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It is known that indoxyl possesses both week acid and basic properties. This has been recorded by A. v. BAYER who noticed the week acid and basic properties of indoxyl prepared from indoxylic acid, therefore, presumably a very pure product. If now the indoxyl should be partly combined with lime, the oxidation must cause a loss of acidity.

The acidity is also bound to become less by the gradual disappearance of the free CO_2 which is always formed during the technical fermentation and in the laboratory experiment. This fully explains the reason why the liquid gradually changes from the acid to an alkaline condition. Finally, I wish to call attention to the following point: If a solution of indican is prepared by crushing the leaves with lime-water and filtering the neutralized liquid, and when to this is added a perfectly neutral solution of enzyme, a solution of indican is finally obtained which yields no indirubin with isatin and sodium hydroxide. If the solution is oxidated in a current of air free from CO_2, the filtrate is distinctly alkaline. It is, therefore, plain that indican forms a neutral saline compound, which is decomposed like free indican by indimulsin (somewhat analogous to myronic acid and its potassium salt).

Klaten (Java), Jan. 1900.

Chemistry. — Prof. S. HOOGEWERFF presents a communication, also on behalf of Mr. H. TER MEULEN, entitled: *"Contribution to the knowledge of indican".*

Observations made lately by BEIJERINCK[1]) and HAZEWINKEL[2]) on indican have shown that this substance is not so readily decomposed as was formerly believed[3]). It is not decomposed by evaporating its aqueous solution, but on the contrary, if free acids and enzymes are absent, it possesses a fair degree of stability and a solid mass of "crude indican" may be obtained by evaporating the decoctions of Indigofera leptostachya and Polygonum tinctorium[4]).

It was only natural that these important observations should lead to an effort to obtain the indican on a pure condition and to deter mine its composition. The formula $C_{26} H_{31} NO_{17}$ proposed by SCHUNCK[3]) as the result of investigations which are in many respects

[1]) Proc. Royal Acad. of Sc. Amsterdam, Sept. 1899 p. 91.

[2]) See preceding article.

[3]) SCHUNCK Phil. Mag. [4] X p. 73 and [4] XV p. 29, 117, 183.

[4]) BEYERINCK l. c. p. 95.

very meritorious, is not based on the analysis of free indican, but on the analysis of lead compounds obtained from extract of woad and has been accepted with a certain amount of reservation [1]). Moreover, the important observations of BEYERINCK communicated at the September meeting on the chromogen of the woad have shaken the foundation of the formula. SCHUNCK's coadjutor MARCHLEWSKI [2]) had, however, already proposed another formula for indican in 1898, starting the hypothesis that it should be looked upon as indoxyl-glucoside; he even gave a structural formula illustrating the connection between the glucose residu and the indoxyl-group. MARCHLEWSKI has apparently not had material at his disposal to prove experimentally the correctness of his hypothetical indican formula $C_{14} H_{17} NO_6$, although in the meantime indican has been proved to be a real indoxyl-glucoside [3]).

The following circumstances enabled us to carry on the investigation. Prof. BEIJERINCK had the kindness to present us with 17 kilos of his own grown Polygonum tinctorium for the extraction of the indican and also with an extract prepared by himself from the leaves of Indigofera leptostachya. From Mr. HAZEWINKEL we received tins containing somewhat purified solutions of indican prepared by himself from indigo-leaves at Klaten. We beg to offer them our best thanks for this co-operation.

The leaves were immersed by us in boiling water, boiled for a few minutes and further systematically exhausted; 2.5 liters of water were used for 1 kilo of the leaves. Without any sensible decomposition the decoctions could be evaporated in vacuo if care was taken to keep the reaction alkaline. The dry residue was extracted with methyl alcohol and to the solution was added ether as long as a precipitate was formed; these precipitates were rich in ash but very poor in nitrogen and were practically free from indican. From the solution, the alcohol and ether were distilled off, the residue was completely dried in vacuo and then dissolved in water. The filtered and concentrated solution deposited on cooling well defined crystals of indican almost colorless and ash free. A large proportion of the impurities may be removed by heating the decoction of the leaves before concentration with baryta-water, filtering and removing the excess of barium by a current of carbon dioxide; the filtrate is then treated as described. If the treatment with baryta

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[1]) Compare BEILSTEIN Org. chem. 3 Aufl. Bd. III p. 595.
[2]) MARCHLEWSKI and RADCLIFFE Journal Soc. chem. Industry 1898 p. 430.
[3]) Compare HAZEWINKEL and BEYERINCK l.c.

