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Botany. — "*Crystallised Starch*". By Prof. Dr. M. W. Beijerinck.

The fact that starch crystallises easily is not generally known. It is true that Arthur Meyer supported the view that the starch grain is a sphero-crystal, [1] but convincing figures he does not give; his considerations are hypothetical and not decisive as he did not make any microscopical examination on soluble starch. Moreover, the highest temperature used by him was but 145° C., and he continued the heating not long enough.

Most species of starch, such as that of potato, wheat, barley, rye, rice, maize, behave as follows.

When a 10% solution, after previous boiling and gelatinising in distilled water, is heated during fifteen minutes or half an hour at 150° to 160° C., the grains dissolve to a perfectly clear, transparent liquid, in which, at slow cooling, a crystalline deposit sets off, consisting of very fine needles, which are either isolated or united in groups of various shapes, not seldom resembling natural starch, and which must undoubtedly be considered as crystallised starch on account of their behaviour towards diastase and chemical reagents.

The free needles, measuring but few microns or parts of microns, make the impression of an amorphous sediment. The groups, formed by longer needles have the shape of corn-sheaves or bundles of arrows (bolidesms); or of discs (bolidiscs), reminding in size and form of the red blood-cells; or they are more or less regular globules (spherites or sphero-crystals), from whose surface, however, here and there project the crystal needles.

Potato starch is very well apt to produce bolidesms and sphero-crystals; it is sufficient to heat to 150° C., during a quarter of an hour, a 10% solution in distilled water, previously boiled and gelatinised. After being kept 24 hours in a cold room loose needles, bolidesms or sphero-crystals are precipitated, and their crystalline nature is easily observable. What circumstances determine the union of the needles to bundles is not yet well known, but certainly slowness of crystallisation favours it, and the concentration has also some influence. Not seldom the whole deposit consists of a magnificent mass of sphero-crystals (Fig. 1). The discs, to which I shall return presently, are formed from potato starch at a somewhat lower temperature than the needles mentioned here.

[1]) Untersuchungen über Stärkekörner, Jena, 1895 Beiträge zur Kenntnis der Stärkegallerten, Kolloidchemische Beihefte Bd. 5, Pag. 1. 1913. The observations and opinions of Bütschli, Untersuchungen über Strukturen, Pag 283, Leipzig 1898, are obscure.

The two constituents of the starch grain, which I described earlier, [1] namely the amylopectose, non-soluble at boiling, which forms the wall of the starch grain, and the granulose (amylose), which does dissolve at boiling and forms the inner part, change both at 150° C. into crystallisable starch.

It is not difficult to convert 40% of the original starch into needles or sphero-crystals. With a lower temperature or a shorter time of heating the quantity of starch, which crystallises increases, but at the same time the needles become shorter and less distinct. When heated at 110° to 120° C. the solution, at first perfectly clear, quite coagulates at cooling and becomes white as porcelain. This coagulated substance or gel, must also be considered as consisting of crystals, but the needles are nearly, or in fact ultra-microscopic. They do not show any orientation.

As the temperature is taken higher, the quantity of dextrine, which does not crystallise, increases. The iodine reaction shows that this dextrine contains much erythrodextrine at lower temperatures, and at higher consists only of leukodextrine. colouring light brown. At temperatures of from 160° to 170° C. the 10% potato starch quite changes into dextrine in from half an hour to three quarters of an hour; besides, the presence of sugar, susceptible to alcoholic fermentation, may then already be observed.

The sphero-crystals and needles of the starch dissolve, when heated in water, more slowly than soluble starch, which I ascribe to the greater size of the artificial needles, compared with that of the needles composing the natural and soluble starch. These needles consist in my opinion of a substance (granulose) impermeable to water, so that the dissolving must begin at the outside and will be the slower as the needles are thicker.

