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Présidence de M. F. KREUTZ.

26. M. L. MARCHLEWSKI m. c. **Filoporfiryna i mezoporfiryna (*Phylloporphyrin and mesoporphyrin, a comparison*).** *(Comparaison de la phylloporphyrine et de la mésoporphyrine).*

It is well known that the absorption spectra of haematoporphyrin and phylloporphyrin resemble each other very closely, the chief difference observed being, that all the bands of haematoporphyrin are shifted slightly towards the red end of the spectrum.

Assuming that the chemical difference between these two substances is caused by two hydroxyl groups, the shifting of the haematoporphyrin bands towards the red is in accordance with a rule deducted from the study of absorption spectra of colouring matters of known constitution, that the hydroxyls, being so called bathochromic groups, have on absorption bands the influence stated. The study of mesoporphyrin, which is derived from haematoporphyrin by substituting a hydroxyl by hydrogen, was therefore of special interest.

It could be expected that the removal of a hydroxyl group from the haematoporphyrin molecule and substituting it by a hy-

drogen atom would cause the formation of a substance with absorption bands moved towards the violet end of the spectrum, i. e. the spectrum of mesoporphyrin will resemble even more that of phylloporphyrin than does its mothersubstance, haematoporphyrin. The comparison of the spectra of mesoporphyrin and phylloporphyrin has indeed shown that the difference between the two is infinitesimal, scarcely measurable by methods hitherto applied in such cases.

This result differs from the result of Nencki and Zaleski [1]), inasmuch as these authors did not notice any difference in the absorption spectra of haematoporphyrin and mesoporphyrin. The preparing of solutions of mesoporphyrin is somewhat tedious, as this substance when applied in the crystalline state dissolves in various solvents only with great difficulty. I found this difficulty can be overcome in the following manner. Mesoporphyrin is dissolved in alcoholic potash, the solution diluted with water, acidulated with acetic acid and quickly extracted with ether.

In this manner strongly coloured solutions are obtained which may be afterwards diluted as required.

The measurement of wavelengths obtained for the absorption bands of equally strongly coloured solutions of phylloporphyrin and mesoporphyrin are as follows:

	Phylloporphyrin	Mesoporphyrin
I	λ 625 — λ 620	λ 626 — λ 622
II	λ 616 — λ 610	λ 618 — λ 611
III	λ 600 — λ 595	λ 601 — λ 596
IV	λ 581 — λ 573	λ 582 — λ 573
V	λ 570 — λ 566	λ 572 — λ 567
VI	λ 536 — λ 520	λ 537 — λ 522
VII	λ 506 — λ 478	λ 508 — λ 479

The absorption of the violet and ultraviolet rays caused by these two substances are also identical. Phylloporphyrin has been studied in this respect before by my friend Mr. C. A. Schunck.

I have found in the spectrum of mesoporphyrin two bands, the position of one of them corresponds exactly to the position of the double band observed by Mr. Schunck in highly diluted phyllo-

[1]) Bull. international de l'Académie des Sciences de Cracovie. Classe des Sciences mathém. et natur., 1901, p. 217.

porphyrin solutions just past the kβ line, and a second just past the thallium line. I was therefore induced to repeat these experiments with phylloporphyrin and again found the two bands in exactly the same position.

Mr. Schunck had also the kindness to examine his old plates of the phylloporphyrin spectrum and found that the two bands are present, but they were not mentioned in his very interesting paper on the subject. Concerning the double band past the kβ line I have been unable to find a split even at considerable dilution, but it is quite possible that I have not been lucky enough to just hit the correct concentration. The second band in the more refrangible part of the spectrum (past the thallium line) may be also found in the haematoporphyrin spectrum, but both bands are moved somewhat towards the red end of the spectrum.

Acid solutions. As will be seen from the reproduction of a photo taken on a spectrum plate of Messrs. Cadett and Neal, the spectra caused by acid solutions of mesoporphyrin and phylloporphyrin are identical.

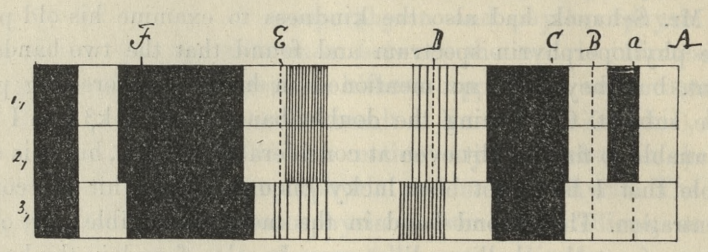
The acid haematoporphyrin solutions cause, as is well known, also three bands, which are shifted slightly towards the red end.

In more concentrated acid solutions all the three porphyrins cause, in addition to the bands shown by the photo, two very faint bands in front of F.

The absorption in the ultraviolet part is characterised in the case of haematoporphyrin and phylloporphyrin, as shown by C. A. Schunck, by a band past the kβ line. Mesoporphyrin shows exactly the same band as phylloporphyrin.

The action of bromine on mesoporphyrin and phylloporphyrin. The study of the behaviour of mesoporphyrin towards bromine had a special interest. As is well known, the chief difference which characterises haematoporphyrin as compared with phylloporphyrin is that the product obtained by the action of bromine on the former lacks an absorption band in the extreme visible red. It has been shown that mesoporphyrin resembles phylloporphyrin still more closely than haematoporphyrin, and it could therefore have been expected that „bromomesoporphyrin“ would show the additional band which we missed in the spectrum of „bromohaematoporphyrin“. These expectations have indeed been justified, as will be seen from the appended drawing showing

the absorption spectrum of solutions obtained by treating the three porphyrins with bromine in the manner described by Mr. Schunck and myself [1]).



1., phylloporphyrin + Br
2., mesoporphyrin + Br
3., haematoporphyrin + Br

The stated properties of mesoporphyrin may be taken as a proof of the contention. previously expressed, that by removing hydroxyls gradually from the molecule of haematoporphyrin and substituting hydrogen we shall in the end obtain phylloporphyrin.

The electrolytic dissociation of haematoporphyrin salts. By a method identical with the one used in the case of phylloporphyrin salts[2]), it is possible to show that haematoporphyrin salts dissociate ellectrolytically in aqueous solutions. Haematoporphyrin is a weaker base than phylloporphyrin and, in order to prevent hydrolytic dissociation, it is necessary to apply solutions containing a greater excess of free acids than in the former case. The reproduction of photographs on plate II show that the absorption spectra are identical, no matter what acid has been used to neutralise the colouring matter.

[1]) Journ. chem. Society, London 1900, p. 1091.

[2]) Bull. Intern. de l'Académie des Sciences de Cracovie, Classe des Sciences mathématiques et naturelles, 1902, p. 5.

27. L. MARCHLEWSKI m. c. **Barwiki, otrzymane przy działaniu izatyny na wyciągi Isatis tinctoria.** ***(On colouring matters obtainable by the action of isatin on extracts of Isatis tinctoria).*** *(Matières colorantes obtenues par l'action de l'isatine sur les extraits d'Isatis tinctoria).*

Isatis tinctoria contains, as shown by Dr. E. Schunck, a substance which under certain conditions splits up yielding indigotin and sugar. Some years ago, when engaged in the study of the constitution of glucosides in general, I expressed the opinion that indican is a glucoside of indoxyl, an opinion which has been proved to be correct by Hoogewerff and ter Meulen in their brilliant experimental research on Polygonum tinctorium[1]). The authors have isolated from this plant a crystalline body which is hydrolised under the influence of acids yielding glucose and indoxyl, which latter in its turn is oxidised under the influence of air giving indigotin. About the same time Beijerinck[2]) had also paid attention to the chemistry of indigo producing plants, and arrived at the conclusion that not all these plants contain the glucoside of indoxyl, but that on the contrary Isatis tinctoria does not contain this glucoside at all, but free indoxyl. These results were very unexpected, especially considering that Dr. Schunck, who for the first time put forward the glucoside nature of indican, based his views upon results obtained from the study of this plant.

Beijerinck supports his contention by the following observations. If extracts of Indigofera leptostachya or Polygonum tinctorium are treated with isatin at elevated temperature, a formation of indirubin, the condensation product of indoxyl and isatin, will take place only after treating the said extracts with acids, the rôle of these acids being to split up the preexisting glucoside into indoxyl and glucose. Now, using an extract of Isatis tinctoria the formation of indirubin takes place without previous treatment with acids, and it may be inferred from this fact, that Isatis tinctoria contains free indoxyl and not a compound of it.

The action of isatin on extracts of woad has been studied

[1]) Koninklijke Akademie van Wettenschappen te Amsterdam. Proceedings etc. 1900, p. 520.

[2]) l. c. 1899, p. 120.

some years ago by Dr. Schunck[1]); his results did not agree with those obtained by Beijerinck, and I have been enabled to clear up the cause of the differences of these two observers. Beijerinck's experiment is carried out as follows. Fresh leaves of Isatis tinctoria are thrown into boiling water and the mixture kept at the boil for some minutes, filtered off and the filtrate treated at once with an aqueous solution of isatin. Very soon there is formed a red precipitate, which is collected on a filter, washed well with water and dried. The colouring matter obtained is next crystallised twice from boiling acetic acid. It does not differ in any respect from indirubin obtained by Baeyer's synthesis and possesses the same composition as will be seen from the following analysis.

O. 1024 gr. gave 0.0378 gr. H_2O and 0.2757 gr. CO_2
found 4.10% H_2O a 73.43% C
calcul. for $C_{16}H_{10}N_2O_2$ 3.85% „ 73.28%

Quite a different result is obtained when operating with dried leaves, that is, when the conditions are observed which led Dr. Schunck to the discovery of indican. I operated as follows. Leaves of Isatis tinctoria which were left to dry first at ordinary temperature and then in a water stove were pulverised and extracted with boiling alcohol. The filtrate was evaporated under reduced pressure, the residue extracted with boiling water. filtered and the filtrate boiled with a solution of isatin. There was formed after some time a dark precipitate which was filtred off, washed with boiling water, then with a dilute solution of caustic soda and again with water. The dry colouring matter was next dissolved in boiling phenol, filtered and the solution precipitated with ether, quickly filtered off and dried. The colouring matter which may for the present be called isatocyanin possesses the following properties. It represents a blackish brown powder easily soluble in acetic acid with a blue colour, with greater difficulty in alcohol and ether, and insoluble in alkalis. In conc. sulphuric acid it dissolves at first with a yellowish colour but after standing the solution turns blue. The following table contains some of the characteristic reactions of indirubin and isatocyanin; it will be seen that the two colouring matters differ very materially in many respects.

[1]) Comp. Chem. News. 1900, p. 176.

	Indirubin	Isatocyanin.
Solubility in glacial acetic acid	dissolves easily with a magenta colour	easily with a blue colour, which disappears on standing.
absorption spectrum	a band in the green part of the spectrum	a band in the yellow part of the spectrum.
solubility in alcohol.	with difficulty giving magenta coloured solution	with great difficulty The blue colour fades away quickly
solubility in conc sulphuric acid.	at first reddish brown, on heating magenta colour	at first yellowish, the solution becomes on standing blue.

I had not enough of isatocyanin to make a complete analysis, but the appended nitrogen determinations of two independently prepared samples seem to show that the method of purifying mentioned above leads to a definite chemical individuum.

1) 0.1174 gr. gave 9.7 cm^3 ($t = 14^0$ $p = 748$ mm) corresponding to 9.56 % N

2) 0.1100 gr. gave 8.8 cm^3 ($t = 12^0$ $p = 747$ mm) corresponding to 9.32 % N.

As regards the chemical nature of isatocyanin I have no suggestions to offer. I may however mention that it resembles somewhat the colouring matter obtained by the action of pyrroline on isatin, and of acetic anhydride on the condensation product of piperidine with isatin. The two latter substances are bye the by not identical, as was supposed by Schotten, as may be seen by comparing the absorptions caused by them in the spectrum. The colouring matter obtained from piperidine and isatin causes a band with a maximum intensity at λ 618—661. The colouring matter from pyrroline and isatin causes general absorption of the red but no bands. Isatocyanin causes a band with a maximum intensity on the sodium line.

