V.—CHEMISTRY AND PHYSICS.

Art. XLVI.—*Studies on the Chemistry of the New Zealand Flora.*

By T. H. Easterfield, Professor of Chemistry, Victoria College, and B. C. Aston, Chemist to the Agricultural Department.

[*Read before the Wellington Philosophical Society, 5th November, 1901.*]

PART II.—THE KARAKA-NUT.

(Preliminary Note.)

The karaka-tree (*Corynocarpus lævigata*) is endemic to New Zealand and the surrounding islands. It is plentiful in the North Island, but its distribution in the South Island is very limited. It is the largest and commonest of all the trees in the Chatham Islands, where it attains a height of over 50 ft.

The kernel of the karaka-berry is known to be very poisonous in its raw state, but if suitably prepared by cooking and subsequent soaking the kernel forms a staple article of Maori food. A detailed account of the process as carried out by the Maoris is given in a paper by Skey.* Owing to the kindness of Mr. H. B. Kirk, Inspector of Native Schools, we have been informed that the process employed by the Morioris in the Chatham Islands is practically identical with that used by the Maoris.

The karaka-kernels have been investigated by Skey. The results of his examination showed—(1) That the kernels contain oil, sugary matter, gum, and amorphous proteids; (2) that the nuts lose their bitter taste when heated to 100° C. for four hours; (3) that animal charcoal removes from the acidified aqueous extract of the kernel a bitter crystalline substance. This compound was named "karakin," but was not obtained in sufficient quantity for a satisfactory examination.

The authors have re-examined the karaka-nut. They find —(1.) That the aqueous extract of the nut yields much prussic acid on distillation. (2.) That air-dried kernels contain 14–15 per cent. of non-drying oil, which yields solid acids on saponification. (3.) That the sugars present are mannose and dextrose. (4.) That the aqueous extract, upon evaporation, even at 35°, in shallow pans, loses the greater part of its bitter taste. The concentrated extract contains no karakin

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* Trans. N.Z. Inst., vol. iv., p. 318.

(see below), but a nitrogenous glucoside, corynocarpin, together with a highly soluble, non-nitrogenous, crystalline compound. These substances have not been detected in the fresh extract. (5.) That a compound agreeing in nearly all respects with Skey's karakin can be readily obtained from fresh kernels by extracting with cold alcohol, and subsequently distilling off the spirit in a partial vacuum. By repeated crystallization from hot alcohol the karakin is obtained in radiating acicular crystals. (6.) The quantity of karakin diminishes rapidly with the age of the nut. The yield from fresh nuts gathered in February, 1901, was 0·3 per cent.; nuts three months old only yielded 0·1 per cent.; after twelve months the nuts were still bitter, but only a small quantity of karakin was obtained from them.

Karakin.

Since this compound is the only substance in the fresh nut of any considerable interest, the method of preparation and properties of it shall alone be given in detail. The fresh kernels are first put through a sausage-machine, and then through the wooden rollers of a wringing-machine, and the mash well stirred with one and a half times its weight of methylated spirit and allowed to stand for thirty-six hours, with repeated stirrings. The spirit is removed by a filter-press and the press-cake again extracted with alcohol. The united filtrates are distilled in a partial vacuum, at a temperature not exceeding 35°, until the greater part of the alcohol is removed. The turbid liquid gradually deposits crystals of karakin, together with a gummy bitter substance which can be removed by recrystallization from boiling alcohol. The pure karakin melts at 122°, dissolves easily in acetone, methyl alcohol, glacial acetic acid, acetic ether, and phenol; with difficulty in cold ethyl alcohol (0·4 gram in 100 cc.) and water. It is very sparingly soluble in ether and benzene. Deposited from hot concentrated solutions in water or alcohol, it separates as an oil, which subsequently becomes crystalline. The compound reduces Fehling's solution readily. After hydrolysis with dilute hydrochloric acid it gives a yellow precipitate when warmed with sodium-acetate and phenyl-hydrazine solution (glucoside reaction). It is highly nitrogenous. Analysis agrees with the formula $(C_5H_8NO_5)_3$.

		Calculated.	Found.
C	=	37·0	37·2
H	=	4·9	4·8
N	=	8·6	8·6
O (by difference)	=	49·5	49·4
		100·0	100·0

Molecular weight in phenol solution : Calculated $(C_5H_8NO_5)_3 = 486$; found $= 450$.

The characters given by Skey for the karakin prepared by the animal-charcoal method differ in two important respects from those above described. The melting-point according to Skey is 100°, and the substance contains no nitrogen. At first sight it would therefore seem that the two substances are not identical. From Skey's paper, however, it would appear that the karakin was not recrystallized, and this would account for the difference in the melting-points. The failure, on the other hand, to detect nitrogen in organic substances has occurred so often in the history of chemical research, more particularly before the application of the metallic-sodium test had become general, that the authors do not attach much importance to this apparent discrepancy. They would add that they have prepared karakin by Skey's method and found it to contain nitrogen, and to have the same melting-point as the compound already described.

The expenses in connection with this investigation have been defrayed by a grant from the Royal Society of London.

ART. XLVII.—*Raoult's Method for Molecular Weight Determination.*

By Professor EASTERFIELD and JAMES BEE, M.A.

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THE teaching of practical chemistry at the present day differs greatly from the teaching in vogue twenty-five years ago. At that time qualitative analysis only was, as a rule, taught to the elementary student, and experimental proof of chemical theory was either ignored or only practised in the lecture-room. Nowadays, however, the teaching of qualitative analysis is usually prefaced by a series of simple quantitative experiments, performed by the students themselves, and designed to illustrate modern chemical principles. Such an introduction greatly facilitates the understanding of the science.

So far as we are aware, no attempt has been made to teach the practice of molecular-weight determination by Raoult's method to the elementary student, it being generally supposed that expensive apparatus is necessary for such determinations. As a matter of fact, the experiment may be successfully carried out with the simplest of school apparatus, and with a very small expenditure of time and material.