

Meletizose (from the larch), *Melitose* (from eucalyptus), *Trehalose* (from Turkish manna), and *Maltose* (from starch), belong to the Saccharons.

"Honey-dew" is a viscid saccharine matter occasionally met with on the leaves of the lime, maple, black alder, rose, and other trees, being a sweet principle exuded from aphides. Sometimes it is sufficiently abundant to dry and fall on the ground, forming a veritable "shower of manna." It is a mixture of cane-sugar, inverted sugar, and dextrin.

Barley-sugar is made by simply heating cane-sugar till it fuses, a change from the crystalline to the uncrystallizable condition occurring. *Treacle* (*Theriaca*, B. P.), *Molasses* or *Melasses* (from *Mel*, honey), or *Golden Syrup*, chiefly results from the application of too much heat in evaporating the syrups of the sugar-cane; it is a mixture of cane-sugar with uncrystallizable sugar and more or less coloring-matter. *Liquorice-root* (*Glycyrrhizæ Radix*, B. P.) contains a considerable quantity of uncrystallizable sugar.

Caramel.—Carefully heat a grain or two of sugar in a test-tube until it blackens; the result is *caramel* or *burnt sugar* (the *Saccharum Ustum* of pharmacy). It is used as a coloring agent for gravies, confectioneries, spirits, and similar materials.

Milk-Sugar, or *Lactose* ($C_{12}H_{22}O_{12}$) (*Saccharum Lactis*, U. S. P.), the sweet principle of the milk of various animals, is not susceptible of alcoholic or vinous fermentation, but it resembles grape-sugar in reducing an alkaline solution of copper with precipitation of suboxide. It is readily obtained from milk by adding a few drops of acid, stirring, setting aside for the curds to separate, filtering, evaporating the whey to a small bulk, filtering again if necessary, and allowing to cool and crystallize. It usually occurs in trade "in cylindrical masses two inches in diameter, with a cord or stick in the axis, or in fragments of cakes—grayish-white, crystalline on the surface and in its texture, translucent, hard, scentless, faintly sweet, gritty when chewed." It is soluble in 6 parts of cold and 3 of boiling water; slightly soluble in alcohol; insoluble in ether. Powdered milk-sugar is used in pharmacy as a vehicle for potent solid medicines. Milk-sugar is convertible, by the action of dilute acids, into "galactose" and "lacto-glucose;" these may be reunited to form milk-sugar. "Milk-sugar, when sprinkled upon 5 parts of sulphuric acid, should acquire not more than a greenish or reddish, but no brown or blackish-brown, color within one hour (abs. of cane-sugar)."—U. S. P.

Saccharic Acid, $H_2C_6H_4O_8$, or $C_4H_4(OH)_4(COOH)_2$, is the result of oxidizing sucrose, dextrose, starch, gum, and lignin by nitric acid. *Mucic acid*, isomeric with saccharic acid, may be obtained in the same way by acting on lactose, gum, and mannite.

QUESTIONS AND EXERCISES.

763. Into what three classes may the carbohydrates be divided?
764. How is grape-sugar obtained from cane-sugar?

765. How are cane-sugar and grape-sugar analytically distinguished?

766. How is dextrose obtained from starch?

767. Mention the chief sources of cane-sugar.

768. Give chemical explanations of the different processes of bread-making.

769. What is the difference between fruit-sugar and honey?

770. What is oxymel?

771. Describe the effect of heat on cane-sugar.

772. How is milk-sugar obtained? In what respects does it differ from other sugar?

773. Whence are mucic and saccharic acids obtained?

Amyloses or Amyloids, $nC_6H_{10}O_5$.

Starch ($nC_6H_{10}O_5$, probably $C_{72}H_{120}O_{60}$) is contained in large or small quantities in nearly every plant. It forms about 60–70 per cent. of wheat, and from 20 to 30 per cent. of potatoes.

