On the *DARWINIAS* of PORT JACKSON and their ESSENTIAL OILS.

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(*a*) Botany of Species.

The genus *Darwinia* was established by A. Rudge in 1817 in the Transactions of the Linnean Society, Vol. xi., 299, on specimens collected in the neighbourhood of Port Jackson by Robert Brown. It was named in honour of Erasmus Darwin, M.D., of Lichfield, author of several botanical works. The first species described was *D. fascicularis.*

Although the genus was founded originally from eastern species it might almost be said to be purely West Australian, as over thirty species are recorded from that colony, whilst only one occurs in Queensland, two in South Australia, two from Victoria, and three from New South Wales.

Darwinia fascicularis, Rudge (B. Fl. iii. 13.) is a virgate shrub, varying in size in different localities, about five feet being the maximum height in the coast form. The mountain variety rarely exceeds two feet. The leaves are slender, numerous and crowded, and vary in length from four to eight lines. The flowers although small are attractive, being sometimes all white, or pink and white.

It occurs on sandy soil mostly, and covers many hundred acres of ground between Botany, La Perouse, and the coast. It has been found north of Manly and also on the Blue Mountains at King's Tableland, Wentworth, and Lawson.

D. taxifolia, A. Cunn., (B. Fl. III., 12) is a shrub of about the same dimensions as *D. fascicularis*, Rudge, but is easily distinguished in the field from that species by the shape of the leaves, their glaucous appearance, and its reddish branchlets. The flowers are not so attractive as those of *D. fascicularis*. Its habitat is almost identical with that of the previous species, although it has, however, been found as far south as Ghunnyenara Mountain (W.B.) It differs botanically from *D. fascicularis* in its laterally flattened, triquetrous leaves.

D. taxifolia, A. Cunn., var. *grandiflora*, Benth. As this variety is very constant throughout its range and it possesses distinctive characters from *D. taxifolia*, it is intended to raise it to specific rank when its chemical constituents have been investigated. It occurs in a very luxuriant form at Berowra. The leaves are much longer and broader than those of the other species, and the flowers are also more showy and larger than those of the other species.

Histological Notes.

A transverse section shows an absence of a midrib, but stomata are very numerous on the whole surface. The contour of a section much resembles a horse-shoe in shape, the flat edge corresponding to the upper surface of the leaf. Some difficulty was experienced in working upon a leaf-section measuring less than half a line in diameter. The very highest power objective was required to determine the form and structure of the various cells, etc. The palisade layers were found to be arranged with their long axes at right angles to the cuticle or surface, and of course containing chloroplastids. The layers were connected to a central body by spongy tissue, without chloroplastids. Vascular bundles were present, being distributed throughout the leaf structure. The oil glands appear to be numerously distributed throughout the leaf, being partly immersed in the cuticle and palisade layers. The oil globule is very minute and not easily detected in the cells. The cell is circular in shape with elongated cells forming the usual guard cells.

(*b*) Chemistry of the Oils.

The Essential Oil of Darwinia fascicularis.

This oil was obtained by steam distillation on fresh material. When first distilled it is reddish-brown in colour, very mobile, with a somewhat strong odour, which when diffused is pleasant. The principal constituent of this oil is the important ester geranyl-acetate. When placed in a freezing mixture a small quantity of a stearoptene separates, but it is difficult to remove, and was not obtained in a separate condition. The specific gravity of the crude oil was ·9154 at 19° C. The colour was too dark to enable the rotation to be taken, but this colour being due to a constituent of an acid character is readily removed by agitating the oil with a very dilute solution of aqueous potash. The oil is then of a very light lemon tint and the rotation in 100 mm. tube was 1·2° to the right.

The yield of crude oil obtained by us from material collected under conditions that would obtain commercially, was ·318 per cent., the mean of several distillations on a total of 1,280 pounds of leaves or terminal branchlets. The collections were made in the months of March, September, October, and November. The yield of oil obtainable during these portions of the year is about the same for each month, and the percentage of ester present in the oil is also about the same, with the exception that the November oil was the richest in geranyl-acetate.

