

CVII.—*The Constituents of the Volatile Oil of the Bark of Cinnamomum pedatinervium, of Fiji.*

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THE bark of *Cinnamomum pedatinervium*, a tree indigenous to the Fiji Islands, possesses a pleasant, aromatic, spicy odour, due to the secretion of a volatile oil. The following account is given by Berthold Seemann in his "Flora Vitiensis" (p. 202).

"The bark of the 'Macou,' as it is termed in the Bau dialect, 'Mou' in that of Kadavu, and 'Maiu' in that of Namosi, is a kind of Cassia bark, which may prove of commercial importance, and is used by the Fijians for scenting cocoa-nut oil. The tree yielding it is about thirty feet high, four to five inches in diameter, and is met with above an elevation of 1500 feet, in dense virgin forests. I found it on Buke Levu, island of Kadavu, and on Voma peak, Viti Levu; and Mr. Pritchard received fine specimens from the islands of Gau, where they had been collected by W. Berwick, a coloured man, residing there. The bark has a fine aromatic smell and flavour, a light brown colour, is thicker than that of the cinnamon of commerce, and resembles some of the laurineous barks, such as the Sintoc and Culilawang, brought from the Moluccas. In Namosi, it is used as a sudorific. Unfortunately, I did not see the tree in flower, and hence am unable to determine whether the 'buds' are equal to the best 'Cassia buds' of commerce. The resemblance of the Fijian names to that of 'Massoy,' given to a fine quality of Cassia bark, from New Guinea, deserves investigation."

A sample of this bark having been sent from Suva, Fiji, to the Imperial Institute in order that its volatile oil might be submitted to examination and commercial valuation, the investigation described in the following pages was carried out in the Laboratories of the Scientific and Technical Department of the Institute.

### EXPERIMENTAL.

A quantity of the powdered bark weighing  $50\frac{1}{2}$  lbs., on distillation with steam, yielded  $7\frac{1}{2}$  oz. of the volatile oil, which is equivalent to 0.92 per cent. The oil is almost colourless when first distilled, but gradually assumes a yellowish-brown colour. It has a sweet, aromatic odour and a pungent, spicy taste. It has a rotatory power of  $-4.78^\circ$  at  $15^\circ$  in a 100 mm. tube, or  $[\alpha]_D -4.96^\circ$ ; when, however, the oil is heated to  $170^\circ$  and allowed to cool again, the rotatory power is increased to  $-5.48^\circ$  or  $[\alpha]_D -5.66^\circ$ . Its index of refraction is 1.4963 at  $15^\circ$ . It is freely soluble in the usual organic solvents, and is neutral to litmus. When the oil is cooled to  $-12^\circ$  for an hour in a mixture of ice and salt, no solid substance separates.

The oil was distilled under atmospheric pressure, and the following fractions were obtained:  $180-205^\circ$ , 22 per cent.;  $205-220^\circ$ , 30 per cent.;  $220-230^\circ$ , 27 per cent.;  $230-255^\circ$ , 18 per cent.; the residue in the distilling flask amounted to 3 per cent. and was of a dark brown colour. The physical characters of the oil and these fractions are given in the following table. The optical rotatory power was in each case determined in a 100 mm. tube by means of a Laurent's half-shadow polarimeter. The refractive indices were determined in a hollow glass prism by means of the spectrometer.

	Boiling at	Specific gravity $15^\circ/15^\circ$ .	$[\alpha]_D$ .	$n_D$ .
Oil .....	—	0.964	$-4.96^\circ$	1.4963
Fraction I.....	$180-205^\circ$	0.915	$-11.37$	1.4816
„ II.....	$205-220$	0.953	$-6.69$	1.4918
„ III.....	$220-230$	0.998	$-2.40$	1.5068
„ IV.....	$230-255$	1.013	$-1.91$	1.5161

### Estimation of Esters.

A quantity of the oil weighing 3.1810 grams was boiled with  $N/2$  alcoholic potassium hydroxide for half an hour. After the solution had cooled, it was titrated with  $N/2$  hydrochloric acid, phenolphthalein being employed as the indicator. It was found that 0.5 c.c. of the

alkali had been neutralised, equivalent to a saponification number 4.4, whence the percentage of esters in the oil amounts to 1.5 per cent. (calculated as  $C_{10}H_{17} \cdot C_2H_3O_2$ ).

