Summary.

We believe that the more commonly occurring vegetable alkaloids may be tentatively identified under the microscope by the form or habit of their picrate crystals prepared under standard conditions. We hope to consider the optical properties of other of their compounds later.

BINGHAMTON, NEW YORK.

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THE DRYING AND SWELLING OF GELATIN. PRELIMINARY NOTE.[1]

BY S. E. SHEPPARD AND F. A. ELLIOTT.

Received October 27, 1921.

The following notes, or more accurately notes and queries, are concerned principally with the influence of the earlier phases of a dehydration-hydration cycle in gelatin jellies on later phases of the cycle. The view that the influence of the history of a gelatin gel on its swelling after drying is explicable in terms of an internal supermolecular structure has been recently clearly expressed by L. Meunier. In a review of recent work "On the Properties of Gelatin"[2] he states "We have already mentioned that according to Hardy's conception, the solid phase of a gelatin jelly has a structure related to its concentration; the cells of the lattice would be open in the case of the less concentrated jellies, and closed in the case of the more concentrated. Admitting this hypothesis, it may be conceived that the absorbing power for water of thin sheets of gelatin will be in relation to the concentrations of the solutions from which they are prepared. If we prepare from the same gelatin two solutions, one at 6%, the other at 20%, and coat thin sheets of gelatin from these on glass, dry at low temperature, the leaves prepared from the diluted solution will absorb more water and will swell more, for equal weight [of gelatin] and time, than the sheets prepared from the concentrated solution."

Similar experiments are recorded by H. R. Procter[3] and by W. D. Bancroft[4] and have been confirmed in this Laboratory. There remains the question as to whether they are due to internal structure, as suggested, or whether a more obvious cause exists.

The Drying of Gelatin Jellies.

Gelatin jellies, of given definite geometrical shape and water content, might be supposed to dry in such a way that the shape would remain un-

[1] Paper read at the Spring Meeting of the American Chemical Society, Rochester, N. Y., April, 1921.

[2] Meunier, *Chimie et industrie*, **5**, (T.) 220 (1921).

[3] Procter, *J. Chem. Soc.*, **105**, 313 (1914).

[4] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., **1921**, p. 251.

affected. Such shrinkage, and a swelling exactly inverse thereto, we may term isometric; actually isometric shrinkage of jellies on drying can be approached only by very slow drying under conditions such that the environment is only slightly unsaturated as to water or water vapor. Ordinarily this is not the case; hence, the rate of diffusion of water to the drying surface is not everywhere the same and equal to the rate of evaporation. The importance of diffusion in regulating the drying and swelling of gelatin masses has been pointed out by (Miss) E. B. Shreve,[5] whose work will be referred to subsequently. The actual balance between the diffusion in the gel and the surface evaporation is affected by a number of factors as follows.

1. **Environment factors.**—*i. e.*, the saturation, temperature, rate of movement of the dehydrating fluid, *e. g.*, air.

2. **Surface factors.**—The surface is not a geometrical boundary of negligible thickness and structure, but a region of discontinuity of physical properties and state of aggregation. If we term the sum total of the surface energy factors the *capillarity*, this becomes of still more pronounced and even critical importance at the intersection of geometrical surfaces, such as edges and corners (dihedral and polyhedral angles).

3. **Elastic factors.**—Although a gelatin jelly is a relatively homogeneous isotropic solid for simple shearing stresses not involving compressions or dilations,[6] it tends to become heterogeneous and aeolotropic for complex stresses such as occur in drying and swelling. This, again reacts on the progress of drying and the properties of the piece of gelatin.

4. **Associated factors.**—Temperature, pressure and chemical conditions are variables associated with both the superficial and the elastic variables; these, as independent variables, define the limits within which gelatin solutions behave as elastic hydrogels. If the temperature and pressure are above certain values, equilibrium is definitely displaced in the direction of the sol condition, in which the rigidity is negligibly small compared with the resistance to compression (bulk elasticity). Again at constant temperature, the chemical potentials, in particular, the hydrogen-ion concentration, definitely limit the concentration region of gel formation. An originally uniform distribution of a chemical potential can readily become nonuniform, again with a definite reaction on the progress of drying and the properties of the dried piece.