The material was obtained from shrubs growing naturally at La Perouse in the neighbourhood of Port Jackson. It was somewhat difficult to obtain the material without a predominance of woody stem; the shrubs, however, lend themselves very readily to clipping, and then grow more compact and bushy. It is to be expected, therefore, that in a state of cultivation (and of course no permanent success can be obtained without cultivation) the yield of oil would be much greater, as a larger quantity of the leafy portion of the plant would be obtainable. That this is so is shown by the fact, that after our September collection we

obtained leaves from the same bushes that had previously been clipped for distillation six months before. The oil obtained was the same in colour and constituents, but the yield was slightly greater, and with careful growing and clipping not less than ·5 per cent. of oil would certainly be obtainable, as in one distillation we obtained ·456 per cent. of oil and ·436 per cent. in another. Of course the yield of oil depends upon the amount of leaves taken in proportion to the stem; the oil is obtained from the leaves of the plant, and as the leaves are very small, this is the more important. Six distillations on material when flowers were present gave a yield of oil equal to ·31 per cent. as a mean, while five distillations in March, when the plant is not in flower, gave ·314 per cent. as a mean yield of oil, so that the yield was actually greater when the plant is not in flower. We thus conclude that the yield of oil is practically the same throughout the whole year, and that it differs little in composition at any time, the average content of geranyl-acetate being about 60 per cent. The oil from the November distillation contained 65 per cent. of geranyl-acetate; this is the time of year when in the neighbourhood of Sydney the vegetation is most vigorous.

These results in regard to the yield and composition of the oil of *Darwinia fascicularis* are the more important when taken in conjunction with the oil from *D. taxifolia*, as this oil contains but just over five per cent. of an ethereal salt calculated as geranyl-acetate, and its value is poor when compared with the oil from *D. fascicularis*.

When the crude oil of *D. fascicularis* was treated with boiling alcoholic potash to saponify the ester, and the regenerated oil distilled under atmospheric pressure, very erratic results were obtained, and it is evident that decomposition or rather alteration takes place under this treatment. Three distillations each of 100 cc. of the saponified oil under different treatment with boiling alcoholic potash gave results as follows:—In the first 54 per cent. distilled between 190° and 195° under ordinary pressure, and 28 per cent. between 225° and 260°. In the second only 3 per cent. came over

below 195° and only 9 per cent. below 205°. In the third only 2 per cent. distilled between 183° and 215°, and only three per cent. more below 220°; between 220° and 235° no less than 58 per cent. was obtained; this fraction was largely geraniol, its specific gravity was ·8874 at 20°; it gave a solid compound with calcium chloride, it formed citral on oxidation, it had an odour of roses. It is thus evident that change had taken place during the process of saponification by the methods used, as these three determinations were made from different portions of the same sample of oil. On ascertaining these facts, attempts were made to remedy this, and it was subsequently found that saponification of the ester takes place readily in the cold, using a semi-normal alcoholic solution of potash, and that the saponification is practically complete under three hours as will be seen from the following determinations :

1·9563 gram oil was added to 20 cc. semi-normal alcoholic potash and allowed to stand ten minutes at ordinary temperatures, it was then found that 4 cc. of potash solution had been absorbed; saponification figure therefore was 57·1, equal to 20 per cent. of ester, calculated as $C_{10}H_{17}O\,OC\,CH_3$.

1·274 gram. oil in 20 cc. alcoholic potash and allowed to stand one hour at ordinary temperatures absorbed 7·3 cc. of potash solution, saponification figure 160·4 equal to 56·1 per cent. of ester. The regenerated oil had still a faint odour of the ester showing that saponification had not been complete.

1·35 gram oil in 20 cc. alcoholic potash and allowed to stand three hours at ordinary temperatures absorbed 8·1 cc. potash solution, saponification figure 168 equal to 58·8 per cent of ester.

On allowing a sample to stand sixteen hours no different results were obtained. From the results of saponification obtained by boiling with the alcoholic potash solution for half an hour, it appears that there is a small quantity of an ester present not decomposed in the cold. When distilling off the volatile acids an odour was detected indicating an acid other than acetic acid,

but it can only be present in minute quantity as will be seen from the result of the analysis of the silver salt obtained from the mixed volatile acids.

A larger quantity of oil was then taken for saponification by semi-normal alcoholic potash at ordinary temperature and allowed to stand four hours; it was found at the end of that time that saponification was practically complete. The regenerated oil is yellowish in tint, specific gravity ·898 at 20°, rotation 100 mm. tube +0·75. It has a pleasant rose odour when diffused, and its freshness and fragrance are excellent. The objectionable odour detected when the ester is saponified by heat is missing, and it is thus seen to be unnecessary to apply heat to obtain separation of the alcohol.

