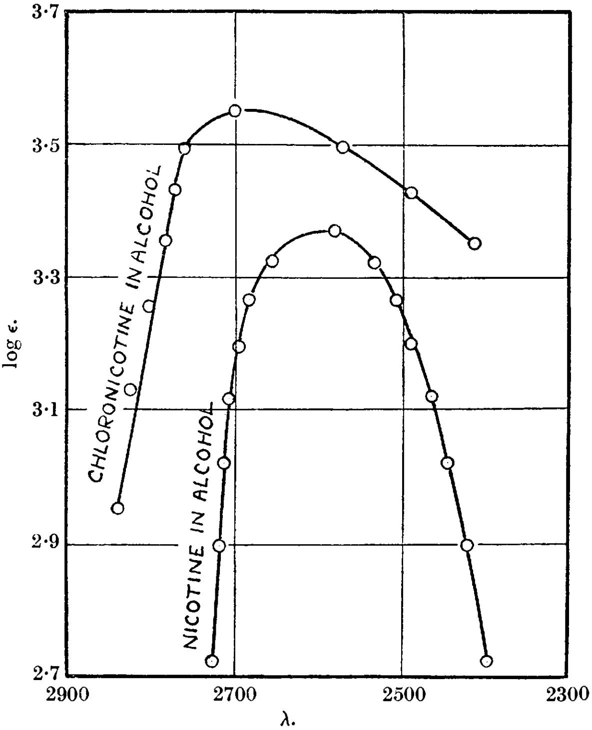
# XLIII.—*The Properties of Nicotine and its Derivatives. Part III. Chloronicotine and Methylnicotone.*

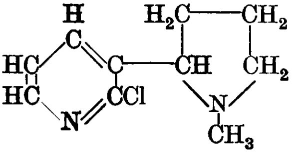
By THOMAS MARTIN LOWRY and HAMID KHAN GORE.

THROUGH the kindness of Professor Karrer in presenting us with authentic specimens of chloronicotine (*Helv. Chim. Acta*, 1926, **9**, 458) and of methylnicotone (*ibid.*, 1925, **8**, 364) we have been able to extend our measurements of absorption spectra and rotatory dispersion (Lowry and Lloyd, J., 1929, 1376, 1771) to these two compounds.

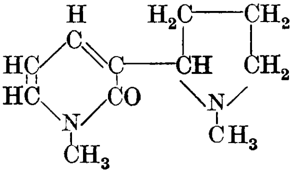
FIG. 1.

*Molecular extinction coefficients of nicotine and chloronicotine in alcohol.*





**Chloronicotine.**

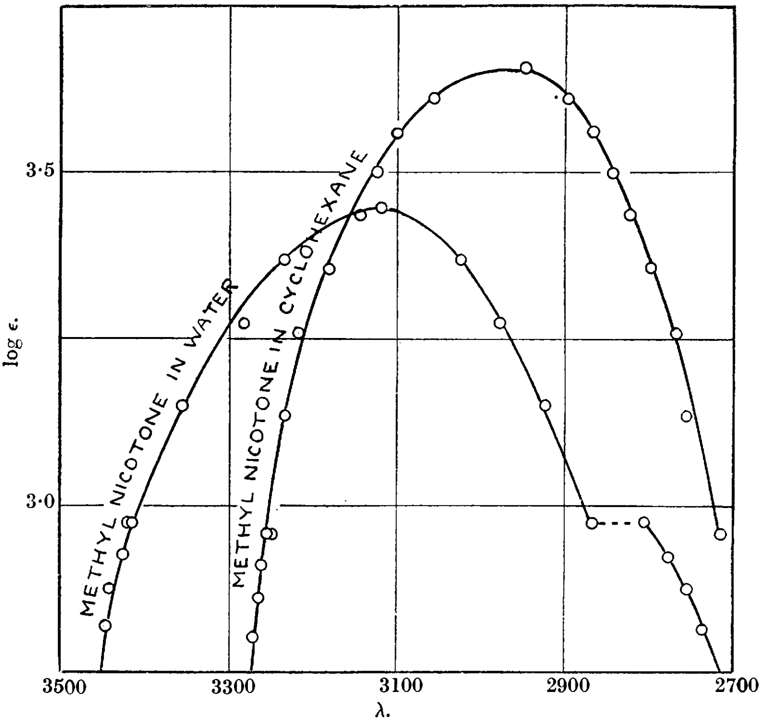


Methylnicotone.

1. *Absorption Spectra.*—The molecular extinction coefficients of a solution of chloronicotine in alcohol at a concentration of 0·2228*M*/1000 are plotted in Fig. 1, and show a maximum log ε = 3·55 at 2700 Å.U., without any minimum at shorter wave-lengths. The curve is therefore of similar type to that of nicotine itself in *cyclo*hexane (J., 1929, 1378). For the purpose of comparison, the molecular extinction coefficients of a solution of nicotine in absolute alcohol at a concentration of 0·3792*M*/1000 have also been plotted in Fig. 1, and show a maximum log ε = 3·37 at 2600 Å.U.