Passing from these preliminary generalities, we note the behavior of gelatin in various forms on ordinary "forced" drying and subsequent swelling.

Leaf Gelatin.

Preparation in "leaf" form is very usual for technical and photographic

[5] Shreve, *Science*, **48**, 324 (1918).

[6] Sheppard and Sweet, THIS JOURNAL, **43**, 539 (1921).

gelatin. The shape and behavior on swelling, for a given stock, are primarily determined by the concentration and thickness at which it was "set," by the fact that it is dried down on a net or mesh, and by the rate of drying. Such a leaf shows in a polariscope local strain areas about the nodes of the net, and evident thickenings at the traces of these nodes and the mesh work on the leaf, as also at the edges. Between the meshlines the gelatin is thinner and has a curved surface. The behavior on swelling is illustrated by the following data.

EXPT. 1

Dimension		0 hrs.	Swelling 1.5 hrs.	ds/s %	Swelling 18 hrs.	ds/s %
Length		23.1 cm.	24.3 cm.	5.2	28.2 cm.	22.2
Breadth		8.5 cm.	9.7 cm.	14.1	10.3 cm.	21.2
	(*a*) Center mesh	0.108	0.83	670.0	1.09	910
Thickness in cm.	(*b*) Nodes	0.70	0.90	14	1.10	50
	(*c*) Edges	0.45	0.90	100		

EXPT. 2

Dimension		0 hrs.	Swelling 1.5 hrs.	ds/s %	Swelling 18 hrs.	ds/s %
Length		22.7 cm.	25.5	12.3	27.5 cm.	21.1
Breadth		8.6	9.0	4.65	10.2	18.6
	(*a*) Center mesh	0.142	0.82	0.477	1.22	760
Thickness in cm.	(*b*) Node	0.75–.80			1.22	50
	(*c*) Edges	0.55			1.3	
	Weight, g.	3.790	20.89	450%	34.46 g.	810%

It will be seen from these that the dilations in length and breadth are very small, compared with the dilation of the thickness of the intermesh elements; this increase in thickness is alone nearly able to take care of the total increase in volume as may be seen by comparing the parallel figures for the increase in weight. It is evident that these results approach the behavior of gelatin jelly coated and dried down on a glass plate, when on swelling the dilation is necessarily confined to the direction perpendicular to the plane of the plate, frilling and stripping excluded. The similar behavior of leaf gelatin is due to similarity of cause. The meshwork of the supporting net initiates the drying by capillarity and thus the sheet receives a skeleton or framework of primarily hardened, rigid gelatin, evident enough upon examination, which is simply a capillary impress of the net. This framework, consisting of more compact gel, is composed of the nodal bosses or cusps (somewhat thicker, as will be seen from the measurements, than the intermesh elements), the internodal

lines of the mesh, and the edges, also thicker. The intermesh elements are curved away from the plane of the mesh, and the flattening out of the curvature on swelling probably plays a considerable part in the approximate re-formation of the original trapezoidal sheet form. On redrying, freely suspended, the sheet is approximately reshrunk to the original leaf form, the intermesh elements going back to their former thickness. This unilateral dilation of the leaf is not peculiar to the leaf as a whole, but is shared by pieces cut out of the intermesh elements, *e. g.*, with a cork borer. Thus, after 3 hours 1.1 cm. diameter became 1.5 cm. (ds/s 36%) and 0.10 mm. thickness became 1.05 mm. (ds/s, 950%).

This was observed by R. Cahal also, in the course of his researches on the microscopic structure of Lippmann images, by microtome sections through gelatin films stripped from a photographic plate. Cahal in order to magnify the distance between the elemental mirrors, employed the device of swelling the section in water, and noticed that the section swelled some 10 times in the direction of the normal to the plane of the plate and but little in the transverse direction. This has been corroborated in this Laboratory.

Initiation of an external skeleton framework, which acts similarly to an adherent plate or film support, appears sufficient to explain the unilateral swelling of a sheet of dried down gelatin as a whole, while the like behavior of pieces and sections indicates that the distribution of strain effected in drying extends to microscopic and perhaps submicroscopic elements. Since the capillary initiation or induction appeared to be a phenomenon of fundamental importance for the drying and swelling of gelatin, experimental attention was directed to reducing this factor progressively as far as possible. If we pass successively from *cubes* to *cylinders* to *spheres*, we have a progressive reduction of the corner and edge factors to zero, and arrive at a figure for which the ratio of surface to volume is a minimum. Experiments were made with such figures, with various modifications of procedure.

