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

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PART V.—THE CHEMISTRY OF PODOCARPUS TOTARA AND PODOCARPUS SPICATUS.

(1.) PODOCARPUS TOTARA.

IN Part iv of this series (Trans. N.Z. Inst., vol. 43, 1911, p. 55) it was mentioned that a crystalline substance can be extracted by alcohol from totara sawdust.

In a preliminary experiment 150 grams of dry totara sawdust were boiled for two hours and a half with 90 per cent. alcohol, and yielded 18 grams of vacuum-dry resinous extract. About 70 per cent. of the extract was soluble in ether, yielding a light-coloured solution. The residue obtained by evaporating the ethereal solution was amorphous, but yielded beautiful crystals when its solution in light petroleum was allowed to evaporate spontaneously. Thirty kilograms of totara sawdust were then percolated with alcohol, and the extract treated in the same way as in the preliminary experiment, but, owing to the difficulty of treating such a large quantity without special appliances, a smaller percentage yield of dry extract was obtained.

The residue left on evaporating the light petroleum extract of the resin prepared by alcohol can be distilled in a partial vacuum without decomposition, and this is the quickest method of purifying the material. The distillate is a light-yellow liquid, which solidifies to a transparent glass if quickly cooled. The glass may be kept for months without showing any sign of crystallization, but, if it be moistened with light petroleum, crystals rapidly begin to form.

The name "totarol" is proposed for this crystalline substance, since, as will be shown, it is a tertiary alcohol.

Pure totarol melts at 127° C. (corrected); in a 4-per-cent. alcoholic solution the specific rotation $[A]_D = 42{\cdot}08°$, in an 8-per-cent. solution the value is 42·18°. It is insoluble in water and aqueous alkali, intensely soluble in alcohol and ether; 100 grams of light petroleum (b.p. 50°–80°) dissolve 18 grams of totarol at 15° C. A very small quantity of alcohol prevents the substance from crystallizing from light petroleum.

An alcoholic solution of totarol is neutral to phenol-phthalein, and does not react with alcoholic potash, hydrochloric acid, or ferric chloride.

The chemical formula for totarol is $C_{20}H_{30}O$, as shown by the following analyses and molecular-weight determinations:—

I. 0·1057 grams yielded 0·3248 gm. CO_2 and 0·0997 gm. H_2O.
II. 0·1003 ,, 0·3076 ,, 0·0949 ,,
III. 0·1162 ,, 0·3569 ,, 0·1099 ,,

Calculated for $C_{20}H_{30}O$.		Found	
	I.	II.	III.
C = 83·9	83·80	83·64	83·76
H = 10·49	10·48	10·50	10·73

Unless the copper oxide was maintained at a very bright-red heat during the analyses the results found were invariably too low (*cf.* the formula $C_{18}H_{26}O$ assigned in the preliminary note, *loc. cit.*; also Dunstan and Henry, J C S, Proc, 1896, p. 48)

The molecular weight was determined by the cryoscopic method, using glacial acetic acid as the solvent. The values found were 285 and 288. The formula $C_{20}H_{30}O$ requires a molecular weight of 286. No compound of this formula is cited in chemical literature

Acetyl Totarol.

Totarol can be recrystallized without change from acetic anhydride, but upon prolonged boiling an acetyl compound results. Acetylation takes place very rapidly and with considerable evolution of heat if a drop of concentrated sulphuric acid be added to acetic anhydride in which finely divided totarol is suspended The compound is conveniently purified by crystallization from alcohol, and melts at 123°–123·5°. The specific rotation in light petroleum (4-per-cent. solution) $[A]_D = 44{\cdot}6°$.

Calculated for $C_{20}H_{29}O.\ C_2H_3O$.	Found. I.	II.
C = 80·49	80·14	80·15
H = 9·75	9·96	9·92

The substance is perceptibly hygroscopic The molecular weight determined by hydrolysis with alcoholic potash gave the values 331·8, 328·7, and 326·7. The calculated value for the above formula is 328.

