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#### LXXIX.—Physical and Physiological Properties of some Hydrogenated Quinoline Compounds.

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It has been shown by Bamberger and his co-workers (Ber., 1890, 23, 1138; 1891, 24, 2463; Annalen, 1890, 257, 1) that a hydrogenated quinoline compound acquires the nature of an alkylated aromatic amine, and the results of the experiments carried out by them led them to adopt a centric formula for naphthalene, quinoline, and similar condensed nuclei.

The present experiments were carried out in the hope of finding if there exists any relation between a hydrogenated quinoline compound and the corresponding aromatic amine in regard to their ultra-violet absorption spectra.

The following compounds were spectrographically examined :

Quinoline compounds.
Quinoline (in alcohol)
1:2:3:4-Tetrahydroquinoline

- (in alcohol). 6-Amino-1:2:3:4-tetrahydro-
- quinoline dihydrochloride (în water).
- $\alpha$ -Naphthaquinoline (in alcohol). 1:2:3:4-Tetrahydro- $\alpha$ -naphtha-
- quinoline (in alcohol).
- 1:2:3:4:7:8:9:10-Octahydroa-naphthaquinoline (in alcohol). β-Naphthaquinoline (in alcohol).
- 1:2:3:4-Tetrahydro-β-naphtha-
- quinoline (in alcohol). 1:2:3:4:7:8:9:10-Octahydro-8-naphthaquinoline (in alcohol).

Aromatic	amines.

Monomethyl-o-toluidine (in alcohol).

2:5-Tolylenediamine dihydrochloride (in water).

1-Methyl-2-naphthylamine (in alcohol).

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From the spectrographic results, the following generalisation can be drawn:

(1) A hydrogenated quinoline compound shows quite a different absorption from that of the original compound, due to the change of structure of the molecule.



(2) The absorption curve shown by a hydrogenated quinoline compound is very similar in its general form to that of the corresponding alkylated aromatic amine. Hence the resemblance of these two series of compounds is proved spectrographically as well as chemically.

(3) As the degree of hydrogenation increases in a quinoline compound, the tendency to exhibit distinct absorption bands decreases.

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(4) A quinoline compound of a higher molecular weight shows more bands than one of a lower molecular weight.





predicted that a compound having a structure



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#### SOME HYDROGENATED QUINOLINE COMPOUNDS.



show an absorption curve similar to that of tetrahydro- $\alpha$ -naphthaquinoline, and so on.

The antiseptic properties of some of these quinoline compounds were examined by Prof. C. H. Browning of Glasgow University, with the following results :

a 1	Staphylococcus pyogenes aureus in peptone	Staphylococcus pyogenes aureus in	Bacillus coli in	Bacillus coli in
Compound.	water.	serum.	peptone water.	serum.
Quinoline hydrochloride	1:4000+ ө.1:2000-	1:1000+ ?-	1:2000+1:1000-	1:1000+ ?-
Tetrahydro- quinoline hydrochloride	1:2000+1:1000-	1:1000+ ?-	1:1000+ ?-	1:1000+ ?-
Methyltetra- hydroquinoliu methiodide.	1:1000+ ne ?-	1:1000+ (some ppt.) ?	1:1000+ ?-	1:1000+
z-Naphtha- quinoline hydrochloride	1 10,000 + 1:4000 - 3.	1 : 2000 + 1 : 1000 inhib	1:2000+(ppt.) . 1:1000-(ppt.)	1:1000+ ?-
Tetrahydro- a-naphtha- quinoline hydrochloride	1:10,000+1:4000-(ppt.)	1:1000+ ?-	1:10,000+(ppt.) 1:4000-(ppt.)	1:1000+ ?-
8-Naphtha- quinoline hydrochloride	1:10,000+ 1:4000-(ppt.)	1 : 2000+ 1 : 1000 inhib.	1:10,000+ 1:4000-(ppt.)	1:1000+ ?-
Fetrahydro- β-naphtha- quinoline hydrochloride	1:10,000+ 1:2000-(ppt.)	1 : 2000+ 1 : 1000 inhib	1:4000+(ppt.) 1:2000-(ppt.)	1:1000+ ?-
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+ = Vigorous growth. inhib. = Inhibition of growth. - = Sterility after twenty-four to forty-eight hours.

