VI.—*On Some New Bases of the Leucoline Series.* PART II. By
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In a former paper read before the Society, and published in the Society's "Transactions,"* on "Some New Bases of the $C_nH_{2n-11}N$ series," obtained from the "vitriol-tar," from the distillation of shale, evidence was given of the isolation of three bases of this series, in addition to the Leucoline, Iridoline, and Cryptidine of G. WILLIAMS.

In this paper it was pointed out that the three new bases, $C_{12}H_{13}N$, $C_{13}H_{15}N$, and $C_{14}H_{17}N$, were obtained by the fractional distillation of the mixed bases after treating alternately with caustic soda and sulphuric acid. In the first experiment, in which a comparatively small quantity of material was used, and where fractional distillation was continued to twenty-five times, the presence of these bases was indicated by the analysis of their chloroplatinates, in those fractions which from theoretic considerations might be expected to contain them; *e.g.*, Cryptidine, the last of G. WILLIAMS' series, was found by him to have a boiling-point of $274^{\circ}C$., whilst Iridoline and Leucoline had boiling-points of $256^{\circ}C$. and $238^{\circ}C$. respectively, showing a difference of $18^{\circ}C$. for each addition of CH_2 to the molecule. The next member in ascending the series would be expected to lie in fraction 290° – $295^{\circ}C$., its theoretic boiling-point being $292^{\circ}C$.; accordingly, analysis of chloroplatinate from fraction 290° – $295^{\circ}C$. showed 26.12 per cent. of platinum, corresponding with percentage of platinum required for chloroplatinate of new base $C_{12}H_{13}N$.†

The quantity of bases in this first experiment being much too small to allow of any satisfactory examination of their fractions, a second and larger quantity was, after going through the same processes of purification, submitted to fractional distillation, and the corresponding fractions 290° – 295° , 310° – 315° , &c., examined. Here a curious anomaly in the boiling-points was observed: the three bases $C_{12}H_{13}N$, $C_{13}H_{15}N$, and $C_{14}H_{17}N$, were obtained; but each was found in the fraction one step lower than was anticipated, *i.e.*, in fractions 270° – 275° , 290° – 295° , 310° – 315° respectively, instead of in fractions 290° – 295° , 310° – 315° , and 325° – 330° . The explanation offered was that in the first experiment twenty-

* "Transactions Royal Society, Edinburgh," vol. xxviii. part ii. "On Some New Bases of the Leucoline Series."

† Trans. Royal Soc. Edin., vol. xxviii. pt. ii. page 563.

five complete fractionations had been made, whilst in the second experiment only sixteen fractionations were made; and it was the desire of more completely isolating the higher members of this series, and, if possible, ascertaining their true position in the series by longer continued fractional distillation, that has given rise to the present paper.

In order to carry out this investigation, we were again kindly supplied by Messrs GELLATLY and THOMSON with a quantity of crude bases, about one gallon; these were purified as follows:—the crude bases, being a mixture chiefly of bases, tarry matter, and paraffin, were digested for several hours with dilute sulphuric acid, the insoluble portion separated by filtration, and the acid liquor neutralised with caustic soda; the so-separated bases were again dissolved in dilute sulphuric acid, again treated with caustic soda, and this process repeated other three times, when the mixture of bases was considered sufficiently pure to be distilled. After eight distillations, a large quantity of black tarry matter being left in the still from each operation, fractional distillation was commenced.

Fractional Distillation of the Mixed Bases.

After twelve complete fractionations, fractions ranging from 250°C. to 390° C. about 5 grms. of fraction 260°–270° C. was dissolved in strong nitric acid, the solution evaporated to dryness on water-bath, the residue treated with water, and to the aqueous solution, cooled in freezing mixture, platinum chloride added. The precipitated platinum salt was washed with ice-cold water, then with a mixture of alcohol and ether, dried over sulphuric acid and finally at 100° C.

Analysis gave—

- I. 25.52 per cent. platinum.
- II. 25.55 „ „

Fractional distillation was then continued to twenty times and platinum salts prepared from fractions 270°–275° and from fraction 290°–295° in same manner as from 260°–270°.

Analysis of platinum salt from fraction 270°–275°—

- I. 24.74 per cent. platinum.
- II. 24.63 „ „

This fraction might be expected to contain Cryptidine, $C_{11}H_{11}N$, and as the chloroplatinate of that base, $2C_{11}H_{11}NHCl$, $PtCl_4$, requires 27.13 per cent. platinum, the small percentage of platinum was quite inexplicable, except on the assumption that during the process of evaporating with nitric acid a nitro-substitution compound had been formed. Assuming that one atom of hydrogen

were replaced by (NO_2) , we should have from cryptidine the body $2\text{C}_{11}\text{H}_{10}(\text{NO}_2)\text{NHCl}$, PtCl_4 , which requires 24.14 per cent. platinum.