Cubes.—Three cases were observed: (a) cube freely suspended, all faces free, (b) cube bounded at one face; (c) cube bounded at two opposite faces. The cubes were cast in special moulds, with a removable suspension consisting of a rigid wire terminated by a small cubical block acting as the center of the cast piece. The relatively slight capillary action of the wire can be reduced by greasing it. The cubes were made in three sizes: 2.5 cm. = 1.0 inch (No. 3), 1.25 cm. = 0.50 inch (No. 2) and 0.62 cm. = 0.25 inch (No. 1). While geometrical similarity induced a similar behavior on drying in the three cubes, the process was the more rapid the smaller the cube. Experiments were made both with dynamic drying (air current) and statically (in a closed vessel) over sulfuric acid of definite concentration. The general results were the same in both cases, but

experiments are being continued over a wider range of condition as to speed, temperature and saturation of the air.[7] The actual progress of drying will be most readily seen from the photographs (Fig. 1).

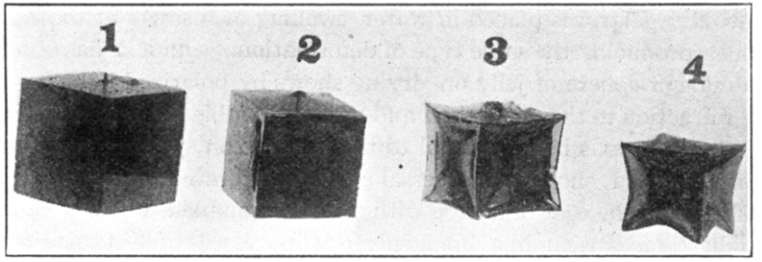

Fig. 1.—Free cube.
1—Original 20% gelatine; 2—Initial drying step; 3—Intermediate; 4— Final drying.

These are for 20 % gelatin jellies. It is evident that drying is *initiated* at the corners or trihedral angles which dry and harden first; at this stage the sides or faces of the cube are bowed or curved outward, giving convex surfaces under tension. This is rapidly followed by hardening of the edges, which tends to flatten the faces again. A rigid framework is thus formed, so that the cube behaves as if suspended inside a relatively unyielding wire cage. The faces now recede, and the edges become somewhat incurved till a sort of inner cube is formed with connected flanges reinforcing it, any cross-section through this having an I-beam structure, as though the drying proceeded in a manner developing the figure with the greatest resistance to stress. The flange-like edges appear to form sections of hyperboloids with a common focus at the center of the cube.

When one face is bounded, as by standing the cube on a sheet of glass, the only noticeable difference is that drying starts at the intersection of the cube with this base. Hence the basal face persists practically unaltered in size. This is duplicated in the case of two parallel faces being bounded when the effect of capillarity at the contact angles in directing the drying becomes still more marked (Fig. 2).

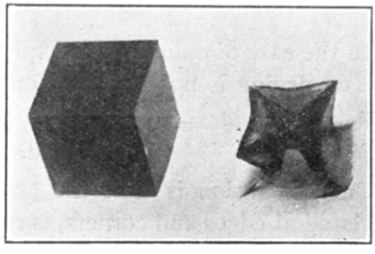

Fig. 2.
Cubes, 1—Face suppression before and after drying 1 inch.

On placing such a cube in water and allowing it to swell, at first the

[7] By very slow drying we have secured isometric shrinkage, and investigation of swelling inverse to this is in progress.

salients formed tend to swell most; this is then followed by restitution of the faces, and an approximate restoration of the original cube. The course of drying—up to about 6 to 10% moisture content—as described, has increased the ratio of surface to volume. If a freshly moulded cube of some 60% gelatin is placed in water, swelling also starts at the corners and edges, producing the same type of deformation. Quincke has observed that a cube or sphere of jelly on drying shows by polarized light negative double refraction in the outer shell and positive double refraction in the interior, the optic axis being normal to the surface; on swelling these conditions are reversed, showing a reversal of the distribution of stress.