At 70° C. the solubility becomes very great, without any sign of production of paste or of gelatinising. With iodine the colour of the solution is pure blue. The effect of diastase on the granulose needles is as usual: erythrodiastase extracted from crude barley-flower, forms erythrodextrine and maltose, whilst leukodiastase prepared from malt, produces leukodextrine and maltose.

Of crystallisable dextrine and amylodextrine, so much discussed in literature, I perceived nothing in my experiments; the latter substance is evidently crystallised starch, with so much erythro- or leukodextrine between the needles, that the pure blue iodine colour of the granulose is modified to violet or reddish brown. When the

[1] Proceedings of the Academy of Sciences. Amsterdam, 11 April, 1912.

crystalline mass, which in fact sometimes colours red with iodine, is washed out with much water, the dextrine, and with it the "amylodextrine reaction" quite disappears, to make place for pure blue.

The crystals may also be obtained from soluble potato starch. Such starch is prepared by keeping raw starch during 10 days under 10 %-ic cold hydrochloric acid.

Crystal discs (bolidiscs) result very easily from wheat starch. The heating must be somewhat longer and the temperature higher than for potato starch. Besides, it is more difficult to obtain a perfectly clear solution from wheat paste.

Fig. 3 shows, 230 times magnified, the discs formed in a beakerglass of 100 cm^3, in which wheat starch, previously boiled in distilled water, is heated to 160° C. The discs are thinnest in the middle and from this centre the needles radiate. The discs resemble natural wheat starch as well in shape as in size. With polarised light I could not, however, perceive anything of the axial cross, which is so very obvious in natural starch. I suppose that it does exist, but is too feeble to be observed. It is, namely, a fact that the structure of the spherites and discs is much looser than that of natural starch, so that in a volume unit of the latter many more needles occur than in the discs and spherites. If now the double refraction of the separate needles be not great, their united power in the discs need not necessarily show the same as is seen in the natural grains.

That the double refraction of the common starch grains reposes on their crystalline nature and not on tangential and radial tensions, may be concluded from the fact, that the axial cross is in the usual way perceptible in soluble starch. As this substance is prepared with strong hydrochloric acid, whereby from 10 to 16 % of the dry substance is extracted, it must be concluded that all tensions, originally present in the grain, disappear.

That the discs may also be obtained from potato starch is demonstrated in Fig. 3, where 10% potato starch, after boiling and gelatinising in distilled water, in a 100 cm^3 beakerglass, heated to 125° C. during $3^1/_2$ hour, and after 24 hours of crystallisation in a room of about 16° C., is figured 600 times magnified.

By moving the coverglass on the slide, many discs may be observed laterally, as is clearly seen in the photo. In the preparation of wheat starch used for fig. 3, all the grains are lying on their broad side.

The crystal discs of the starch are now and then referred to in literature as "Jacquelain discs", but without any allusion to their crystalline structure. JACQUELAIN himself, who first mentioned these grains, called them "granules de fécule".[1])

After having become acquainted with the described facts and found them confirmed for other species of starch, I convinced myself that the natural starch grain also is built up of crystal needles radiating from the dot or hilum. This may best be seen in soluble potato starch, very cautiously heated in the microscopic preparation on the slide under the coverglass, when all the stages of the dissolving in hot water can be followed. The tiny radiating crystal needles then become visible in a ring-shaped arrangement, such as might be expected from the structure of the starch grain itself. It seems that the length of the needles corresponds with the thickness of the rings.

From the preceding I conclude, that the formation of the starch grain takes place in the following way. The amyloplast produces granulose, which in the interior crystallises to small spherites, just as in a solution. But this granulose production occurs periodically; and so the process of crystallisation gives rise to the formation of the layers of the grain.

To explain the great difference existing between starch gelatinised at 100° C. and that heated to 150° and 160° C. it must be accepted that in the starch grain, beside the granulose, an incrustating substance exists, functioning as a "protecting colloid", whose presence makes the needles remain short, the shorter the more of the colloid is present. It remains active unto about 100° C., but above this temperature it slowly decomposes, quite to vanish at about 150° C.