When this regenerated oil from the cold saponification was distilled under ordinary pressure (760 mm.) less than three per cent. distilled below 225°, between 225° and 235° 43 per cent. was obtained, and between 235° and 240° 26 per cent. distilled. The fraction (225 – 235°) had no rotation, its specific gravity was ·890 at 15° C., and it was principally geraniol. The fraction 235 – 240° had a specific gravity ·892 at 21° C. Some decomposition had taken place under atmospheric pressure, but when distilled under reduced pressure about 60 per cent. of a fraction could be obtained, largely geraniol, as there are no terpenes or low boiling constituents to interfere. It is thus apparent that when the ester is decomposed in the cold but little alteration, if any, of the alcohol takes place, but it cannot be boiled with alcoholic potash without undergoing alteration. It is also apparent that the alteration is in the direction of the formation of lower boiling constituents.

We have obtained in four different directions during this research, a product boiling at 183 – 185° (uncor.) and having a very low specific gravity ·836 at 15°. It has no rotation when obtained under the most favourable conditions. It is worthy of remark that this product obtained by four different routes has

the same boiling point in all; three gave practically the same specific gravity, while the fourth was a little higher. It is certain that it is a product of alteration formed when the crude oil is saponified by boiling with alcoholic potash under ordinary atmospheric pressure, as it does not exist in the oil obtained by cold saponification. When gently oxidised citral was obtained, and on further oxidation a viscid brown substance having an aromatic odour. On boiling with acetic anhydride and sodium acetate a determination showed 24·1 per cent. of ester to have been formed. It should not now be difficult to obtain it in a pure condition, and further investigation will be made concerning it.

In a paper by Bertram and Gildmeister[1] it is stated that the essential oils of the pelargoniums (the French, African, and Reunion geranium oils) contain a considerable proportion of geraniol which boils at 225 - 230°, but there is also present a second alcohol which has not yet been obtained in a pure condition, and whose properties and composition have in consequence not been determined. This second alcohol, they say, appears to be differentiated from geraniol by its lower boiling point, its lower specific gravity and its behaviour towards hydrogen chloride and towards calcium chloride with which it forms no solid compound. Possibly this may be also a product of alteration.

Barbier[2] obtained an alcohol by heating geraniol with alcoholic potash, this he stated to be dimethylheptenol $C_9H_{18}O$. This being questioned, he supports his statement in a paper[3] by publishing results of a synthetical dimethylheptenol.

Tiemann[4] shows that when geraniol is heated with alcoholic potash the product is methylheptenol $C_8H_{16}O$. This boils about 173° under atmospheric pressure.

It thus appears that different bodies are obtainable from geraniol or geraniol bearing compounds when these are heated with alcoholic potash under different conditions.

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[1] J. Pr. Chem. 1896 [2] 53, 225 - 237—Abstract Journ. Chem. Soc., June 1896, 381.

[2] Compt. rend. 126, 1423. [3] Compt. rend. 128, 110. [4] Ber. 31, 2989.

The crude oil of *D. fascicularis* contains free alcohol, probably geraniol, as practically no constituent was present boiling below 222°.

By referring to Schimmel & Co's list of known constituents of essential oils, Report, April, 1897, we find that geraniol occurs in the oil from the following:—

Fresh flowers N.O. Rosaceæ (Roses).
Herb N.O. Geraniaceæ (Pelargonium sp.)
Grass N.O. Gramineæ (Andropogon sp.)
Flowers N.O. Rutaceæ (Citrus sp.)
Flowers N.O. Anonaceæ (Cananga sp.)
Wood N.O. Burseraceæ (Bursera sp.)
To this list may now be added; Shrub N.O. Myrtaceæ (Darwinia sp.)

With the doubtful exception of the oil from *Eucalyptus citriodora* this appears to be the first time that geraniol has been found occurring in plants belonging to the Myrtaceæ, although this genus consists so largely of oil-yielding plants.

Distillation of the original oil.

