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(1177)

| | | | | | | |
|---------------------|--------|-------|-------|-------|-------|--|
| <i>a.</i> | 98.36 | 0 | 0 | 1.64 | 0 | Na ₂ SO ₄ .10H ₂ O |
| <i>t.</i> | 95.83 | 2.24 | 0 | 1.93 | 0 | Na ₂ SO ₄ .10H ₂ O + CuSO ₄ .5H ₂ O |
| <i>t.</i> | 95.83 | 2.24 | 0 | 1.93 | 0 | Na ₂ SO ₄ .10H ₂ O + CuSO ₄ .5H ₂ O |
| line <i>t u.</i> | 95.861 | 2.099 | 0 | 1.502 | 0.538 | " + " |
| <i>u.</i> | 95.901 | 2.038 | 0 | 1.094 | 0.967 | Na ₂ SO ₄ .10H ₂ O + CuSO ₄ .5H ₂ O + D |
| <i>t.</i> | 95.83 | 2.24 | 0 | 1.93 | 0 | Na ₂ SO ₄ .10H ₂ O + CuSO ₄ .5H ₂ O |
| <i>d.</i> | 97.89 | 2.11 | 0 | 0 | 0 | CuSO ₄ .5H ₂ O |
| <i>u.</i> | 95.901 | 2.038 | 0 | 1.094 | 0.967 | Na ₂ SO ₄ .10H ₂ O + CuSO ₄ .5H ₂ O + D |
| | 95.572 | 2.032 | 0.277 | 0 | 2.119 | CuSO ₄ .5H ₂ O + D |
| | 94.701 | 1.158 | 2.137 | 0 | 2.004 | " + " |
| line <i>u n.</i> | 94.433 | 1.060 | 2.533 | 0 | 1.974 | " + " |
| | 93.166 | 0.773 | 4.192 | 0 | 1.869 | " + " |
| | 92.056 | 0.508 | 5.628 | 0 | 1.718 | " + " |
| | 91.118 | 0.523 | 6.652 | 0 | 1.707 | " + " |
| <i>n.</i> | 90.023 | 0.455 | 7.959 | 0 | 1.563 | CuCl ₂ .2H ₂ O + CuSO ₄ .5H ₂ O + D |
| <i>d.</i> | 97.89 | 2.11 | 0 | 0 | 0 | CuSO ₄ .5H ₂ O |
| <i>e.</i> | 91.020 | 0.231 | 8.749 | 0 | 0 | CuCl ₂ .2H ₂ O + CuSO ₄ .5H ₂ O |
| surface <i>D.</i> | 93.365 | 0.621 | 3.325 | 0 | 2.681 | D |

In most cases the appertaining residues at 15°, 25°, and 35° have been analysed as well as the solutions, and the solid phases with which the solutions were saturated have been deduced therefrom by means of the usual method.

(To be continued).

Chemistry. — "*Hypaphorine and the relation of this substance with tryptophane*". By Prof. P. VAN ROMBURGH.

(Communicated in the meeting of March, 25, 1911).

In the seeds of *Erythrina Hypaphorus* Boerl. (*Hypaphorus subumbrans* HASSK.) which, under the name of "dadap minjak" is generally cultivated, in Eastern Java, as a shading tree in coffee gardens, GRÜSSTOFF¹⁾ has found a poisonous alkaloid.

In the end of 1891 Dr. GRÜSSTOFF had invited me to take in hand, jointly, the study of this alkaloid in order to determine its structure. Shortly afterwards Dr. GRÜSSTOFF was obliged, in the course of 1892, to return to Europe. In the beginning of 1892 I

¹⁾ Mededeelingen uit 's Lands Plantentuin 7, 29 (1890).

was engaged for some time on the investigation of the "dadap substance", but suspended the work after his departure from Java. -

In 1898 appeared a communication¹⁾ on hypaphorine, the name meanwhile given to the substance obtained from the "dadap seeds", from the hand of Dr. GRESHOFF, in which, however, the results obtained by myself, were not included.

In that communication are given the method of preparation of hypaphorine and also its properties.