Similarly, the chloroplatinate from fraction 290° – 295° showed 23.37 per cent. platinum, this being far too low for platinum salt of base $\text{C}_{12}\text{H}_{13}\text{N}$, that salt requiring 26.12 per cent., the presence of a nitro-compound was inferred from the fact that the percentage of platinum obtained agreed closely with the calculated quantity for the body having the formula $2\text{C}_{12}\text{H}_{12}(\text{NO}_2)\text{NHCl}$, PtCl_4 , this body requiring 23.34 per cent. platinum, found 23.37 per cent.

In order to more completely separate the bases five more fractional distillations were made, this making twenty-five fractionations in all, and involving some six hundred distillations.

Again a platinum salt was prepared from fraction 290° – 295° by dissolving the base in nitric acid as on former occasions, this yielded 23.54 and 23.52 per cent. platinum, agreeing with the salt made after twenty fractionations, thus showing that the last five fractional distillations had not effected any further separation, and further strengthening the supposition that the bodies obtained by the action of nitric acid were nitro-compounds. The further examination of these bodies was not proceeded with at this stage, as we considered it more advisable to attempt the identification of the bases in the first instance without the use of nitric acid, employing only hydrochloric acid as the solvent.

The method adopted for obtaining the chloroplatinates was therefore as follows:—About 3–5 grms. of the fraction under examination was dissolved in 20–30 cc. of dilute hydrochloric acid and the solution boiled, when a small quantity of a black tarry substance separated; this was filtered off, and the clear solution, diluted with five to six times its volume of water, was cooled in freezing mixture. To the diluted solution was added platinum chloride, the chloroplatinate precipitated as a fine granular yellow mass was collected on a filter washed several times with ice-cold water, then with a mixture of alcohol and ether, dried over sulphuric acid, and finally dried at 100°C .

Examination of Fraction 270° – 275° .

Chloroplatinate prepared as above,

0.2805 grms. gave
0.0765 „ platinum = 27.27 per cent.

This agrees with percentage of platinum demanded by chloroplatinate of cryptidine, bg. pt. 274°C ., the formula for which $2\text{C}_{11}\text{H}_{11}\text{NHCl}$, PtCl_4 , requires 27.13 per cent., this being sufficient evidence of the presence of cryptidine, and also indicating that this time the increased number of fractional distillations to which the bases had been subjected had brought them up to their hypothetical boiling-points, the carbon and hydrogen in this salt was not determined.

Examination of Fraction 290°-295°.

Analysis of chloroplatinate—

I.	0.198	grms.	salt gave				
	0.051	„	platinum = 25.76	per cent.	platinum.		
II.	0.164	„	salt gave				
	0.04225	„	platinum = 25.77	„	„		
III.	0.31175	„	salt gave				
	0.082	„	platinum = 26.30	„	„		
IV.	0.2895	„	salt gave				
	0.40085	„	CO ₂	= 37.76	„	carbon.	
	0.122	„	H ₂ O	= 4.49	„	hydrogen.	
V.	0.52525	„	salt gave				
	0.72675	„	CO ₂	= 37.70	„	carbon	
	0.208	„	H ₂ O	= 4.37	„	hydrogen.	
VI.	0.44725	„	salt gave				
	0.62275	„	CO ₂	= 37.75	„	carbon.	
	0.17375	„	H ₂ O	= 4.35	„	hydrogen.	

These results agree with the percentage composition of chloroplatinate of first new base C₁₂H₁₃N, the formula for which 2C₁₂H₁₃NHCl, PtCl₄, requires—

	Calculated.	Found.					
		I.	II.	III.	IV.	V.	VI.
Carbon, .	38.19	37.76	37.70	37.75	...	...	...
Hydrogen, .	3.72	4.49	4.37	4.31	...	...	...
Platinum, .	26.12	...	...	...	25.76	25.77	26.30

Examination of Fraction 305°-310°.

Analysis of chloroplatinate—

I.	0.216	grms.	salt gave				
	0.054	„	platinum = 25.00	per cent.	platinum.		
II.	0.2165	„	salt gave				
	0.054	„	platinum = 24.94	„	„		

Examination of Fraction 310°-315°.

Analysis of chloroplatinate—

I.	0.277	grms.	salt gave				
	0.07	„	platinum = 25.27	per cent.	platinum.		
II.	0.301	„	salt gave				
	0.076	„	platinum = 25.25	„	„		

III.	0.458	grms. salt gave				
	0.1145	„	platinum = 25.00	per cent.	platinum.	
IV.	0.54275	„	salt gave			
	0.77875	„	CO ₂	= 39.47	„	carbon.
	0.233	„	H ₂ O	= 4.79	„	hydrogen.
V.	0.42525	„	salt gave			
	0.62	„	CO ₂	= 39.95	„	carbon.
	0.18	„	H ₂ O	= 4.70	„	hydrogen.

