

Fig. 25. Continuous curve: cranial indices of Smith Sound Eskimoes, recorded by BESSELS. Dotted curve: indices of the Long Barrow skulls, measured by THURNAM and PARSONS.

Fig. 26. Continuous curve: cranial indices of the New-England skulls, measured by BOAS. Dotted curve: cranial indices of the neolithic skulls from North-East and Middle-Germany, recorded by SCHLIZ.

---

**Biochemistry.** — *A few remarks on the iodine-amylum reaction.* By G. v. ITERSON JR. and J. COUMOU.

(Communicated at the meeting of June 29, 1935).

1. F. MYLIUS (16) contended in 1887 that besides the presence of iodine the presence of iodides or of hydriodic acid is required to form the blue iodo-amylum. Results apparently in contradiction with this should be explained, according to MYLIUS, by the formation of potassium iodide or hydriodic acid, the glass being of special influence in this matter.

This idea has been contested among others by L. BERZELLER (4) in 1917, who stated that the iodine reaction may take place without the presence of iodine ions, for example, by using pure iodine in boiled quartz glass-ware.

In point of fact the iodine reaction succeeds, if executed according to the method of C. NÄGELI (17), with a slight variation, a crystal of pure iodine in water on a quartz slide being used. If, however, it is considered that grains of starch contain exchangeable ash constituents, then neither BERZELLER's observation nor the experiment indicated by us proves convincing. BERZELLER's statement is besides impaired since he assumes that the presence of iodine ions intensifies the colour of iodo-amylum, omitting to state, however, why this should be the case.

Furthermore, the arguments against MYLIUS put forward by N. VON EULER and K. MYRBÄCK (8) in 1922 are weak, thus making MYLIUS' conception still maintainable.

2. In the course of time a great number of compounds have become known which produce a blue coloration with iodopotassium iodide, similar to the one produced with starch. In particular G. BARGER (1, 2 and 3) and cooperators have enlarged our knowledge in this respect. Only recently D. KRÜGER (14) added a new example.

From these data it appears that the occurrence of the blue reaction is connected with either the presence or formation of crystals, or with the colloidal state of the reacting product. In the real solutions no blue iodine reaction has been observed up to now. Assuming that "crystallites" are present in the colloidal state, we can reduce the condition necessary for the occurrence of the reaction to the requirement that the matter must be in crystalline state.

In this connection especially the agreement of the iodine reaction of narceine crystals and the iodo-amylum reaction indicated by W. STEIN (19) as early as 1869 is of importance. We call special attention to the "dichroism" of narceine crystals coloured blue with iodine and that of many periodides of alkaloids, of which herapathite forms the most interesting example. This dichroism, namely, makes it probable that the iodine has been fixed in the crystal lattice in very specific spots.

The presence of iodides or hydriodic acid besides that of iodine appeared to be required, or at any rate to act favourably, in many of the above-mentioned reactions. Sometimes other ions also, especially polyvalent cations, were effective. G. BARGER and E. FIELD (1) draw attention to the fact that double transpositions could have taken place here and that iodides could have been formed, but they prefer a colloid chemical explanation for this phenomenon (the iodine is considered to be colloidal in this case).

3. In 1915 G. BARGER and W. W. STARLING (2) concluded that "it is probable that the addition of iodine by the organic substance is a result of residual affinity". Although G. BARGER and F. D. EATON determined in 1924 that the physical nature of the material is also of essential importance for the occurring of the iodine reaction, the first mentioned conclusion had not to be withdrawn.

The observations of M. BERGMANN (5) and those of M. BERGMANN and M. GIERTH (6) in 1925 and 1926 on iodine reactions with compounds containing "etheroxygen" (where hydriodic acid or potassium iodide were also required) led BERGMANN to the supposition that "molecular compounds" are formed, in which the ether-oxygen atom should be active. BERGMANN supposes that something similar happens with the formation of iodo-amylum.

In this connection we refer to the investigation of W. v. KAUFMANN and A. LEWITE (13) who concluded in 1919 that the behaviour of starch to formaldehyde may best be explained by supposing that ether groups in the starch with formaldehyde may form a compound which decomposes in water.

With reference to P. PFEIFFER's *Org. Molekülverbindungen* 2. Aufl. 1927, and especially to the recent treatise of G. BRIEGLEB and W. LAUPPE (7) we emphasize that there are three possible structures of compounds of starch, iodine and potassium iodide or hydriodic acid. Firstly a "pseudosalt" may be formed in which oxygen is active with four valencies. Secondly a salt of "oniumform" may develop, where ions are bound together. Thirdly, a coordinative trivalent oxygen may play a role.