Processes.—Rasp or grate, or, with a knife, scrape, a portion of a clean raw potato, letting the pulp fall on to a piece of muslin placed over a small dish or test-glass, and then pour a slow stream of water over the pulp; minute particles of granules of starch pass through the muslin and sink to the bottom of the vessel, fibrous matter remaining on the sieve. This is potato-starch. Even diseased potatoes furnish good starch by this method. Wheat-starch (*Amylum*, U. S. P.) may be obtained by tying up some flour in a piece of calico, and kneading the bag in a slow stream of water flowing from a tap, the washings running into a deep vessel, at the bottom of which the white starch collects; the sticky matter remaining in the bag is *gluten*.

The blue starch of the shops is artificially colored with smalt or indigo to neutralize the yellow tint of recently washed linen; it should not be used for medicinal purposes. Starch dried in mass splits up into curious columnar masses resembling the basaltic pillars of Fingal's Cave in Staffa or those of the Giant's Causeway in the north of Ireland. The cause of the phenomenon, which may also be seen in grain tin, is not conclusively known.

Gluten is the body which gives tenacity to dough and bread. It seems to be a mixture of vegetable fibrin, vegetable casein, and an albuminous matter termed gluten. These substances and gluten itself are closely allied; each contains about 16 per cent. of nitrogen. *Wheaten Flour* (*Farina Triticæ*, B. P.) contains about 72 per cent. of starch and 11 of gluten, as well as sugar, gum, fine bran, water, and ash. The compactness of barley, well seen in Husked or Pearl Barley (*Hordeum Decorticatum*, B. P.), is said to be due to the large amount of vegetable fibrin present. During germination

the fibrin is destroyed; hence, probably, the cretaceous character of malt. *Oatmeal* (*Avena Farina*, U. S. P.) is very rich in albumenoid or flesh-forming constituents, containing nearly 16 per cent.. *Sago* is granulated starch from the Sago Palm. *Tapioca* is granulated starch from the Bitter Cassava. The white translucent grains known as Rice are the husked seeds of *Oryza sativa*. Rice (*Oryza*) and the Flour of Rice, or Ground Rice (*Oryza Farina*), are official in the Pharmacopœia of India. Rice is quite a staple article of food in tropical countries. Ground rice resembles flour of wheat in composition, but contains from 85 to 90 per cent. of starch.

Mucilage of Starch.—Mix two or three grains of starch with first a little and then more water, and heat to the boiling-point; mucilage of starch (*Mucilago Amyli*, B. P.) results. 1 part of starch to 200 of water gives *Gelatinized Starch*, U. S. P.

This mucilage or paste is not a true solution; by long boiling, however, a portion of the starch becomes dissolved. In the latter case the starch probably becomes somewhat altered.

Chemical Test.—To some of the mucilage add a little free iodine; a deep blue color is produced.