100 cc. of the crude oil of *D. fascicularis* was distilled under atmospheric pressure, only a few drops came over below 170°, principally water; the thermometer then rises rapidly with an occasional drop to 215°, between 215° and 222° 5 per cent. distilled, three fractions were then obtained:

1. 222° to 230° obtained 32 per cent.
2. 230 „ 240 „ 32 „
3. 240 „ 270 „ 22 „

Specific gravity first fraction ·897 at 20°
„ second „ ·906 „ 20°
„ third „ ·913 „ 20°

Another distillation gave—

222° to 230° = 34 per cent.
230 „ 235 = 47 „
235 „ 240 = 67 „

This was taken as one fraction, it had no rotation, its specific gravity at 18° = ·9036.

Some decomposition had taken place, the odour of acetic acid being most marked, so that the oil cannot be distilled under atmospheric pressure without alteration. The distillation results show an entire absence of terpenes and other constituents boiling at a low temperature, and the same results were also secured from the oil obtained by cold saponification.

When the fraction (222 – 240°) was saponified by alcoholic potash in the cold and the oil treated with dry calcium chloride, a solid mass was obtained; this was ground up with ether and dried at pump as much as possible, then pressed between drying paper until dry. On decomposing this with water 30 cc. of a slightly coloured oil was obtained; this had a fine rose odour, specific gravity at 16° = ·886, on distillation the greater portion distilled between 228 - 230° was practically colourless, had no rotation, and formed citral on oxidation. These characters indicate geraniol. It is also readily soluble to a clear solution in 55 per cent. alcohol. The crude oil of *D. fascicularis* does not form a clear solution with two volumes of 70 per cent. alcohol, but does so with 90 per cent. alcohol.

Saponification of the Ester.

Several determinations of the percentage of ester in the crude oil of *D. fascicularis* from several distillations obtained at different times, gave 57·05 per cent. as the least, and 65·1 per cent. as the greatest; this was from oil distilled in November. When the dark colour was removed by shaking with a very dilute solution of aqueous potash, the determination on the same sample of oil showed a diminution of 1·4 per cent. or 60·9 reduced to 58·5 per cent. A determination on the fraction 222 – 240° obtained on distilling the crude oil gave 73·1 per cent. of ester. The method adopted in these determinations was to weigh the oil into a flask, add 20 cc. of correctly standardised alcoholic potash (semi-normal) and heat to boiling on the water bath for half an hour with air condenser. It was then cooled, water added, also a few drops of

phenolphthalein and the solution titrated with semi-normal sulphuric acid. The weight of potash used in the saponification was then calculated, the saponification figure determined, then

$$\frac{\text{saponification figure} \times 19{\cdot}6}{56} = \text{per centage of ester.}$$

1. 2·6468 gram required ·4312 gram potash
   S.F. 163 = 57·05 per cent. ester.
2. 1·6502 gram required ·2688 gram potash
   S.F. 163 = 57·05 per cent. ester.
3. 1·8938 gram required ·3248 gram potash
   S.F. 171·5 = 60 per cent. ester.
4. 1·8769 gram required ·3248 gram potash
   S.F. = 170·5 = 59·7 per cent. ester.
5. 1·777 gram required ·3108 gram potash
   S.F. = 174 = 60·9 per cent. ester.
6. 1·7649 gram required ·3276 gram potash
   S.F. = 185·6 = 64·9 per cent. ester.
7. 1·8509 gram required ·3444 gram potash
   S.F. = 186 = 65·1 per cent. ester.

(Nos. 6 and 7 represent the November oil.)

Determination of the free Alcohol.

10 cc. of the November oil containing 65 per cent. of geranyl acetate was mixed with an equal volume of acetic anhydride and a little anhydrous sodium acetate; this was boiled for three hours, water was then added and the whole again heated, the oil was separated, washed and dried.

1·3558 gram of this oil required ·3164 gram potash S.F. = 233·4 = 81·68 per cent. ester. We thus obtain 16·68 per cent. increase of ester, which calculated from $C_{10}H_{17}OOCCH_3$ represents 13·11 per cent. of free alcohol. From the distillation figures this alcohol is probably geraniol.

Oxidation of the alcohol to aldehyde.