The hypothesis that this protecting colloid might be a phosphoric ester of granulose, is contrary to the properties of soluble starch, for this behaves at crystallisation of the solutions, prepared between 100° and 150° C., precisely in the same manner as natural starch so that the protecting colloid is still present in this substance, whereas it might be expected that an ester would be decomposed by the strong, 10%-ic hydrochloric acid used for its preparation.

Perhaps the colloid is the amyloplast itself, which, at the formation of the starch grain, remains partly enclosed between the fine granulose needles. Its greatest accumulation would then occur in the amylopectose wall of the grain, which does not yet dissolve at boiling.

[1]) J A. JACQUELAIN, Mémoire sur la fécule. Annales de Chimie et de Physique. T. 63, Pag. 173, Paris 1840. Much in this treatise is incorrect and obscure, else the discs would certainly already earlier have drawn general attention.

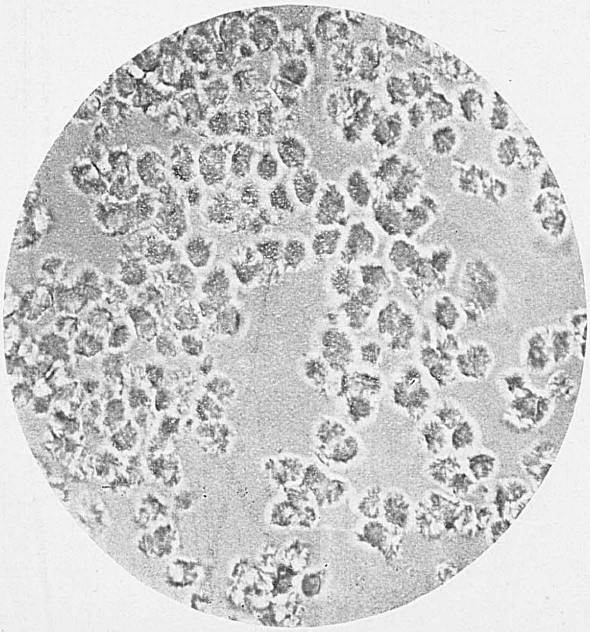

Fig. 1 (600).

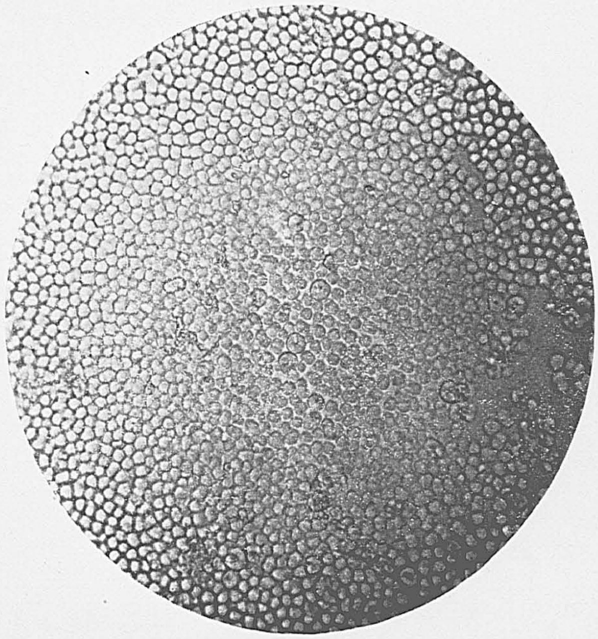

Fig. 3 (230).