### EXPERIMENTAL.

### Tetrahydroquinoline.

Quinoline was reduced with tin and hydrochloric acid according to Hoffmann's method (*Ber.*, 1883, **16**, 728). The crude tetrahydroquinoline, containing some unchanged quinoline, was warmed with concentrated hydrochloric acid on a water-bath until crystals of the hydrochloride appeared. The hydrochloride was pressed on a porous plate and washed with a little hot benzene, and then recrystallised from alcohol. The hydrochloride, consisting of colourless, slender needles, melted at  $180-181^{\circ}$ .

The free base was obtained from its hydrochloride as an almost colourless oil, boiling at  $160^{\circ}/72$  mm.

# 6-Aminotetrahydroquinoline.

This compound was prepared according to Bamberger (Annalen, 1890, 257, 24) by combining tetrahydroquinoline hydrochloride with diazotised sulphanilic acid and subsequently reducing the azo-compound with stannous chloride.

The free base crystallises from benzene in colourless leaflets, m. p.  $97^{\circ}$ , and is extremely oxidisable, changing slowly into a black mass. It was kept in the form of the hydrochloride (m. p.  $243^{\circ}$ ), which was quite stable.

# Methyltetrahydroquinoline methiodide.

Tetrahydroquinoline, obtained from 2 grams of the hydrochloride, was mixed with 14 grams of freshly distilled methyl iodide, whereby oily drops soon appeared, which gradually solidified to a crystalline mass (Hoffmann and Königs, Ber., 1883, 16, Wedekind, Ber., 1902, 35, 773). It was warmed on the 732; water-bath for one hour and left to stand overnight. After an excess of methyl iodide had been driven off, the residue was dissolved in water, made alkaline with ammonia, and the separated oil extracted with ether. The aqueous solution, thus freed from any kairoline, was evaporated nearly to dryness on the waterbath, and the residue dissolved in hot alcohol and precipitated by careful addition of ether. This procedure was repeated several times to obtain the methiodide in colourless needles, which melted at about 172° with decomposition.

## Monomethyl-o-toluidine.

Crude monomethyl-o-toluidine was prepared by heating 23 grams of o-toluidine, 12·3 grams of methyl alcohol (acetone-free) and 21·5 grams of concentrated hydrochloric acid in a sealed tube

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at 200—220° for eight hours (Nölting, *Ber.*, 1878, **11**, 2278). It was converted into its nitroso-compound, and by subsequent reduction by stannous chloride the pure monomethyl compound was obtained as a colourless oil, when freshly distilled; but it soon oxidised and became discoloured. It boiled at  $206-208^{\circ}$ .

## 2: 5-Tolylenediamine.

(Beilstein and Kuhlberg, Annalen, 5-Nitro-o-toluidine 1871, 158, 348, 352).-Eight grams of powdered aceto-o-toluidide were added little by little to 28 grams of fuming nitric acid which had been previously cooled by a freezing mixture. Nitration was carried out at about  $-5^{\circ}$ . The mixture was left to stand overnight, then poured into a large bulk of cold water, whereby the nitro-product separated as a vellow precipitate, which was subsequently hydrolysed with boiling dilute sulphuric acid (30 grams of concentrated acid in 90 c.c. of water). After all had been hydrolysed, it was subjected to steam distillation (Cohen and Dakin, T., 1901, 79, 1127), in the course of which a small amount of 3-nitroo-toluidine distilled with water as fine, orange-yellow needles (m. p. 92-97°). The residue in the flask was made alkaline with ammonia, and the 5-nitro-o-toluidine separated and purified by recrystallisation from a large bulk of hot water. It was obtained in lemon-yellow needles, m. p. 134-135°.