Both these fractions, 305°–310° and 310°–315°, therefore consist of the second new base, C₁₃H₁₅N, the theoretical boiling-point of which is 310° C., the formula of its chloroplatinate 2C₁₃H₁₅NHCl, PtCl₄, requiring—

		Found.					
	Calculated.	I.	II.	III.	IV.	V.	
Carbon, . . .	39.89	39.47	39.95	...	...	...	
Hydrogen, . . .	4.09	4.79	4.70	...	...	...	
Platinum, . . .	25.19	...	...	25.27	25.25	25.00	

Examination of Fraction 325°–330°.

Analysis of chloroplatinate—

I.	0.287	grms. salt gave				
	0.0695	„	platinum = 24.21	per cent.	platinum.	
II.	0.183	„	salt gave			
	0.044	„	platinum = 24.03	„	„	
III.	0.271	„	salt gave			
	0.066	„	platinum = 24.35	„	„	
IV.	0.388	„	salt gave			
	0.5885	„	CO ₂	= 41.36	„	carbon.
	0.16	„	H ₂ O	= 4.56	„	hydrogen.
V.	0.2965	„	salt gave			
	0.4515	„	CO ₂	= 41.51	„	carbon.
	0.1205	„	H ₂ O	= 4.52	„	hydrogen.

These results show this fraction to consist of the third new base, C₁₄H₁₇N, the theoretical boiling-point of which is 328° C. The formula of its chloroplatinate 2C₁₄H₁₇NHCl, PtCl₄, requiring—

		Found.				
	Calculated.	I.	II.	III.	IV.	V.
Carbon, . . .	41.48	41.36	41.51	...	...	...
Hydrogen, . . .	4.44	4.56	4.52	...	...	...
Platinum, . . .	24.37	...	...	24.21	24.03	24.35

Examination of Fraction 345°-350°.

Analysis of chloroplatinate—

I.	0.3695	grms. salt gave			
	0.8725	„	platinum = 23.61	per cent. platinum.	
II.	0.23025	„	salt gave		
	0.055	„	platinum = 23.84	„	„
III.	0.2825	„	salt gave		
	0.4475	„	CO ₂	= 43.18	„ carbon.
	0.1135	„	H ₂ O	= 4.40	„ hydrogen.
IV.	0.5685	„	salt gave		
	0.896	„	CO ₂	= 42.99	„ carbon.
	0.2295	„	H ₂ O	= 4.48	„ hydrogen.

These analyses show the salt to be the chloroplatinate of the fourth new base, C₁₅H₁₉N, theoretical boiling-point 346° C. Its chloroplatinate has the formula 2C₁₅H₁₉NHCl, PtCl₄, and composition—

		Found.			
	Calculated.	I.	II.	III.	IV.
Carbon,	42.95	42.99	43.18	...	...
Hydrogen,	4.53	4.48	4.40	...	...
Platinum,	23.50	...	...	23.61	23.84

Examination of Fraction 360°-365°.

Analysis of chloroplatinate—

I.	0.2525	grms. salt gave			
	0.058	„	platinum = 22.96	per cent. platinum.	
II.	0.288	„	salt gave		
	0.066	„	platinum = 22.91	„	„
III.	0.414	„	salt gave		
	0.667	„	CO ₂	= 43.96	„ carbon.
	0.186	„	H ₂ O	= 4.97	„ hydrogen.
IV.	0.435	„	salt gave		
	0.702	„	CO ₂	= 44.00	„ carbon.
	0.199	„	H ₂ O	= 5.08	„ hydrogen.

These analyses show this salt to be the chloroplatinate of the fifth new base, C₁₆H₂₁N, theoretical boiling-point 364° C. Its chloroplatinate has the formula 2C₁₆H₂₁NHCl, PtCl₄, and composition—

		Found.			
	Calculated.	I.	II.	III.	IV.
Carbon,	44.34	43.96	44.00	...	...
Hydrogen,	5.08	4.97	5.08	...	...
Platinum,	22.75	...	...	22.96	22.91