The facts described above tend to show that the chemical compositions of dried and fresh leaves of Isatis tinctoria vary very considerably.

That the extracts of dried leaves contain a substance which under certain conditions produces indigotin, follows from the clas-

sical researches of Dr. Schunck, and further researches are necessary to clear up the nature of the substance which yields in the presence of isatin isatocyanin, as well as to establish definitely Beijerinck's contention, that Isatis tinctoria does contain free indoxyl. Schunck [1]) pointed out, that in case Beijerinck's views were correct an extract of the leave of the plant ought to yield indigotin on passing air through it, as a matter of fact he could notice no formation of the colour. Against Beijerinck's contention may be put still another objection: that it is not impossible, that isatin dissolved in boiling water partly forms isatic acid, the hydrogen ions of which may cause hydrolytic action. One thing however to my mind has been proved by the experiment of Beijerinck, namely that the indigoproducing substances present in Isatis on the one hand and in Indigofera and Polygonum tinct. on the other are not identical, although indoxyl is the intermediate product in all cases.

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28. M. L. BIER et M. L. MARCHLEWSKI m. c. **Absorbcya ultrafioletowych promieni przez barwiki żółci, urobilinę i proteinochrom.** ***(Absorption of ultra-violet rays by bilirubin, biliverdin, urobilin and proteinchrom).*** *(L'absorption des rayons ultraviolets par les matières colorantes de la bile, l'urobiline et le protéinochrome).*

It is well known that the colouring matter of the blood and its derivatives, as well as chlorophyll and its derivatives, cause in the ultraviolet part of the spectrum very characteristic absorption bands. According to Hartley [2]) and his co-workers the absorption of ultraviolet rays is a preeminently constitutional property of substances, and it might therefore have been expected that in the face of the proved [3]) convertibility of haematogenic urobilin, which is undoubtedly closely related to the hepatic urobilin, — the colouring mat-

[1]) l. c.

[2]) Proc. Royal Society **28**, 233, **29**, 290. Phil. Trans, **170**, 257. Proc. Royal Society **31**, 1. Journal chem. Society. **47**, 685. Ber. d. deutsch. chem. Gesellsch. **18**, 592, Journ. chem. Society, **50**, 58, Journ. chem. Society, **53**, 641. Ber. der deutsch. chem. Gesellsch. **21**, 689. etc.

[3]) Bulletin International de l'Académie des Sciences de Cracovie. Classe des Sciences mathématiques et naturelles 1901, p. 277.

ters extracted from the gall, and their derivatives, which, with the exception of urobilin, do not cause any characteristic absorption in the visible part of the spectrum, will cause in the more refrangible part bands, similiar to chlorophyll and haemoglobin or their derivatives. Our investigations do not confirm this supposition.

Neither bilirubin, or urobilin and biliverdin studied in various solvents cause any characteristic absorption bands in the ultraviolet. Proteinchrom which might be, according to Nencki's hypothesis, the mothersubstance of the blood colouring matter behaved similarly. This result alters, to a certain extent, the conclusions drawn from the very important researches of Hartley. It seems that the absorption of ultraviolet rays does not in the first instance depend upon the constitution of the nucleus forming the base of complicated substances, but is caused rather by certain atomic groups, which may not be present in all the derivatives of the same mothersubstance. This explains the totally different behaviour of urobilin and phylloporphyrin or haematoporphyrin. The next conclusion to be drawn is that urobilin, which is formed so easily by oxidation of haemopyrrolline, obtained from haematoporphyrin or phyllocyanin, and also the other gall colouring matters, must differ constitutionally far more from the chromogen of the blood colouring matter, than does the latter from chlorophyll.

The photographs, reproductions of which accompany this paper, were obtained with an apparatus constructed by A. Hilger of London. A train of two quartz lenses and an Iceland spar prism were used. The solutions were placed in a cell with quartz facings. The source of light was an Auer-Welsbach burner, the photographic plates were the lightening plates of Messrs. Cadett and Neal of Surrey, England.

The material. Bilirubin and biliverdin were procured from E. Merck, urobilin we made ourselves by Hoppe-Seylers method, or by oxidation of haemopyrroline obtained from phyllocyanin, proteinchrom, by selfdigestion of pancreatic glands according to Kurajeff's prescription.

The results. Bilirubin which, as is well known, is very imperfectly soluble in alcohol has been studied in chloroformic solutions and also in alcoholic alkaline. Various photographs disclosed no characteristic absorption bands in the ultraviolet but only

a total endabsorption. Biliverdin has been studied in alcoholic solutions, no characteristic band being observed.

Urobilin and proteinchrom were dissolved in alcohol and photographs of various concentrations taken, the result being, so far as characteristic bands were concerned, negative. The reproduction of photographs shown on plates A, I, II, III, and B I illustrate the totally different behaviour of the above colouring matters towards the ultraviolet rays as compared with blood colouring matter or chlorophyll derivatives.

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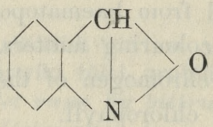
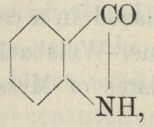
29. M. S. NIEMENTOWSKI m. c. **Amidynowe pochodne bezwodnika antranilowego.** ***(Amidinartige Derivate des inneren Anhydrides der Anthranilsäure).*** *(Sur les dérivés amidinés de l'anhydride anthranilique)*

Seitdem durch die neuesten Untersuchungen von Bamberger und Demuth [1]) die Formel



als Ausdruck der Constitution des Anthranils viel wahrscheinlicher geworden ist als die früher gebrauchte



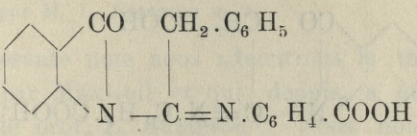
verdienen die Derivate des wahren Anhydrides der Anthranilsäure erhöhtes Interesse. Solche am Stickstoffatom des Anhydrides substituierten, der Klasse der Amidine angehörenden Derivate, sind vor längerer Zeit von Kowalski und Niementowski [2]) und neuerdings von letzterem in grösserer Anzahl aufgefunden worden.

Durch mehrtägiges Erhitzen der Anthranilsäure mit Phenyles-

[1]) Eug. Bamberger u. Ed. Demuth: Ber. d. chem. Ges. **34.** 4015 [1901].

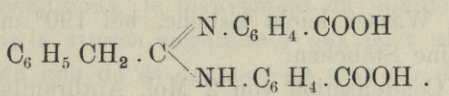
[2]) Mieczysław Kowalski i Stefan Niementowski: Rozpr. XXXIII. 120 i Ber. d. chem. Ges. **30.** 1186. [1897].

sigsäure oder phenylessigsaurem Aethylester entsteht das bei 283° schmelzende Phenylaethenyldianthranilsäureanhydrid



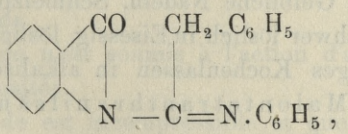
in einer kaum 2·5% der Menge der Ausgangsmaterialien erreichenden Ausbeute, neben viel Phenylacetanilid und wenig eines olivengrün fluorescierenden, näher nicht untersuchten Körpers. Grünlich gelbe längliche Blättchen, in Benzol und Alkohol sehr schwer, in Aceton und Eisessig etwas leichter löslich. Das Platinsalz $(C_{22}H_{16}N_2O_3)_2.H_2PtCl_6$ schmilzt mit Zersetzung bei 256 bis 258°.

Durch längeres Kochenlassen der alkalischen Lösung addiert der Körper 1 Mol. Wasser und liefert die Phenylaethenyldianthranilsäure



Farblose Stäbchen, die mit Aufschäumen bei 190° schmelzen und in organischen Solventien leicht löslich sind. Silbersalz, $C_{22}H_{16}Ag_2N_2O_4$, weisser, lichtempfindlicher Niederschlag.

Durch Erhitzen mit concentrierter Salzsäure im zugeschmolzenen Rohre auf 210° verliert der bei 283° schmelzende Körper ein Molekel Kohlensäure und ergiebt ein Phenylaethenylanilantranilsäureanhydrid

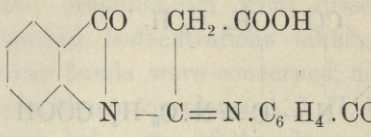


welches in seideglänzenden weissen Nadeln krystallisiert, bei 229° schmilzt und in organischen Solventien löslich ist.

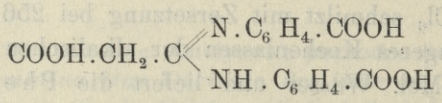
Die Condensation der Anthranilsäure mit Malonsäureäthylester erfolgt verschieden, je nachdem die Componenten in aequimolekularem Verhältnis oder 2 Mol. Anthranilsäure auf 1 Mol. Ester zur Reaktion gelangen.

In ersterem Falle entsteht in einer Ausbeute bis zu 20% der Masse der ursprünglichen Componenten nach der Gleichung

$2\,C_7H_7NO_2 + C^7H_{12}O_4 = C_{17}H_{12}N_2O_5 + 2\,C_2H_6O + H_2O$ das Anhydrid der Methenyldianthranilessigsäure

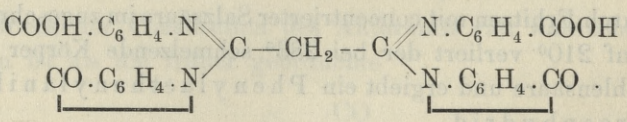


ein in sämmtlichen Solventien entweder unlöslicher, oder äusserst schwer löslicher, in mikroskopischen Platten (bei 302° Schm. mit Zersetzung) krystallisierender Körper, welcher durch mehrstündiges Erhitzen in alkalischer Lösung zur entsprechenden Methenyldianthranilessigsäure

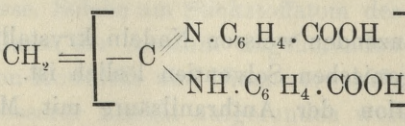


aufgespalten wird. Diese letztere bildet in organischen Solventien und in heissem Wasser leicht lösliche, bei 190° mit Aufschäumen schmelzende feine Stäbchen.

Aus der Condensation von 2 Mol. Anthranilsäure mit 1 Mol. Malonsäureester geht nach der Gleichung $4\,C_7H_7NO_2 + C_7H_{12}O_4 = C_{31}H_{20}N_4O_6 + 2\,C_2H_6O + 4\,H_2O$ das Di-Anhydrid der Malontetranthranilsäure hervor



Ausbeute bis 30%. Gelbliche Nadeln, Schmelzpunkt mit Aufschäumen bei ca. 275°, schwer löslich in Eisessig, löslich in Phenylhydrazin. Durch mehrstündiges Kochenlassen in alkalischer Lösung ergiebt es die zugehörige Malontetranthranilsäure



weisse, unter Aufschäumen bei 263—265° schmelzende Nadeln. In organischen Solventien sehr schwer löslich; in Laugen löslich, in verdünnten Säuren unlöslich.

30. M. C. ZAKRZEWSKI. **O oscylacyi krążka w płynie lepkim.** ***(Sur les oscillations d'un disque plongé dans un liquide visqueux).*** Mémoire présenté par M. L. Natanson m. t.

Dans la présente note nous admettrons la théorie de la viscosité indiquée par Maxwell et qui, depuis, a été développée et approfondie par le prof. L. Natanson [1]). Nous nous proposons de l'appliquer au cas particulier d'un disque plan qui, suspendu par un fil élastique, oscille au sein d'un liquide.

On sait que le problème auquel nous venons de faire allusion a été traité par Maxwell [2]), par MM. O. E. Meyer [3]), Th. Schmidt [4]) et par d'autres savants, en partant de la théorie habituellement admise de la viscosité. Ces travaux nous ont servi de point de départ. Nous admettrons que le disque est assez mince et que son diamètre est assez grand pour qu'on puisse négliger l'influence exercée par le bord.

