

THE ACID OF WILLOW BARK.

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THE chemistry of the willow seems to have been little studied, and what attention it has received has been almost entirely devoted to its active principle, salicin. All the information I have been able to obtain regarding the constituents of the bark is very meagre, the majority of works on chemistry and materia medica merely mentioning that salicin is extracted therefrom; while, curiously enough, the 'Pharmacographia' of Flückiger and Hanbury omits all notice of the subject. Neligan states (authority not given) that the bark contains resinous matter, gum, chlorophyll, tannin, an organic salt of magnesia, and salicin; and that is as complete an account as I have found in any of the other books.

When an infusion of willow bark is made, the liquor is distinctly acid to litmus. In the preparation of salicin by Erdmann's process this acid is neutralised by the excess of lime, and the salt thereby formed passes into solution. On evaporating to dryness and exhausting the residue with spirit the salt is redissolved and remains in the spirituous solution after the salicin has crystallized out. The salt may be obtained by distilling off the spirit and allowing the residue to crystallize. These crystals are then purified by recrystallization from water. Thus prepared the lime-salt separates in the form of a cauliflower-like mass composed of radiate groups of prismatic crystals.

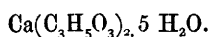
A portion of these crystals when heated fused, and inflamed, left a residue of calcic carbonate, indicating an organic salt of lime. It was found that the substance lost weight but slowly in the exsiccator, and likewise in the water-bath. A portion of the

air-dried salt was therefore dried in the air-bath at 130°C . 9.140 grs. lost 2.745 grs. = 30.03 per cent. In another determination with a different crop of crystals 7.85 grs. lost 2.275 grs. = 28.98 per cent. A quantity of the salt was then incinerated in a platinum crucible, the residue being treated with excess of sulphuric acid and the crucible again ignited. 6.41 grs. gave 4.00 grs. $\text{CaSO}_4 = 1.176$ grs. $\text{Ca} = 18.34$ per cent. In the second determination 6.12 grs. gave 3.82 grs. $\text{CaSO}_4 = 1.12$ grs. $\text{Ca} = 18.35$ per cent.

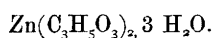
One or two methods for preparing the acid were tried, the following being the process finally adopted:—To a solution of the lime-salt in water solution of oxalic acid is added—not in excess. The precipitate is then separated by filtration, the filtrate concentrated and extracted with ether, which dissolves the acid. The ether being now driven off, a syrupy solution of the acid is left. A few ounces were prepared by this method and placed over sulphuric acid under a bell-glass for two days. The acid then remained in the form of a syrup, almost odourless, with an intensely sour taste. As in these respects it exactly resembled lactic acid, and seeing that the calcium salt in its crystalline form and in its percentages of H_2O and Ca corresponded with calcic di-lactate, there could be little doubt that the acid under examination was lactic acid. To make more certain, however, some further tests were applied. A little was heated in a test-tube, when water and carbonic anhydride were given off, and a residue left which shortly solidified. A portion was then boiled with sulphuric acid, which liberated an inflammable gas burning with a blue flame—no doubt carbon monoxide. When a small quantity was heated with sulphuric acid and manganese dioxide, a vapour smelling like aldehyde was evolved. A portion of the acid was distilled and the fraction coming over and above 130°C . was evaporated and treated with cold alcohol, which separated small white crystals, having the form of rhomboidal plates, and in other respects resembling lactide.

From the acid as above obtained the zinc-salt was prepared by warming with excess of zinc carbonate, filtering, and allowing to crystallize. The crystals were pressed between blotting paper and exposed for a short time to the air. In these air-dried crystals the H_2O was determined by drying in the water bath; 6.065 grs. lost 1.125 grs. = 18.46 per cent. In a second determination with another crop of crystals 9.275 grs. lost 1.695 grs. = 18.27 per cent. The zinc was determined in the dry salt by ignition in the blow-pipe flame; 6.33 grs. gave 2.12 grs. $\text{ZnO} = 33.49$ per cent. In another determination 7.58 grs. gave 2.55 grs. $\text{ZnO} = 33.64$ per cent.

The above numbers are here compared with those calculated for the normal calcium and zinc salts of lactic acid respectively—



	per cent	I.	Found.	mean.
H_2O	29.22	30.03	28.98.	29.505
Ca	18.34	18.34	18.35	18.345



	per cent.	I.	Found.	mean.
H_2O	18.33	18.46	18.27	18.36
ZnO	33.38	33.49	33.64	33.56

The ZnO is too high, owing either to an impurity in the salt, or to a fault in the analysis;

but I had not time to examine into the matter. The zinc-salt crystallized in four-sided truncated prisms, which were insoluble in alcohol.

I am unable to state from what species of *salix* the acid was prepared, but as all the samples of bark I have examined give acid infusions, it is not improbable that lactic acid exists in all the members of the Salicaceæ.
