ON A NEW SPECIES OF *LEPTOSPERMUM* AND ITS ESSENTIAL OIL.

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Leptospermum citratum sp. nov.

L. flavescens var. *citratum* Bailey and White, Queensl. Agric. Journ. Vol. v, p. 161, pl. 13 (1916); Bot. Bull. xviii, p. 8, pl. 2 (1916).

Frutex, nonnunquam ad arborem minorem auctus, 4—20 pedalis, ramis junioribus angulatis mox teretibus. Foliis linearibus vel angustato-lanceolatis, obtusis, glabris, membranaceis obsolete-3-nerviis pellucido-punctatis, 2—4½ c.m. longis, 3—4 mm. latis. Floribus albis, solitariis axillaribus, sessilibus vel brevissime pedicellatis nonnunquam terminalibus in ramis lateralibus. Bracteis 2, caduceis. Calicibus glabris, lobis ovatis marginibus fimbriatis. Petalis spathulatis vel laminis orbicularibus. Ovario glabro; fructibus quinque-locularibus.

A glabrous shrub or small tree, varying in height from 4 to 20 feet, the main stem up to and occasionally exceeding 3 inches in diameter, bark light brown colour and comparatively thin and smooth on the upper branches, more or less fibrous and furrowed on the lower part of the stem. Juvenile branchlets at first somewhat angular, afterwards terete.

Leaves alternate, linear or narrow linear-lanceolate, obtuse, 2 to 4½ cm. long, 3 - 4 mm. broad.

Flowers white, solitary in the axils of the leaves or occasionally terminal on the lateral branchlets, sessile or

very shortly pedicellate. Bracts 2, greenish, enveloping the buds and soon falling off when the flowers reach maturity. Calyx-tube glabrous, sepals 5, ovate, valvate, more or less sprinkled with prominent oil-glands, the margins fimbriate with a woolly fringe. Petals 5, white, orbicular but distinctly clawed, giving them a somewhat spathulate appearance. Style 2–3 mm. long, with a capitate stigma. Stamens about 25 to 30. Ovarium glabrous. Capsules 5-celled, the valves slightly domed and usually about the same size as the calyx-tube.

Credit is due to Rev. H. M. R. Rupp for the first discovery of this interesting species. He forwarded some specimens (in fruit only) to the National Herbarium in August 1911, from Copmanhurst, Clarence River, New South Wales.

Additional specimens were obtained from Mr. G. Savidge from the same locality in December 1912, but were not sufficiently perfect for complete investigation.

In September 1916, during a trip to the northern rivers with Dr. T. Guthrie, Mr. A. D. Ollé, and one of us (E.C.) visited Copmanhurst, and made special investigation of this species and secured a fair amount of material, including a quantity of ripe fruits and seeds, for the purpose of studying the plants in different stages of growth to see if they were really distinct from *Leptospermum flavescens* var. *grandiflorum*, which it very closely resembles. As a result of this trip, one of us (E.C.) has been able to raise a large number of seedlings, and has planted them in various localities in different kinds of soil, and finds that the characters, as well as the citron-scented oil contained in the leaves, are constant and identical with the parent plants, and quite distinct from any other species of *Leptospermum*. Some difficulty was encountered during the early stages of growth of the seedlings, as it was found that the plants require careful nursing; this probably

accounts for the limited number of plants and restricted areas.

In January 1917, Mr. R. W. Challinor collected some additional fresh material from Copmanhurst, and in November 1917, Mr. Cheel supplemented this, and, as a result of our investigations, we are now able to state that the oil from the leaves of the cultivated plants agrees in every way with that from the original plants. Its nearest ally seems to be *L. flavescens* var. *grandiflorum* Benth., but from this the new species may be distinguished by the more obtuse leaves, which have a distinctly fragrant citron-like odour, and the smaller flowers and different habit of growth. It is interesting to note that *L. flavescens* var. *grandiflorum* is chiefly found in the beds of creeks and rivers, and seems to be confined to Port Jackson and southern localities. The typical form of *L. flavescens* also seems to be absent from the neighbourhood of Copmanhurst.

There is, however, an abundance of *L. flavescens* var. *microphyllum* in the neighbourhood of Copmanhurst; in fact this latter seems to be common in the northern parts of this State and Queensland, but it is quite distinct, and cannot in any way be confused with *L. citratum*.

The distribution is as follows:—New South Wales—Copmanhurst (Rev. H. M. R. Rupp, August 1911; G. Savidge, December, 1912 (in flower); E. Cheel, Dr. T. Guthrie, and A. D. Ollé, September 1916).

Queensland—Springbrook, Macpherson Range (C. T. White).

The Essential Oil.