Dans ces conditions, le mouvement du liquide et du disque est déterminé par la vitesse angulaire ψ qui, pour une molécule du liquide, ne dépend que de sa distance au plan du disque. Prenons pour origine des coordonnées O le centre du disque, dirigeons l'axe des z de haut en bas suivant la verticale et choisissons pour plan des (x, y) le plan du disque. La vitesse d'un point du liquide dont la distance à l'axe Oz est égale à r a pour composantes parallèles aux axes des x et des y

$$u = -\psi y$$

$$v = \psi x.$$

Nous admettrons

1) que le liquide n'est soumis à l'action d'aucune force autre que celle de la viscosité;

2) que le liquide est incompressible et que par conséquent la pression hydrostatique au sein du liquide est constante;

3) que le mouvement est extrêmement lent en sorte que l'on peut négliger les produits de la vitesse par ses dérivées.

[1]) L. Natanson: Bull. Intern. de l'Académie des Sc. de Cracovie, Février 1901 et Janvier 1902.

[2]) Maxwell: Phil. Trans., Vol. 156, pag. 249.

[3]) Oscar E. Meyer: Crelle's Journal, vol. 59, p. 229.

[4]) Th. S. Schmidt: Wied. Ann., Vol. 16, p. 633.

Dans ces hypothèses u et v vérifient les équations suivantes

$$\frac{\partial^2 u}{\partial t^2} + \frac{1}{T}\frac{\partial u}{\partial t} - A^2 \frac{\partial^2 u}{\partial z^2} = 0$$

$$\frac{\partial^2 v}{\partial t^2} + \frac{1}{T}\frac{\partial v}{\partial t} - A^2 \frac{\partial^2 v}{\partial z^2} = 0,$$

T désignant la durée du temps de relaxation pour le liquide en question et A^2 le rapport de la rigidité à la densité [1]). Ces équations donnent, pour la vitesse angulaire ψ, l'équation suivante:

1) $$\frac{\partial^2 \psi}{\partial t^2} + \frac{1}{T}\frac{\partial \psi}{\partial t} - A^2 \frac{\partial^2 \psi}{\partial z^2} = 0.$$

Elle a la même forme que les précédentes: c'est l'équation connue sous le nom de „l'équation des télégraphistes".

Pour écrire l'équation du mouvement du disque il faut calculer les déformations initiales du liquide, les vitesses de ces déformations, enfin les tensions intérieures.

Désignons par χ_0 l'angle de torsion d'une particule du liquide au moment $t = 0$. Cette variable ne dépend que de la variable z. La torsion χ_0 entraîne dans le sens des axes Ox et Oy les déplacements suivants:

$$\xi_0 = -\chi_0 y \quad \text{et} \quad \eta_0 = \chi_0 x$$

qui donnent, pour les valeurs des éléments de la déformation initiale, les expressions suivantes

$$\alpha_0 = \frac{\partial \eta_0}{\partial z} = x\frac{\partial \chi_0}{\partial z} \quad \text{et} \quad \beta_0 = \frac{\partial \xi_0}{\partial z} = -y\frac{\partial \chi_0}{\partial z}.$$

Les vitesses de la déformation s'expriment au moyen de ψ comme α_0 et β_0 au moyen de χ_0. Il vient:

$$a = x\frac{\partial \psi}{\partial z} \quad \text{et} \quad b = -y\frac{\partial \psi}{\partial z}.$$

Les expressions des tensions au sein du liquide sont, d'après la théorie de M. Natanson [2]),

[1]) L. Natanson, loc. cit. Janvier 1902, p. 32.
[2]) L. Natanson, loc. cit. Janvier 1902, p. 19.

$$\left.\begin{aligned} p_{yz} &= (p_{yz})_0\, \varepsilon^{-\frac{t}{T}} - \varepsilon^{-\frac{t}{T}} \int_0^t dt\, \varepsilon^{\frac{t}{T}}\, n\, a \\ p_{zx} &= (p_{zx})_0\, \varepsilon^{-\frac{t}{T}} - \varepsilon^{-\frac{t}{T}} \int_0^t dt\, \varepsilon^{\frac{t}{T}}\, n\, b \end{aligned}\right\} \quad 2)$$

où l'on doit poser dans notre cas:

$$(p_{yz})_0 = -nx \frac{\partial \chi_0}{\partial z}$$

$$(p_{zx})_0 = ny \frac{\partial \chi_0}{\partial z},$$

le symbole n désignant le module de rigidité instantanée du liquide.

Pour calculer les forces que le liquide exerce sur le disque, il faut substituer dans les équations 2) les valeurs des déformations et de leurs vitesses en y posant $z = 0$. Désignant par $\overline{X}$ et $\overline{Y}$ les pressions exercées à la surface du disque, nous aurons:

$$-\overline{X} = ny \left(\frac{\partial \chi_0}{\partial z}\right)_{z=0} \varepsilon^{-\frac{t}{T}} + \varepsilon^{-\frac{t}{T}} \int_0^t dt\, \varepsilon^{\frac{t}{T}}\, ny \left(\frac{\partial \dot{\psi}}{\partial z}\right)_{z=0}$$

$$-\overline{Y} = -nx \left(\frac{\partial \chi_0}{\partial z}\right)_{z=0} \varepsilon^{-\frac{t}{T}} - \varepsilon^{-\frac{t}{T}} \int_0^t dt\, \varepsilon^{\frac{t}{T}}\, nx \left(\frac{\partial \dot{\psi}}{\partial z}\right)_{z=0}.$$

Le moment de ces pressions par rapport à l'axe Oz a pour expression

$$M_z = (x^2 + y^2)\, n \left(\frac{\partial \chi_0}{\partial z}\right)_{z=0} + (x^2 + y^2)\, \varepsilon^{-\frac{t}{T}} \int_0^t dt\, \varepsilon^{\frac{t}{T}}\, n \left(\frac{\partial \dot{\psi}}{\partial z}\right)_{z=0}.$$

Bornons-nous à la considération du cas où le liquide ne mouille qu'une seule surface du disque; c'est le cas des expériences effectuées par M. Schmidt; le moment intégral agissant sur la surface du disque sera

$$\frac{\pi R^4 n}{2} \left(\frac{\partial \chi_0}{\partial z}\right)_{z=0} \varepsilon^{-\frac{t}{T}} + \frac{\pi R^4}{2} \varepsilon^{-\frac{t}{T}} \int_0^t dt\, n \left(\frac{\partial \dot{\psi}}{\partial z}\right)_{z=0} \varepsilon^{\frac{t}{T}}$$

en désignant par R le rayon du disque. Pour obtenir l'équation du mouvement du disque nous désignerons:

par φ l'angle de déviation du disque de sa position d'équilibre,

par $\tau\varphi$ le moment des forces élastiques engendrées par le fil de suspension,

par M le moment d'inertie du disque. L'équation du mouvement du disque sera:

$$3)\quad M\frac{\partial^2\varphi}{\partial t^2} = -\tau\varphi + \frac{\pi R^4}{2} n\left(\frac{\partial \chi_0}{\partial z}\right)_{z=0} \varepsilon^{-\frac{t}{T}} + \frac{\pi R^4}{2}\varepsilon^{-\frac{t}{T}} \int_0^t dt\, n\left(\frac{\partial \psi}{\partial z}\right)_{z=0} \varepsilon^{\frac{t}{T}}$$

Suivant M. Meyer [1]) il faut considérer cette équation comme une des conditions „aux limites" définissant l'intégrale ψ de l'équation 1). Les autres conditions aux limites dépendent des circonstances de l'expérience. Nous admettrons qu'à une certaine distance du disque mobile se trouve un second disque immobile parallèle au premier.

Une solution particulière de l'équation 1) est la suivante:

$$\psi = \varepsilon^{-m^2 t}\,[C \sin(\nu z) + D \cos(\nu z)],$$

où m et ν vérifient l'équation

$$4)\quad m^4 - \frac{m^2}{T} = -\nu^2 A^2 \ .$$

Les conditions relatives aux surfaces sont

1) $\psi = 0$ pour $z = c$

ou $C = -D\,cotg\,(\nu c)$;

2) $\psi = \frac{d\varphi}{dt}$ pour $z = 0$

ou

[1]) loc. cit., p. 249.

$$\left.\begin{aligned} \frac{d\varphi}{dt} &= D\varepsilon^{-m^2 t} \\ \frac{d^2\varphi}{dt^2} &= -m^2 D\,\varepsilon^{-m^2 t} \\ \frac{d^3\varphi}{dt^3} &= m^4\ D\ \varepsilon^{-m^2 t} \\ \varphi &= -\frac{1}{m^2} D\,\varepsilon^{-m^2 t} \end{aligned}\right| \qquad 5)$$

On peut omettre la constante arbitraire dans l'expression de φ si l'on choisit convenablement l'angle initial φ_0.

En dérivant par rapport à la variable z l'expression de ψ nous trouvons:

$$\left(\frac{\partial\psi}{\partial z}\right)_{z=0} = -\varepsilon^{-m^2 t} D\,\nu\,cotg\,(\nu c). \qquad 6)$$

En intégrant cette équation par rapport au temps il vient:

$$\int_0^t dt\,\varepsilon^{\frac{t}{T}}\left(\frac{\partial\psi}{\partial z}\right)_{z=0} = -\frac{D\,\nu\,cotg\,(\nu c)}{1-m^2 T}\left(\varepsilon^{\frac{t}{T}-tm^2}-1\right). \qquad 7)$$

On pourrait déterminer la quantité $\left(\frac{\partial\chi_0}{\partial z}\right)_{z=0}$ au moyen de la condition $\chi_0 = \left(\int\psi dt\right)_{t=0}$; mais il est préférable d'éliminer χ_0, car on obtient ainsi une équation qui se prête plus facilement à l'analyse. En dérivant l'équation 2) par rapport au temps on obtient:

$$M\frac{\partial^3\varphi}{\partial t^3} = -\tau\frac{\partial\varphi}{\partial t} - \frac{\pi R^4 n}{2T}\left(\frac{\partial\chi_0}{\partial z}\right)_{z=0}\varepsilon^{-\frac{t}{T}} +$$

$$+\frac{\pi R^4}{2}\frac{\partial}{\partial t}\left\{\varepsilon^{-\frac{t}{T}}\int_0^t dt\ n\left(\frac{\partial\psi}{\partial z}\right)_{z=0}\varepsilon^{\frac{t}{T}}\right\}.$$

En déterminant par cette équation $\frac{\pi R^4}{2}\,n\left(\frac{\partial\chi_0}{\partial z}\right)_{z=0}\varepsilon^{-\frac{t}{T}}$ et en portant la valeur trouvée dans l'équation du mouvement du disque (3) nous obtenons

$$M\frac{\partial^2\varphi}{\partial t^2} = -\tau\varphi - TM\frac{\partial^3\varphi}{\partial t^3} - T\tau\frac{\partial\varphi}{\partial t} +$$

$$+\frac{\pi R^4}{2}\left[\varepsilon^{-\frac{t}{T}}\int_0^t dt\; n\left(\frac{\partial\psi}{\partial z}\right)_{z=0}\varepsilon^{\frac{t}{T}} + T\frac{\partial}{\partial t}\left\{\varepsilon^{-\frac{t}{T}}\int_0^t dt\; n\left(\frac{\partial\psi}{\partial z}\right)_{z=0}\varepsilon^{\frac{t}{T}}\right\}\right].$$

Les valeurs 5) 6) 7) portées dans cette équation donnent

8) $$cotg\,(\nu c) = \frac{M m^4 - T m^6 + \tau - \tau T m^2}{\frac{\pi R^4}{2}\nu m^2 n T}$$

Il existe entre les quantités m et ν la relation 4). Nous écrirons cette relation sous la forme

$$T m^4 - m^2 + A^2 T\nu^2 = 0.$$

Les équations de l'Hydrodynamique classique se déduiraient de nos équations en posant

$$T = 0 \text{ et } A^2 T = \frac{\eta}{\rho}$$

où l'on désigne par η le coefficient de viscosité du liquide et par ρ sa densité.

