PROCEEDINGS

OF

THE ROYAL SOCIETY

December 11, 1884.

THE TREASURER in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read:—

I. "The Absorption-spectra of the Alkaloids." By W. N. HARTLEY, F.R.S., Professor of Chemistry, Royal College of Science, Dublin. Received November 19, 1884.

(Abstract.)

While studying the molecular constitution of various organic substances by means of their action on the ultra-violet rays in the manner described in the "Philosophical Transactions," vol. 170, p. 257, 1879, it was considered of importance to ascertain whether absolute physical measurements could not be substituted for the uncertain chemical reactions and variable physiological tests at present employed as a means of detecting the alkaloids in medico-legal examinations. About forty alkaloids and derivatives therefrom have been examined, authentic specimens having been procured from the chemists by whom they were prepared. Solutions were carefully made of the same strength in most cases, only diactinic solvents, most generally alcohol, being employed. The cells with quartz sides for holding the solutions were of various thicknesses, ranging from 1 mm. to 20 mm. The electrodes employed to give a well-defined spectrum consisted, one of an alloy of tin with 25 per cent. cadmium, the other of lead with cadmium in the same proportion. Spectra are thus obtained with lines of the same intensity, numerous and evenly distributed throughout a spectrum extending

from wave-length 4414·5 to 2145·8. The prominent lines of cadmium are distinguished by their extension across the spectrum from pole to pole, while those of lead are on one side only and those of tin on the other. As a weaker continuous spectrum fills the intervals between the lines, there is no difficulty in obtaining accurate measurements. To secure well-defined spectra the photographs were taken with the solutions placed in front of the slit, upon which the rays from the sparks were concentrated by a quartz lens of 2 inches diameter and 3 inches focal length. The spectra were measured by means of an ivory scale applied to the surface of the photographs; this had bevilled edges and was divided thereon into hundredths of an inch. The linear measurements are termed scale numbers and are arbitrary, but they were reduced to wave-lengths by the use of an interpolation curve. The oscillation frequencies were also read off on a second curve whenever it was considered desirable to record them. The wave-lengths were taken from those published in the "Philosophical Transactions," vol. 175, p. 63, 1884, but for use in recording these measurements the fractions of a tenth-meter were disregarded. The total number of lines employed, including two or three air-lines, was seventy. For the convenience of those who may be engaged in similar work, the wave-lengths of the lines and their reciprocals are given on page 3. The wave-lengths of a magnesium line and a calcium triplet are also inserted, as it is sometimes convenient to refer to them.

The absorption curves which have been drawn differ from those figured in my previous communications, owing to the use of wave-length numbers. The curves have been made continuous, and so the necessity for shading has been avoided; but very careful descriptions of the spectra are furnished in addition, so that no detail has been omitted. Nearly all the samples of alkaloids examined were obtained from Messrs. T. and H. Smith and Co., of Edinburgh, Mr. David Howard, of the firm of Howard and Sons, of Stratford, and Dr. C. R. A. Wright, F.R.S. The bodies may be divided into two groups, those which exhibit spectra with absorption-bands and those with continuous spectra.

Alkaloids and Derivatives exhibiting Absorption-bands.

Aconitine.
Pseudaconitine.
Japaconitine.
Morphine.
Narcotine.
Codeïne.
Thebaïne.
Papaverine.
Oxynarcotine.
Apomorphine Hydrochloride.
Cotarnine Hydrobromide.
Tetracetyl Morphine.
Diacetyl Codeïne.
Quinine.
Quinine Sulphate.
Cinchonine Sulphate.

Quinidine Sulphate.	Piperine.
Cinchonidine Sulphate.	Brucine.
Veratrine.	Strychnine.

Alkaloids transmitting continuous Spectra.

Narceïne.	Hyoscyamine.
Aconitine (foreign).	Digitaline.
Cevadine.	Picrotoxine.
Atropine.	Nicotine.
Solanine.	Caffeïne.

