2,3-Diphenyl-X-methylpyrido(2,3)pyrazines.—These were prepared by the condensation of the above 2,3-diaminopicolines with benzil following the procedure of Chichibabin and Kirsanow.[6] The yields of pure product after recrystallization from ethanol were about 30%.

2,3-Diphenyl-8-methylpyrido(2,3)pyrazine.—M. p. 143-144°. *Anal.*[5] Calcd. for $C_{20}H_{15}N_3$: N, 14.14. Found: N, 14.00.

2,3-Diphenyl-7-methylpyrido(2,3)pyrazine.—M. p. 160-161°. *Anal.*[5] Calcd. for $C_{20}H_{15}N_3$: N, 14.14. Found: N, 14.15.

2,3-Diphenyl-6-methylpyrido(2,3)pyrazine.—M. p. 169-170°. *Anal.*[5] Calcd. for $C_{20}H_{15}N_3$: N, 14.14. Found: N, 14.00.

3- and 5-Nitro-2-picolinols.—These were prepared by the reaction of the corresponding nitro-2-aminopicolines with nitrous acid at 0° following the usual procedure. The products were purified by recrystallization from water to give nearly quantitative yields.

TABLE I

3- AND 5-NITRO-X-METHYL-2-PYRIDINOLS

Nitro	Methyl	M. p., °C.	N Anal.,[5] % Calcd. for $C_6H_5O_3N_2$	N Anal.,[5] % Found
5	3	234–235	18.18	18.26
5	4	189–190	18.18	18.17
5	6	235–236	18.18	18.20
3	4	234–235	18.18	18.09
3	5	253–255	18.18	18.11
3	6	223–224	18.18	18.21

3-Amino-5-methyl-2-pyridinol.—Low pressure catalytic reduction of 5.0 g. (0.033 mole) of 3-nitro-5-methyl-2-pyridinol dissolved in 100 ml. of ethanol using palladium-on-charcoal catalyst gave 3.8 g. (80%) of this compound, m. p., after recrystallization from benzene, 119-120°. *Anal.*[5] Calcd. for $C_6H_8ON_2$: N, 22.58. Found: N, 22.63.

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[6] Chichibabin and Kirsanow, *Ber.*, **60**, 766 (1927).

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Oxonium Salts of Khellin

New compounds believed to be oxonium salts have been prepared by direct treatment of khellin[1] with sulfuric and hydrochloric acids.

Khellin Sulfate.—Powdered khellin (0.5 g.) in 1 cc. 98% sulfuric acid turned orange and then formed an orange-red viscous solution. On the addition of 50 cc. of ethyl acetate an orange solid separated which was filtered off, washed and dried; yield 0.7 g. Crystallization from ethyl acetate gave orange plates which melted at 210° with decomposition to a violet liquid. The solid was stable for a long time but decomposed almost quantitatively in aqueous solution or in dilute ammonia at room temperature to give khellin. This oxonium compound is practically insoluble in dry organic solvents, *e.g.*, benzene and toluene.

Anal. Calcd. for $C_{14}H_{12}O_5$, H_2SO_4: C, 46.9; H, 3.9; S, 8.9. Found: C, 46.7; H, 4.01; S, 8.9.

Khellin Hydrochloride.—Powdered khellin (0.5 g.) was dissolved in hot absolute alcohol and after cooling externally with ice, hydrogen chloride was passed into the solution. An orange color immediately developed, followed by the precipitation of yellow needles which were filtered off, washed with a little absolute alcohol, saturated with hydrogen chloride and then dried at room temperature. This substance melted at 98° decomposing to a red liquid. In aqueous solution it decomposed to khellin; yield, 0.4 g.

Anal. Calcd. for $C_{14}H_{12}O_5$, HCl; Cl, 11.9. Found: Cl, 12.1.

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[1] Khellin has been isolated from *Ami Visnaga* (*cf.* Späth and Gruber, *Ber.*, **71B**, 106-113 (1938).

3-Amino-4-ethyl-, 3-Amino-4-*t*-butylbenzoic Acids and 4-Bromo-3-*t*-butylaniline

The two amino acids were prepared from *p*-ethyl and *p*-*t*-butylbenzoic acids by nitration and reduction. 3-Nitro-4-ethylbenzoic acid so obtained[1] (90.5%) melted at 157.5-158.3° (lit.,[2] 155-156°), the *t*-butyl analog (90.7%) at 162.7-163.2° (lit.,[3] 161°).

Reduction was carried out according to the general procedure of Jacobs and Heidelberger.[4] A solution of 0.40 mole of the 3-nitro-4-alkylbenzoic acid in dilute ammonium hydroxide was added dropwise during a few minutes to a vigorously stirred, boiling solution of 780 g. (2.8 moles) of ferrous sulfate crystals in 1 l. of water. The mixture was then immediately treated with concentrated ammonium hydroxide, added dropwise at the rate of about 200 ml. an hour, while heating and vigorous stirring was maintained. Water lost by evaporation was made up from time to time by washing down the sides of the beaker with water. Addition of ammonium hydroxide was continued until the boiling solution became strongly ammoniacal and the mixture was then filtered hot. The cake was washed thoroughly by removing it from the filter, heating and stirring it with about 500 ml. of water containing 100 ml. of concentrated ammonium hydroxide, and then refiltering. The combined filtrates, which were dark in color, were concentrated to about 1 l., boiled with decolorizing charcoal, and refiltered. The warm filtrate was made barely acidic with acetic acid, resulting in the immediate separation of a solid precipitate or of an oil which solidified upon stirring. After cooling, this amino-acid was removed by filtration and dried at 105°. The amino-acids were purified further by recrystallization from boiling water. 3-Amino-4-ethylbenzoic acid was obtained in 73% yield, m. p. 149.4-149.7°.

Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.78; H, 6.66; N, 8.66.

The *t*-butyl analog (75%) melted at 154-155°.

Anal. Calcd. for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.50; H, 7.64; N, 7.47.

4-Bromo-3-*t*-butylaniline.—*t*-Butylbenzene was converted to the 2,4-dinitro derivative (72%) m. p. 62.3-63.0° (lit.,[5] 61-62°), which was partially reduced to 4-amino-2-nitro-*t*-butylbenzene (97%), m. p. 56.6-57.7° (lit.,[5] 55°) and deaminated by diazotization and hypophosphorus acid to *o*-nitro-*t*-butylbenzene, b. p. 118° (12 mm.) (lit.,[5] 114-115° 10 mm.). Reduction gave 78% of *o*-*t*-butylaniline, b. p. 103-105° (11 mm.) (lit.,[5] 102° (10 mm.)). This material (34.5 g.) was boiled in 100 ml. of glacial acetic acid for three hours to convert it to *o*-*t*-butyl-acetanilide. After cooling, an equivalent of bromine was added dropwise over half-an-hour with shaking at room temperature. After standing an additional half-hour, the mixture was poured into a liter of water containing enough bisulfite to destroy any excess bromine. The precipitate of crude 2-*t*-butyl-4-bromoacetanilide was collected and hydrolyzed without further purification by

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[1] Kloeppel, *Ber.*, **26**, 1733 (1893).

[2] Aschenbrandt, *Ann.*, **216**, 221 (1882).

[3] Kelbe and Pfeiffer, *Ber.*, **19**, 1726 (1886).

[4] Jacobs and Heidelberger, THIS JOURNAL, **39**, 1435 (1917).

[5] Shoesmith and Mackay, *J. Chem. Soc.*, 2336 (1928).