Si l'on adopte cette hypothèse, l'équation 8) prendra la forme:

$$cotg\left(\frac{m c}{\sqrt{\frac{\eta}{\rho}}}\right) = \frac{M m^4 + \tau}{\frac{\pi R^4}{2} m^3\sqrt{\rho\eta}}$$

c'est-à-dire

9) $$cotg\,(m c_1) = \frac{m^4 + \alpha^4}{2\beta m^3}$$

où l'on a posé

$$c_1 = \frac{c}{\sqrt{\frac{\eta}{\rho}}},\quad \frac{\pi R^4}{2M}\sqrt{\rho\eta} = 2\beta,\quad \frac{\tau}{M} = \alpha^4.$$

L'expression 9) constitue l'équation fondamentale qui a servi à MM. Meyer et Schmidt dans leurs travaux cités plus haut.

Nous n'entreprendrons pas l'analyse de l'équation 8) dans toute sa généralité; nous supposerons qu'il suffit, pour obtenir une

première approximation, de poser *cotg* (νc) égal à $\frac{1}{\nu c}$. Dans cette hypothèse l'équation 8) prendra la forme

$$m^6 - \frac{m^4}{T} + \left(\frac{\tau}{M} + \frac{\pi R^4}{2McT}\right)m^2 - \frac{\tau}{TM} = 0. \qquad 9)$$

Dans le cas du mouvement périodique cette équation a deux racines réelles et quatre racines complexes de la forme $\pm(a \pm b\,i)$. Par conséquent

$$a^2 - b^2 = l$$

représente le décrément logarithmique de l'amplitude de l'oscillation et

$$\frac{\pi}{2\,a\,b} = t_1$$

la période d'une oscillation du disque dans le liquide. En substituant ces valeurs dans l'équation 9) et en égalant à zéro séparément les parties réelle et imaginaire, il vient:

$$\left.\begin{aligned} &l^3 - 3\,l\,\frac{\pi^2}{t_1^2} - \frac{l^2 - \frac{\pi^2}{t_1^2}}{T} + \left[\frac{\tau}{M} + \frac{\pi R^4 \eta}{2\,M\,c\,T}\right] l - \frac{\tau}{M\,T} = 0 \\ \text{et} \\ &3\,l^2 - \frac{\pi^2}{t_1^2} - \frac{2\,l}{T} + \left[\frac{\tau}{M} + \frac{\pi R^4 \eta}{2McT}\right] = 0. \end{aligned}\right\} \qquad 10)$$

Écrivons la dernière équation sous la forme

$$T\left\{3\,l^2 + \frac{\pi^2}{t^2} - \frac{\pi^2}{t_1^2}\right\} = 2l - \frac{\pi R^4 \eta}{2\,Mc} \qquad 11)$$

où nous désignons par t la période d'une oscillation du disque dans l'air. L'équation 11) constitue une généralisation de la formule donnée par M. Schmidt

$$2\,l\,c = \frac{\pi R^4 \eta}{2\,M},$$

formule qui résulte de l'équation 11) moyennant l'hypothèse particulière $T = 0$.

On sait que la valeur du coefficient de viscosité trouvée à l'aide de la méthode du disque oscillant, surpasse dans toutes les expériences celle qui résulte des observations fondées sur l'écoulement par un tube capillaire. Il résulte de l'équation 11) que tout au moins une partie de cette différence pourrait être attribuée à l'influence de ce fait que le temps de la relaxation est différent de zéro.

M. Schmidt a exécuté, pour l'eau, des expériences très soigneuses en se plaçant dans des circonstances à peu près conformes aux hypothèses adoptées dans notre calcul. Malheureusement, la méthode basée sur l'application de l'équation (11) ne se prête guère dans ce cas, à la détermination de la constante fondamentale T, puisque la valeur du temps T se présente dans ce cas sous la forme d'un rapport de quantités tellement petites que l'ordre de leur grandeur est comparable à celui des erreurs inévitables de l'expérience.

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31. M. MICHEL SEŃKOWSKI. **O metodzie badania czynności wydzielniczej wątroby.** ***(Ueber eine Methode zur Untersuchung der Secretionsthätigkeit der Leber).*** *(Sur une méthode pour servir à l'étude de la fonction de sécrétion du foie).* Mémoire présenté par M. L. Marchlewski m. c.

Der Verf. hebt die Mangelhaftigkeiten hervor, die an die bisherigen Untersuchungen der menschlichen Galle und der Faeces gebunden sind. Die Untersuchungen der Galle stützten sich auf die vereinzelten Fälle, in denen die infolge eines chirurgischen Eingriffs entstandene Gallenfistel es möglich gemacht hat, einen Theil der secernierten Galle zu erhalten und zu untersuchen, wogegen ein unbekannter Rest in das Duodenum einfloss und sich der Untersuchung entzog. Andererseits ist die Untersuchung der Faeces in Hinsicht auf Gallenbestandtheile und besonders auf Gallensäuren auch sehr mangelhaft. Die in der Litteratur notierten Arbeiten beschränken sich auf die quantitative Bestimmung der in den Faeces sich findenden Fetten und Fettsäuren, ohne sie näher zu untersuchen; von den Gallensäuren wurde höchstens bemerkt: „Die Cholalsäure wurde regelmässig gefunden". Am weitesten gingen die Arbeiten Müller's, welcher die Aufmerksamkeit auf die Schmelz-

und Erstarrungstemperatur der aus den Faeces erhaltenen Fettsäuren lenkte.

Die Versuche des Verf's. erwiesen, dass die achttägige Menge des normalen menschlichen Kothes 200 gr. Trockensubstanz ergab. Diese wurde mit heissem Alkohol extrahiert, die Lösung mit Aetzkali verseift, mit Wasser verdünnt und mit Benzin zum Zwecke der Cholesterinentfernung mehrfach ausgeschüttelt. Die alkoholisch-wässerige Lösung wurde im Wasserbade von Alkohol befreit und die Fettsäuren mit Salzsäure ausgefällt. Die erhaltenen Fettsäuren schmolzen bei 38°—45°, erstarrten bei 43° bis unter 35°; ihre Säurezahl, durch Titrieren mit $^1/_{10}$ N. Kalilauge bestimmt, betrug 154·2. die daraus berechnete mittlere Moleculargrösse war 364. Da die gewöhnlichen Fettsäuren wie Palmitin, Öl und Stearinsäure ein weit niedrigeres Moleculargewicht besitzen (256—284), deutet die erhaltene Zahl auf ein Gemisch mit Säuren von einem weit grösseren Moleculargewichte. Cholsäure wurde zwar in der Säuremischung gefunden, ihre Menge aber war so klein, dass es unmöglich war anzunehmen, sie allein sollte eine so grosse Moleculargewichtserhöhung hervorrufen. Die Controluntersuchungen vermittelst der Siedemethode in Benzollösung ergaben keine geeigneten Resultate, weil die Fettsäuren in Benzollösung, in etwas grösserer Concentration (1—10%), Zahlen nahe dem doppelten Moleculargewichte zeigen.

Um die vorausgesetzten höher constituierten Säuren zu ermitteln, wurden 10 gr. der Faecesfettsäuren in absolutem Alkohol gelöst, mit trockenem Chlorwasserstoffe esterificiert, die Alkohollösung mit Wasser verdünnt und mit Benzin ausgeschüttelt. Die Benzinlösung wurde mit verdünntem Alkohol gewaschen und dann mit einer verdünnten wässerig-alkoholischen Aetzkalilösung ausgeschüttelt. Die alkalische Lösung zeigte nach Verjagen des Alkohols und Zusatz eines Ueberschusses an Alkali (über 10%) einen Niederschlag, der auf dem Asbestfilter gesammelt, in Wasser gelöst und mit Salzsäure zersetzt wurde. Der entstandene voluminöse Niederschlag, auf dem Filter gewaschen und mehrmals unter Wasser geschmolzen, erstarrte zu einer tiefbraun gefärbten harzähnlichen Masse. Die Elementaranalyse des erhaltenen Productes entsprach am nächsten der Desoxycholsäure von Mylius, die durch Reduction der Cholsäure während der Fäulnis entsteht. Auch die Reactionen und die mögliche Bildungsweise im faulenden Kothe entsprachen

dieser Säure bis auf die Thatsache, dass die Säure von Mylius krystallinisch, die des Verfassers amorph und stark verunreinigt war, ihre Menge aber zu klein war, um sie besser zu reinigen, ohne sich der Gefahr auszusetzen, die erhaltene Substanz zu verlieren. Die Fettsäuren aus acholischem Stuhle ergaben eine mittlere Moleculargrösse von 292, keine Cholsäure und keine Desoxycholsäure.

Auf Grund dieser Untersuchungen giebt der Verf. eine Methode an, die Gallensäuren in den Faeces quantitativ zu bestimmen, und zwar:

Die Faeces von 1—2 Tagen werden womöglich mit Kohlenpulver abgegrenzt, getrocknet, die Trockensubstanz gewogen, mit heissem Alkohol extrahiert, die Lösung mit Kali- oder mit Natriumalkoholat verseift, mit Wasser verdünnt und mit Benzin ausgeschüttelt. Die Benzinlösung giebt nach dem Abdampfen die Menge des rohen Cholesterins bezw. Koprosterins an. Die verbleibende Seifenlösung, von Alkohol befreit und mit Salzsäure versetzt, giebt die freien Fettsäuren, die mit Wasser ausgekocht, getrocknet, gewogen und mit $^1/_{10}$ N. Kalilösung titriert werden. Aus der mittleren Moleculargrösse bestimmt man den Gehalt der Gallensäuren, indem man als Moleculargewicht der Fettsäuren (wegen der möglichen Verunreinigung mit Nichtsäuren) 290 und als Moleculargewicht der Gallensäuren 400 im Mittel zwischen Chol- und Desoxycholsäure annimmt.

Die erhaltenen Zahlen aus der achttägigen Menge des normalen menschlichen Kothes sind:

Trockensubstanz 200 gr., pro die 25 gr.

Rohe Fettsäuren 18 gr., pro die 2·25 gr.

Säurezahl der Fettsäuren 154·2.

Mittleres Moleculargewicht der Fettsäuren 364.

Reine Fettsäuren (Mittl. Mol. Gew. 290) 26%, pro die 0·485 gr.

Gallensäuren (Mittl. Mol. Gew. 400) 74%, pro die 1·765 gr.

Im acholischen Stuhle sinkt das mittlere Moleculargewicht auf 292, die Menge der Gallensäuren fällt also beinahe auf Null. Cholesterin wurde auch im acholischen Stuhle gefunden.

