ON AN UNDESCRIBED DARWINIA AND ITS ESSENTIAL OIL.

By R. T. Baker and H. G. Smith.

With Plates VII and VIII.

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Darwinia grandiflora, Sp. nov.

(Syn. *D. taxifolia* var. *grandiflora*, Benth.)

Remarks.

In a paper read by us before this Society in 1899 we state p. 164, *inter alia*, that "it is intended to raise this variety to specific rank when its chemical constituents have been investigated."

At that time its botanical affinities to and specific differences from its congeners, *D. taxifolia*, A. Cunn., and *D. fascicularis*, Rudge, were worked out, but we preferred to wait until the oil had been procured and analysed, before specially describing it.

Several attempts were made from time to time to procure leaves, but it was not until Dr. Cleland informed us of a locality on the Hawkesbury River that sufficient material was procurable for a distillation.

Even in this case the amount of leaves was not what we could have wished, but sufficient was obtained to give the required data for this paper.

In botanical sequence it stands between *D. taxifolia*, A. Cunn., and *D. fascicularis*, Rudge, having some characters of each and differences from both, and the same remarks apply to the chemistry.

The flowers have a greater resemblance to those of the latter rather than the former, and the leaves to the former rather than the latter.

It differs from *D. taxifolia* in being a more erect and higher growing shrub, and the leaves being distinctly decussate and not nearly so much crowded, larger and flatter, and not glaucous. Its flowers are also more fleshy, and the calyces lack the ribs so prominent a feature in both the other species. The bracts also differ in shape from both species, whilst the disposition and the shape of the leaves clearly separate it from *D. fascicularis*.

Chemically the constituents obtained from the leaves place the oil intermediate between those of its congeners.

Description of Species.

It is an erect shrub growing to a height of fifteen feet, never arborescent as far as seen, with reddish terminal branchlets.

Leaves decussate, distant in the upper branchlets, and never so close together or crowded as in *D. taxifolia* and *D. fascicularis*, nor glaucous as obtains in the former species; falcate, laterally compressed, acute, 7 to 8 lines long, the mid-rib not showing, the upper surface channelled with acute edges, oil glands not so pronounced as in the above species, uniform colour to the articulation with the decurrent petiole in the stem.

Flowers terminal, about 5 lines long, in clusters of 3 to 4, pink, white, and green in colour.

Bracteoles broad, with scarious edges, oil glands very numerous, acuminate, not so long as the calyx.

Calyx fleshy, the lower half quite round, not ribbed or corrugated, shining and much pitted, the upper portion with five narrow channels between each portion of sepal, which may be said to be here valvate, the free lobes small, acuminate and incurved.

Petals white, broad, about 1 line long.

Staminodia very small, subulate, about as long as the filaments.

Style well exserted, sometimes over an inch long.

Histology of Leaf.

In a transverse section the usual leaf structure of angiosperms obtains, except the guard cells of the stomata, which are of rather unusual form, being shaped in transverse section like the arms of a pair of callipers.

In the centre is the midrib, proportionately small to the area of the section, and surrounded by a ring of endodermic cells supported by a very loose mesophyll or spongy tissue which is bounded by parenchyma carrying chloroplastids, followed outward by palisade layers, the whole encircled by a single row of deep epidermic cells in length equalling the depth of the palisade cells. Sparsely scattered throughout the latter are the oil glands.

Interpolated between the palisade and loose parenchyma tissue are found elongated water storage tracheides with spiral thickenings, a useful provision of nature for this arenaceous plant.

The stomata are not numerous, but are interesting, for the guard cells are quite unique in shape, being curved like the mandibles of some coleopterous insect or a pair of callipers, the free ends in section tapering to a sharp point.

A high magnification shows a few scattered hairs on the surface of the leaf.

Essential Oil.

The material for distillation was collected at the Hawkesbury River, New South Wales, early in November, and when distilled was quite fresh. The average yield of oil from the leaves with terminal branchlets was 0·12 per cent.