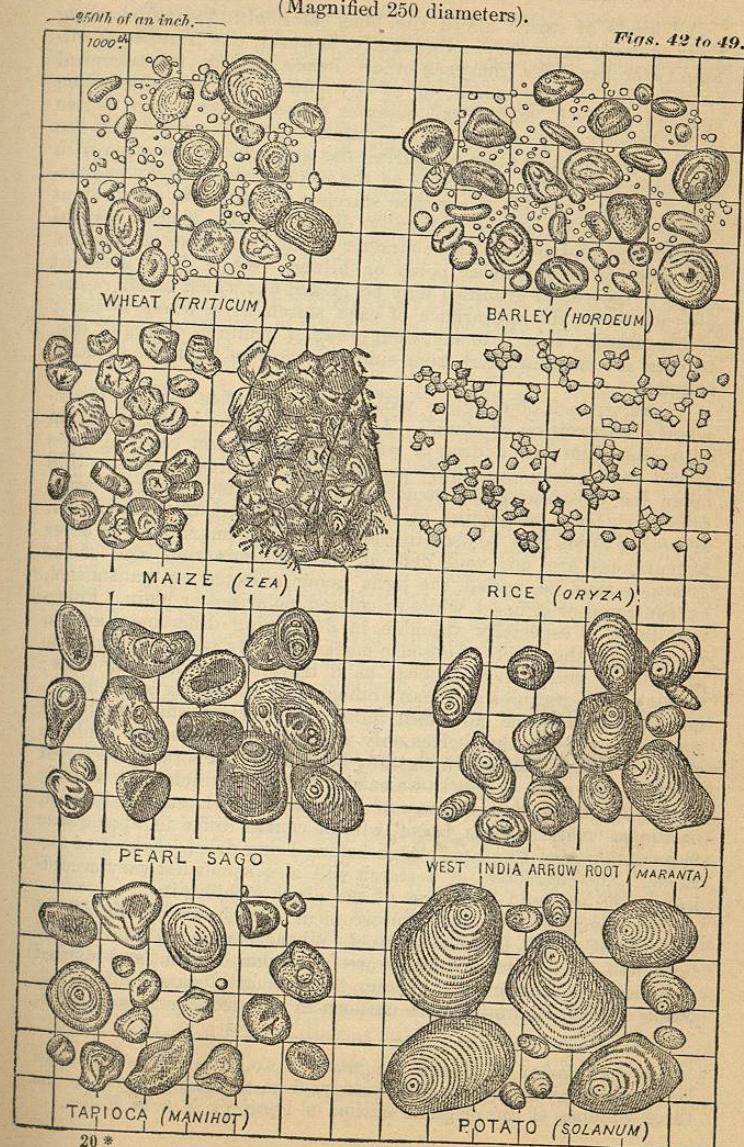
This reaction is a very delicate test of the presence of either iodine or starch. The starch must be in the state of mucilage; hence in testing for starch the substance supposed to contain it must be first boiled with water. The solutions used in the reaction should also be cold, or nearly so, as the blue color disappears on heating, though it is partially restored on cooling. The iodine reagent may be iodine-water or tincture of iodine. In testing for iodine, its occurrence in the free state must be ensured by the addition of a drop, or even less, of chlorine-water. Excess of chlorine must be avoided or chloride of iodine will be formed, which does not color starch.

The so-called *iodide of starch* scarcely merits the name of a chemical compound, the state of union of its constituents being so feeble as to be decomposed at 100° F. Substances that attack free iodine remove that element from iodide of starch. The alkalis, hydro-sulphuric acid, sulphurous acid, and other reducing agents destroy the blue color. With nitric acid starch yields an explosive compound (*Xyloidin*) $C_{12}H_{16}(NO_2)_4O_{10}$.

Composition of Starch-Granules.—Starch-granules consist mainly of *granulose*, soluble in cold water and giving an indigo color with iodine, and *starch cellulose*, insoluble in water and giving with iodine a dirty-yellow color, with, possibly, other carbohydrates. The starch cellulose forms an external coating upon the granule, and also exists mixed with the granulose inside the granule. If this coating be broken by mechanical means, the continued application of cold water will remove all the granulose, leaving the cellulose insoluble. By the action of diastase, ptyalin, and other ferments, and by other means, the granulose may be converted into sugar and dextrin, leaving the starch cellulose unacted upon.

STARCHES

(Magnified 250 diameters).



Microscopical Examination of Starches.

All kinds of starch afford the blue color with iodine, showing their chemical similarity. Physically, however, the granules of different starches differ from each other; hence a careful microscopical examination of any starch, or of any powder or vegetable tissue containing starch, enables the observer to state, with a high degree of probability, the source of the starch—either at once if he has much experience, or after comparing the granules in question with authentic specimens. A glance at the accompanying eight engravings* (Figs. 42 to 49) of common starches will show to what extent different starch-granules naturally differ in size, shape, general appearance, distinctness and character of the rugæ, and position of the more or less central point or hilum. While from different starches individual granules may be picked out which much resemble each other, the appearance of each starch as a whole is fairly characteristic; that is to say, each *group* of granules differs in one, two, or several characters from similar *groups* of granules of other starches.