32. M. A. KORCZYŃSKI et M. L. MARCHLEWSKI m. c. **Studya nad izatyną.** ***(Contributions to the chemistry of isatin).*** *(Contribution à la Chimie de l'isatine).*

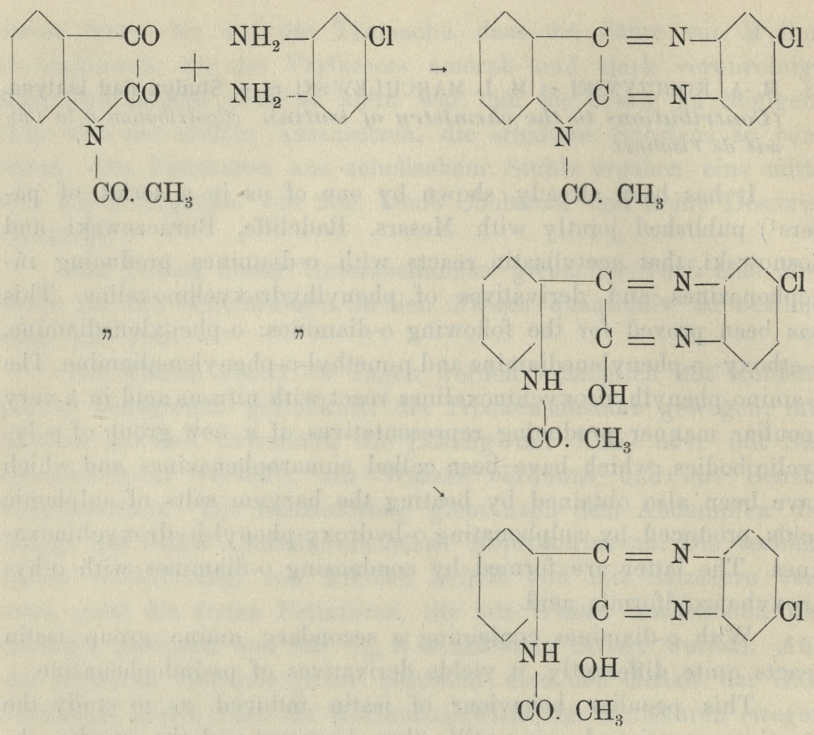
It has been already shown by one of us in a series of papers[1]) published jointly with Messrs. Radcliffe, Buraczewski and Sosnowski, that acetylisatin reacts with o-diamines producing indophenazines and derivatives of phenylhydroxychinoxaline. This has been proved for the following o-diamines: o-phenylenediamine, p-ethoxy- o-phenylenediamine and p-methyl-o-phenylenediamine. The o-amino-phenylhydroxychinoxalines react with nitrous acid in a very peculiar manner producing representatives of a new group of polycyclic bodies, which have been called cumarophenazines and which have been also obtained by heating the baryum salts of sulphonic acids, produced by sulphonating o-hydroxy-phenyl-hydroxychinoxalines. The latter are formed by condensing o-diamines with o-hydroxybenzoylformic acid.

With o-diamines containing a secondary amine group isatin reacts quite differently, it yields derivatives of ps-indophenazine.

This peculiar behaviour of isatin induced us to study the reactions mentioned using still other diamines and the results obtained fully endorse the former trials.

Acetylisatin reacts with p-chloro- o-phenylenediamine yielding acetyl-chloro-indophenazine, and a mixture of two isomeric o-acetamino-phenyl-hydroxy-chlorochinoxalines. The latter gives after saponification two isomeric o-amino-phenyl-hydroxy-chloro-chinoxalines, which can be separated utilising their unequal solubility in alcohol. These reactions may be expressed by the following formulae:

[1]) Bull. international de l'Académie des Sciences de Cracovie. Classe des Sciences mathém. et natur., **1900**, **1901**, 160, 308. Ber. d. deutsch. chem. Gesellsch. **1901**, 1113.

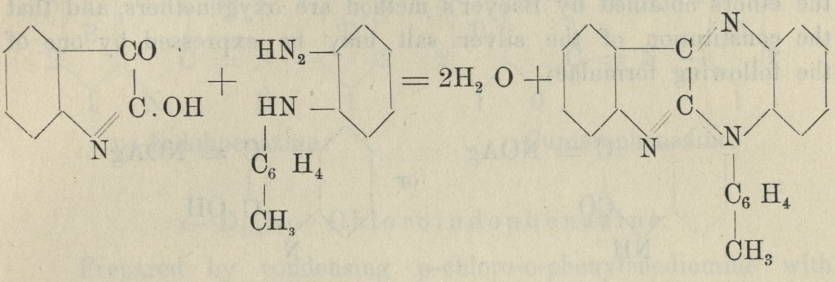


The formation of the second chloroindophenazine in this reaction, foreseen by theory, we did not establish with certainty. We succeeded however in obtaining this second isomere in the following manner. Similarly as all o-amino-phenyl-hydroxychinoxalines hitherto examined may be converted into the corresponding indophenazines by the action of boiling acetic acid, so may also the two mentioned chlorinated compounds. The isomere melting at a higher temperature gives under the said conditions a chloroindophenazine, which has been found to be identical with the compound formed by condensation of chlorophenylenediamine with isatin. The isomere, on the other hand, which melts at a lower temperature gives a chloroindophenazine identical with the one obtained, when acetylisatin is brought to act upon chloro-o-phenylenediamine.

Acetyl-bromoisatin behaves in quite the same manner as acetylisatin, it yields when treated with o-diamines a mixture of indophenazine derivatives and o-amino-phenylhydroxychinaxaline derivatives.

From amongst representatives of the cumarophenazine group we have studied this time the product of distillation of the baryum salt of the sulphonic acid of o-hydroxy-phenyl-hydroxy-chloro-chinoxaline. The latter has been obtained by condensing chloro-o-phenylenediamine with hydroxybenzoyl formic acid.

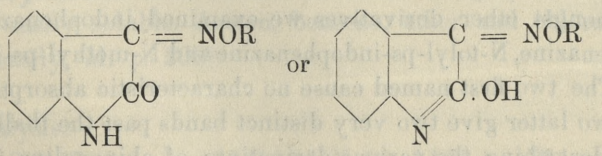
The reaction of p-methyl-o-amino-diphenyl-amine with isatin takes place quite in accordance with former experiences, viz. isatin behaves in this case like an o-hydroxyketon yielding an alkylated azine and not an ammonium base:



We dont consider the above result by any means as a proof for the hydroxyl-formula for isatin, on the contrary we think it highly probable, that the above reaction takes place in two stages producing first an imesatin, containing a hydroxyl group, which is split off afterwards with the hydrogen atom of the secondary amine group to close the azine ring.

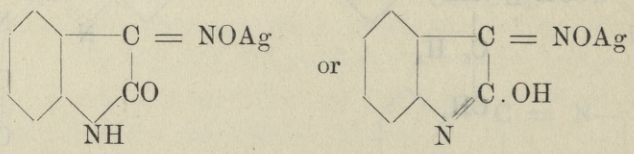
The behaviour of isatin towards hydroxylamine has been studied on several occasions before, it remains however still undecided by which formula to express the constitution of the ethers of isatinoxime.

These ethers may be obtained according to Baeyer's method by the action of alkylhaloids on the silver salt of the oxime and, lead by analogy. one of the following formulae may appear acceptable:



In other words it is supposed, that the silver salt of isatin-oxime contains the silver atom attached to oxygen, and being sub-

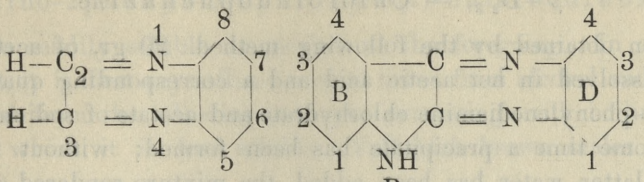
stituted by an alkyl or aryl will yield oxygen ethers. Wishing however to prove this contention definitely, we endeavoured to prepare these ethers by a method, which would leave no doubt as to the position of the alkyl or aryl introduced, and compare them with the substances obtainable by the old method. To this end we condensed isatin with α-benzylhydroxylamine and compared the thus formed isatinoxime benzyl ether with the product of interaction of benzylchloride and isatinoxime silver. This comparison has shown, that the two substances are identical, and it follows therefrom, that the ethers obtained by Baeyer's method are oxygenethers, and that the constitution of the silver salt may be expressed by one of the following formulae:



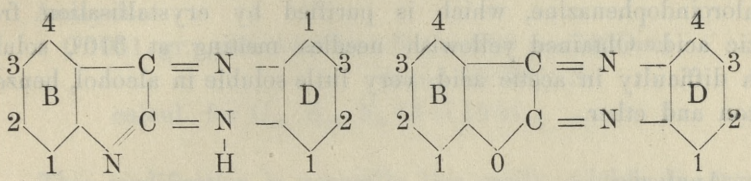
It remains yet to be shown whether they contain a hydroxylgroup or not.

In the last part of the paper results are described which were obtained studying the absorption of ultraviolet rays by isatin and its various derivatives in alcoholic solutions. Isatin, chloroisatin and methyl-isatin cause, in accordance with Hartley's results, a well defined band in the region of the kβ line and a strong end-absorption. On the other hand nitroisatin and acetylisatin show no characteristic band, a fact, which may be explained by supposing, that the solutions of these substances contain in reality nitro or acetylisatic acid, for the sodium salt of isatic acid behaves quite similarly, and nitroisatin and acetylisatin yield with ease chinoxaline-derivatives. The oxime of isatin and its benzylether, as well as the oxime of methylisatin cause no characteristic absorption bands. From amongst other derivatives we examined indophenazine, chloroindophenazine, N-tolyl-ps-indophenazine and N-methyl-ps-indophenazine. The two first named cause no characteristic absorption bands but the two latter give two very distinct bands past the thallium line.

In describing the various derivatives of chinoxaline, indophenazine, ps-indophenazine and cumarophenazine we will make use of the following formulae:



chinoxaline Indophenazine



ps-Indohpenazine Cumarophenazine.

α—$D_{2(3)}$ — Chloroindophenazine.

Prepared by condensing p-chloro-o-phenylenediamine with isatin in aequimolecular proportions in acetic acid solution at the boiling temperature of the mixture. Light yellow needles or scales from alcohol. M. p. above 300°. Easily soluble in aceton and chloroform. The alcoholic solution yields with ammoniac. silver nitrate solution a red precipitate.

Analysis:

0.1561 gr. gave 22·8 cm^3 N (p=742*mm* t=18°)

found 16·46% N

calcul. for $C_{14}H_8N_3Cl$ — 16·67% N

α—$D_{2(3)}$ — Chloro-Pr-acetylindophenazine

may be obtained by boiling the former with anhydrous acetic acid. It crystallises from alcohol in white needles, in which it is not very easily soluble. Aceton, benzene, ether and chloroform dissolve it easily. M. p. 208°.

Analysis:

0.1157 gr. gave 15·0 cm^3 N (t=14·5° p=734*mm*)

found 14·49% N

calcul. for $C_{16}H_{10}N_3OCl$ 14·24 „

β—$D_{2\,3)}$ — Chloroindophenazine

has been obtained by the following method. 20 gr. of acetylisatin were dissolved in hot acetic acid and a corresponding quantity of chloro-o-phenylenediamine chlorhydrate and acetate of sodium added. After some time a precipitate has been formed; without filtering off the latter, water has been added, the mixture rendered alkaline, boiled for 15 minutes and filtered. The insoluble part represents β-chloroindophenazine, which is purified by crystallisation from acetic acid. Obtained yellowish needles melting at 310°, soluble with difficulty in acetic acid, very little soluble in alcohol, benzene aceton and ether.

Analysis:

0.1032 gr. gave 15·7 cm^3 N (t=18° p=730 *mm.*)
found 16·86% N
calcul. for C_{14} H_8 N_3 Cl — 16·67 „

β-o-amino-2-Phenyl-3-Hydroxy-6(7)-chlorochinoxaline

In order to obtain this substance the filtrate from β-chloroindophenazine is acidulated and the precipitate containing two isomeric o-acetamino-phenyl-hydroxychlorochinoxalines dissolved in conc. hydrochloric acid and the solution heated on a water bath for six hours. After that the solution was diluted with water, filtered, neutralised by adding an alkali. In order to separate the two isomeric o-amino-phenyl-hydroxy-chlorochinoxalines the precipitate mentioned is crystallised from alcohol. The more soluble part melting at 229°—230° and crystallising in orange needles we will call the β-modification, because it yields β-chloro-indophenazine on being boiled with glacial acetic acid. It is easily soluble in aceton, with difficulty in benzene, chloroform and ether. Its solution in conc. hydrochloric acid gives a red coloration with ether. The hydrochloride is white.

Analysis:

0.1061 gr. gave 14·2 cm^3 N (t=10·5° p=740 *mm*)
found 15·56% N
calcul. for C_{14} H_{10} N_3 Cl O 15·51 „ „

α-o-amino-2phenyl-3-hydroxy-6(7)-chlorochinoxaline is not so readily soluble in alcohol as the foregoing. In order to purify it, it is first crystallised several times from alcohol and finally separated from the adhering β-isomer extracting with boiling benzene in which it is less soluble. Yellowish brown scales melting at 265°.