Fig. 2.

*Molecular extinction coefficients of methylnicotone in* cyclo*hexane and in water.*



The molecular extinction coefficients of methylnicotone in *cyclo*hexane at a concentration of 1·072*M*/1000 and in water at a concentration of 1·104*M*/1000 are plotted in Fig. 2 and show the following maxima :

In *cyclo*hexane : log ε = 3·445 at 3100 Å.U.
In water : log ε = 3·656 at 2950 Å.U.

The wave-length of the maximum is longer by about 400 Å.U. than in the simple derivatives of nicotine, where the maximum is always at or below 2700 Å.U. The curves therefore clearly represent a *ketonic* band; but this is evidently reinforced by the conjugated double bonds of the pyridone ring, in the same way as in benzylidenecamphor (Lowry and French, J., 1924, **125**, 1921), since the intensity of the maximum in camphor itself is only $\log \varepsilon = 1{\cdot}45$ at 2880 Å.U. for a solution in *cyclo*hexane. The right-hand arm of each curve shows a break on passing to a solution of higher concentration. This is due in the first instance to deviations from Beer's law; the widening of the curve on the side of shorter wavelengths may, however, be regarded as evidence of the persistence of the nicotine band in a spectrum that is predominantly ketonic.

### TABLE I.

*Rotatory Dispersion of Chloronicotine in Alcohol.*

1·2226 G. per 100 g.; $D_{4^\circ}^{20^\circ} = 0{\cdot}80064$; $l = 2$ dcm.; $[\alpha]_{\mathrm{D}}^{20^\circ} = -120^\circ$; $[\alpha]_{5461}^{20^\circ} = -145^\circ$; $\alpha_{4358}/\alpha_{5461} = 1{\cdot}87$; $\alpha = 0{\cdot}66/(\lambda^2 - 0{\cdot}065)$; $\lambda_0 = 2550$ Å.U.

| λ, Å.U. | α obs. | α calc. | Diff. | λ, Å.U. | α obs. | α calc. | Diff. |
|---|---|---|---|---|---|---|---|
| Li 6708 | −1·71° | −1·71° | ±0 | Hg 5461 | −2·83° | −2·83° | ±0 |
| Cd 6438 | −1·90 | −1·90 | ±0 | Cu 5218 | −3·20 | −3·18 | −0·02 |
| Li 6104 | −2·15 | −2·15 | ±0 | Cu 5153 | −3·29 | −3·29 | ±0 |
| Na 5893 | −2·35 | −2·34 | −0·01 | Cd 5086 | −3·40 | −3·41 | +0·01 |
| Cu 5782 | −2·45 | −2·45 | ±0 | Cd 4800 | −3·98 | −3·99 | +0·01 |
| Hg 5780 | −2·44 | −2·45 | +0·01 | Zn 4722 | −4·20 | −4·18 | −0·02 |
| Cu 5700 | −2·55 | −2·54 | −0·01 | Hg 4358 | −5·28 | −5·28 | ±0 |

### TABLE II.

*Rotatory Dispersion of Methylnicotone in Ethyl Acetate.*

1·3578 G. per 100 g.; $D_{4^\circ}^{20^\circ} = 0{\cdot}90613$; $l = 2$ dcm.; $[\alpha]_{\mathrm{D}}^{20^\circ} = -90{\cdot}2^\circ$; $[\alpha]_{5461}^{20^\circ} = -109^\circ$; $\alpha_{4358}/\alpha_{5461} = 1{\cdot}91$; $\alpha = 0{\cdot}6065/(\lambda^2 - 0{\cdot}0712)$; $\lambda_0 = 2668$ Å.U.

| λ, Å.U. | α obs. | α calc. | Diff. | λ, Å.U. | α obs. | α calc. | Diff. |
|---|---|---|---|---|---|---|---|
| Li 6708 | −1·61° | −1·60° | −0·01 | Cu 5218 | −3·01° | −3·02° | +0·01 |
| Cd 6438 | −1·77 | −1·78 | +0·01 | Ag 5209 | −3·02 | −3·03 | +0·01 |
| Li 6104 | −2·01 | −2·01 | ±0 | Cu 5153 | −3·12 | −3·12 | ±0 |
| Na 5893 | −2·22 | −2·20 | −0·02 | Cd 5086 | −3·24 | −3·24 | ±0 |
| Cu 5782 | −2·30 | −2·30 | ±0 | Cd 4800 | −3·81 | −3·81 | ±0 |
| Hg 5780 | −2·30 | −2·31 | +0·01 | Zn 4722 | −4·00 | −4·00 | ±0 |
| Hg 5461 | −2·68 | −2·67 | −0·01 | Hg 4358 | −5·12 | −5·11 | −0·01 |

