

tion, and HCN is evolved, which in its turn attacks the zinc plates, or anodes, and combines therewith to produce additional double cyanide of zinc and potassium— ZnK_2CN_4 .

Thus, the solution during passage through the box is deprived of its copper, the place of the double cyanide of copper and potassium being taken for an equivalent amount of the double cyanide of zinc and potassium, from which latter salt the cyanide may readily be obtained in the available form of free potassium-cyanide by the method explained previously in Case 1.

Should it be desired to ship the cyanogen product to market, it is shipped readily as the simple zinc-cyanide $ZnCy_2$, the precaution being taken to pack it, while damp, in airtight cases. When allowed to dry much of it is converted to carbonate. To make the $ZnCy_2$ available for gold-extraction purposes it is, as previously explained, dissolved in a caustic alkali, the excess of zincate of soda or potash being removed by addition of an alkaline sulphide.

N.B.—It is advantageous, to promote perfect precipitation both in the precipitation of the cyanides with zinc salt and in the precipitation of the zinc as ZnS , and in the electrical precipitation of the copper and bullion, to cause active circulation, which is best occasioned by the employment of compressed air.

In the electrical precipitation-box the distance between cathode and anode should be $\frac{1}{2}$ in. Beginning with a thick plate of zinc and a very thin sheet of copper, you end with a thin frayed sheet of zinc and a thick plate of copper containing small amounts of bullion.

ART. XLIII.—*Studies on the Chemistry of the New Zealand Flora.*

By THOMAS H. EASTERFIELD, Professor of Chemistry in the Victoria College, and B. C. ASTON, Chemist to the Department of Agriculture.

[Read before the Wellington Philosophical Society, 2nd September, 1903.]

PART III.—RIMU-RESIN.

THE wide distribution of resinous substances in the vegetable kingdom naturally raises three questions: (1.) What is the function of resins in the plant-economy? (2.) What is the chemical origin of the resins? (3.) Are all the plant-resins closely related from the chemical standpoint? It is in the hope of finding evidence which may help in arriving at an

answer to these questions that the present investigation has been commenced.

The rimu (*Dacrydium cupressinum*) is one of the best known and most widely used of the New Zealand forest-trees; its timber is highly resinous, and the heart-shakes, which are frequently large, contain an opaque pinkish resin which may completely fill the cracks or only occur in warty globules having a concentric structure.

Rimu-resin dissolves for the most part in alcohol, but leaves a small residue of a red amorphous substance, which has a bitter and astringent taste. If water be added to the alcoholic solution until a faint turbidity results, and the solution be allowed to stand for some hours, the greater part of the resin separates in the form of almost colourless hexagonal plates, which can be completely decolourised by recrystallisation from dilute alcohol. The crystalline compound thus obtained is strongly acid, and the name "rimuic acid" is proposed for it.

Rimuic acid is very sparingly soluble in water, benzene, and light petroleum; easily soluble in alcohol, ether, and hot acetic acid. It melts at 192°–193° C., and has the specific rotation $[\alpha]_D = -150^\circ$.

Two preparations of the acid were analysed. The analyses and molecular-weight determinations agree with the formula $C_{16}H_{20}O_8$.

Calculated for $C_{16}H_{20}O_8$.	Found.	
	I.	II.
C = 73.8	... 73.8	73.7
H = 7.7	... 7.9	7.95
O = 18.5		
<hr/>		
M.W. = 260	... 266 and 288 by cryoscopic methods,	264 by titration.

The following salts have been analysed:—

Acid Ammonium Salt— $(C_{16}H_{20}O_8)_2, NH_3, H_2O$.—This salt is sparingly soluble in water; it is readily obtained by saturating a solution of ammonia with the acid, filtering at once, and gently warming the filtrate.

Calculated.	Found.
$NH_3 + H_2O = 6.7$... 6.3
$NH_3 = 3.14$... 3.0

Barium Salt— $(C_{16}H_{19}O_8)_2, Ba, 14 H_2O$.—This most characteristic crystalline salt separates in well-developed square plates when a solution of barium-chloride is added to a solution of the acid in excess of ammonia. Three preparations gave—

Calculated.	Found.		
	I.	II.	III.
H ₂ O = 27·7	... 27·7	27·1	27·7
Ba = 15·1	... 15·8	15·3	15·1

Silver Salt—C₁₈H₁₉O₈, Ag.—An amorphous flocculent precipitate prepared from a solution of the barium salt.