Passing from the case of a cube with one face bounded, we may consider any right 6-face, with one bounded (or suppressed) and the *thickness*, taken perpendicular to this face, small compared to the other dimensions. In the limit this corresponds to photographic plates and films. In this case drying proceeds very similarly at first to the cube, but the sides soon become incurved and case-hardened, so that in the second stage drying proceeds by gradual envelopment and reduction in area of a central humid zone, proceeding inward from the corners and edges.

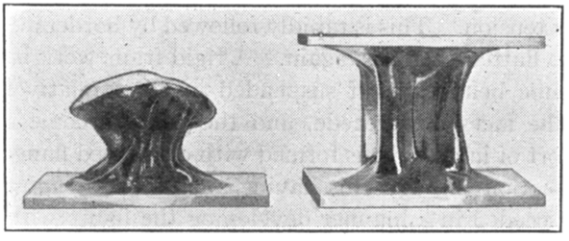

Fig. 3.
Cylinders, 1—Face, and 2—Face suppression after drying, side view.

In the case of cylinders and spheres, the photographs show that shrinkage on drying is not uniform, but produces a puckered or wrinkled surface (Fig. 3).

Case Hardening vs. Structure.

Our conclusion is that the "case hardening" effect, in particular as initiated at edges and corners, is responsible for two important phenomena in the hydration-dehydration cycle of gelatin jellies. The first of these is the fact noted in reference to "leaf" gelatin, and pointed out by Miss E. B. Shreve[5] "that the greatest shrinkage and subsequent swelling takes place perpendicular to the largest evaporating surface." The second is the apparent influence of the original concentration of the gelatin jelly on its swelling limit subsequent to drying. This we regard as being due to the initial case-hardening, which preserves an approximate "skin

extension" corresponding to the original figure. If this is correct, there appears no need to postulate an internal sub-microscopic but supermolecular structure of the gelatin. Any "structure" is not inherent in the gelatin, but is an environment impress, a strain structure in the original mass.[8] We are continuing the investigation of this with controlled humidity, to adjust the rate of evaporation.

The influence of hydrogen-ion concentration on swelling of gelatin masses with different drying histories is also under investigation, in relation to the Procter-Wilson-Loeb theory of gelatin swelling.[9]

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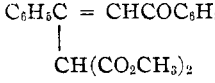
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE ADDITION OF MALONIC ESTERS TO BENZOYL-PHENYLACETYLENE.

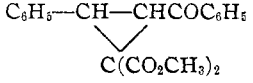
BY E. P. KOHLER.

Received October 28, 1921.

The following investigation was originally undertaken for the purpose of making the unsaturated δ-ketonic acid (I) for comparison with an isomeric cyclopropane derivative (II).



(I).



(II).

It was abandoned for a time because the addition reaction gave substances of a different type, and then taken up again in the hope of finding

[8] This view may be compatible with a development of the 2-phase theory for gelatin gels, with the proviso, however, that the structure elements are resultants of the physico-chemical changes of environment, not native to gelatin. Thus Miss J. Lloyd (*Biochem. J.*, **14**, 166 (1920)) pictures gelation as follows: "gelation will only occur on the cooling of a sol which contains in solution iso-electric gelatin and gelatin salts in equilibrium with free electrolytes. As the sol is cooled the insoluble iso-electric gelatin is precipitated in a state of suspended crystallization and forms a solid framework throughout the system. The more soluble gelatin salts remain in solution and by their osmotic pressure keep the framework extended. Gels, therefore, are 2-phase systems, the solid phase consisting of iso-electric gelatin, the liquid of gelatin in salt form." With regard to this conception, if the insoluble iso-electric gelatin forms a rigid "solid framework," one does not quite see how the osmotic pressure is necessary to keep it extended. It appears, however, that this precipitation theory can be extended to drying, the solid framework growing by accretion as the concentration changes in the liquid phase, and building up the skin extension to which we have referred.

[9] H. R. Procter, Ref. 3. Also Procter and J. A. Wilson, *J. Chem. Soc.*, **109**, 307 (1916). J. A. Wilson and W. Wilson, THIS JOURNAL, **40**, 886 (1918). J. Loeb, *J. Gen. Physiol.*, **1918–1921**; *Science*, **52**, 449 (1920).