### TABLE III.

*Rotatory Dispersion of Methylnicotone in Water.*

2·1209 G. per 100 g.; $D_{4^\circ}^{20^\circ} = 1{\cdot}0012$; $l = 2$ dcm.; $[\alpha]_{\mathrm{D}}^{20^\circ} = -56{\cdot}75^\circ$; $[\alpha]_{5461}^{20^\circ} = -70^\circ$; $\alpha_{4358}/\alpha_{5461} = 1{\cdot}91$; $\alpha = 0{\cdot}6764/(\lambda^2 - 0{\cdot}0704)$; $\lambda_0 = 2654$ Å.U.

| λ, Å.U. | α obs. | α calc. | Diff. | λ, Å.U. | α obs. | α calc. | Diff. |
|---|---|---|---|---|---|---|---|
| Li 6708 | −1·77° | −1·78° | +0·01 | Cu 5218 | −3·35° | −3·35° | ±0 |
| Cd 6438 | −1·98 | −1·98 | ±0 | Cu 5153 | −3·45 | −3·46 | +0·01 |
| Li 6104 | −2·25 | −2·24 | −0·01 | Cd 5086 | −3·60 | −3·59 | −0·01 |
| Na 5893 | −2·41 | −2·44 | +0·03 | Cd 4800 | −4·23 | −4·23 | ±0 |
| Cu 5782 | −2·56 | −2·56 | ±0 | Zn 4722 | −4·44 | −4·43 | −0·01 |
| Hg 5780 | −2·56 | −2·57 | +0·01 | Hg 4358 | −5·66 | −5·66 | ±0 |
| Hg 5461 | −2·97 | −2·97 | ±0 | | | | |

2. *Rotatory Dispersion.*—Tables I—III show the rotatory dispersion of solutions of chloronicotine in alcohol and of methylnicotone in ethyl acetate and in water. In each case the rotatory dispersion is simple within the limits of experimental error. The constants of the equations are set out in Table IV with those of nicotine and of one of its salts for comparison.

TABLE IV.

*Rotatory Powers and Dispersion Constants.*

| Substance. | Solvent. | Conc., %. | $[\alpha]_{5461}$. | $\frac{\alpha_{4358}}{\alpha_{5461}}$ | $\lambda_0^2$. | $\lambda_0 \times 10^4$, Å.U. |
|---|---|---|---|---|---|---|
| Chloronicotine | Alcohol | 1·2226 | $-145°$ | 1·87 | 0·065 | 2550 |
| Methylnicotone | EtOAc | 1·3578 | $-109$ | 1·91 | 0·0712 | 2668 |
| Methylnicotone | Water | 2·1209 | $-70$ | 1·91 | 0·0704 | 2654 |
| Nicotine | Acetone | 28·8 | $-209·0$ | 1·817 | 0·0664 | 2400 |
| Nicotine | Water | 25·5 | $-97·64$ | 1·876 | 0·0627 | 2575 |
| $ZnCl_2$ compound | Water | 17 | $+20·17$ | 1·644 | 0·0217 | 1480 |

In spite of the elimination of a hydrogen atom by chlorine in one compound and by oxygen in the other, it is obvious that the lævorotation and the characteristic high dispersion of the parent base are preserved in these two derivatives. The reversal of sign and the fall in the dispersion constant which are observed in the salts of nicotine and in its mono- and di-methiodide (but not in the *iso*methiodide) are therefore not due to the interlocking of this hydrogen atom with the nitrogen of the pyrrolidine ring.

It is also noteworthy that, although the absorption spectrum of methylnicotone is dominated by a ketonic band, the characteristic wave-length deduced from the measurements of rotatory dispersion still corresponds closely with that of nicotine. For this reason, it would be of great interest if measurements of optical rotatory power could be made *within the region of absorption.* It has been found, however, both by calculation and by experiment, that this cannot be done in the case of nicotine, on account of the enormous value of the extinction coefficient at and near the maximum; and this limitation is even more severe in the case of derivatives, such as methylnicotone, which are of lower optical rotatory power, but show a still more intense selective absorption. For this reason the further analysis of the curve appears to be impossible under the conditions of experiment now available.

## *Summary.*

(*a*) Chloronicotine in alcohol shows an absorption band with maximum $\log \varepsilon = 3·55$ at 2700 Å.U., as compared with $\log \varepsilon = 3·37$ at 2600 for nicotine. Methylnicotone gives a maximum $\log \varepsilon = 3·44$ at 3100 Å.U. in *cyclo*hexane and 3·66 at 2950 in water.

(*b*) The rotatory dispersion of lævorotatory nicotine can be expressed by one term of Drude's equation with characteristic wave-length $\lambda_0 = 2550$ Å.U. Methylnicotone gives $\lambda_0 = 2668$ Å.U. in *cyclo*hexane and 2654 in water. Both compounds therefore behave like the parent base, and not like its salts, which are dextrorotatory and of much lower dispersion.

Laboratory of Physical Chemistry,
University of Cambridge.

[*Received, December* 19*th*, 1930.]