A quarter-inch object-glass will commonly suffice for the microscopical observation of starch. A very little of the starch is mixed on a glass slide with a drop of water, a piece of thin covering-glass placed on the drop and gently pressed, so as to provide a very thin layer for observation. Instead of water, diluted spirit of wine, diluted glycerin, turpentine or other essential oil, Canada balsam, and other fluids may be used in cases where the markings or other appearances are not well defined. The illumination also of the granules may be varied, the light being reflected or transmitted, concentrated or diffused, white or colored, polarized or plain. Polarized light is especially valuable in developing differences and in intensifying the effects of obscure markings. By polarized light the granules of potato-starch appear as if traversed by a black cross; wheat starch-granules and many others also peculiarly and characteristically influence polarized light. Distinctive characters will sometimes present themselves only when the granules are made to roll over in the fluid in which they have been temporarily mounted or when the slide is gently warmed. Starches which have already been subjected to the influence of heat, partly, as in sago or tapioca, or almost entirely, as in bread, will of course differ in appearance from granules of the same starch before being dried, cooked, or torrifed. The characters of a starch will also somewhat vary according to the age and condition of the plant yielding it.

The description of the microscopical characters of the official varieties of starch is as follows: 1. Wheat starch: A mixture of large and small granules, which are lenticular in form, and marked with faint concentric striæ surrounding a nearly central hilum. 2. Maize starch: Granules more uniform in size, frequently polygonal,

* By permission of Messrs. Longmans & Co. these engravings have been copied, with very few modifications, from the plates in two of the three volumes of the original edition of Pereira's *Materia Medica*.

somewhat smaller than the large granules of wheat starch, and having a very distinct hilum, but without evident concentric striæ. 3. Rice starch: Granules extremely minute, nearly uniform in size, polygonal, hilum small and without striæ.

(For plates and descriptions of the characters of other starches occurring in plants used for medicinal purposes, the reader is referred to works on *Materia Medica*, and to the indexes of Journals of Pharmacy, as well as to general works and magazines on microscopy. For engravings of starch-granules *in situ*, vide Berg's *Anatomischer Atlas*, published by Gaertner, Berlin.)

The student may place fair confidence in the accompanying lithographs, and in most of the published engravings of starch-granules; but in microscopical analyses of importance the worker should, if possible, himself obtain actual specimens of starches for comparison from the respective seeds, fruits, and other tissues.

Inulin ($C_6H_{10}O_5$) is a white powder apparently occupying the place of starch in the roots of many plants, especially those of the natural order *Compositæ*. 20 to 45 per cent. has been obtained from elecampane (*Inula helenium*). It is also contained in the dahlia, colchicum, arnica, dandelion, chicory, artichoke, etc. It is soluble in boiling water, nearly all being redeposited on cooling. Iodine turns it yellow. Long ebullition converts it into a kind of gum. Like starch, inulin is convertible into sugar, but by its own special ferment, the existence of which, in the Jerusalem artichoke, has been demonstrated by Professor J. R. Green. It differs from diastase in being without the power of converting starch into sugar.

Lichenin ($C_6H_{10}O_5$) is a white, starch-like powder largely contained in many lichens—Iceland "moss," *Cetraria islandica*, and many others. It is soluble in boiling water, and the fluid gelatinizes on cooling. It may be precipitated from its aqueous solution by alcohol. With iodine it gives a reddish-blue color.

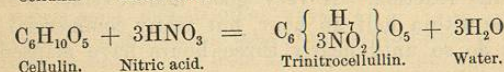
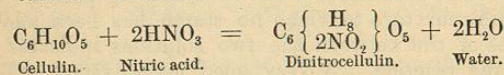
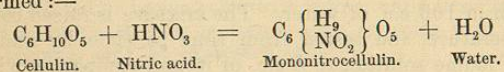
Glycogen, or *animal starch*, is the name given to the solid matter stored in the liver, and resulting from the dehydration of the digested hydrated food which has been carried to the liver by the portal vein.