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is omitted the leaves of Indigofera leptostachya yield a gelatinous body which greatly impedes the purification of the indican. 17 kilos of the leaves of Polygonum tinctoria yielded 5 grams of pure indican.

Indican crystallized from aqueous solutions consists of spear-shaped crystals which Prof. SCHROEDER VAN DER KOLK, as the result of a preliminary nomination, declares to belong to the rhombic system. The crystals contain 3 mols. of water of crystallisation, melt at 51° and losing some of the water are transformed into a gummy-like mass which is gradually decomposed on heating above 100°. Dried in vacuo over sulphuric acid indican loses its water of crystalisation, but when the anhydrous mass is exposed to the air, it reabsorbs moisture and practically regains its original weight. Dried indican melts at 100°—102°, is tolerably soluble in water, methyl- or ethyl-alcohol and acetone, but only slightly soluble in benzene, carbon-disulphide and ether.

Heated on a platinum foil or in a test-tube purple-coloured fumes are given off which condense on the sides of the tube: this does not take place in a current of carbon dioxide. When an aqueous solution of indican is decomposed by the galvanic current, indigotin is formed at the anode. .
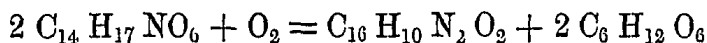
Indican has a bitter taste. It is optically active, a 2 per cent solution gives a polarization of — 2° when examined in a 20 c.m. tube at 15°. After acting on the solution with hydrochloric acid and oxidizing the resulting indoxyl the liquid shows a right-handed polarisation [1]. As soon as we shall have again at our disposal larger quantities of indican, we wil make further experiments with a view to determine its specific rotary power and we will also try to isolate the sugar formed in the hydrolysis of the indican.

As will be seen from the subjoined analyses and the determination of the molecular weight, the molecular formula of the vacuum- dried indican is $C_{14} H_{17} NO_6$ this confirming MARCHLEWSKI's hypothesis. The crystallized compound contains 3 mols. of water of crystallization; it may be observed here that amygdaline also contains 3 mols. of water of crystallization and also polarises to the left [2].
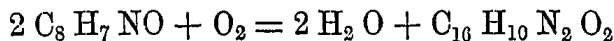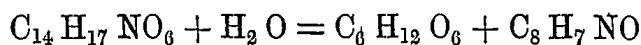
By passing a current of air through a hot solution of indican in dilute hydrochloric acid, containing a little ferric chloride as oxygen carrier, 91 per cent of indican was converted into indigotin according to the equation:

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[1] Compare C. J. VAN LOOKEREN CAMPAGNE. Landw. Versuch. XLV, 195.

[2] Indican is, therefore isomeric with FISCHER's amygdonitril. Ber. D. Chem. Ges. XXVIII, 1508.

$$2\,C_{14}\,H_{17}\,NO_6 + O_2 = C_{16}\,H_{10}\,N_2\,O_2 + 2\,C_6\,H_{12}\,O_6$$

or rather:

$$C_{14}\,H_{17}\,NO_6 + H_2\,O = C_6\,H_{12}\,O_6 + C_8\,H_7\,NO$$
$$2\,C_8\,H_7\,NO + O_2 = 2\,H_2\,O + C_{16}\,H_{10}\,N_2\,O_2$$

but the experiment will have to be repeated on a larger scale so as to be able to judge of the purity of the indigo-blue and ascertain its percentage of indigo-red which also seems to be formed.

We also wish to state that during this investigation not the least difference was noticed between the indican prepared from Indigofera leptostachya and that obtained from Polygonum tinctorium and we, therefore incline to the belief that both plants contain the same indican. As soon as larger quantities of indican are again at our disposal, we hope to continue and extend the investigation of this important compound.

The following results were obtained when subjecting indican to ultimate analysis. The sample was dried in vacuo over sulphuric acid.

I. 0.2416 gram of indican (Indigofera) yielded on combustion with copperoxide in a current of oxygen 0.4960 gram of carbon dioxide and 0.1257 gram of water.

