The Essential Oil of Melicope Ternata (Wharangi).

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THE material used in this investigation was collected in the late summer at Titirangi and Anawata. About 10 cwt. of leaves and terminal branchlets were steam distilled the day following their collection and the products of distillation collected, the oil being separated off and dried over anhydrous sodium sulphate. The condensed steam was made alkaline and evaporated to dryness. The amount of sodium salts obtained in this way was very small. Although the material collected was quite fresh and the leaves possessed a pronounced aromatic odour, the yield of oil was surprisingly small, being only 0.016% by weight. The volume of oil obtained was about 100 c.c., the low yield being possibly due to the abnormally dry season. The total amount of oil collected was insufficient for a complete analysis and unfortunately no more of the leaves could be obtained.

The oil was a dark brownish-red, mobile liquid possessing a pleasant aromatic odour. It was miscible in all proportions with absolute alcohol and soluble in 10 volumes of 90% alcohol, and had the following constants: absolute density at 20°C. = 0.8449, refractive index at 20°C. = 1.4902, acid value = 2.0, ester value = 7.2. Determinations of the percentage of aldehydes in the oil were made in two ways, viz., by absorption with sodium bisulphite, and by the hydroxylamine method. The bisulphite method gave a result of 1.5% by volume, and the hydroxylamine method 2.1% by weight (calculated as citronellal). Of these two methods, the latter is the more reliable, the bisulphite method being inaccurate for oils obtaining only a small percentage of aldehyde. The percentage of phenols and free acids in the oil, found by absorption with 4% caustic potash solution, was 1%. Thus it will be seen that the oil contains only small amounts of esters, aldehydes, phenols and acids.

The aldehydes were removed from the collected oil in the usual manner with a 30% solution of sodium bisulphite, a small amount of yellow-coloured liquid being obtained with a sweet lemon-like odour indicative of citral or citronellal. There was insufficient for definite identification.

Acids and phenols were removed from the remaining oil by extraction with 3% caustic soda and found to consist of (1) cinnamic acid identified by its m.p. 133° and by oxidation to benzaldehyde by potassium permanganate; (2) a trace of isovaleric acid recognised by its odour, and (3) a very small amount of a phenol too small for identification.

The remaining oil was washed with concentrated brine till neutral, then with water, and finally dried over anhydrous sodium sulphate. It was then fractionally distilled using a rod and disc fractionating column, the following fractions being collected, leaving a residue which did not distil when the pressure was lowered to 3.5 mm.

Fraction.	Pressure.	Boiling Range.	Weight.	% By Weight.	Refractive Index at 15°C.
1	760 mm.	174°-184°	16.1 gm.	27.6	1.4864
2	10 „	130°-141°	8.6 „	14.8	1.5070
3	10 „	141°-155°	4.2 „	7.2	1.5105
4	10 „	155°-190°	4.2 „	7.2	1.5144
Residue	—	—	23 „	40	

Systematic refractionation of fraction 1, finally over sodium, yielded 14 gm. of a liquid (b.p. 172°-175°) having refractive index at 15°C. of 1.4750 and absolute density at 15°C. of 0.8495. Its specific rotation at 22° C. using the yellow mercury line was 76.12°. The molecular refraction, 45.12, agreed with the calculated value for a monocyclic terpene, viz., 45.24. The liquid was identified as limonene by the preparation of the tetrabromide m.p. 103.5°-104°C. The low optical rotation indicates the presence also of some dipentene.

From the physical constants of fractions 1, 3 and 4, it seems probable that these fractions contain sesquiterpenes and sesquiterpene alcohols. Insufficient material was however available for the separation and identification of the constituents.

Summary.

From the foregoing results the essential oil of Melicope ternata (Wharangi) contains:

Aldehydes (probably citral or citronella) 2%
Phenols and free acids (cinnamic acid and a trace of isovaleric acid) 1%
Esters 2%
Terpenes (limonene and dipentene) 25%

The remainder consists probably of sesquiterpenes and sesquiterpene alcohols, unidentified, 29% and resinous residue, 40%.

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