Dextrin.—Mix a grain or two of starch with about half a test-tubeful of cold water and a drop or two of sulphuric acid, and boil the mixture for a few minutes; no mucilage is formed, and the liquid, if sufficiently boiled, yields no blue color with iodine; the starch has become converted into *dextrin* and some sugar. Dextrin is also produced if starch is maintained at a temperature of about 320° F. for a short time. Dextrin is now largely manufactured in the latter way, and a paste of it is used by calico-printers as a vehicle for colors; it is termed *British gum*. The change may also be effected by *diastase*, a peculiar ferment existing in malt. Mix two equal quantities of starch with equal amounts of water, adding to one a little ground malt; then heat both slowly to the boiling-point: the mixture without malt thickens to a paste or pudding; that

table Jelly ($C_{32}H_{40}O_{28}, 4H_2O$), is the body which gives to expressed vegetable juices the property of gelatinizing: it forms the chief portion of Irish or Carrageen "Moss" (*Chondrus crispus*). Ceylon "Moss" (*Gracillaria lichenoides* and *G. confervoides*, P. I.) contains from one-third to three-fourths of vegetable jelly.

The mucilage of marshmallow-root (*Althea officinalis*) and of linseed or common flaxseed (*Linum usitatissimum*) is a gum-like substance containing much mineral matter. It is the basis of the infusions termed *mallow tea* and *linseed tea*. Somewhat similar mucilage occurs in infusion of bael; it is also largely yielded by the seeds of the quince (*Cydonium*, U. S. P.), as well as by the bark of the Red or Slippery Elm (*Ulm Fulva*) (*Ulmus*, U. S. P.). *Salep*, the powdered dried tubers of many species of *Orchis*, contains a large quantity of such matter. *Squill* also. The Indian Okra (*Hibisci Capsula*, P. I., from *Hibiscus esculentus*) and *Ispaghul* or *Spogel* seeds (*Ispaghula semina*, P. I., from *Plantago ispaghula*) also appear to contain a considerable quantity. In *Sassafras-pith* (*Sassafras Medulla*, U. S. P.) starch and much mucilage occur.

Cellulin or *cellulose*, the woody fibre of plants, familiar, in the nearly pure state, under the forms of "cotton-wool" (*Gossypium*, U. S. P., hairs of the seed of various species of *Gossypium*), paper, linen, and pith, is another substance isomeric, probably polymeric, with starch. Lignin is a closely-allied body, lining the interior of woody cells and vessels. By the action of nitric acid of various strengths on cellululin, peroxide of nitrogen (NO_2) is substituted for one, two, or three atoms of hydrogen—mono-, di-, or trinitrocellulin being formed:—



Trinitrocellulin is highly explosive gun-cotton; dinitrocellulin is not sufficiently explosive for use instead of gunpowder; mononitrocellulin is scarcely at all explosive. The heat of a water-bath may explode trinitrocellulin, but not dinitrocellulin, if pure. The three movable atoms of hydrogen in cellululin may be displaced by bodies other than peroxide of nitrogen.

Dinitrocellulin (*Pyroxylinum*, U. S. P.).—Mix 6 parts of sulphuric acid and 5 of nitric in an earthenware mortar. When cooled to about $32^\circ C.$ ($90^\circ F.$), immerse 1 part of cotton-wool in the mixture, and stir it with a glass rod so that it is thoroughly and uniformly wetted by the acids. Macerate for about ten hours, or until a sample washed with water and then with alcohol is soluble in a mixture of 1 vol.

of alcohol and 3 of stronger ether. Transfer the cotton to a vessel containing a considerable volume of water, stir it rapidly and well with a glass rod, decant the liquid, pour more water upon the mass, agitate again, and repeat the affusion, agitation, and decantation until the washing ceases to give a precipitate with chloride of barium or to taste acid. Drain the product on filtering-paper, and dry on a water-bath.