Scale numbers.	Wave-lengths.	Reciprocals.	Scale numbers.	Wave-lengths.	Reciprocals.
17	4480 Mg	2232	190	2812 Sn	3556
17·7	4454 Ca	2245	192·5	2801 Pb	3571
18·9	4434 Ca	2255	197	2778 Sn	3599
20·0	4424 Ca	2260	203·5	2747 Cd	3640
20·5	4414 Cd	2265	213	2705 Sn	3696
22·5	4386 Pb	2280	223	2662 Pb	3756
30·5	4245 Pb	2355	235	2613 Pb	3827
42·7	4061 Pb	2462	240	2593 Sn	3856
62·0	3800 Sn	2503	244	2576 Pb	3882
67·3	3739 Pb	2674	245	2572 Cd	3888
72	3683 Pb	2715	245·5	2570 Sn	3891
76·3	3639 Pb	2748	247	2561 Pb	3904
79	3610 Cd	2770	251·5	2545 Sn	3929
82·7	3572 Pb	2799	266·5	2495 Sn	4008
93·7	3465 Cd	2886	270	2483 Sn	4027
97	3437 Air	2909	272	2475 Pb	4040
101	3403 Cd	2938	281·3	2445 Pb	4090
106·5	3352 Sn	2983	282	2443 Pb	4095
109·5	3330 Sn	3003	286·5	2429 Sn	4116
115	3283 Sn	3045	289	2422 Sn	4128
118	3262 Sn	3065	295	2402 Pb	4163
119·5	3260 Cd	3067	298	2393 Pb	4178
129·5	3174 Sn	3150	306	2368 Sn	4223
135	3137 Pb	3187	311	2355 Sn	4246
151	3033 Sn	3297	318	2335 Sn	4282
155	3008 Sn	3324	320	2329 Cd	4293
159·5	2980 Cd	3355	322·7	2321 Cd	4308
165	2949 Pb	3391	325·7	2313 Cd	4323
171	2912 Sn	3434	335	2288 Cd, Sn	4370
177	2880 Cd	3472			
178·5	2872 Pb	3481	344	2265 Cd	4415
180	2862 Sn	3494	351	2247 Sn	4450
182·5	2849 Sn	3510	353·5	2241 Cd	4462
185	2837 Sn	3524	368·5	2205 Pb	4535
186	2832 Pb	3531	372·5	2195 Cd	4555
188	2822 Pb	3543	395	2145 Cd	4662

The conclusions to be drawn from this investigation are the following:—

1. The absorption-spectra offer a ready and valuable means of ascertaining the purity of preparations of the alkaloids, and particularly of establishing their identity.

The quantity of some of the alkaloids present in a solution may be estimated by means of the absorption curves.

The different character of the various specimens known as aconitines may be recognised; thus the comparatively harmless base may be distinguished from those of great physiological activity by its transmission of a continuous spectrum, while the three specimens of physiologically active aconitines are distinguished from one another by their characteristic absorption curves.

That the three active aconitine bases are substances each with a different chemical constitution, is a conclusion confirmed by optical examination.

The purity of quinine and absence of any admixture of cinchonine can be readily determined by reason of the latter substance being much less diactinic than the former; but for the same reason quinine cannot be estimated in presence of cinchonine. Drugs of such potency as aconitine, morphine, quinine, strychnine, &c., which ought to be prescribed only when of absolute purity, should have their exact nature and degree of purity guaranteed by an examination of their absorption-spectra.

2. In comparing the spectra of substances of similar constitution, it is observed that such as are derived from bases by the substitution of an alkyl radical for hydrogen and acid radicals for hydroxyl, the curve is not altered in character, but may vary in length when equal weights of substances are examined. This is explained by the absorption-band being dependent upon the compactness of structure of the carbon and nitrogen nucleus of the molecule, and because equal weights are not molecular weights. Examples are afforded by morphine and codeïne (methyl-morphine), diacetyl-codeïne, and tetracetyl-morphine.

3. Bases which contain oxidised radicals, as hydroxyl, carboxyl, or methoxyl, diminish in diactinic quality in proportion to the amount of oxygen they contain. Examples are papaverine, narceïne, narcotine, and oxynarcotine.

The apo-derivatives are less diactinic than the parent bases in a degree which indicates that the molecular weights have been nearly doubled. Examples are apo-morphia and pseudaconitine.

4. Bodies with the pyridine and quinoline nucleus exhibit absorption-bands extending between wave-lengths 350 and 280, those with a benzene nucleus generally from 290 to 260, or rays even more refrangible; while the aconitines and opium bases, likewise strychnine, give evidence of a benzene nucleus, the cinchona bases, with piperine and brucine, appear to contain a nucleus of quinoline or pyridine.