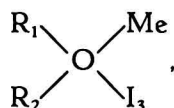
From the considerations of A. HANTZSCH (11) on the relation between the constitution and the colour the first mentioned type of structure would appear the most probable one for the blue iodo-amylum (according to

HANTZSCH, iodine, of all halogens, shows the greatest tendency to form "pseudosalts").

4. A. LOTTERMOSER and A. OTT (15) made it probable in 1930 that starch from an iodo-potassium iodide solution fixes the following ions or molecules :

$I_3$ -ions,  $I_2$ -ions,  $I$ -ions,  $KI_3$ - and  $KI$ -molecules. The  $I_3$ -ions are fixed by preference, then come the  $I_2$ -ions, and so on.

If all these facts are combined, it becomes probable that, in dealing with the blue starch iodine reactions, inside the crystallites molecules of the following type are present :



where  $Me$  represents a monovalent metal atom or a hydrogen atom. We leave it undecided as to whether the etheroxygen, present in the hexagons of the starch molecule according to HAWORTH, plays a role here, or whether this is done by the etheroxygen supposed to be present as a connecting link between the hexagons.

The objection might be raised that F. L. GILBERT, R. R. GOLDSTEIN and T. M. LOWRY (10), when determining the absorption spectra of 7 aromatic polyhalides and of 8 caesiumpolyhalides, found absorptions characteristic of the "brown iodine solutions". However, it should be borne in mind that these spectra have been determined for "real" solutions and that the solid  $CsI_3$  (as well as several solid polyiodides of alkaloids) is blue-black. We shall not enter further into discussions as to how the iodine in the group  $I_3$ , present in the crystallites, may be connected up, but will only indicate how it is possible that iodine occurs bound in such a way that during light absorption a process occurs of the nature proposed by J. FRANCK (9) which causes the violet colour of iodine vapours.

5. To confirm the above conception, we have asked ourselves whether it might not be possible to demonstrate the influence of iodine ions, while reacting with iodine for starch, more convincingly than is done according to the method of MYLIUS.

We took as our starting point the observation that a suspension of starch in  $KI$  solution of 10 % concentration, saturated with iodine, could not be brought to "gelatinization" by boiling. This appeared to be particularly striking because of the observations of M. SAMEC (18) and of J. VAN DER HOEVE (12) who found that a potassium iodide solution of this strength without iodine lowered the gelatinization point of starch considerably.

It is known that iodo-amylum is a negative lyophobic colloid ; the possibility exists, therefore, that the observed raising of the gelatinization point is due to the precipitation of the iodo-amylum by the  $K$ -ions, added in

great excess. The lyophobic properties of iodo-amylum, however, are not strong — vide BARGER and FIELD (1) — that is why it was considered of importance to investigate whether the raising of the gelatinization point could be observed also with low concentrations of iodo-potassium iodide. With these low concentrations the precipitating action of the *K*-ions may be considered improbable. In fact, this appeared to be the case.

L. BERZELLER (4) described a few observations in 1917 on the gelatinization of iodo-amylum. He experimented with starch which had first been soaked with iodo-potassium iodide solution (e.g. a saturated solution of iodine in a normal solution of potassium iodide). Next, the supernatant liquid was decanted and replaced by distilled water. In the most favourable case he observed a raising of the gelatinization point of 1° C. We obtained definitely greater increases by our method.

6. For the determination of the gelatinization point we applied the method of M. SAMEC (18), with the one variation that the temperature of the water-bath was not allowed to rise during the experiment but kept at 74.0° C. The suspension of potato starch used contained 1 gram of air-dry starch in 800 cm<sup>3</sup> of liquid. Below we give a few of our observations. We note that the liquids of the concentrations indicated were poured onto the air-dry starch in the above-mentioned ratio. The solution, which contained iodine only, had been prepared by shaking pure iodine with distilled water; no special care was taken to obtain electrolyte-free solutions, it being sufficient for our purpose to obtain a comparison of the gelatinization temperatures.

Liquid in which starch was suspended	Observed temp. of gelatinization in °C.	Raise with respect to starch in water
1. Distilled water . . . . .	{ 64.0 64.1	— —
2. 0.014% I sol. . . . .	{ 65.2 65.4	{ 1.2 1.4
3. 0.014% I sol. + 1% KI sol. . .	{ 70.4 69.6	{ 6.4 5.6
4. 1% KI sol. . . . .	63.8	—0.4
5. 0.006% I sol. + 1% KI sol. . .	{ 68.0 68.1	{ 4.0 4.1
6. 0.014% I sol. + 0.05% KI sol. .	69.6	5.9

After our remarks sub 1., it will not be considered surprising that an iodine solution without potassium iodide produces a slight raise of the temperature of gelatinization. We call special attention to the last observation, because it demonstrates clearly, in comparison with the results

of the experiments numbered 2 and 3, how large an influence is exerted on the point of gelatinization by the addition of a very low concentration of potassium iodide in the presence of free iodine.