2:5-Tolylenediamine.—5-Nitro-o-toluidine was easily reduced by granulated tin and concentrated hydrochloric acid. Colourless plates of the tin double salt of the base separated from the cooled filtrate, which were dissolved in water and decomposed by hydrogen sulphide. Slightly greyish-white hydrochloride of 2:5-tolylenediamine was obtained by evaporating the filtrate from tin sulphide. The free base is very unstable.

# 1:2:3:4-Tetrahydro- $\alpha$ -naphthaquinoline.

Tetrahydro- $\alpha$ -naphthaquinoline was prepared according to Bamberger's method (*Ber.*, 1891, 24, 2475) by reducing  $\alpha$ -naphthaquinoline with tin and hydrochloric acid.

The hydrochloride, which crystallises from alcohol in thick, colourless prisms, melts at  $260^{\circ}$  with decomposition. The free base melts at about  $45^{\circ}$ .

## 1:2:3:4:7:8:9:10-Octahydro- $\alpha$ -naphthaquinoline.

 $\alpha$ -Naphthaquinoline was reduced with metallic sodium and boiling amyl alcohol according to the method of Bamberger and Stettenheimer (*Ber.*, 1891, **24**, 2488).

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The base was purified by distillation in a vacuum, and boiled at  $192-193^{\circ}/8-10$  mm.

# 1:2:3:4-Tetrahydro- $\beta$ -naphthaquinoline.

This compound was obtained in the same way as the  $\alpha$ -compound, by reducing  $\beta$ -naphthaquinoline with tin and hydrochloric acid (Bamberger and Müller, *Ber.*, 1891, 24, 2643).

The hydrochloride crystallises from hydrochloric acid in colourless leaflets, which shrink and then melt at 231°.

# 1:2:3:4:7:8:9:10-Octahydro- $\beta$ -naphthaquinoline.

 $\beta$ -Naphthaquinoline was treated like the  $\alpha$ -compound with sodium and amyl alcohol (Bamberger and Müller, *Ber.*, 1891, 24, 2658). A trace of *ac*-octahydro-compound was precipitated as carbonate by passing a current of carbon dioxide through the ethereal solution of the reduced products. The base was purified by distillation under reduced pressure.

# 1-Methyl-2-naphthylamine.

This compound was prepared according to the method of Fries and Hübner (*Ber.*, 1906, **39**, 439). The scheme of reactions is as follows:



2:2'-Dihydroxydi- $\alpha$ -naphthylmethane crystallises from glacial acetic acid in a felted mass of colourless needles, m. p. 199.5—200°.

1-Methyl-2-naphthol crystallises from hot water in colourless, fibrous needles, m. p. 110°.

1-Methyl-2-naphthylamine.—In order to replace the hydroxyl group of 1-methyl-2-naphthol by the amino-group, Bucherer's method of conversion of  $\beta$ -naphthol into  $\beta$ -naphthylamine was tried (J. pr. Chem., 1904, [ii], **69**, 88), that is, heating 3 grams of 1-methyl-2-naphthol with a mixture of 5 c.c. of 40 per cent. solution of ammonium sulphite and 5 c.c. of concentrated ammonia in a sealed tube at 150—160° for seven hours. But no change was

found to have taken place, due probably to the steric hindrance of the methyl group in the ortho-position to the hydroxy-group.

Amination, however, can be brought about by heating the naphthol with four times its weight of calcium chloride-ammonia in a sealed tube at 270° for eight hours.

1-Methyl-2-naphthylamine crystallises from light petroleum in thick, colourless prisms, m. p. 50-51°.

# Spectrography.

The experiments were carried out by using Adam Hilger's rotating sector spectrophotometric attachment, the spark from a nickel-iron alloy being employed as a source of light.

The absorption curves are drawn on wave-lengths against logarithms of molecular extinction coefficients,  $\log\left(\frac{I_0}{I}\right) - dc$ , where  $I_0$  and I are the intensities of the incident and emergent light respectively, d the thickness of the absorbing layer, and c the molecular concentration.

The authors take this opportunity to express their hearty thanks to Prof. E. C. C. Baly, of Liverpool University, for his kindness in placing his spectrophotometer at their service.

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[Received, March 18th, 1921.]

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