Pyroxylin may also be made by soaking 7 parts of white filtering-paper, which has been washed in hydrochloric acid and dried, in a mixture of 140 parts of sulphuric acid (sp. gr. 1.82) and 70 of nitric acid (1.37) for three hours, and well washing the product (Guichard).

Mononitrocellulin and *trinitrocellulin* are insoluble in a mixture of alcohol and ether; *dinitrocellulin* or *pyroxylin* is soluble, the solution forming ordinary collodion (*Collodium*, U. S. P.). The official proportions are 4 parts of pyroxylin dissolved in a mixture of 70 of stronger ether and 26 of alcohol. After digesting for a few days the liquid is decanted from any insoluble matter and preserved in a well-corked bottle. It is a colorless, highly inflammable liquid, with ethereal odor, which dries rapidly upon exposure to the air, and leaves a thin, transparent film, insoluble in water or rectified spirit. Flexible collodion (*Collodium Flexile*, U. S. P.) is a mixture of collodion (92 parts), Canada balsam (5 parts), and castor-oil (3 parts). *Blistering Collodion* (*Collodium Vesicans*, B. P.) is a solution of pyroxylin in acetic ether containing the active blistering principle of cantharides. A *Styptic Collodion* (*Collodium Stypticum*, U. S. P.) is also official.

Tunicin, or animal cellulose, is extracted from ascidians and cynthians.

Isomerism.—Allotropy.—Polymorphism.

The composition of dextrin is represented by the same formula as that of starch—namely $C_6H_{10}O_5$ —for it has the same percentage composition as starch. Inulin (p. 466) and cellulose (p. 468) have also a similar formula. There are many other bodies similar in centesimal composition, but dissimilar in properties; such substances are termed *isomeric* (from *ἴσος*, *isos*, equal, and *μέρος*, *meros*, part); and their condition is spoken of as one of *isomerism*. There is sometimes good reason for doubling or otherwise multiplying the formula of one of two *isomers*, *isomerides*, or isomeric bodies. Thus a molecule of ethylene (olefiant gas), the chief illuminating constituent of coal gas, is represented by the formula C_2H_4 , while a molecule of amylene, an anæsthetic liquid hydrocarbon, obtained from amylic alcohol, though having the same percentage composition as olefiant gas, is represented by the formula C_5H_{10} ; for amylene, when gaseous, is about twice and a half as heavy as ethylene, and must contain, therefore, in each molecule, twice and a half as many atoms, for (Avogadro) these equal volumes must contain equal numbers of molecules; its formula is consequently constructed to represent those proportions. (Read again pages 36 to 56.) This variety of isomer-

