

The Glucosides.

BY MR. J. C. UMNEY.

THE author defined glucosides as bodies which, under the action of ferments, of dilute acids, or in some cases of electricity, split up into one or more molecules of glucose, and a second non-saccharine substance. They were not esters, but ethers, of the glucoses, derived from the combination of the latter with other hydroxyl compounds. The classification still adopted was that introduced in 1867, namely, substances yielding one or two molecules of true glucose, phloroglucosides, compounds containing mannite, and glucosides containing tannin.

The author proposed to deal consecutively with the constitution, methods of preparation, decompositions, general characters and reactions, and occurrence in plants of glucosides, followed by an epitome of the features of the glucosides most interesting pharmaceutically.

CONSTITUTION.

Glucosides were compound ethers containing the group $C_6H_{12}O_6$, which was turned out on hydrolysis. Their constitution was by no means simple. Attempts have been made to synthesise them with partial success; phenol glucoside had been prepared, for instance. Naturally, glucosides were neutral bodies, though there were exceptions; some were acid, salicin was basic, and almost alkaloidal; the sugar was mostly glucose. In some cases sugars were separated, which were considered peculiar, but they were shown later to be ordinary dextro-glucose. The second body which results from the splitting up of the glucoside was, in some cases, a hydrocarbon, sometimes an alcohol or aldehyde or phenol, whilst in many cases the chemical nature of the decomposition product had not been correctly determined.

METHODS OF PREPARATION.

The author mentioned five methods as follows:—(1) Extraction with alcohol alone when the glucoside was in the free state with little tannin; (2) The lime process; (3) The litharge method, not always suitable, as it involved long boiling, which converted some glucosides into resinoid bodies; (4) Precipitation with subacetate of lead and separation of the glucoside from the lead compound formed; and (5) The mixed method adopted when the plant contains much tannin, or the application of sulphuretted hydrogen is contra-indicated. The author did not describe the processes, as they are well known, and detailed in the text books.

DECOMPOSITION.

The characteristic splitting up of these bodies could be accomplished by high temperatures, dilute acids, ferments, or, in some instances, by electrolysis. *Esculin* and *salicin* could be split up at 170° and 240° C. respectively, while *arbutin* was unaffected. Others were decomposed by prolonged heating with water only. Of dilute acids, hydrochloric and sulphuric

were effective, but not equally so; saponin was readily split up by hydrochloric acid, but not at all easily by sulphuric acid. In some cases organic acids could affect the decomposition. Alkalies were also able to determine the dissociation, but when the alkali was strong the sugar first formed was decomposed further. With respect to the effect of ferments, it might take place at ordinary or elevated temperatures. Emulsin decomposed *amygdalin* with which it was associated in the almond, but also *salicin* and *esculin*, though the effect was less complete than that of dilute acids. The ferment of saliva, *myrosin* (found in mustard seed), the bacteria of alcoholic and of lactic fermentation, were also effective dissociators of glucosides. The action of such bodies on a glucoside could not, however, be prejudged by analogy. *Salicin* was easily decomposed by emulsin, while *benzoyl salicin* could not be. *Amygdalin* was not decomposed by the digestive ferments, but its poisonous action was probably due to ferments producing putrescent decomposition in the intestines.

By the use of 450 Bunsen elements *salicin* had been decomposed, and *amygdalin* split up into benzoic aldehyde, prussic acid, and a small quantity of ammonia.

GENERAL CHARACTERS AND REACTIONS.

The majority of glucosides contained carbon, hydrogen, and oxygen; some included nitrogen in the molecule and a few sulphur. Many were difficult to isolate in a state of purity, but when thus obtained, crystalline. Glucosides were characterized by a marked insolubility in ether, and most, but not all, reduced alkaline copper solution on boiling. Some coagulated when the aqueous solution was heated with ammonia. They might be distinguished by the property of splitting up when heated with dilute acids, by the reduction of copper solution, by precipitation of molybdate of ammonia, slightly acidulated with hydrochloric acid. Many glucosides when treated with benzoic chloride gave very stable benzoyl compounds.

OCCURRENCE IN PLANTS.

It had been maintained the glucosides were the first assimilation products of the activity of chlorophyll. This theory had more recently received support from further research. Certain acids of a glucosidal nature did occur in unripe fruits, but disappeared in the process of ripening. The weight of evidence was in support of the view that adopted by Sachs that starch and not the glucoside must be considered the first assimilation product of plants. Liebig promulgated the theory that carbon dioxide is converted into carbohydrate by the condensation of the molecule with water, but Bayer formed the hypothesis that carbonic oxide is first reduced to formic aldehyde, six molecules of which condense to form sugar in the presence of some body not yet determined. He assumes that under favorable conditions the molecule of glucose may lose

three molecules of water forming a body isomeric with phloroglucinol.

The author had drawn up a table showing the approximate constitution of those glucosides already determined.

PHARMACEUTICAL GLUCOSIDES.

Esculin obtained from the bark of the horse-chestnut (*Esculus hippocastanum*), from the root bark of *Gelsemium semper-virens* and other plants. Soluble in hot water and alcohol, it crystallises in fine needles. The aqueous solution exhibits a fine blue fluorescence, which is destroyed by acids. It is decomposed by boiling hydrochloric acid, or by heat alone at 236° C. into glucose and *esculetin*.

Amygdalin occurs in the bitter almond and in an amorphous modification in the cherry laurel. Woehler and Liebig showed (1837) that both bitter and sweet almonds contained emulsin, which in the presence of water is capable of splitting up the glucoside. The dissociation was affected by pure water alone at 150° C.

Arbutin was first discovered in 1852. It is found in many plants of the Ericaceae, and is always contaminated by methylarbutin. It crystallises in fine needles with a bitter taste, and when boiled with dilute acids splits up into hydroquinone and glucose; methylarbutin is resolved in methylhydroquinone.

Carminic acid was found not only in the insect (*Coccus cacti*), but in the leaves of *Monarda spec.* and a few other plants. Boiled with dilute sulphuric acid it separated into carmine red—a dark red mass, soluble in water and alcohol—and an unfermentable sugar.

Chinovin.—The *a* variety is obtained from cinchona barks, and the *B* from cupreas. By hydrochloric acid *chinovin* is resolved into *chinovic acid*, and a sugar $C_6H_{12}O_4$, which is dextrogyre and not fermentable by yeast. The work of Dr. Passmore upon *B-chinovin* had shown it to be a mixture of dextro-glucose and another body.

Coniferin was obtained from species of *Abies*, *Pinus* and *Larix*. By means of emulsin it can be resolved into sugar and another crystallisable body, and by the oxidation of this second substance (or of *coniferin* itself) *vanillin* was obtained.

Convallarin was obtained from the lily of the valley, where it was associated with *convallamarin*.

Crocin, the peculiar glucoside of saffron was split up by dilute acids into another coloring matter and sugar. The latter was dextrogyre, and had only half the reducing power of dextro-glucose.

Daphnin, isomeric with *esculin*, yielded glucose and *daphnetin* or *dioxy coumarin*.

Digitalin.—The active constituents of digitalis were partly glucosidal. According to Schmiedeberg, pure digitalin was only one constituent of the commercial article. *Digitalcin* was an amorphous yellow substance, soluble in water.

Frangulin, by the action of dilute acids, was hydrolysed into glucose and *frangulic acid*, probably isomeric with *alizarin*, and found to give the same reactions as emio-