7. Immediately the question arises whether in this experiment hydriodic acid may be substituted for the potassium iodide. As will be apparent from the following data, this happens to be the case. It may be noted that the solution of hydriodic acid was made iodine-free by means of hydrogen sulphide.

Liquid in which starch was suspended	Observed temp. of gelatinization in °C.	Raise with respect to starch in water
7. 0.01 % I sol. + 0.05 % HI sol. . . . .	68.7	4.7
8. 0.01 % I sol. + 1 % HI sol. . . . .	71.3	7.3
9. 1 % HI sol. . . . .	64.1	0

Thus in this case also the addition of *HI* in a concentration which of itself has no effect appears, in the presence of iodine, to have a definite influence on the gelatinization point.

8. If our theory is right, it is to be expected that iodine ions will show a specific action on the gelatinization point, compared with other anions, if present together with free iodine.

The results of experiments made to determine this point, to which a few

Liquid in which starch was suspended	Observed temp. of gelatinization in °C.	Raise with respect to starch in water
10. 0.01 % I sol. + 0.5 % H <sub>2</sub> SO <sub>4</sub> sol. . . . .	65.5	1.4
11. 0.01 % I sol. + 0.06 % H <sub>2</sub> SO <sub>4</sub> sol. . . . .	65.1	1.0
12. 0.01 % I sol. + 0.07 % KNO <sub>3</sub> sol. . . . .	65.7	1.6
13. 0.01 % I sol. + 1 % KNO <sub>3</sub> sol. . . . .	68.4	4.3
14. 0.01 % I sol. + 0.01 % HCl sol. . . . .	64.3	0.3
15. 0.01 % I sol. + 0.035 % Ca Cl <sub>2</sub> sol. . . . .	65.9	1.9
16. 0.01 % I sol. + 0.035 % Ba Cl <sub>2</sub> sol. . . . .	65.5	1.5
17. 0.01 % I sol. + 0.075 % Ba Cl <sub>2</sub> sol. . . . .	66.5	2.5
18. 0.015 % I sol. + 0.05 % K <sub>2</sub> SO <sub>4</sub> sol. . . . .	65.7	1.6
19. 0.01 % I sol. + 0.1 % La(NO <sub>3</sub> ) <sub>3</sub> sol. . . . .	{ 68.3 67.7	{ 4.3 3.7
20. 0.015 % I sol. + 0.04 % Al Cl <sub>3</sub> sol. . . . .	69.3	5.3
21. 0.015 % I sol. + 0.1 % Ca I <sub>2</sub> sol. . . . .	>74.0	>10.0
22. 0.1 % CaI <sub>2</sub> sol. . . . .	64.3	0.3

observations on the influence of cations have been added, follow below.

Comparison of the data 7 and 11, 6 and 12, and also 7 and 14, supports our opinion that among the anions the iodine ions exert a specific action. The polyvalent cations produce a definitely higher increase than the monovalent ones. This is not surprising, however, if we consider the fact that iodo-amylum is a negatively charged colloid. The interesting effect of the combination of iodine and calcium iodide (vid. Nr. 21 and compare with Nr. 15 and Nr. 22) is in agreement with this explanation.

The result with 1 %  $\text{KNO}_3$ -solution bids us to be careful; the possibility exists however that potassium iodide is formed by double exchange.

9. The investigation of the possible influence of other free halogens on the gelatinization point of starch was next taken in hand. SAMEC's method being used, neither a bromine or a chlorine solution as such, nor with the addition of potassium chloride, showed an appreciable influence on the gelatinization point. At most, differences of a few tenths of a degree could be seen.

It appeared, however, that with some of the experiments with bromine no "complete" gelatinization of the starch grains occurred. As a matter of fact it could be observed macroscopically and without doubt that the presence of bromine and potassium bromide together had its effect on the gelatinization. A starch suspension in water saturated with bromine could be made to gelatinize completely by boiling, but the addition of potassium bromide prior to boiling produced only a swelling of the starch grains on boiling. The swelling resulted in a yellow mass, which settled as a gel on standing. A solution of soluble starch is changed neither by the addition of potassium bromide nor by the addition of bromine; however, a mixture of bromine and potassium bromide produces a gelatinous precipitate.

With chlorine, no similar results could be observed.

*Delft*, June 1935.