The oil was red in colour, somewhat mobile, and had a terpene like odour. In general characters and appear-

ance it more closely resembled the oil of *Darwinia fascicularis* than that of *D. taxifolia*, and the study of the chemistry of the oil indicates its intermediate position between those two species. The crude oil had

Specific gravity at 15° C. = 0·9150

Optical rotation a_D = + 23·1°

Refractive index at 20° C. = 1·4773

Scarcely soluble in 10 volumes 80 per cent. alcohol.

Determination of ester with alcoholic potash.

(*a*) Heated to boiling on water bath for half an hour, 1·5345 gram required 0·154 gram KOH ∴ S.N. = 100·4

(*b*) In cold with two and three-quarter hours contact, 1·5340 gram required 0·1484 gram KOH ∴ S.N. = 96·7 equal to 33·84 per cent. geranyl-acetate.

This result shows that the saponification number 3·7 represents an ester not saponified in the cold with two and three-quarter hours contact, and as butyric acid was detected during the determination of the fatty acids, it is possible that this ester is a butyrate.

Determination of the fatty acids.

Sulphuric acid was added to the aqueous portion after saponification, which was then distilled until all the volatile acids had come over. The perfectly clear distillate was exactly neutralised with barium hydrate solution, evaporated to dryness and heated in air bath at 100 – 105° C. The sulphate was prepared from a weighed portion in the usual way; 0·2716 gram of the barium salt gave 0·2446 gram $BaSO_4$ = 90·07 per cent.

The odour of butyric acid was distinctly marked, and, assuming the two combined acids to be acetic and butyric, the results show the barium salt to contain 92·15 per cent. barium acetate, and 7·85 per cent. barium butyrate. The separated oil after saponification had a distinct odour of geraniol.

The investigation of the oil of *Darwinia fascicularis*[1] showed the ester to be geranyl-acetate, the alcohol being separated in a pure condition. The amount of oil of the present species, at our disposal, did not permit the isolation of the alcohol, but from the saponification results in the cold, together with the odour of the saponified oil, it is evident that the principal ester in this species is geranyl-acetate also.

Determination of the chief terpene.

When the oil was distilled directly a considerable portion came over between 156 - 160° C., and no less than 30 per cent. distilled below 165° C. This fraction had a pinene-like odour and had:—

Specific gravity at 15° C. = 0·872.
Optical rotation a_D + 41·6°.
Refractive index at 20° = 1·4685.

The nitrosochloride was prepared with it, and this, when purified, melted at 104° C. It is thus evident that the lower boiling terpene in this oil is a highly dextrorotatory pinene.

The pinene in the oil of *D. taxifolia* is lævorotatory, while the corresponding terpene in the oil of *D. fasicularis* has a dextro rotation. The presence of a small quantity of a volatile acid with a higher molecular weight than that of acetic was also determined in the esters of *D. fascicularis*, so that the resemblances between the characters of the oils of *D. grandiflora* and *D. fascicularis* are distinctly shown.

For comparison the results obtained with the crude oils of the three species of Darwinia are here tabulated.

[1] This Journal, Vol. xxxiii, (1899), p. 163.

	D. fascicularis.	*D. grandiflora.*	*D. taxifolia.*
Sp. gr. at 15° C. ...	0·9184	0·915	0·8779
Rotation a_D ...	+ 1·2°	+ 23·1°	− 6·5°
Ref. index at 20°C.	...	1·4773	...
Ester by boiling ...	60%	35·1%	5·3%
Ester in the cold...	58%	33·8%	...
Yield of oil ..	0·318%	0·12%	0·313%

Distribution.

Berowra, R. T. Baker. Left bank of the Hawkesbury River, opposite Milson Island, Dr. J. B. Cleland.

EXPLANATION OF PLATES.

Plate VII.

1. Flowering twig.
2 Individual flower.
3. Transverse section of calyx.
4. Transverse section of calyx.
5. Longitudinal section of lower portion of flower.
6. Flower cut open to show disposition of stamen and staminodia.
7 and 8. Two bracts.

1 to 8 enlarged.

Plate VIII.

Transverse section of leaf, showing anatomical structure.