ism is termed *polymerism* (from *πολύς*, *polús*, many or much, and *μέρος*, part). Metastannic acid (*vide* p. 240) is a polymeric variety, or *polymeride*, of stannic acid. An illustration of a second variety of isomerism is seen in the case of cyanate of ammonium and urea, bodies already alluded to in connection with cyanic acid. These and several other pairs of chemical substances have dissimilar properties, yet are similar not only in elementary composition and in the centesimal proportion of the elements, but also in the fact that each molecule possesses the same number of atoms. But the reactions of these bodies indicate the probable nature of their construction; and this is shown in their formulæ by the disposition of the symbols. Thus cyanate of ammonium is represented by the formula NH_4CNO , urea by $\text{CO}(\text{NH}_2)_2$. Such bodies are termed *metamerie* (from *μετά*, *meta*, a preposition denoting change, and *μέρος*), and their condition spoken of as one of *metamerism*. Acetate of ethyl (p. 404) is metamerie with butyric acid (p. 493), for they have the same percentage composition and their vapors have the same specific gravity, and each therefore might be represented by the formula $\text{C}_4\text{H}_8\text{O}_2$; but their properties warrant us in assuming that their atoms occupy different positions in the two molecules—justify us in giving $\text{CH}_3\text{CO.OC}_2\text{H}_5$ as a picture of a molecule of acetate of ethyl, and $\text{C}_3\text{H}_7\text{COOH}$ as a picture of a molecule of butyric acid. Acetate of methyl ($\text{CH}_3\text{COO.CH}_3$), propionic acid ($\text{C}_2\text{H}_5\text{COOH}$),* and formate of ethyl ($\text{H.CO.OC}_2\text{H}_5$) are isomers of the metamerie variety, or *metamerides*; also quinine and quinidine, cinchonine and cinchonidine, and many of the volatile oils, etc. The isomerism of starch and dextrin may be of a polymeric or of a metamerie character; but we do not yet know which, and must therefore at present give them identical formulæ, though it is most probable that many of the carbohydrates are multiples of the mere empirical formulæ, since dextrin ($\text{C}_6\text{H}_{10}\text{O}_5$)_x by hydration produces maltose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, which would point to the formula of dextrin as being at least ($\text{C}_6\text{H}_{10}\text{O}_5$)₂. Substances similar in composition and constitution, yet differing in properties, are termed *allotropic* (*ἄλλος*, *allos*, another; *τρόπος*, *tropos*, condition). Thus ordinary phosphorus, kept at a temperature of about 450° F. in an atmosphere from which air is excluded, becomes red, opaque, insoluble in liquids in which ordinary phosphorus is soluble, oxidizes extremely slowly, and only ignites when heated to near 500° F. (red or amorphous phosphorus). A black allotropic variety of phosphorus is known. There are also three *allotropes* of carbon which are respectively crystalline, graphitic, and amorphous. Sulphur may be obtained in the viscous as well as in the hard, brittle condition. Another illustration of *allotropy* is seen in the varieties of tartaric acid, which have different optical properties, but otherwise are identical; they are in neither of the above-mentioned states of isomerism, but are allotropic modifications of the same substance. Occasionally one and the same substance crystallizes in two distinct forms; its state is then described as one of *polymorphism* (*πολύς*, *polus*, many;

* For explanation of formulæ, see chapter on Aldehydes and Acids.

μορφή, *morphe*, form). Sulphur is polymorphous. It crystallizes by slow cooling in (1) prismatic crystals of sp. gr. 1.98, while in nature it occurs in (2) octahedra of sp. gr. 2.07. Melted and poured into water, sulphur takes up (3) the form of caoutchouc of sp. gr. 1.96. These differences warrant the statement that sulphur occurs in three distinct allotropic conditions. Possibly, such conditions result from the association of different numbers of atoms in the molecule of the element; that is, allotropic bodies may simply be *physically polymeric*, or in some other way be mere *physical isomerides*.

QUESTIONS AND EXERCISES.

774. How is wheat-starch or potato-starch isolated?
775. Define gluten and gluten.
776. Enumerate the proximate principles of wheaten flour.
777. Is starch soluble in water?
778. Which is the best chemical test for starch?
779. Distinguish physically between the varieties of starch.
780. Into what compound is starch converted by heat?
781. What occurs when a mixture of starch and water is allowed to flow into hot diluted sulphuric acid?
782. If two equal amounts of starch with water be heated, one containing a small quantity of ground malt, what effects ensue?
783. Write a short article on the chemistry of malting.
784. What is the nature of gum arabic? and how is it distinguished from "British gum"?
785. Mention the properties of the products of the action of nitric acid of various strengths on cellulose.
786. How is pyroxylin prepared?
787. Explain *isomerism*, giving several illustrations.
788. Give examples of polymeric bodies.
789. State the formula of a body metamerie with urea.
790. Define allotropy and polymorphism, giving illustrations.

ALDEHYDES AND ACIDS.

General Formation.—The aldehydes and acids may be artificially formed by oxidation of the primary alcohols, glycols, etc. Monohydric alcohols, having only one hydroxyl (OH) group, form monobasic acids, dihydric alcohols (glycols), having two hydroxyl groups, yield monobasic and dibasic acids; and so on. Thus:—