*Laboratory for Technical Botany.*

#### LITERATURE CITED.

1. G. BARGER and E. FIELD. Blue Adsorption Compounds of Iodine, Part I. Starch, Saponarin, and Cholic Acid, *J. Chem. Soc. London*, **101**, 1394—1408, 1912.
2. G. BARGER and W. W. STARLING. Blue Adsorption Compounds of Iodine, Part II and III. Derivatives of  $\alpha$ - and of  $\gamma$ -Pyrone, *J. Chem. Soc., London*, **108**<sup>1</sup>, 411—424, 1915.
3. G. BARGER and F. J. EATON. Blue Adsorption Compounds of Iodine, Part IV, *J. Chem. Soc.* **125**, 2405—2414, 1924.
4. L. BERZELLER. Unters. üb. Adsorptionsverb. u. Adsorption. *Biochem. Ztf.* **84**, 106—117, 1917.
5. M. BERGMANN. Jodverbindungen einfacher 1, 2-Cyclo-acetale vom Typus der Jodstärke. *Ber. d. D. chem. Ges.* **57**<sup>1</sup>, 753—757, 1924.
6. M. BERGMANN und M. GIERTH. Ueber isomere Alkylverbindungen des Cyclo-hexanol-2-on-1, *Ann. d. Chem.* **448**, 48—76, 1926.

7. G. BRIEGLEB und W. LAUPPE. Zur Frage der Affinitätsabsättigung des Sauerstoffes in Molekülverbindungen der Alkohole, Aether, Ketone und Aldehyde, Ztf. physik. Chem. B **28**, 154—166, 1935.
8. H. v. EULER und K. MYRBÄCK. Verbindungen von Iod mit Bestandteilen der Stärke, Ann. d. Chemie **428**, 1—25, 1922.
9. J. FRANCK. Elementarprozesse photochemischer Reaktionen. Bemerkungen über die homöopolare Bindung. Ztf. physik. Chem. **120**, 144—150, 1926.
10. F. L. GILBERT, R. R. GOLDSTEIN and T. M. LOWRY. Adsorption Spectra of Polyhalide Ions, J. Chem. Soc. London, 1931, 1092—1103.
11. A. HANTZSCH. Ueber Isomerie zwischen echten und Pseudo-Haloidsalzen, Ber. d. D. chem. Ges. **52**<sup>II</sup>, 1544—1572, 1919.
12. J. VAN DER HOEVE, Verstoffseling van aardappelmeel, Diss. Utrecht, 1930.
13. W. VON KAUFMANN und A. LEWITE. Ueb. die Natur der Lösungen von Stärke in Formalin und die quantitative Rückverwandlung von Formalin Stärke in Stärke, zugleich ein Beitrag zur Kenntnis des Farbentons von Jodlösungen, Ber. d. D. chem. G. **52**, 616—627, 1919.
14. D. KRÜGER. Ueber die gefarbtten Jodderivate eines Acridinderivates, Ber. d. D. chem. G. **65**, 13—18, 1932.
15. A. LOTTERMOSER and A. OTT. Unters. üb. die Konstitution der Jodstärke. Koll. Ztf. **52**, 138—159, 1930.
16. F. MYLIUS. Ueb. die blaue Jodstärke, Ber. d. D. chem. Ges. **20**, 688—695, 1887.
17. C. NÄGELI. Die Reaktion von Iod auf Stärkekörner und Zellmembranen, Sitz. ber. d. Kön. Bay. Akad. Wiss. München, 1862, 251—321 and 1863, 483—586.
18. M. SAMEC. Die Lösungsquellung der Stärke bei Gegenwart von Kristalloiden, Koll. chem. Beih. **3**, 122—160, 1912.
19. W. STEIN. Ueb. das Verhalten des Narceins gegen Jod, Journ. f. prakt. Chem. **160**, 310—312, 1869.

---

**Mathematics.** — *Über allgemeine konforme Geometrie in projektiver Behandlung.* Von J. A. SCHOUTEN und J. HAANTJES.

(Communicated at the meeting of June 29, 1935).

Wir kündigen hier ein Theorem an, dessen Beweis an anderer Stelle veröffentlicht werden soll.

In einer  $X_n$  <sup>1)</sup> sei ein Fundamentaltensor bis auf einen beliebigen Zahlenfaktor gegeben. Entweder ist dann die konforme Geometrie in der  $X_n$  *konformeuklidisch*, d. h. der Konformkrümmungsaffinor verschwindet, oder dieser Affinor verschwindet nicht. Im ersten Falle gilt bekanntlich der Satz:

*Die Geometrie der  $X_n$  ist identisch mit der Geometrie einer quadratischen Hyperfläche in einer  $P_{n+1}$  <sup>2)</sup>,*

der sich genauer folgendermassen formulieren lässt:

---

<sup>1)</sup>  $X_n = n$ -dimensionale Mannigfaltigkeit mit gewöhnlichen nicht homogenen Koordinaten.

<sup>2)</sup>  $P_{n+1} = (n + 1)$ -dimensionale Mannigfaltigkeit einer gewöhnlichen projektiven Geometrie.