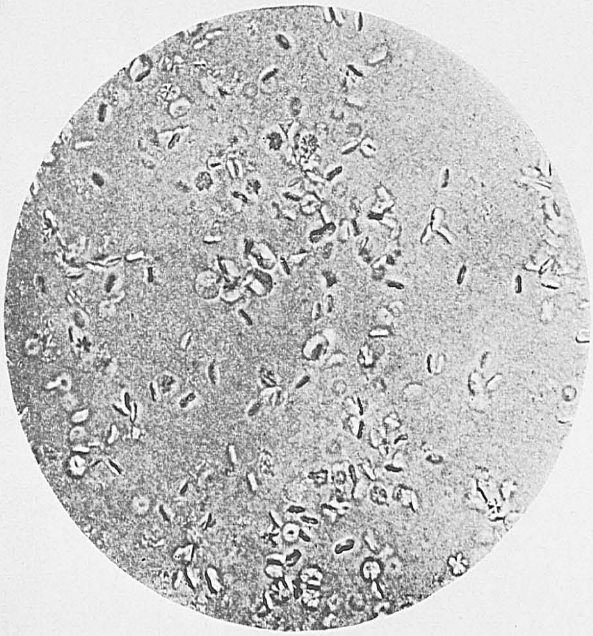

Fig. 2 (600).

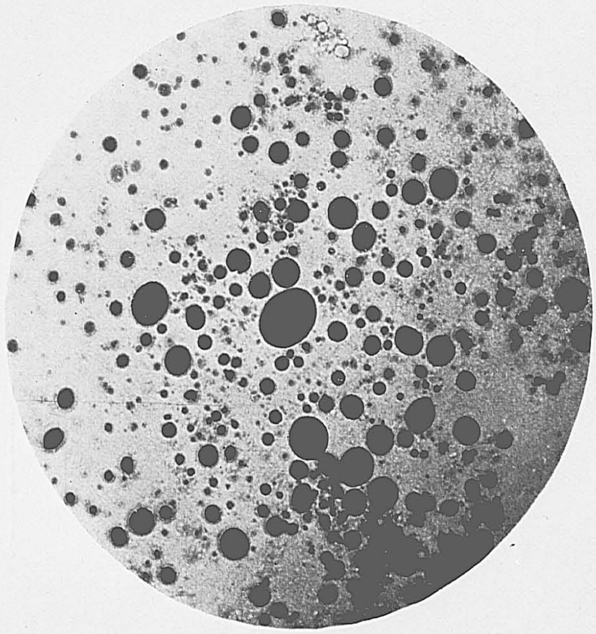

Fig. 4 (200)

That no difference could be found in the rate of nitrogen between the granulose and the amylopectose of the starch grain, to which circumstance I directed attention in my communication of 11 April 1912, I ascribe to the extremely small absolute rate of nitrogen in both constituents; but I think that the relative difference is considerable.

I will not omit to draw attention to the existence of starch species, which after heating, do not crystallise in the usual way. To these belongs arrowroot. If a 10 % paste of arrowroot is precisely treated as above described, it becomes after cooling, as usually, turbid and precipitates; but instead of a crystalline deposit we find in the microscopic preparation drops of various sizes, and homogeneous structure (Fig. 4), which later, however, become turbid and granulous. With iodine these drops turn deep blue and evidently consist of granulose like the crystal needles of the other starch species. The liquid between the drops is also a granulose solution, but less concentrated. The drops remind of a heavy oil, but they differ from it by such a small surface tension that notwithstanding their liquid state many may be pear- or egg shaped, and even pointed. Double refraction I could not perceive, but, nevertheless, I think it probable that they must be reckoned to the liquid crystals. That after some time the drops become turbid can be explained by the growing in length and thickness of the ultra-microscopic needles, which constitute the liquid crystal drops, hence, by the same process of crystallisation by which the needles originate,

The facts here briefly described deserve further attention from a physico-chemical view.

EXPLANATION OF THE FIGURES.

Fig. 1 (600). Sphero-crystals of 10 % potato starch, half an hour at 150° C.

Fig. 2 (600). Bolidiscs or JACQUELAIN discs of potato starch, half an hour at 125° C.

Fig. 3 (230). Bolidiscs or JACQUELAIN discs of wheat starch, three quarters of an hour at 160° C.

Fig. 4 (200). Drops or liquid crystals of 10% arrowroot, three quarters of an hour at 140° C., coloured with iodine.