THE OCCURRENCE OF TWO PHYSIOLOGICAL FORMS OF *LEPTOSPERMUM CITRATUM* (CHALLINOR, CHEEL AND PENFOLD) AS DETERMINED BY CHEMICAL ANALYSIS OF THE ESSENTIAL OILS.

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Manuscript received, March 24, 1942. Read, May 5, 1942.

Leptospermum citratum was described as a distinct species and the chemical composition of the essential oil revealed by Challinor, Cheel and Penfold in 1918.[1] Since that date experimental plots have been established in various parts of New South Wales and Queensland, as well as in Kenya Colony, South Africa, and in the Netherlands East Indies. The essential oils from a number of these plots have been examined, and without exception the results confirmed the chemical composition of the original oils examined in 1918.[2]

The oil from the type species, which consists principally of the aldehydes citral and citronellal, has been an article of commerce for several years past. The war has been responsible for an unprecedented demand, with the result that the price rose to £10 per gallon at the stills in September, 1941. The principal localities for the supply of the oil have been Punchbowl, Whiteville, Baryulgil and Copmanhurst, all in the Grafton district of northern New South Wales.

The tree grows in rocky ledges in inaccessible parts of the Dividing Range, and is very sparsely distributed. The increasing demand for the oil has caused an intensive search for new areas. The essential oils distilled from material collected from these new areas were found to differ markedly in chemical composition from the type species. Field investigations revealed the occurrence of at least two forms growing at Tyndale on Woodford Island, situated a few miles west of Maclean on the Clarence River of New South Wales. One form was observed at Copmanhurst.

Botanically the two forms are identical with each other and the type species. Specimens of each were submitted to Mr. R. H. Anderson, Chief Botanist of the Botanic Gardens, Sydney, who confirmed our own determinations. He did, however, comment on the fact that the characteristic odour of the type species could not be detected in the forms.

The description given in the original paper[1] fits the forms exactly, although flowers of the latter have not yet been seen.

In order to distinguish the two forms, they have been designated variety A and B respectively. The leaves of variety A when crushed between the fingers emit a terpene-like odour resembling γ-terpinene, whilst the foliage of variety B gives a rose-like odour characteristic of geraniol.

The chemistry of the essential oils has not yet been completely elucidated, and further work has been deferred owing to the war.

The purpose of this note is to place on record the occurrence of the two forms, together with sufficient chemical data to enable them to be readily

TABLE 1.

Essential Oils of Leptospermum citratum, *Varieties "A" and "B".*

Date.	Locality.	Yield of Oil.	$d_{15^\circ}^{15^\circ}$	$a_D^{20^\circ}$	$n_D^{20^\circ}$	Solubility in Alcohol.	Ester No.	Ester No. after Acetylation.	Citral Content.	Remarks.
16/4/1941	Woodford Is., N.S.W.	1·0%	0·8841	+1·68°	1·4760	1·4 vol., 70%			16%	Leaves supplied by C. Savidge, Var. "B".
,,	,, ,,	1·2%	0·8634	+2·35°	1·4795	Insol 10 vol., 80%			—	Leaves supplied by C. Savidge, Var. "A".
25/9/1941	,, ,,	1·3%	0·862	+2·08°	1·4789	Insol. 10 vol., 80%	8·3		—	Collected by authors, Var. "A".
,,	,, ,,	1·0%	0·881	+1·75°	1·4780	1·8 vol., 70%			20%	Collected by authors, Var. "B".
				Samples of Oil Furnished by Distillers.						
4/10/1940	Copmanhurst.	—	0·8764	−1·25°	1·4760	10·0 vol., 80%	3·9	43·7	—	Furnished by J. Pocock, Var. "A".
29/9/1941	,,	—	0·876	+1·47°	1·4753	6·3 vol., 80%	3·2	5·7	—	Furnished by J. Pocock, Var. "A".
,,	,,	—	0·864	+2·63°	1·4790	9·7 vol., 80%	8·9	51·3	—	Furnished by C. Savidge, Var. "A".
				Leptospermum citratum *Type—for comparison.*						
		1·0% to 1·5%	0·8792 to 0·8856	+3·6° to +5·0°	1·4688 to 1·4757	1·0–1·2 vol., 70%			45–50%	Also contains citronellal 35%. Total aldehyde, 75–85%.

identified and separated from the type species. The accompanying table gives the chemical and physical characters of the essential oils distilled from material collected by ourselves in September, 1941, together with those of samples supplied by distillers. For comparative purposes the chemical and physical characters of *L. citratum* type are also included in the table.

The constituents which have so far been identified are as follows :

Variety A.—γ-terpinene b.pt. 179-181° C. (762 mm.), ($d_{15}^{15°}$ 0·851, $a_{20°}^{D}$ +0·24°, $n_{20°}^{D}$ 1·4781 ; m.p. of the erythritol, 235-236°), d-a-pinene (pinonic acid, m.p. 69-70°), cymene (p-hydroxy-isopropylbenzoic acid, m.p. 155-156°), cineol, unidentified terpenes, linalool (?), with small quantities of sesquiterpenes and eugenol, 0·6% (benzoate m.p. 69-70°).

Variety B.—Citral 16% to 20% ($d_{15}^{15°}$ 0·8928, $n_{20°}^{D}$ 1·4883, semicarbazones m.p. 163-164° and 135-136°), geraniol, free and combined as formate and acetate, ($d_{15}^{15°}$ 0·880, $a_{20°}^{D}$ +1·44°, $n_{20°}^{D}$ 1·4699, silver salt of phthalic acid ester m.p. 133°, diphenylurethane m.p. 82-83°), with citronellol and similar esters.

Acknowledgments.

Our thanks are tendered to Mr. C. Savidge, Copmanhurst, and Mr. J. Pocock, Punchbowl, for samples of oil and consignments of foliage and for the valuable assistance during our visit to Copmanhurst in September, 1941, and also to the Forestry Commission of New South Wales, and its officers at South Grafton, for valuable cooperation in this investigation.

References.

(1) Challinor, R. W., Cheel, E., and Penfold, A. R., 1918. *J. Proc. Roy. Soc. N.S.W.*, **52**, 175.

(2) Penfold, A. R., and Morrison, F. R., 1918. Syd. Tech. Mus. Bull. 14, part II, Australian Tea Trees of Economic Value.