Calculated.	Found.	
Ag = 29·4	29·0 and 29·7

Benzoyl Rimuic Acid.—This compound was prepared by shaking the alkaline solution of rimuic acid with excess of benzoyl-chloride. It is sparingly soluble in cold alcohol; from hot alcoholic solutions it separates on rapid cooling as a transparent jelly, which becomes crystalline on standing.

Calculated for	Found.		
C ₁₆ H ₁₆ O, C ₆ H ₅ CO, CO ₂ H.	75·6
C = 75·8	6·6
H = 6·6

Rimuic acid boils at 296°–300° at 21 mm. By continued heating at 300° it loses water, and is converted into a colourless compound which is no longer soluble in alkalis, ether, or the usual organic solvents, and cannot be distilled without decomposition. Rimuic acid does not yield an ethereal salt when treated with absolute alcohol and hydrochloric-acid gas. It readily forms two crystalline nitro-acids and a sulphonic acid, which will be described in a later paper.

It is of interest to note that *Podocarpus cupressinum*, a tree occurring in Java, contains as the chief constituent of its heart-resin an acid (podocarpic acid) which is so similar to rimuic acid that the two compounds might readily be mistaken for one another. Upon comparison it becomes clear that the two acids belong to the same homologous series—C_nH_{2n-8}OH, CO₂H.

	Rimuic Acid, C ₁₆ H ₂₀ O ₈ .	Podocarpic Acid, C ₁₇ H ₂₂ O ₈ .
M.P.	192–193° C. ...	186–188° C.
[α] _D	–150° ...	+ 136°

The acids differ in the number of molecules of water with which their salts crystallize. The following points of resemblance are remarkable: Both yield sparingly soluble acid ammonium salts which crystallize with one molecule of water. Both yield anhydrides when heated to 300° C. Both yield crystalline mono and dinitro derivatives the acid salts of which are yellow, the normal salts scarlet or crimson. The dinitro derivatives are peculiarly sensitive to the action of light. Both acids, again, dissolve readily in cold concentrated sulphuric acid, and yield sulphonic acids the barium salts of which are sparingly soluble and highly

crystalline. Upon diluting the crude sulphuric-acid solution with water the smell of valeric acid is in each case distinctly perceptible.

The solution of either of the sulphonic acids when warmed with very dilute nitric acid gives a yellow precipitate, the formation of which may be used as a test for nitric acid.

ART. XLIV.—*Note on Interaction of Citric and Sulphuric Acids.*

By JAMES BEE.

[*Read before the Wellington Philosophical Society, 4th November, 1903.*]

DURING the preparation of aconitic acid by Hentschel's method (in which citric acid is heated with a 66-per-cent. sulphuric acid under a reflux condenser) it was found that the yield varied very considerably according to the length of time during which the acids were heated together. If the reaction were carried on for too short a time unchanged citric acid was left behind; if the heating was continued for twelve hours instead of six very little aconitic acid separated from the mixture on cooling; and in a third experiment, in which the materials were heated on a reflux apparatus for twenty-four hours, no crystallization took place after cooling.

It was found that, on pouring off the black liquid from the vessel in which the reaction had taken place, a small black deposit resembling charcoal was left. This turned out to be undecomposed aconitic acid. Suspended in the dark liquid was a flocculent dark-brown precipitate, which was separated from the liquid by straining through a large Buchner filter. From this a little aconitic acid was isolated.

The filtrate was diluted with water and extracted many times with ether. The united residues were recrystallized from glacial acetic acid, whereby aconitic acid was separated. The mother liquors were freed from acetic acid by evaporation with water, the residue taken to dryness and recrystallized from chloroform and acetone. By this means a small quantity of an acid which melted at 206° C. (uncorrected) was obtained. Upon combustion it gave numbers agreeing accurately with those of diconic acid, $C_9H_{10}O_6$.

Calculated for $C_9H_{10}O_6$.		Found.
C = 50.47 per cent.	...	50.49
H = 4.67 "	...	4.56
O = 44.86 "	...	44.95