The fraction 222 – 240° was saponified and the oil distilled; the fraction 227 – 230° was oxidised by bichromate of potassium,

using Beckmann's method. Oxidation takes place readily, giving an oil with a strong lemon odour. The separated oil was agitated with a solution of acid sodium sulphite, the crystalline mass separated, purified, and decomposed by sodium carbonate. The aldehyde thus obtained had a strong odour of lemons. It was treated with pyrotartaric acid in absolute alcohol with β-naphthylamine, also dissolved in absolute alcohol (Doebner's reaction).[1] A lemon-yellow crystalline substance was obtained on cooling, melting at 197 – 198° and is the alcyl-β-naphtocinchoninic acid characteristic of citral. The same aldehyde was also obtained when the alcohol from the calcium chloride compound was oxidised. Citral is therefore, the aldehyde obtained on oxidising the alcohol of the ester in the oil of *D. fascicularis*.

Determination of the acid.

The liquid obtained after saponification and separation of the oil was made alkaline and evaporated nearly to dryness, this was then acidified with sulphuric acid, the sulphate of potassium separated and the liquid distilled. The volatile acid obtained in the distillate was almost entirely acetic acid, although the odour indicated the presence of a small quantity of another volatile acid. The silver salt was obtained, purified, and the molecular value of the acid determined. 0·2796 gram of the silver salt gave on ignition 0·1789 gram silver = 63·98 per cent.; CH_3COOAg requires 64·6 per cent. silver. The molecular value also shows 61·6 for the acid instead of 60 acetic acid. The probable presence of a small quantity of an acid with a higher molecular value is thus indicated. The reactions were those of acetic acid, no formic acid could be detected. The distillate was neutralised, evaporated down and allowed to crystallise; a good quantity of crystallised acetate of sodium was obtained showing some well developed monoclinic crystals. The principal acid of this ester is, therefore, acetic acid.

[1] Ber. 27, 352.

Essential oil of Darwinia taxifolia.

This oil was distilled from fresh material. It differs largely from the oil of *D. fascicularis* in all its characters. The specific gravity of the crude oil was ·8734 at 21° C. and its rotation in 100 mm. tube was 6·5° to the left.

When distilled 4 per cent. came over below 165°, and by 175° 54 per cent. had been obtained, by 185° 65 per cent. had distilled. From 165 – 185° was considered as first fraction. Second fraction 185 – 230° = 6 per cent. Third fraction 230 – 255° = 16 per cent.

Specific gravity, first fraction = ·8545 at 21° C.
„ third fraction = ·9062 „
Rotation 100 mm. tube, first fraction – 10·6
„ „ „ third fraction + 4·7

The lower boiling portion of the first fraction consisted largely of lævopinene shown by its boiling point and the formation of its nitrosochloride melting point 103°. Neither phellandrene nor cineol could be detected. The ester determination gave results as follows:—1·3381 gram crude oil required ·0196 gram potash
S.F. = 14·5 = 5 per cent ester.
1·2176 gram required ·0196 gram potash
S.F. = 16 = 5·6 per cent. ester.

An ester determination on the third faction gave the following result:—
1·5175 gram required ·0532 gram potash
S.F. 35 = 12·3 per cent. ester.

Determination of free alcohol.

10 cc. of the crude oil was boiled three hours with an equal volume of acetic anhydride and a little anhydrous sodium acetate. The separated oil was washed and dried:
1·7198 gram required ·0756 gram potash
S.F. = 44 = 15·4 per cent. ester.

The oil thus contains some free alcohol, but it is doubtful if it be geraniol, as the regenerated oil, after saponification of the ester had a marked odour of linalool. If the alcohol be considered as

having a formula $C_{10}H_{18}O$ there was 7·9 per cent. of alcohol present in the free condition in this oil. The bromide obtained from the first fraction was liquid.

The commercial prospects of this oil, in comparison with that from *D. fascicularis*, being poor, no further investigation of its remaining constituents was undertaken.

The yield of oil from *D. taxifolia* is almost identical with that from *D. fascicularis*, being ·313 per cent. The crude oil is much lighter in colour than that from *D. fascicularis*. The crude oil did not form a clear solution with two volumes of 90 per cent. alcohol.

(*c*) Possibilities of Cultivation.

As these species do not present any very marked horticultural attractions they have received little or no attention from gardeners and are therefore only known in the wild state, and so very little data can be given under this heading. However, as *D. fascicularis* has such good commercial possibilities it is hoped that experiments will be taken up at once in regard to it.

