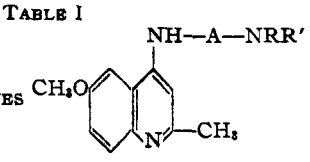
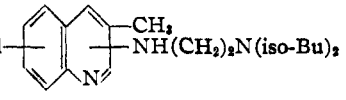
TABLE I

6-METHOXYQUINALDINES



| SN[a] | -A- | R | R' | Yield, % | Formula | M. p., °C. | Analyses, %[b] Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|---|---|---|---|
| .. | $-(CH_2)_3-$ | H | Iso-Pr | 34 | $C_{17}H_{25}ON_3\cdot 2HCl\cdot 2H_2O$[c] | 150–153 | 56.65 | 7.56 | 56.54 | 7.55 |
| | | | | | | | | | 56.62 | 7.59 |
| 5204 | $-(CH_2)_3-$ | H | Iso-Bu | 32 | $C_{18}H_{27}ON_3\cdot 2HCl\cdot H_2O$[d] | 283–284 | 57.75 | 7.81 | 57.83 | 7.75 |
| .. | $-(CH_2)_3-$ | Iso-Bu | Iso-Bu | 43.5 | $C_{22}H_{35}ON_3$ | 159–160 | 73.90 | 9.87 | 73.85 | 9.72 |
| 6556 | $-p-C_6H_4-$ | Me | Me | 45 | $C_{19}H_{21}ON_3\cdot 2HCl$ | 276–277 | 60.00 | 6.10 | 59.90 | 6.08 |
| 6557 | $-HC(CH_2CH_2)_2CH-$ | Me | Me | 31 | $C_{19}H_{27}ON_3\cdot 2HCl$ | 295–297 | 59.05 | 7.57 | 59.70 | 7.67 |
| 6560 | $-HC(CH_2CH_2)_2CH-$ | Et | Et | 32 | $C_{21}H_{31}ON_3\cdot 2HCl$ | 270–272 | 60.85 | 8.03 | 60.74 | 8.03 |

3-METHYLQUINOLINES



| | Diamine position | Cl position | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 9215 | 2 | 7 | 38 | $C_{20}H_{30}N_3Cl\cdot 2HCl\cdot H_2O$[e] | 203–206 | 57.10 | 7.67 | 57.16 | 7.62 |
| 6562 | 4 | 7 | 53 | $C_{20}H_{30}N_3Cl\cdot 2HCl$ | 213–215 | 57.10 | 7.67 | 57.16 | 7.64 |
| 9216 | 4 | 5 | 29.5 | $C_{20}H_{30}N_3Cl\cdot 2HCl$[f] | 215–217 | 57.10 | 7.67 | 57.03 | 7.64 |

[a] The reference number of compounds listed in "A Survey of Antimalarial Drugs," ed. by Wiselogle, J. W. Edwards, Ann Arbor, Mich., 1946. [b] Analyses on the anhydrous material, in the case of the hydrates. [c] *Anal.* calcd. for dihydrate: $Cl^-$, 17.89. Found: $Cl^-$, 17.85. [d] Moisture loss at 125°: 4.82%; calcd. for monohydrate: 4.59%. Free base, 66.5% yield, b. p. (0.5 mm.) 200–215°. [e] Moisture loss at 125°: 4.07%; calcd. for monohydrate: 4.28%. [f] Free base had m. p. 129–131°.

## Some Quinaldine and 3-Methylquinoline Derivatives

BY KEITH W. WHEELER, CHARLES H. TILFORD, M. G. VAN CAMPEN, JR., AND ROBERT S. SHELTON

Termination of our work on antimalarials left unfinished a proposed series of 4-substituted-6-methoxyquinaldines and a similar group of 3-methylquinoline derivatives. Since further work in this direction is not anticipated, it seems desirable to record the preparation and properties of those compounds we did obtain and which have not been previously described in the literature. None of these compounds was appreciably active against the malaria parasite, the activities ranging from $Q<0.03$ for SN9215 to $Q<1.0$ for SN5204, although serveral of them showed moderate activity against *T. equiperdum* in mice.[1]

The intermediates 4-chloro-6-methoxyquinaldine,[2] 4,5-dichloro-3-methylquinoline,[3] 4,7-dichloro-3-methylquinoline[3] and 2,7-dichloro-3-methylquinoline[4] were prepared by standard procedures. The required diamines were obtained from the catalytic hydrogenation of the β-(di)-alkylaminopropionitrile, or the commercially available *p*-aminodiethyl (or methyl) anilines, and from the phthalimide synthesis.

**Procedure.**—A mixture of 0.1 mole of the chloroquinoline and 0.2 mole of the diamine was heated for eight to fifteen hours at 175–200° or for twenty-four to thirty-six hours at 145–150°. Water and ether were added to the mixture, the layers were separated, and the ether layer was washed with 10% hydrochloric acid. The aqueous layer and acidic extracts were combined and made strongly basic. The liberated oil was taken up in ether, dried, and distilled under reduced pressure in some cases, while in other cases only the more volatile material was distilled, leaving the crude free base as a residue. The hydrochloride salts were prepared in the usual manner and recrystallized from mixtures of ethanol and butanone or from aqueous ethanol.

The yields, properties, and analyses of the new compounds prepared are recorded in Table I. The yields reported here do not take into account the quinoline bases recovered in some instances.

**Acknowledgment.**—We wish to express our appreciation to Mr. Wm. J. Corbett for technical assistance.

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(1) We are indebted to Dr. Lloyd D. Seager, Woman's Medical College of Pennsylvania, for these tests.

(2) Conrad and Limpach, *Ber.*, **21**, 1650 (1888).

(3) Steck, Hallock and Holland, THIS JOURNAL, **68**, 380-383 (1946).

(4) This compound, m. p. 125–127°, was obtained along with the known 4,7-dichloro isomer from the action of phosphoryl chloride on 7-chloro-3-methylquinoline N-oxide. Although no analytical data are available, it is assumed to be the 2,7-isomer.

## Optically Active 2-Methylbutyl 3,5-Dinitrobenzoate

BY JONATHAN W. WHITE, JR., AND W. P. RATCHFORD

A lack of agreement in the literature concerning the melting point of optically active 2-