Analysis:

0.1051 gr. gave 14·2 cm^3 N (t=9·5° p=740 *mm*)

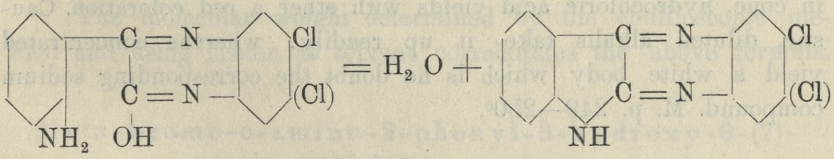
found 15·78% N

calcul. for C_{14} H_{10} N_3 Cl O 15·51 „ „

This modification is generally less easily soluble in organic solvents than the foregoing one. The solution in conc. hydrochloric acid yields a red coloration with ether and on standing deposits white needles, which are no doubt the corresponding hydrochloride.

Conversion of α & β-amino-phenyl-hydroxy-chloro-chinoxalines into the corresponding chlorophenazines

This reaction is attained easily by boiling the chinoxaline-derivatives with glacial acetic acid and may be expressed by the following formulae:



The α isomere, melting at 265°, yields α-D-chloro-indophenazine, which crystallises from alcohol in glistening scales, whereas the β isomere yields β-D-chloroindophenazine, crystallising from alcohol in yellowish needles.

Br_3 Bromoindophenazine

has been obtained in the following manner. Acetylbromoisatin was dissolved in boiling acetic acid and aequimolecular quantities of o-phenylenediamine hydrochloride and sodium acetate added. After heating the mixture on a water bath for an hour, water has been

added, then the liquid rendered alkaline and heated for a short time to the boil. The substance left undissolved has been filtered off, washed well with water and crystallised several times from glacial acetic acid. Obtained yellow needles melting at 279—280°, which dissolve with difficulty in alcohol, ether, aceton, benzene and chloroform. The alcoholic solution yields with an ammoniacal solution of silver nitrate a red precipitate.

Analysis:

0.1102 gr. gave 13·8 cm^3 N (t=17° p=743)

found 14·21% N

calcul. for $C_{14}H_8N_3Br$ 14·12 „ „

m-Bromo-o-amino-2-phenyl-3-hydroxychinoxaline.

The alkaline filtrate from the above yielded, on being neutralised, a white precipitate, which was dissolved in a concentrated solution of sodium hydrate and the solution kept boiling for several hours in order to split off the acetyl group. The alkaline solution was then diluted with water and the free amino compound precipitated by adding hydrochloric acid. After washing it thoroughly with water it has been crystallised several times from alcohol. It represents orange needles, soluble with difficulty in alcohol, benzene, chloroform, easier soluble in ether and aceton. The solution in conc. hydrochloric acid yields with ether a red coloration. Caustic, diluted alkalis take it up readily, whereas concentrated yield a white body which is no doubt the corresponding sodium compound. M. p. 249—250°.

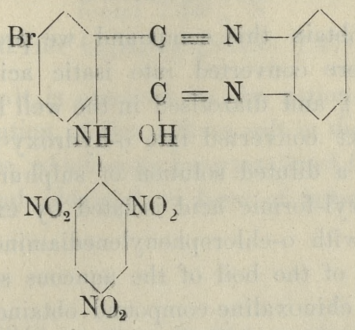
Analysis:

0.1560 gr. gave 18·4 cm^3 N (t=17° p=734 *mm*)

found 13·12% N

calcul. for $C_{14}H_{10}N_3OBr$. 13·35 „ „

Picrylo-meta-bromo-o-amino-2-phenyl-3-hydroxychinoxaline.



This compound can be obtained easily by boiling the alcoholic solution of the above chinoxalinederivative with picrylchloride. It crystallises from acetic acid in red needles melting at 287—8°, soluble with difficulty in alcohol, ether, benzene, chloroform, but easily soluble in aceton. Alkalis take it up readily.

Analysis:

0.1063 gr. gave 14·8 cm^3 N (t=17° p=740)
found 15·72% N
calc. for $C_{20}H_{11}N_6O_7$ Br 16·00 „ „

The molecular weight determined by the ebullioscopic method and using aceton as solvent corroborates the above formula.

Meta-bromo-o-amino-2-phenyl-3-hydroxy-6-(7)-methylchinoxaline

can be obtained exactly in the same manner as the not methylated compound using o-toluylenediamine instead of o-phenylenediamine. Yellow orange needles, melting at 243°, crystallised from chloroform.

Analysis:

0.1330 gr. gave 15·0 cm^3 N (t=17° p=733)
found 12·61% N
calcul. for $C_{15}H_{12}N_3OBr$ 12·75 „ „

o-Hydroxy-2-phenyl-3-hydroxy-7(6)-chloro-chinoxaline.

In order to obtain this compound we proceeded as follows: 15 gr. of isatin were converted into isatic acid under conditions previously related [1]), and diazotised in the well known manner. The diazobody was next converted into o-hydroxy-benzoyl-formic acid by boiling it with a diluted solution of sulphuric acid and finally the o-hydroxy-benzyl-formic acid isolated by extraction with ether. The condensation with o-chlorophenylenediamine takes place easily at the temperature of the boil of the aqueous solutions of the reacting bodies. The chinoxaline compound obtained was finally purified by crystallising from alcohol. We obtained yellow needles, melting at 286—7° which dissolve easily in caustic alkalis, conc. acids and in boiling alcohol, but with difficulty in benzene, ether and chloroform.

Analysis:

0.1702 gr. gave 15.4 cm^3 N (t = 17.5° p. 757° *mm*)

found 10.43 % N

calcul. for $C_{14}H_9O_2N_2$ Cl 10.26 % N

Sulphonic acid of o-hydroxy-2-phenyl-3-hydroxy--7(-6)- chlorochinoxaline

is formed by heating the sulphuric acid solution of the chinoxaline compound on the water bath. The formerly dark reddish brown solution changes gradually its colour to a yellow one. The product of sulphonation can be isolated by pouring the warm sulphuric acid solution into water and adding sodium chloride. The sodium salt formed can be purified by crystallising from boiling water. It contains three molecules of water of crystallisation:

1.4029 gr. lost on being heated to 125° 0.1754 gr.

found 12.52% H_2O

calcul. for $C_{14}H_8N_2O_2$ Cl. $SO_3Na + 3H_2O$ 12.35% H_2O

[1]) Bull. Int. de l'Acad. des Sciences de Cracovie. Classe des Sciences mathém. et natur., **1901**, 303.

Analysis of the sodium salt dryed at 125°.

0.1025 gr. gave 6.5 cm^3 N (t = 7° p = 736 *mm*).

found 7.44% N

calcul. for $C_{14}H_8N_2O_5SClNa$ 7.47% N

The baryum salt is obtained by the action of baryum chloride on the aqueous solution of the sodium salt in the form of a yellowish white precipitate which may be crystallised from a large amount of boiling water and obtained in form of minute yellowish white needles.

Analysis:

0.6843 gr. gave 0.1914 gr. $BaSO_4$

found 16.45% Ba

calcul. for Ba $(C_{14}H_8N_2ClSO_5)_2$ 16.27% Ba

D_2(3) Chlorocumarophenazine.

This substance is formed readily by dry distillation of the baryum salt described above. It has been purified by crystallising from alcohol. The small admixture of a colouring matter can be removed by charcoal. Chlorocumarophenazine represents white needles, which are readily soluble in alcohol, ether, benzene and chloroform. The solutions fluoresce faintly green. M. p. 149—150°.

Analysis:

0.1043 gr. gave 9.5 cm^3 N (t = 9° p = 745 *mm*)

found 10.73% N

calcul. for C_{14} H_7ON_2 Cl 11.02% N

II.

Derivatives of ps-Indophenazine.

N-tolyl-ps-indophenazine.

The p-methyl-o-nitrodiphenylamine necessary for this synthesis we obtained by Schöpf's method, which consists in condensing p-toluidine with o-chlornitrotoluene. This nitrocompound we dissolved in acetic acid, reduced it with zinc dust and combined the aminocompound formed with isatin, which had been also dissolved in acetic

acid. The solution was heated on a boiling water bath for $^1/_2$ hour, diluted with water and neutralised by adding a solution of sodium-hydrate. The precipitate obtained we dissolved in conc. hydrochloric acid, diluted the solution by adding water, filtered off some undissolved substances and precipitated the ps-indophenazine derivative by adding an alkali. This procedure has been repeated three times and finally the N-tolyl-ps-indophenazine crystallised repeatedly from alcohol. We obtained glistening brownish red needles melting at 255—255·5°, which were easily soluble in boiling alcohol, with greater difficulty in benzene and chloroform. The solutions in concentrated acids possess a yellow or reddish brown colour, according to the concentration of them.

Analysis:

0.1089 gr. gave 13.1 cm^3 N (t = 10.5°, p = 738 *mm*)

0.1798 gr. gave 0.5359 gr CO_2 and 0.0826 gr. H_2O

	found	calcul. for C_{21} H_{15} N_3
N:	13.49%	13.61%
C:	81.28%	81.50%
H:	5·10%	4.89%

The chlorhydride of the base may be obtained by passing a current of hydrochloric acid through its solution in benzene. It represents a yellow crystalline powder which dissociates very easily giving off hydrochloric acid.

Br_3-N-tolyl-ps-indophenazine

has been obtained from bromoisatin by a method analogous to the foregoing one. It crystallises from alcohol in brownish red needles melting at 290—291°, which dissolve easily in boiling alcohol, not so readily in benzene, chloroform and aceton and with difficulty in ether.

Analysis:

0.1091 gr. gave 10.6 cm^3 N (t = 14.5°, p = 742 *mm*)

found 11.12% N

calcul. for C_{21} H_{14} N_3 Br 10.89 % N

In acids it dissolves like all the hitherto examined derivatives of ps-indophenazines with a yellow colour.

III.

On isatin-oxime ethers and derivatives.

These substances may be obtained, as already pointed out, by two different methods. The first consists in heating the silver salt of the oxime with an alkylhaloide and the second in condensing isatin with α alkyl-hydroxylamine.

Benzylether of isatin-oxime.

First method. The silver salt of isatin-oxime, which has been obtained according to Baeyer's prescription, we heated with benzylchloride in presence of alcohol on a water bath for several hours. The silver chloride formed was filtered off and the filtrate heated with some charcoal, filtered again and left to cool. The ether crystallised out in form of yellow needles; these were purified by several recrystallisations from alcohol.

The isatinoxime benzylether dissolves easily in alcohol, aceton, benzene, ether. Caustic alkalis take it up with difficulty. The alcoholic solution yields with ammoniac. silver nitrate a red precipitate, which is dissolved easily by an excess of ammonia. M. p. 168.5—169°.

Analysis:

0.1866 gr. gave 18.2 cm^3 N (t = 20° p = 760 *mm*)

found	calcul. for $C_{15}H_{12}N_2O_2$
N 11.19%	11.13%

Second method.

1.4 gr. isatin and the aequimolecular quantity of the hydrochloride of α benzyl hydroxylamine and sodium carbonate were heated in alcoholic solution in a sealed tube for three hours at 100°. The contents of the tube were then treated with caustic soda in order to remove the unaltered isatin and the part undissolved therein crystallised twice from alcohol. The yield is almost quantitative. The product obtained did not show any differences when compared with the one obtained by the first method.

Analysis:

0.1022 gr. gave 10.0 *cm* N (t = 13°, p = 738 *mm*)

found 11.22% N

calcul. for $C_{15}H_{12}N_2O_2$ 11.13 „ „

The benzylether of bromoisatin-oxime

The reaction between isatin and α benzyl hydroxylamine takes place already in the cold. In order to complete it, however, we heated the ingredients just as stated in the foregoing example in a sealed tube for 2 hours. The purification of the benzylether has been carried out exactly as stated in the case of isatinoxime benzylether. M. p. 200°. Yellow needles easily soluble in boiling alcohol, aceton, benzene and chloroform.

