conveniently by chromatographic methods. The identification of pyrrole, 2-methylpyrrole, phenol, *o*-cresol, 3,5-dimethylphenol, 1-naphthol, 4-picoline, 2,6-lutidine, 3,4 lutidine, 2,5-lutidine, 3,5-lutidine and 2,3,5-trimethylpyridine is described.

The pyrolysis of Gilsonite, an asphaltite,[1] yields a distillate in an amount of about 55%. Saturated and unsaturated hydrocarbons as well as basic nitrogen compounds have been reported[2] to be present in this distillate. The probable absence of aromatic hydrocarbons also was indicated.[2a] Evidence for the presence of 3-ethylpyridine and 2,3,5-trimethylpyridine in the basic fraction has been derived.[3]

In the work herein described the procedure developed permitted the processing of relatively small amounts of materials. The distillate A, derived in the pyrolysis of Gilsonite, was subjected to a distillation to obtain 6.5% of a low-boiling fraction B (b.p. 35–120°) and 31% of a fraction C (b.p. 60–150°, 13 mm.). Fraction B did not contain any nitrogen- or sulfur-containing compounds, as shown by analyses. The separation of basic and acidic compounds from C by conventional methods using aqueous acids and bases was attended with much tar formation and concomitant loss of the desired fractions. Any pyrroles contained might be expected to be degraded to a considerable extent upon contact with mineral acids. For these reasons pyrroles and phenols were first removed from C by reaction with potassium metal.[4] The solid mixture of salts was treated with water to hydrolyze pyrrole salts. The pyrroles then were extracted with ether, leaving the salts of phenols in the aqueous phase, which could be acidified and ether-extracted to obtain a phenol fraction. Basic compounds were separated by extraction with an aqueous solution of phosphoric acid.

Pyridine and alkylpyridines are reported[5] to yield dipyridyls by condensation with sodium in the presence of air. The comparable reaction with potassium[6] proceeds much more slowly. The extent of condensation of pyridine and its alkyl derivatives during the initial separation procedure with potassium, whereupon phenols and pyrroles were converted into salts, would undoubtedly be limited. When pyridine was added to the neutral fraction, obtained after phenols, pyrroles and pyridines were removed, 92% of a chromatographically homogeneous fraction was recovered. This fraction was demonstrated to be unchanged pyridine.

The separation of relatively small amounts of each of the fractions was accomplished by a chromatographic procedure. Pyrroles were located on the absorbent using *p*-dimethylaminobenzaldehyde[7] as a streak indicator. The location of phenols was effected with an alkaline solution of potassium permanganate and of pyridines with tetraiodophenolphthalein. Pyridine compounds were found to react rapidly with the sodium salt of tetraiodophenolphthalein to yield a colorless solution. The colored form of the indicator was presumed to form a complex of the type indicated by I. Dilute mineral acids could readily regenerate the violet color of the indicator.

From the pyrrole fraction, pyrrole and 2-methylpyrrole were isolated. Tetraiodopyrrole, pyrrole picrate, 1-pyrroleacetic acid, 1-pyrroleacetamide, 2-pyrrolecarboxanilide and the condensation product of pyrrole and phthalic anhydride were prepared and compared with authentic samples. 5-Methyl-2-pyrrolecarboxanilide, 1-*p*-nitrobenzoyl-2-methylpyrrole and the condensation product of

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(2) (a) W. C. Day, *J. Franklin Inst.*, **140**, 221 (1895); (b) C. F. Mabery, THIS JOURNAL, **39**, 2015 (1917).

(3) R. E. Reusser, Master's thesis, University of Utah, 1949.

(4) A. G. Janssen, E. R. Scherz, R. Van Meter and John S. Ball, THIS JOURNAL, **73**, 4040 (1951), extracted pyrroles from shale-oil naphtha with solid potassium hydroxide.

(5) C. R. Smith, *ibid.*, **46**, 414 (1924), and earlier references, which are therein cited.

(6) B. Emmert, *Ber.*, **49**, 1060 (1916).

(7) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. I, Academische Verlagsgesellschaft, G.m.b.H., Leipzig, 1934, p. 66.