Fractions of higher boiling-points were not examined, one other within the series, viz., 380° – 385° , was obtained (which would probably contain the base $C_{17}H_{23}N$) but only in very small quantity and containing paraffin; but from those fractions examined, viz., 290° – 295° , 305° – 310° , and 310° – 315° , 325° – 330° , 345° – 350° , and 360° – 365° , we have been able, by the analysis of the platinum salts, to separate and identify five new members of the series of Leucoline bases, viz., the base $C_{12}H_{13}N$ from fraction 290° – 295° , $C_{13}H_{15}N$ from fractions 305° – 310° and 310° – 315° , $C_{14}H_{17}N$ from fraction 325° – 330° , $C_{15}H_{19}N$ from fraction 345° – 350° , and $C_{16}H_{21}N$ from fraction 360° – 365° . Taking Leucoline, Iridoline, and Cryptidine with boiling-points 238° , 256° , and 274° respectively, it will be seen that the boiling-points of the five higher members of the series would be 292° , 310° , 328° , 346° , and 364° ; we have not been able to ascertain the actual boiling-points of these higher members of the series, but have shown that the fractions, within a range of 5° C., consist practically of such bases; and, as is seen from analyses of chloroplatinate from fractions 305° – 310° and 310° – 315° , also from other analyses not noted, the same base extends over a considerable range of temperature.

In a former paper on these bases,* wherein the identification of $C_{12}H_{13}N$, $C_{13}H_{15}N$, and $C_{14}H_{17}N$ was recorded, an apparent anomaly in their boiling-points was observed; the base $C_{12}H_{13}N$ being found in fraction 270° – 275° instead of in fraction 290° – 295° , $C_{13}H_{15}N$ in fraction 290° – 295° , instead of fraction 310° – 315° , &c., and the explanation was offered that fractional distillation had not been pushed far enough, that were it continued at least twenty-five or thirty times, these three bases would be found in fractions 290° – 295° , &c. The present investigation has shown this to be the case, fractional distillation being continued to twenty-five times before the bases were submitted to examination, with the result already stated.

It is necessary to mention that fractional distillation at these very high temperatures was effected by means of the high-range thermometers made by the late Dr GEISSLER of Bonn; these thermometers are so constructed as to indicate temperatures up to 460° C. All distillations above 300° C. were made in the above manner, distillation being pushed as long as any distillate was produced, the limit to this being found to lie about 390° C., when a thick tarry residue was left in the flask.

When recently distilled these bases are of a pale brown colour; they rapidly darken when exposed to the atmosphere, and even when enclosed in hermetically sealed tubes the same darkening in colour goes on, but more slowly. They thicken and appear to become resinous when kept for some time in an imperfectly closed vessel, and, as the series is ascended, the more rapidly do they become resinous.

* Trans. Royal Society, Edinburgh, vol. xxviii. part ii. p. 569.

The salts of these bases, if we except the lower members of the series, do not appear to crystallise. As already stated, the chloroplatinates are precipitated in the form of granular yellow masses, which under the microscope appear to consist of tufts of silky crystals, but we have hitherto completely failed to re-crystallise the precipitated chloroplatinate, as was effected by G. WILLIAMS with the platinum salt of cryptidine.

We would suggest, that in order to distinguish these five bases from their isomers of the Chinoline series—Tetrahiroline, &c., they should be termed Tetracoline, Pentacoline, &c., thus WILLIAMS' bases being Leucoline, Iridoline, and Cryptidine, the series will now consist of—

Leucoline,	C_9H_7N	Pentacoline,	$C_{13}H_{15}N$
Iridoline,	$C_{10}H_9N$	Hexacoline,	$C_{14}H_{17}N$
Cryptidine,	$C_{11}H_{11}N$	Heptacoline,	$C_{15}H_{19}N$
Tetracoline,	$C_{12}H_{13}N$	Octacoline,	$C_{16}H_{21}N$

Action of Nitric Acid on these Bases.

The study of the action of nitric acid on these five bases has not as yet yielded any very promising results. As was stated in an early part of this paper, we were led to believe from the analysis of the platinum salts prepared by evaporating the bases with strong nitric acid, that "nitro-compounds" were formed. At two stages of the fractional distillation—at the twentieth and the twenty-fifth—platinum salts were prepared from fraction 290° – 295° by dissolving the base in strong nitric acid, evaporating the solution on water-bath, treating the residue with water, and from this precipitating the platinum salt by addition of platinum chloride; both salts yielded 23·37 per cent. platinum, this corresponding with the calculated percentage of platinum in substance having the formula $2C_{12}H_{11}(NO_2)NHCl$, $PtCl_4$, but further examination did not bear out this theory, for the same platinum salt yielded on combustion—

	I.	II.
Carbon,	39·42	39·00
Hydrogen,	4·5	4·5

whereas the above formula requires only—

Carbon,	34·12 per cent.
Hydrogen,	3·08 „

It is apparent also from these analyses that the chloroplatinate prepared with nitric acid have not the same composition as those prepared with hydrochloric acid.