Analysis:

0.1075 gr. gave 7.8 cm^3 N (t = 14.5°, p = 736 *mm*)

found 8.24% N

calcul. for $C_{15}H_{11}N_2O_2Br$ 8.48% N

The benzylether of chloroisatin-oxime

has been obtained by heating chloroisatin with α benzyl hydroxylamine hydrochloride and sodium carbonate in alcoholic solution under pressure at 100°. Yellow needles, which dissolve with difficulty in alcohol and ether, easier in benzene and chloroform. M. p. 224.5°.

Analysis:

0.1104 gr. gave 9.4 cm^3 N (t = 16°, p = 742 *mm*)

found 9.69% N

calcul. for $C_{15}H_{11}N_2O_2Cl$ 9.83% N

The Benzylether of nitroisatin-oxime

Golden yellow scales, which dissolve with difficulty in alcohol, easier in aceton and benzene. M. p. 234—235°

Analysis:

0.1133 gr. gave 14.6 cm^3 N (t = 18.5° p = 733 mm^3)

found 14.21% N

calcul. for $C_{15}H_{11}O_4N_3$ 14.17% N

IV.

Absorption of ultraviolet rays by isatin and some of its derivatives.

All substances with one exception were studied in alcoholic solutions.

1) Isatin (Table F. III).

1.47 gr. were dissolved in 100 cm³ alcohol. This solution has been diluted further in the following manner:

a., 1 cm³ sol. + 20 cm³ alcohol, corresponding to 0.00061 gr. in 1 cm³
b., 1 „ „ + 30 „ „ „ „ 0.00047 „ „ „
c., 1 „ „ + 40 „ „ „ „ 0.00036 „ „ „
d., 1 „ „ + 50 „ „ „ „ 0.00029 „ „ „
e., 1 „ „ + 60 „ „ „ „ 0.00024 „ „ „

The thickness of the solution layer was in all cases 19 mm.

2., Chloroisatin (Table F. II.)

0.4536 gr. dissolved in 50 cm. alcohol, and this solution diluted further as follows:

a., 1 cm³ sol. + 10 cm³ alcohol, corresponding to 0.00082 gr. in 1 cm³
b., 1 „ „ + 15 „ „ „ „ 0.00056 „ „ „
c., 1 „ „ + 20 „ „ „ „ 0.00043 „ „ „
d., 1 „ „ + 25 „ „ „ „ 0.00035 „ „ „

3., Nitroisatin (Table F. I).

0. 4810 gr. nitroisatin were dissolved in 25 cm³ alcohol, 1 cm³ of this solution has been mixed with 60 cm³ of alcohol and 1 cm³ of this solution diluted further as follows:

a., 1 cm³ + 1 cm³ alcohol, corresponding to 0.000157 gr. in 1 cm³
b., 1 „ + 3 „ „ „ „ 0.0000787 „ „ „
c., 1 „ + 7 „ „ „ „ 0.0000393 „ „ „
d., 1 „ + 15 „ „ „ „ 0.0000197 „ „ „

4., Meltylisatin (Meltyl-ps-isatin) (Table E. III).

1.61 gr. were dissolved in 100 cm³ alcohol. Further dilutions as follows:

a., 1 cm³ + 20 cm³ alcohol, corresponding to 0.00077 gr. in 1 cm³
b., 1 „ + 30 „ „ „ „ 0.00052 „ „ „
c., 1 „ + 40 „ „ „ „ 0.00040 „ „ „
d., 1 „ + 50 „ „ „ „ 0.00031 „ „ „

5., Acetylisatin (Table E. II).

1.89 gr. acetylisatin were dissolved in 100 cm³ alcohol. 1 cm³ of this solution has been mixed with 60 cm³ of alcohol and 1 cm³ of this latter solution diluted further as follows:

a., 1 cm³ + 1 cm³ alcohol, corresponding to 0.000157 gr. in 1 cm³
b., 1 „ + 3 „ „ „ „ 0.0000787 „ „ „
c., 1 „ + 7 „ „ „ „ 0.0000393 „ „ „
d., 1 „ + 15 „ „ „ „ 0.0000197 „ „ „

6., Sodium salt of isatic acid (Table E. I)

1·47 gr. isatin were dissolved in boiling caustic potash solution and then filled up to 100 cm³. Taken 1 cm³ of this + 60 cm³ of water and diluted further as follows:

a., 1 cm³ + 1 cm³ H_2O, correspond. to 0.000120 gr. in 1 cm³
b., 1 „ + 3 „ „ „ „ 0.000060 „ „ „
c., 1 „ + 7 „ „ „ „ 0.000030 „ „ „
d., 1 „ + 15 „ „ „ „ 0.000015 „ „ „

7., N-tolyl-ps-indophenazine (Table G. II)

1,546 gr. were dissolved in 200 cm³ alcohol. 1 cm³ of this solution was mixed with 25 cm³ of alcohol and then diluted further as follows:

a., 1 cm³ + 31 cm³ alcohol, corresp. to 0.0000096 gr. in 1 cm³
b., 1 „ + 63 „ „ „ „ 0.0000048 „ „ „

8., N-methyl-ps-indophenazine (Table G. I)

0.1166 gr. were dissolved in 20 cm³ alcohol and then diluted as under 7.

All the N-alkyl-(aryl)-ps-indophenazines hitherto examined show, besides the two bands in the ultraviolet, an ill defined band in the green and blue part of the spectrum.

33. PUBLICATIONS DE LA CLASSE.

Le Secrétaire dépose sur le bureau les dernières publications de la Classe:

Wł. Natanson. „O rozchodzeniu się małych ruchów w płynach lepkich". *(Sur la propagation d'un petit mouvement dans un fluide visqueux)*, 8-o, p. 19.

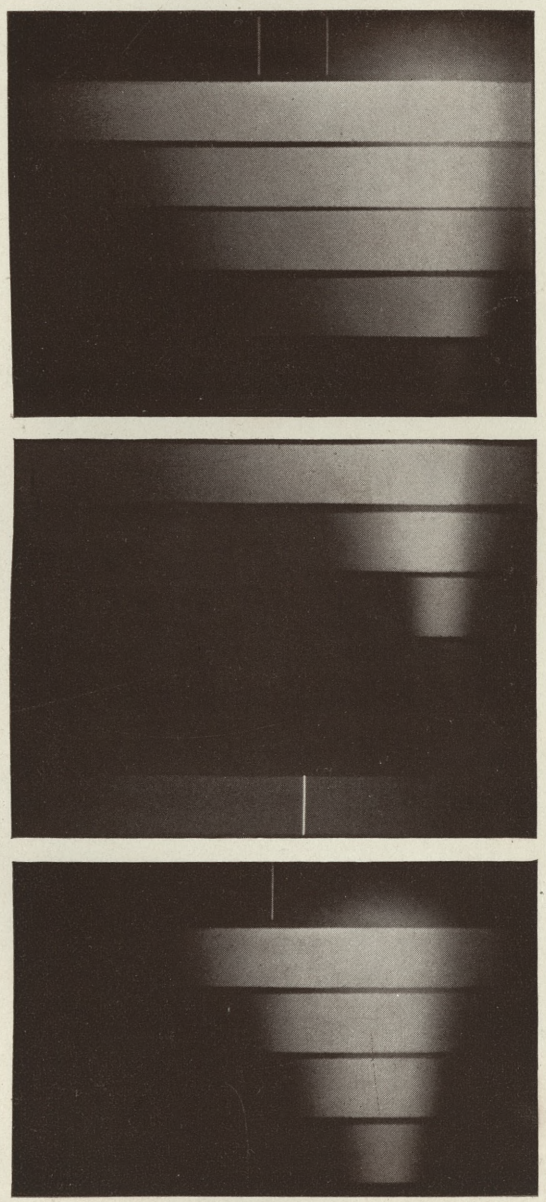
K. Rogoziński. „O fizyologicznej rezorbcyi bakteryi z jelita. *(Sur l'absorption des microbes par l'intestin à l'état physiologique)*, 2 planches, 8-o, p. 105.

Nakładem Akademii Umiejętności.

Pod redakcyą
Członka delegowanego Wydziału matem.-przyr., Dra Władysława Natansona.

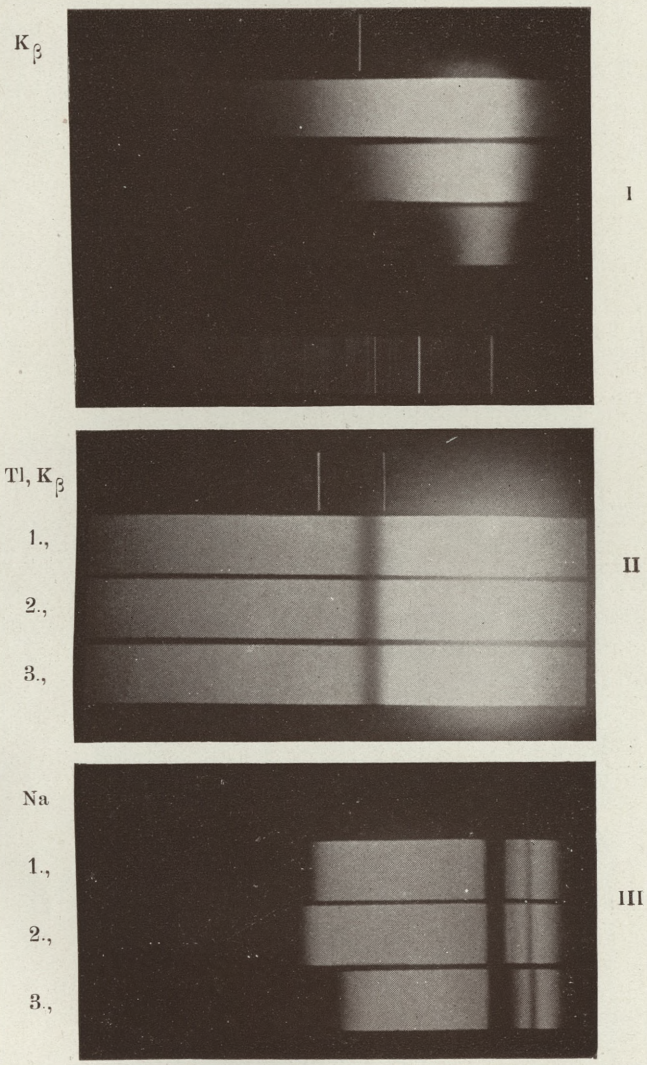
Kraków, 1902. — Drukarnia Uniwersytetu Jagiellońskiego, pod zarządem J. Filipowskiego.

17 Maja 1902.



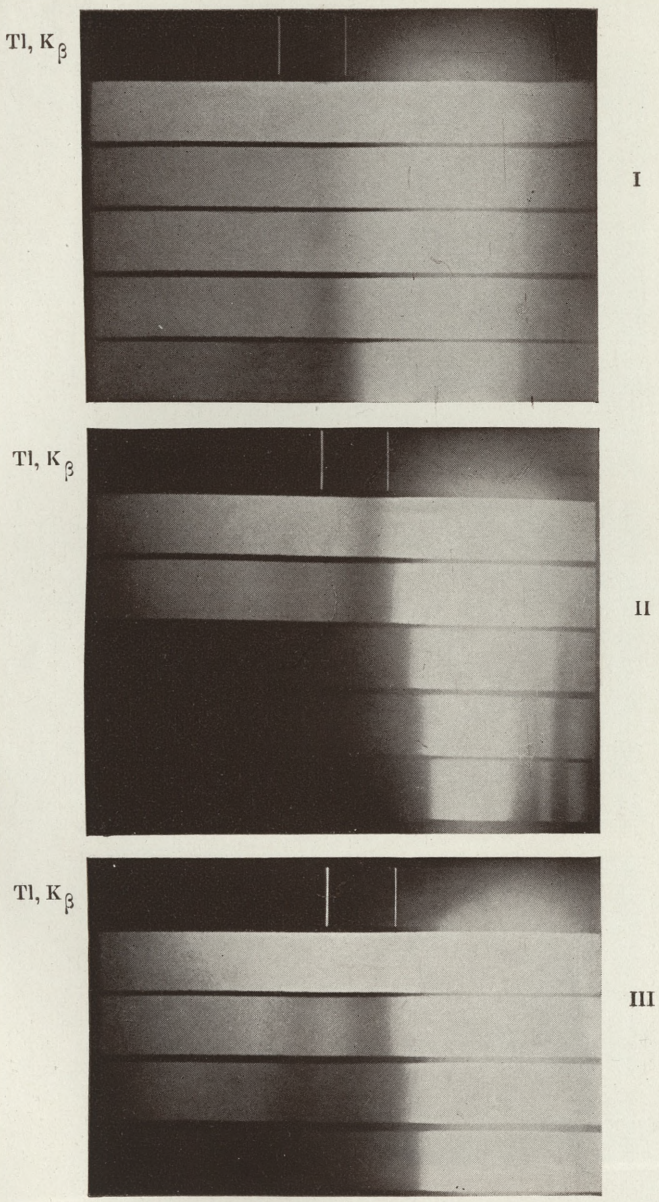
I., Urobilin fr. haemopyrrol in ether
II., Bilirubin in alcohol + Na O H
III., Proteinchrome in alcohol.