#### *Estimation of Alcohols.*

A mixture of 5 c.c. of the oil, 10 c.c. of acetic anhydride, and 1 gram of anhydrous sodium acetate was boiled for  $1\frac{1}{2}$  hours in a small flask attached to a reflux condenser. About 15 c.c. of water were now added, and the flask was heated for half an hour on the water-bath. The acetylated oil was separated by the addition of a considerable quantity of water to the liquid, which had been transferred to a separating funnel; it was washed with sodium carbonate solution and afterwards with water until the washings were neutral to litmus, and was then dried with anhydrous sodium sulphate. 1.4262 grams of the acetylated oil were hydrolysed with  $N/2$  alcoholic potassium hydroxide, and the resulting solution was titrated with  $N/2$  hydrochloric acid; it was found that 5.9 c.c. of the alkali solution had been neutralised by the acids formed in the hydrolysis, whence the saponification number of the acetylated oil is 115.8, corresponding with 31.85 per cent. of total alcohols (calculated as  $C_{10}H_{17} \cdot OH$ ) in the original oil; 1.1 per cent. of the alcohols being present in the form of esters, the free alcohols amount to 30.75 per cent.

#### *Estimation of Methoxyl.*

The estimation of methoxyl in the oil was effected by a modification of Zeisel's method:

- I. 0.3233 gave 0.0281 AgI. OMe = 1.15 per cent.  
 II. 0.5010 „ 0.0443 AgI. OMe = 1.16 per cent.

#### *Separation of the Terpene.*

The oil (150 grams) was distilled under 10 mm. pressure by means of a paraffin bath, and the distillate was collected until the temperature rose to  $110^\circ$ . The fraction thus obtained was redistilled under the same pressure and collected below  $100^\circ$ . This product was heated with and redistilled from metallic sodium under the ordinary pressure. A specimen of the terpene which had been treated five times in this way gave, on analysis, figures which pointed to the formula  $C_{10}H_{16}$ , but it evidently still contained a small quantity of oxygenated compounds. Unfortunately, the quantity of terpene remaining was too small to admit of further attempts to purify it.

0.2699 gave 0.8586  $\text{CO}_2$  and 0.2731  $\text{H}_2\text{O}$ .  $\text{C} = 86.8$ ;  $\text{H} = 11.3$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$ ;  $\text{H} = 11.8$  per cent.

The terpene boils at  $167\text{--}172^\circ$  and has a specific gravity 0.8659 at  $15^\circ/15^\circ$ . Its rotatory power in a 100 mm. tube is  $-15.48^\circ$  or  $[\alpha]_D -17.72^\circ$ . It possesses a pleasant lemon-like and slightly camphoraceous odour, and gives an orange-red coloration with concentrated sulphuric acid.

Determinations of the vapour density by V. Meyer's method, using aniline as the heating agent, gave the following results: I. 0.0612 gram gave 9.3 c.c. at  $17^\circ$  and 755 mm. measured over water. Hence the vapour density = 80.1 and the molecular weight = 160.2. II. 0.1027 gram gave 16.0 c.c. at  $17^\circ$  and 751 mm. measured over water. Hence the vapour density = 78.1 and the molecular weight = 156.2.  $\text{C}_{10}\text{H}_{16} = 136$ . These results are somewhat high, but this is due to polymerisation of some of the terpene with formation of resin in the course of the experiment; the formula  $\text{C}_{10}\text{H}_{16}$  is, however, clearly indicated.

*Preparation of the Dibromide.*—Bromine was added drop by drop to a well cooled solution of the terpene in glacial acetic acid until the colour was no longer discharged. Since nothing had separated from the solution after 24 hours, the product was precipitated by the addition of water and dissolved in ether; the ethereal solution was washed with solution of sodium carbonate and afterwards with water and dried with calcium chloride. After the removal of the ether by distillation, the residue consisted of a nearly colourless, syrupy liquid. It was left over calcium chloride for four weeks in a vacuum desiccator, at the end of which time it had become slightly yellow, but otherwise remained unchanged. Estimation of the bromine by Carius's method showed that the substance is a *dibromide*,  $\text{C}_{10}\text{H}_{16}\text{Br}_2$ .

0.3945 gave 0.5116 AgBr.  $\text{Br} = 55.2$ .

$\text{C}_{10}\text{H}_{16}\text{Br}_2$  requires  $\text{Br} = 54.1$  per cent.

Attempts to prepare a crystallisable nitrosochloride or nitrosite were unsuccessful.

After the removal of the greater part of the terpene, the residual oil was shaken with solution of sodium carbonate (5 per cent.). Subsequent examination of the solution showed that nothing had been extracted from the oil except a little brown colouring matter; the absence of free acids was thus established.

The oil was washed with water and shaken with a strong solution of sodium hydrogen sulphite for about half an hour; the aqueous liquid was then run off and washed with ether. Since no solid substance separated from the solution, it was treated with an excess of sodium carbonate and distilled. The first few drops of the distillate

had an odour resembling that of fatty aldehydes, and on further distillation a slight citral-like odour was observed, but no appreciable quantity of aldehydes was obtained.

