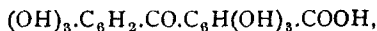


NOTES AND COMMENTS.

CHEMISTRY.

THE CHEMISTRY OF TANNINS—C. Etti (*Monatsh*, **10**, 647 and 805, through *Journal of Society of Chemical Industry*).—The results of previous investigations have shown that the tannin $C_{17}H_{16}O_8$ obtained from *Quercus robur* L, and that obtained from *Quercus pubescens* W, occur in the oak bark not only in the form of tannic acid, but also as the anhydride; it was also found that the tannic acids, which are almost insoluble in water, do not occur in combination with a sugar, and are not therefore glucosides; their basis is not tannin, but a substance isomeric therewith, namely, a ketone acid (gallylgallic acid) of the constitution—



formed from two molecules of gallic acid with elimination of one molecule of water.

In this paper the author gives an account of experiments, which show that the tannic acid $C_{16}H_{14}O_8$ is a derivative of the ketone acid referred to above; as this tannic acid closely resembles the acids previously investigated both in physical and chemical properties, it follows that they also are derivatives of the same ketone acid.

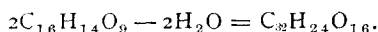
The greater part of the sparingly soluble ketone tannic acid occurs in the plant in combination with a metallic base, probably magnesium, and as these salts are very readily soluble in water, they can be easily and completely extracted. After concentrating the aqueous extract and acidifying with hydrochloric acid, the tannic acid is precipitated in an insoluble condition, and can be washed free from hydrochloric acid and then purified by extracting with alcohol or ether. The most suitable source of these acids are the commercial extracts, which are obtained from the bark and wood of various trees and largely used in tanning.

The author has isolated the following tannic acids by the method described above. An acid of the composition $C_{16}H_{14}O_8$ from the extract obtained by the Oak Extract Company in Slavonia, from the wood of the stalk-oak. An acid of the composition $C_{18}H_{18}O_9$ from the oak-bark used in a tannery at Pesth. An acid $C_{20}H_{22}O_9$ obtained from the bark of the copper-beech in the neighborhood of Salzburg. An acid of the composition $C_{22}H_{26}O_9$ from the hop cones obtained from Saaz. All these tannic acids have a different color, varying from brownish-red to bright red; those obtained from the stalk-oak and holm-oak give in dilute alcoholic solution a deep blue, the others, however, a green coloration with ferric chloride. It seems that all the tannic acids obtained from the oak are simply different derivatives of the same ketone tannic acid.

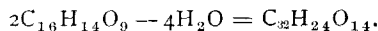
The tannic acid $C_{16}H_{14}O_8$ is a brownish-red amorphous compound; under the microscope it is seen to consist of small spherical nodules, which

are all so much alike that the presence of impurities can be easily detected. It is almost insoluble in water and ether, but readily soluble in alcohol and acetone. Its solution in dilute alcohol has an acid reaction, gives a precipitate with lead acetate and a dark blue coloration with ferric chloride. The formation of the phenylhydrazine-derivative, $C_{22}H_{26}N_2O_8$, and the oxime, $C_{16}H_{15}NO_9$, proves that the acid contains a ketone group.

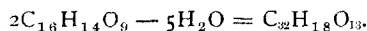
When the acid is heated with dilute sulphuric acid at 120° – 130° , it gives gallic acid (m. p. 238° – 240°) and a large quantity of insoluble anhydro-derivatives. It forms a soluble neutral salt and several very sparingly soluble basic salts with magnesium. When heated alone at 130° – 135° , or at 100° , with water in sealed tubes, or when boiled with hydrochloric or dilute sulphuric acid, it yields various very stable anhydrides, a property which is especially characteristic of the ketone tannic acids, and serves to distinguish them from tannin. When the acid is boiled with dilute (1–10) sulphuric acid, for example, as long as a red precipitate is produced it is converted into an acid anhydride, $C_{32}H_{24}O_{18}$, according to the equation—



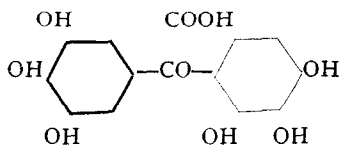
When heated at 120° – 130° , under the same conditions, it gives two anhydrides. The one is soluble in ninety-six per cent. alcohol and is formed according to the equation—



The other is insoluble in ninety-six per cent. alcohol, and no longer contains a carboxyl group, its formation being expressed thus:



These experiments show that the tannic acid contains four hydroxyl groups; its behavior with hydrochloric and with hydriodic acid shows that it contains two methoxy groups. The acid, $C_{16}H_{14}O_9$, is therefore a dimethyl derivative of a ketone acid of the constitution—



but the position of the two methoxy groups has not yet been determined.

H. T.

ON A NEW REACTION OF TANNIN—Dr. Carl Böttinger (Liebig's *Annalen*, No. 256, p. 341).—When tannin and phenylhydrazin are boiled together in watery solution in the proportion of 2 to 1 or better 1 to 1, or heated to 100° in the proportion of 1 to 2, with exclusion of water, a solution is effected, there occurs an evolution of gas, and a mixture of several bodies is formed. Some of these bodies are soluble in ether and some are not, the latter are not completely soluble in sodium hydrate solution, the ether-alcohol solution of the former is quickly decolorized by zinc dust and hydrochloric acid.