

ON THE BUTYL ESTER OF BUTYRIC ACID OCCURRING  
IN SOME EUCALYPTUS OILS.

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IN a paper by the Curator (Mr. R. T. Baker, F.L.S.) and myself, read before the British Association for the Advancement of Science when that body met in Sydney in August last, the announcement was made that a previously undescribed ester, with a low refractive index, occurred in some quantity in the oil of *Eucalyptus Perriniana*, collected both in Tasmania and in New South Wales, and that the presence of this ester in such quantity was one of the distinguishing features for this species when compared with the closely related one, *E. Gunnii*. Considerable work was done on these species with material collected at both localities, and it is evident from the results that these two Eucalypts are not identical.

It is the purpose of this paper to record the chemical results obtained with this ester, which is evidently a constant constituent in the oils of a certain class of Eucalypts, although in most cases occurring but in small amount. This is another instance of the peculiarity, so pronounced with chemical constituents in the genus *Eucalyptus*, namely a progressive increase throughout a whole series of closely agreeing forms until the maximum is reached in one of them. Not only is this the case with the oils, but with the exudations and other secretions also, the sequence running through a whole group being sometimes remarkably complete.

Butaldehyde, perhaps the parent substance of this ester, is present in most crude Eucalyptus oils, and is one of the constituents which give to unrectified oils a somewhat objectionable odour. The formation of the ester might perhaps be accounted for by a rearrangement in the aldehydic groups of two molecules of the butaldehyde. Normal butyric acid has already been identified as occurring in small quantity in several of these oils, and this acid was probably derived from the hydrolysis of the ester, because a corresponding change does take place when the oil of *E. Perriniana* has been stored for a sufficiently long time.

The material of *E. Perriniana* from which this oil was distilled, was collected at Tingiringi Mountain, southern New South Wales, in September, 1913. The crude oil was rich in eucalyptol, but phellandrene was not detected at this time of the year. The general characters of this oil agreed with those obtained with the material of the same species from Strickland, in Tasmania, collected July 1912. The analysis of the Tasmanian sample is recorded in a paper by Mr. Baker and myself, in Proc. Roy. Soc. Tasmania, October, 1912.

The abnormally low refractive index of the lower boiling fractions of the oil led to the determination of this ester, as so low a refractive index as 1.4538 at 16° C., in ordinary fractions, had not previously been detected in Eucalyptus oils.

#### Determination of the Acid.

The portion of 200 cc. of the crude oil distilling below 190° C., was boiled with aqueous potash under a reflex condenser for some hours. The aqueous portion was separated and distilled, but nothing came over below the boiling point of water, so that methyl, ethyl, and propyl alcohols were absent. The remainder was evaporated to dryness and the potassium salt decomposed by sulphuric acid and distilled

until all the volatile acid had come over. This had an odour of butyric acid strongly marked. The free acid in the distillate was exactly neutralised with barium hydrate solution, evaporated to dryness and heated in air bath to  $105^{\circ}$  C.

A molecular weight determination with this barium salt gave the following:—

0.3592 gram gave 0.2668 gram.  $\text{BaSO}_4 = 74.28$  per cent.

Barium butyrate gives theoretically 74.91 per cent.  $\text{BaSO}_4$ , so that most probably no other acid than butyric was present. The odour and other indications suggested the normal form for this acid, and the ethyl ester gave the characteristic pine-apple odour. To decide the point the calcium salt was prepared by decomposing the remainder of the barium salt with sulphuric acid, and distilling over the volatile acid. The distillate was exactly neutralised with freshly prepared and filtered lime water, using a trace of phenolphthalein as indicator. It was then carefully evaporated to a small bulk on the water bath until a portion of the solid salt separated, but this took up again when the liquid cooled. The precipitation was again brought about when heated in test tube, but this was also dissolved on cooling. It is thus apparent that the acid of this ester is normal butyric.

#### Determination of the Alcohol.

On distilling the oil separated after saponification, about 1.2 per cent. came over below  $150^{\circ}$  C. A trace of eucalyptol was present and perhaps a trace of pinene also. This portion was carefully oxidised with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ , by heating to boiling, and allowing to stand for twenty-four hours. A volatile acid with the odour of butyric was then readily detected, this was distilled over, filtered through wet paper, exactly neutralised with barium hydrate solution, and evaporated to dryness and heated in air oven.

The barium salt thus obtained was identical in odour and reactions with that from the acid of the ester. Although the amount of salt at disposal was small, yet, sufficient was obtained with which to make a quantitative determination for molecular weight.

0.0354 gram gave 0.0264 gram  $\text{BaSO}_4 = 74.58$  per cent.

Barium butyrate gives 74.91 per cent.  $\text{BaSO}_4$

It might reasonably be considered that as this ester is butyl-butyrate that both the alcohol and the acid are identical in form, and although sufficient acid from the alcohol was not available with which to prepare the calcium salt, yet, the odour of this acid, as well as that of its ethyl ester, was identical with those of the acid, and again corresponded with those given by pure normal butyric acid.

That the greater portion of the total ester in the oil of *E. Perriniana* is the low boiling butyl-butyrate is shown from the saponification results with the freshly distilled oil. The saponification number for the crude oil was 52.6, representing 13.52 per cent. of an ester having a molecular weight 144. The saponification number in the portion distilling below  $190^\circ \text{C}$ . (75 per cent.) was 57.2, representing 14.7 per cent. of ester in this fraction. The ester was not decomposed on direct distillation, no free acid being detected in the lower boiling fractions.

In future analyses of Eucalyptus oils from trees belonging to this class, it will be necessary to determine the ester value in the lower boiling fractions, particularly when the saponification number for the crude product is at all high.

When the identity of the ester in the oil of *E. Perriniana* from New South Wales had been determined, the amount of ester in the first fraction of the oil of this species from Tasmania was taken. This fraction—although investigated

over a year previously had fortunately been preserved—represented 18 per cent. of the crude oil distilling below 173° C. It contained, however, some free acid at this time, as a portion of the ester had hydrolysed. The saponification number for the ester and free acid in this fraction was 45·8. This result also shows the ester in the oil of *E. Perriniana* of Tasmania to be a low boiling one, and that the greater portion distilled over in the first fraction.

These chemical results support the botanical evidence that the trees growing both in Tasmania and on the mainland of Australia are the same species.

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Smith, Henry George. 1914. "On the butyl ester of butyric acid occurring in some Eucalyptus oils." *Journal and proceedings of the Royal Society of New South Wales* 48, 464–468. <https://doi.org/10.5962/p.359668>.

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