As regards its properties it may be mentioned here that hypaphorine crystallises in hydrated transparent crystals, which effloresce in a desiccator. At 255° it melts without decomposition. On being heated strongly in the air it burns with evolution of vapours having an odour resembling indol. It has a right-handed rotation $[\alpha]_D = +91^\circ - 93^\circ$. Although hypaphorine possesses a neutral reaction, it yields with acids crystallised compounds of which the sparingly soluble nitrate is particularly characteristic. No formula could be deduced from the recorded analyses of the hypaphorine and its nitrate. In the "Index Phytochemicus" by RITSEMA and SACK, published in 1905, the formula $C_{14}H_{18}N_2O_2$ is, however, given for hypaphorine, but without any mention being made of the source.

After the decease of Dr. GRESHOFF, I applied to the Committee of the Colonial Museum at Haarlem with the request to forward me the preparations of hypaphorine from the laboratory of the Museum in order to enable me to continue the investigation, started previously at Buitenzorg. I have to tender my sincere thanks to that Committee for the great willingness with which, a few months ago, my request was complied with.

The elementary analysis of the anhydrous hypaphorine gave me, at Buitenzorg, the following results:

C 68.4; 68.4. H 7.68; 7.63. N 10.9; 11.—.

Calculated for $C_{14}H_{18}N_2O_2$: C 68.24, H 7.38, N 11.37.

The hydrochloride gave: 13.1 %; 13.1 % HCl.

Calculated for $C_{14}H_{18}N_2O_2 \cdot HCl$: 12.95 % HCl.

On heating with strong aqueous potassium hydroxide, hypaphorine is decomposed. A gas having an amine-like odour is evolved and the aqueous distillate contains oily drops, which solidify after a while. The gas evolved was collected in dilute hydrochloric acid and the solid matter was separated by filtration from the aqueous distillate. The aqueous solution was united with the hydrochloric acid in which the said amine had been absorbed and evaporated. From the brown

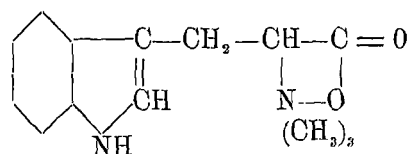
¹⁾ Mededeelingen uit 's Lands Plantentuin 25, 54 (1898).

of 0.2 gram of tryptophane. This, according to the classic method of PETER GRIESS ¹⁾, was mixed in methyl alcohol solution with sodium hydroxide and an excess of methyl iodide. After a few hours, the alcohol and the excess of methyl iodide were removed by distillation in a waterbath. If now the residue is taken up with a little water and mixed with dilute nitric acid a nitrate crystallises in delicate needles when the sides of the beaker are rubbed with a glass rod. I obtained about 0.12 gram of the nitrate.

The nitrate exhibits in its reactions the greatest resemblance with the nitrate of hypaphorine. Like the latter it has no sharp melting point; at about 220° the two preparations contained in capillary tubes were converted amid effervescence into a black mass. This decomposition point depends on the manner of heating.

On boiling with aqueous potassium hydroxide the synthetic nitrate also yields vapours having an odour of amine and indol ²⁾.

From the experiments described we may draw the conclusion that it is highly probable, that hypaphorine is identical with α -trimethyl- β indolpropio-betaïne:



derived from tryptophane.

In order to get perfect certainty and also to be able to perform the required analyses, I intended to carry out the synthesis of this betaïne on a larger scale, when last week I received from Dr. BARGER in London a letter communicating that by methylating tryptophane according to ENGELAND ³⁾ and treating the product formed in this reaction with dilute aqueous potassium hydroxide, he had obtained a betaïne, the nitrate of which has the same properties as that of hypaphorine. A determination of the rotatory power could be made. Found $[\alpha]_D = +94^\circ$ whereas GRIESSHOFF states $+91-93^\circ$.

In consequence, I limit myself to the short, preliminary communication of my results and intend to return to the synthesis, jointly with Dr. BARGER.

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Org. Chem. Lab. University.

¹⁾ B. 8, 1406 [1875].

²⁾ Tryptophane when boiled with strong aqueous potassium hydroxide certainly yields a distillate which gives with HNO₃ the indol reaction, but with hypaphorine the splitting takes place much more easily, which fact is not readily accounted for by the formula.

³⁾ B. 42, 2962 [1909]; 43, 2662 [1910].