The oil obtained from this species of Leptospermum is of a pale amber colour, and possesses a strong, pleasant modified lemon odour, suggestive of the principal constituents, which have now been identified as citronellal and citral. The crude oil contains 90% of these two aldehydes

in nearly equal proportion, and in this respect appears to occupy a position intermediate between the oils from *Eucalyptus citriodora* and *Backhousia citriodora*, both of which give the highest recorded yields of the respective aldehydes citronellal and citral.

The relative proportions of these two aldehydes are also apparent from the specific gravity and refractive index of the oil, these constants being approximately what might be obtained when citronellal and citral are mixed in equal proportions.

Experimental.—Three lots of material were collected at Copmanhurst, New South Wales, in September 1916, by Dr. T. Guthrie, Messrs. E. Cheel, and A. D. Ollé; in January 1917 by Mr. R. W. Challinor; and in November 1917 by Mr. E. Cheel. Altogether 686 lbs. of leaves and terminal branchlets were distilled, the yield of oil averaging from 1·73 to 1·85%. The crude oil was of a pale amber colour, of specific gravity $\frac{15^\circ}{15^\circ}$ C. 0·8841; optical rotation a_D +3·6 at 18° C.; refractive index n_D 20° C. 1·4730; contained 90% aldehydes and was soluble in 2 volumes of 70% alcohol (by weight).

The Aldehydes.—The aldehyde content of the oil was determined quantitatively by the sodium bisulphite method. 5 c.c. of oil leaving 0·55 c.c. unabsorbed oil, another 5 c.c. left a residue of 0·5 c.c., which indicates 89% and 90% respectively of constituents absorbed by sodium bisulphite.

A larger quantity of the oil was then treated, 50 c.c. at a time, and the non-aldehydic portion separated, the aqueous solution was extracted several times with ether to remove undissolved oily matter, the ether was distilled off, and the aldehydes regenerated by means of alkali, dried over anhydrous Na_2Suc_4 and separated into two fractions; fraction 1, boiling at 93-94° C. (12 m.m.) and consisting approximately of 48% of the original oil, and Fraction 2,

boiling at 110–112° (12 m.m.) which was about 42% of the oil.

Identification of Citronellal.—The fraction of lower boiling point was a colourless oil of a strong citronellal odour, its specific gravity at $\frac{15}{15}$° C. was 0·8577; optical rotation at 20° C., a_D + 8·61°, equal to a specific rotation $[a]_D$ 20° of + 10; refractive index n_D 20°, 1·4482.

Molecular weight.—The molecular weight of this aldehyde, determined by the Landsberger boiling point method, using acetone as solvent, gave the following results:—1·1612 gms. of aldehyde in 27·5 c.c. of acetone elevated the boiling point 0·6° C. indicating a molecular weight of 156·2. 1·1612 grams in 36·5 c.c. acetone gave an elevation of 0·45° C. Molecular weight 156·8. The molecular weight of citronellal = 154.

Derivatives.—The naphthocinchoninic acid derivative was prepared in the usual way from pyruvic acid and β. naphthylamine and the crystalline product purified; it melted sharply at 225° C.

Citronellyl β. naphthocinchoninic acid melts at 225° C. With semicarbazide hydrochloride it gave a crystalline semicarbazone which melted at 78 – 79° C.

Citronellyl semicarbazone melts at 82·5° C. On reduction it yields an alcohol of specific gravity $\frac{15}{15}$° C. 0·8602, boiling at 226° C. (761 m.m.) and giving a silver salt of its phthalic acid ester melting at 123° C. Records of the melting point of the silver salt of citronellyl phthalic acid vary from 120 to 125° C. It is thus evident that the aldehyde boiling at 93–94° C. (12 m.m.) is citronellal.

Identification of citral.—The aldehyde fraction boiling at 110–112° C. (12 m.m.) is a pale yellow oil with a very strong lemon odour like citral. When submitted to treatment with sodium sulphite by Burgess's method, it is completely absorbed, showing the absence of non aldehydic

constituents. Its specific gravity at $\frac{15}{15}$° C. is 0·8929; optical rotation zero; refractive index at 20° C. 1·4875.

The β naphthocinchoninic acid derivative prepared in the usual way and purified, was crystalline and melted at 200° C.

Citryl naphthocinchoninic acid melts at 200° C. These results show this aldehyde to be citral.

The non aldehydic portion of the oil is still under investigation, sufficient material for a complete examination not yet being accumulated.

There appears to be a small amount of a phenol present, which gives a crystalline benzoate with benzoyl chloride, melting at 67° C. Acetylation of a small portion of this residue also indicates the presence of a small amount of an alcohol resembling geraniol or citronellol, but this requires confirmation.

From colour reactions obtained with bromine and with hydrochloric acid, there is also evidence of the presence of small amounts of aromadendrene.

The oil of this Leptospermum is therefore quite distinctive in character, and differs from that of any other species of Leptospermum so far recorded.

This work has been carried out in the Research Laboratory of Messrs. Gillard Gordon Ltd., Sydney, and our thanks are due to this firm for their courtesy in this matter.