II. 0.2397 gram yielded 0.4928 gram of carbon dioxide and 0.1244 gram of water.

III. 0.1539 gram of the indican treated by the KJELDAHL-GUNNING process yielded 5.12 cc. of $N/_{10}$ ammonia.

IV. 0.6310 gram similarly treated yielded 20.60 cc. of $N/_{10}$ ammonia.

On comparing the percentages of carbon-hydrogen and nitrogen with those calculated from MARCHLEWSKI's formula:

	I.	II.	III.	IV.	Calculated for $C_{14}\,H_{17}\,NO_6$.
C	56.0 pCt.	56.1 pCt.	—	—	56.95 pCt.
H	5.8 pCt.	5.8 pCt.	—	—	5.76 pCt.
N	—	—	4.7 pCt.	4.7 pCt.	4.75 pCt.

it is apparent that while the figures for the hydrogen and nitrogen practically agree, those of the carbon are somewhat too low. We, therefore, repeated the determination of carbon by means of the

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MESSINGER-FRITSCH[1]) moist combustion process so as to make more sure about the true percentage of carbon. We first tested the accuracy of the process by some blank experiments and some combustions of salicylamide.

V. 0.1371 gram of indican (Indigofera) heated with sulphuric acid and potasium dichromate yielded 0.2341 gram of carbon dioxide = 56 5 percent of carbon.

VI. 0.2169 gram of indican (Polygonum) yielded 0.4517 gram of carbon dioxide = 56.8 percent of carbon.

If we now take take the mean of these two determinations the composition of indican is:

56.7 pCt. C
5.8 pCt. H
4.7 pCt. N

which satisfactorily agrees with that calculated from MARCHLEWSKI's formula.

For the determination of the molecular weight the cryoscopic method was used, as indican is too little soluble in the liquids generally used in the process based on the increase of the boiling point.

Two determinations were made:

I. 0.1935 gram of indican (Polygonum) dissolved in 24.89 gram of water lowered the freezing point to the extent of 0.058°.

II. 0.8301 gram of indican dissolved in 24.89 gram of water lowered the freezing point to the extent of 0.208°.

From these determinations the following figures-are calculated for the molecular weight:

I 248 en II 297

which shows that it is not a multiple of 295. $C_{11}H_{17}NO_6$ must be accepted as the molecular formula of indican.

The determinations of the water of crystallization were done with indican from Polygonum.

I. 0.4149 gram of indican lost on drying in vacuo 0.0594 gram of water.

II. 3.2262 gram lost 0.4943 gram.

III. 0.2291 gram of the dried indican when exposed to the air until the weight was constant, absorbed 0.0393 gram of water[2]).

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1) Lieb. Ann. 294. p. 79.
2) The amount of water which is reabsorbed depends on the state of humidity of the air.

The percentage of water contained in crystallized indican is, therefore:

I 14.3 pCt.

II 15.4 pCt.

III 17.2 pCt.

the formula $C_{14} H_{17} NO_6 + 3 H_2O$ requires 15.5 pCt.

Chemical Laboratory of the Polytechnical School.

Mathematics. — *"A special case of the differential equation of* MONGE.*"* by Prof. W. KAPTEYN.

To the communications inserted in the Proceedings of Nov. 25th and Dec. 30th 1899 we here add the results of our investigation of a case where the equation of MONGE consists of three terms.
If the equation of MONGE has the form

$$s + \lambda t + \mu = 0$$

this equation will admit of two intermediate integrals, only when

$$\lambda = \frac{1}{\varrho} \frac{\partial}{\partial q} (p \varrho + v) \quad , \quad \mu = \frac{1}{\varrho} H (p \varrho + v),$$

where ϱ represents any function of x, y, z, q, and the function v satisfies the differential equation

$$\frac{1}{\varrho} \frac{\partial \varrho}{\partial q} \frac{\partial v}{\partial y} + \left(1 + \frac{q}{\varrho} \frac{\partial \varrho}{\partial q}\right) \frac{\partial v}{\partial z} - \frac{1}{\varrho} H(\varrho) \frac{\partial v}{\partial q} = \frac{\partial \varrho}{\partial x}$$

and H denotes the operation $\frac{\partial}{\partial y} + q \frac{\partial}{\partial z}$.
Then one of the intermediate integrals is

$$p \varrho + v = f(x),$$

where f denotes an arbitrary function, the second being found by connecting the two integrals of the complete system