The totarol regenerated during hydrolysis had the same melting-point and optical activity as the original totarol

The slow rate at which totarol undergoes acetylation suggests that it is a tertiary alcohol. The same conclusion is to be drawn from the fact that it yields no acid phthalic ester when the benzene solution is boiled with phthalic anhydride, and that no acetyl ester results when totarol is heated with glacial acetic acid in a sealed tube

Oxidation experiments also indicate that totarol is neither a primary nor secondary alcohol Chromic acid in glacial acetic-acid solution attacks totarol very slowly at first; subsequently the action becomes vigorous, and much carbon dioxide is evolved. Unchanged totarol, but no oxidation product, can be isolated after the reaction has ceased. Similarly no acid or ketonic products could be isolated when totarol was oxidized with potassium bichromate and dilute sulphuric acid, though the experiment was tried at various temperatures.

A neutral crystalline oxidation product, but no acid, results when totarol dissolved in pure benzene or purified light petroleum is agitated for some hours with decinormal permanganate solution. The yield is about 20 per cent of the weight of the totarol taken. The substance is readily purified by crystallization from ether, and when pure melts at 205°, at which temperature sublimation commences.

Calculated for $C_{40}H_{60}O_3$.	Found. I.	II.
C = 81·63	81·41	81·47
H = 10·21	10·31	10·29

The formula suggests that during oxidation two molecules of totarol have condensed and an atom of oxygen has been added. Until further evidence as to the constitution of totarol has been obtained it would be useless to speculate on the relationship of the two compounds to each other

Bromine and Iodine Absorption.

Totarol in chloroform solution absorbs bromine very rapidly. At the same time a little hydrobromic acid is evolved Very slight temperature differences make such large differences in the percentage of bromine absorbed that it is impossible to state definitely the number of unsaturated "linkings" in the molecule. The iodine absorption by Wij's method indicates that six atoms of iodine are absorbed by one molecule of totarol Totarol yielded no definite products when submitted to sulphonation and nitration

(2.) PODOCARPUS SPICATUS.

The occurrence of matai-resinol in the heart-cracks of this species has already been reported (Easterfield and Bee, Trans Chem. Soc, 1910, p. 1028). The heart-cracks of old matai-trees frequently contain a considerable quantity of a liquid known as matai-beer The liquid can be tapped by means of an auger, and is said to be eagerly drunk by the bushmen. A sample of matai-beer was kindly procured by Mr Phillips-Turner, Secretary to the Forestry Commission. The liquid was of a light-brown colour; its smell suggested the presence of butyric or caproic acid, and its taste was styptic and sweetish, followed by a bitter after-taste 10 c c of the liquid left on evaporation a brown sticky residue weighing 0·265 gram 10 c.c. required 5 c c $\frac{N}{10}$ sodium hydrate for neutralization Practically the whole of the acidity disappears during evaporation

In a 20 cm. tube the liquid rotated the ray of polarized sodium light 0·64°; this value was unchanged after the liquid had been heated with hydrochloric acid

The liquid instantly reduced Fehling solution in the cold, and gave a silver mirror with ammoniacal silver solution It reduced mercuric chloride slowly on warming. With phenyl hydrazine in acetic acid it yielded a scarlet crystalline precipitate, but the amount obtained was too small for further examination. Ferric chloride produced a greenish-brown tint

For the identification of the volatile acid 250 c.c were distilled with steam The distillate exactly neutralized with ammonia and excess of silver nitrate added. Analysis of the micro-crystalline silver salt showed it to be silver caproate

Calculated for $C_6H_{11}O_2Ag$.	Found I.	Found II
C = 32 28 .	32·49	32·10
H = 4·93 ..	4·81	4·83
Ag = 48·43	49·00	48·66

Caproic acid exists in *Goupia tomentosa* (*Celastraceae* family), a timber-tree used for boatbuilding in British Guiana (Dunstan and Henry, Trans. Chem. Soc., 1898, p. 228), and which is closely allied to the well-known garden shrub *Euonymus*. Its occurrence in other plants does not appear to have been recorded.

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