L. Marchlewski.



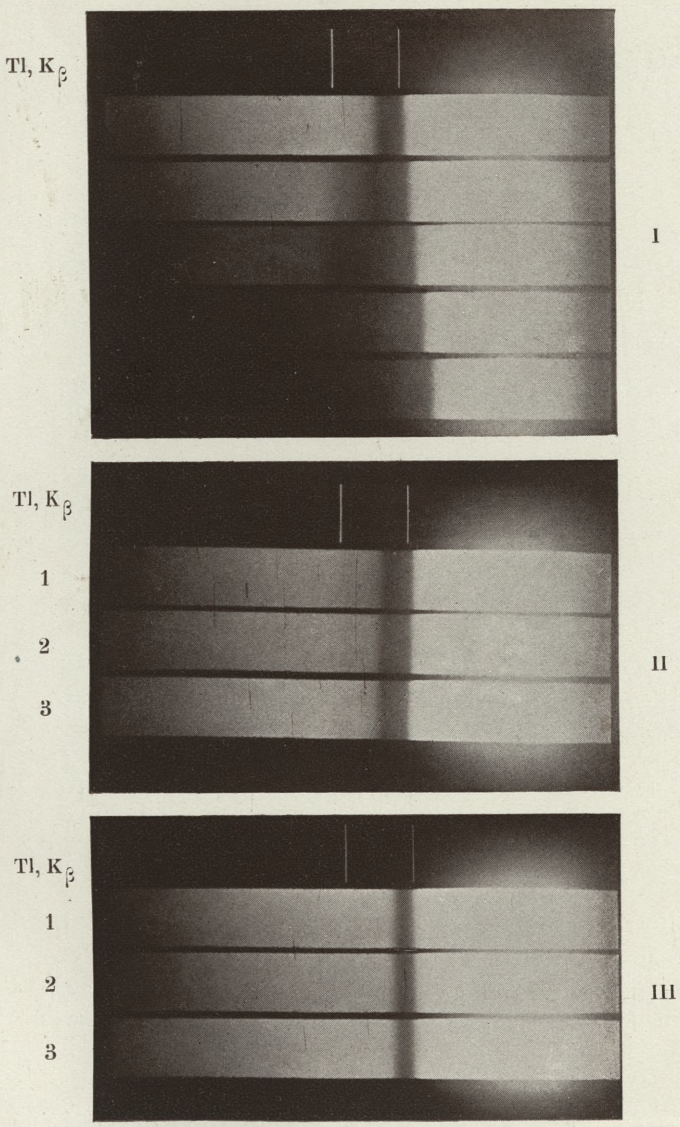
I., Biliverdin in alcohol
II., 1., Phylloporphyrin + H_2O + HCl
2., Mesoporphyrin + H_2O + HCl
3., Haematoporphyrin + H_2O + HCl
III., 1., Phylloporphyrin + H_2O + HCl
2., Mesoporphyrin + H_2O + HCl
3., Haematoporphyrin + H_2O + HCl

L. Marchlewski.



I., Phylloporphyrin, various concentrations
II., Haematoporphyrin, „ „
III., Mesoporphyrin, „ „

L. Marchlewski.

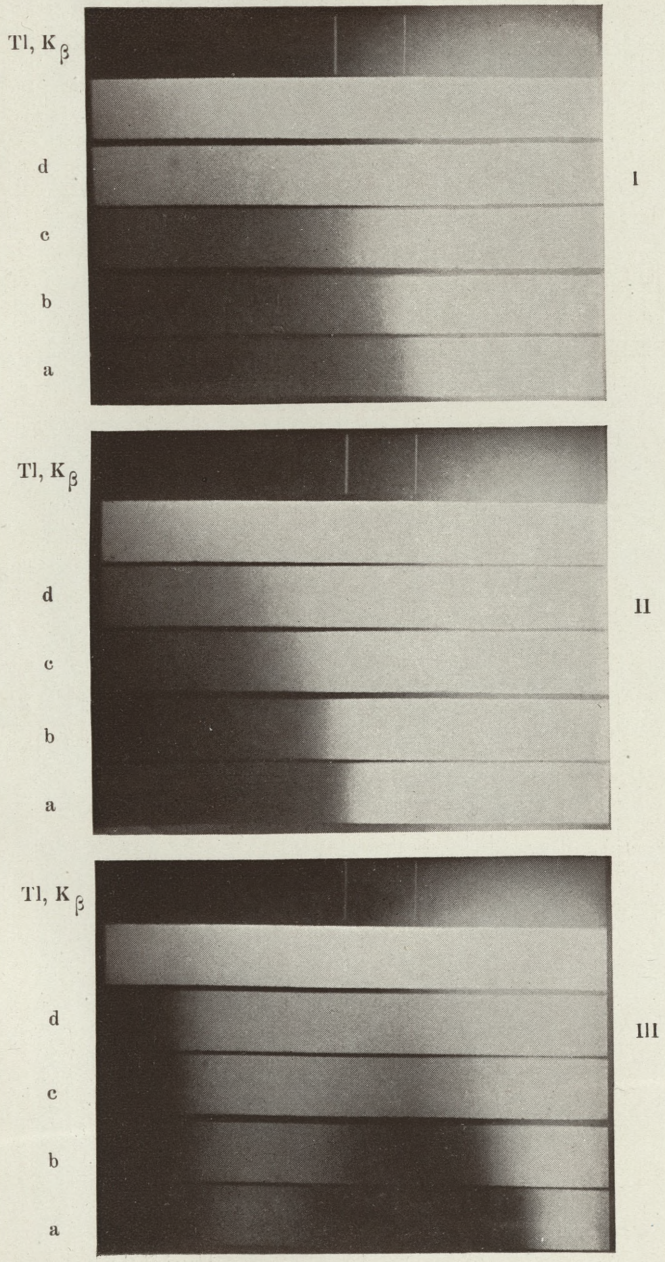


I., Haematoporphyrin in hydrochloric acid solution, various concentrations

II., 1., Haematoporphyrin + HCl + H_2O
2., „ + HNO_3 + H_2O
3., „ + H_2SO_4 + H_2O

III 1., Haematoporphyrin + HCl + H_2O
2., „ + HNO_3 + H_2O
3., „ + H_2SO_4 + H_2O

L. Marchlewski.



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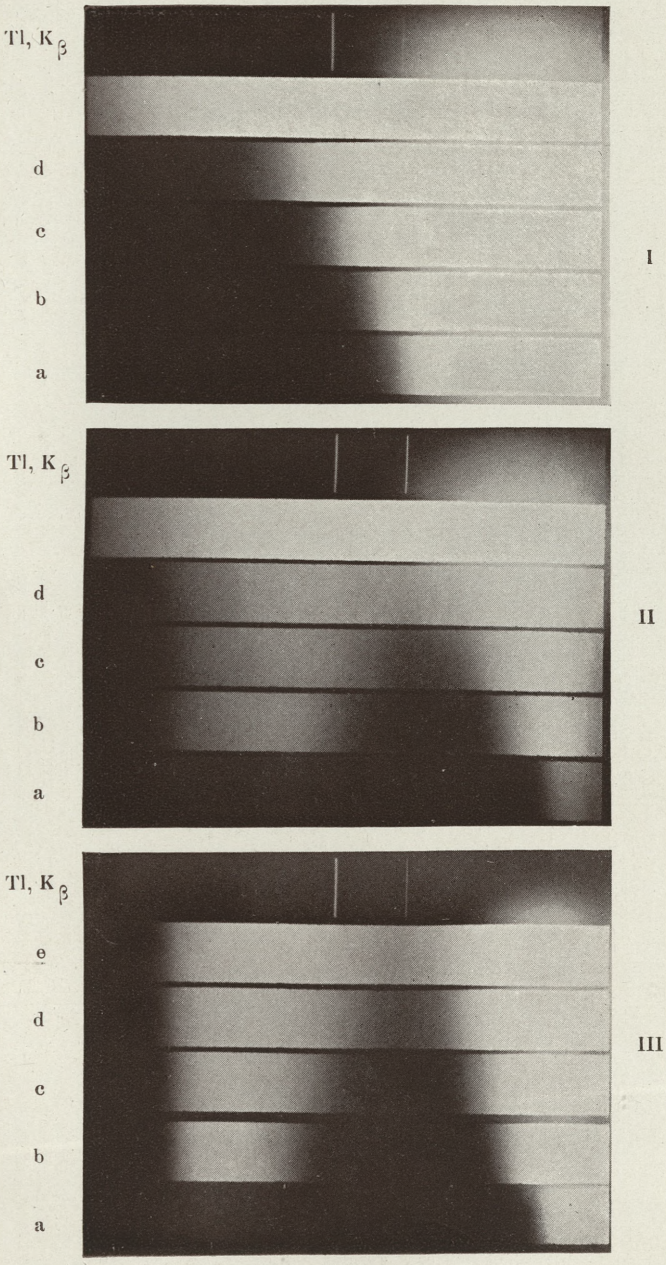
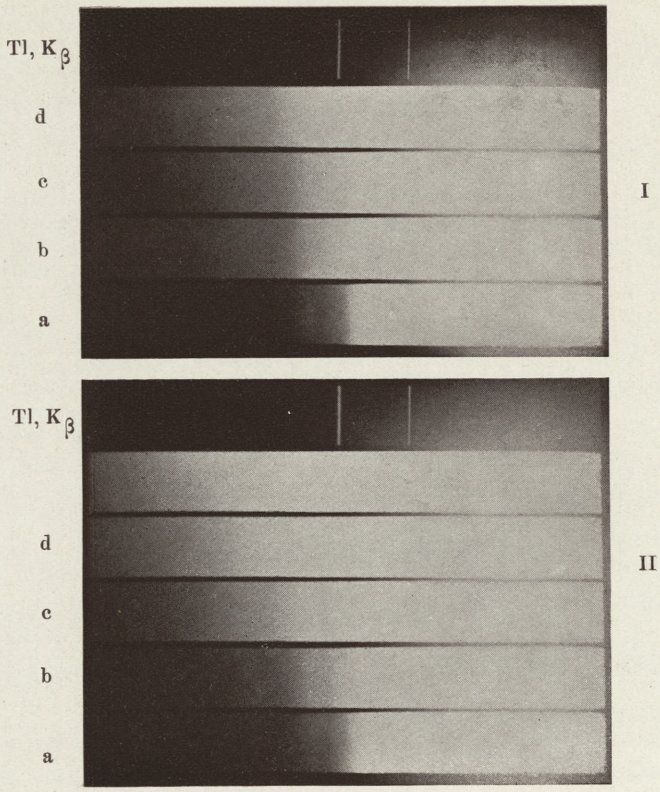


L. Marchlewski.



L. Marchlewski.