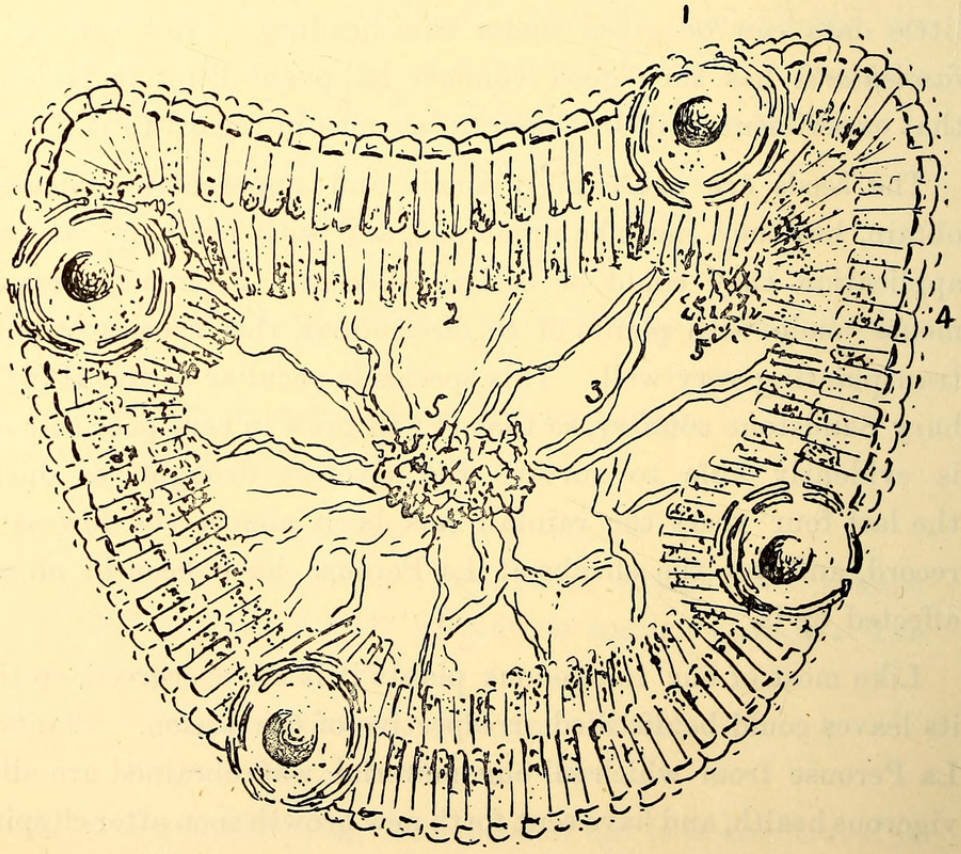
The seeds are exceedingly small and apparently difficult to obtain, but they must be numerous, and with ordinary care and application they could be easily collected. From a few experiments made with plants of *D. fascicularis*, this species survives transplanting very well. This species is peculiar to the Hawkesbury Sandstone country, so that it will grow in very poor soil, and is evidently able to survive the severest drought, as during the last four years the rainfall has been almost the lowest on record, and yet the shrubs at La Perouse have been in no way affected by it.

Like most of our indigenous plants it is an evergreen, so that its leaves could be distilled irrespective of the season. Plants at La Perouse from which all our material was obtained are all in vigorous health, and have sent forth new growth soon after clipping. In no instance were the trees cut down or uprooted, but only the terminal branchlets cut off.

In its natural state it has a tendency to run very much to wood, but this is probably owing to the plants growing so very close together—in many cases almost forming an impenetrable bush. Under cultivation and with the trees planted some distance apart this defect should be removed, and bushy foliaceous plants produced. The results of the experiments in transplanting now being carried out at this Museum will be available to the general public at any time.

We wish to express our acknowledgements to Miss S. Hynes, B.A. for the locality of *Darwinia taxifolia* at Randwick, to Mr. Connelly for photographs of the plants, and to Mr. H. Oakes (one of the Technical College Students in organic chemistry) who gave up much time to assist.

TRANSVERSE SECTION OF LEAF OF *Darwinia fascicularis*, A. Rudge
(Highly magnified.)



1—Lysigenous oil gland with oil globules. 2—Palisade-layers. 3—Spongy tissue. 4—Epidermis of Leaf. 5—Vascular bundles.