### *Identification of Eugenol.*

The oil was now washed with a small quantity of solution of sodium carbonate and afterwards with water; it was then shaken with about 30 c.c. of solution of sodium hydroxide (5 per cent.). After the aqueous solution had been washed with ether, it was acidified with dilute sulphuric acid. A substance with a clove-like odour separated in oily drops and was extracted with ether. The ethereal solution was dried with calcium chloride and the ether carefully removed by distillation. The residue consisted of about  $1\frac{1}{2}$  grams of a brown oil which gave with ferric chloride the blue colour characteristic of eugenol. It was dissolved in dilute solution of potassium hydroxide, benzoyl chloride was added drop by drop, and the mixture was warmed and well shaken. A benzoyl derivative separated, and was washed with dilute potassium hydroxide, and afterwards with water. When crystallised from alcohol, it formed well-defined, rhombic prisms; it was recrystallised from the same solvent and dried between filter papers. It melted sharply at  $70^{\circ}$ , and, on analysis:

0.1865 gave 0.5179  $\text{CO}_2$  and 0.0997  $\text{H}_2\text{O}$ .  $\text{C} = 75.74$ ;  $\text{H} = 5.94$ .

$\text{C}_{17}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 76.12$ ;  $\text{H} = 5.97$  per cent.

Determination of the methoxyl was made by a modification of Zeisel's method:

0.2950 gave 0.2603 AgI.  $\text{OMe} = 11.64$ .

$\text{OMe} \cdot \text{C}_6\text{H}_3(\text{C}_3\text{H}_5) \cdot \text{OBz}$  requires  $\text{OMe} = 11.57$  per cent.

The benzoyl derivative of eugenol was prepared for comparison; this melted at  $70^{\circ}$ , and when mixed with that obtained from the phenol from the oil, the melting point was unchanged.

### *Eugenol Methyl Ether (?)*

After removing the eugenol from the oil by shaking it with aqueous potassium hydroxide, the oil still possessed a pungent taste which closely resembled that of eugenol methyl ether, a small quantity of which was prepared for comparison. Further, since the amount of eugenol present only accounts for a small proportion of the methoxyl found in the oil, some other substance containing methoxy-groups must be present. It is, therefore, highly probable that the oil contains a little eugenol methyl ether; the quantity of this compound demanded

by the percentage of methoxyl (after deducting that due to the eugenol) amounts to about 3 per cent.

*Hydrolysis with Alcoholic Potassium Hydroxide.*

In order to hydrolyse the esters, the oil (from which the terpene and eugenol had been removed) was boiled for two hours with alcoholic potassium hydroxide in a flask connected with a reflux condenser. After the greater part of the alcohol had been removed by distillation, the liquid was transferred to a separating funnel and water was added in sufficient quantity to effect the separation of the oil. The oil which had separated was run off, and the last portions were removed by shaking with ether; the oil was then dissolved in this ether, and the ethereal solution washed with a little water and dried quickly with calcium chloride. After the ether had been removed by distillation, the oil was distilled under 10 mm. pressure and afterwards separated into four fractions (I, II, III, and IV) by distillation under atmospheric pressure.

The alkaline liquid was concentrated to a small volume and was then acidified with sulphuric acid and distilled with steam. The first portion to distil over was turbid and contained small oily drops of a substance with the odour of eugenol; the whole of the distillate was rendered slightly alkaline with sodium carbonate and extracted with successive portions of ether. After distilling off the ether, a small residue of eugenol was obtained, which gave a blue coloration with ferric chloride and yielded a benzoyl derivative melting at 69–70°. A small quantity of eugenol was therefore present in the oil in the form of an ester.

The sodium carbonate solution (from which the eugenol had been extracted) was concentrated, acidified with sulphuric acid, and distilled with steam. The distillate was again neutralised with sodium carbonate, was concentrated to a very small volume, and was acidified with sulphuric acid and shaken repeatedly with ether. The ether was carefully removed by distillation, and a very small residue was obtained, which had a pale brown colour and an odour of fatty acids (especially that of propionic acid); when boiled with a little alcohol and strong sulphuric acid, an ethereal odour recalling that of ethyl propionate was produced.

The four fractions of oil obtained after the hydrolysis of the esters were collected at the following temperatures: I, 200–215°; II, 215–223°; III, 223–232°; IV, 232–255°. After refractionation, six fractions were obtained which boiled within the following ranges of temperature: (1) 195–205°; (2) 205–215°; (3) 215–223°; (4) 223–227°; (5) 227–235°; (6) 235–245°; owing, however, to

the small volume operated on, the separation was necessarily incomplete. The specific gravity and optical rotatory power of each fraction were determined; the results are given in the following table,

Fraction.	Boiling point.	Specific gravity 15°/15°.	$[\alpha]_D$ .
1	195—205°	0·9156	—9·49°
2	205—215	0·9468	—6·26
3	215—223	0·9756	—3·62
4	223—227	1·0019	—2·04
5	227—235	1·0027	—1·60
6	235—245	1·0272	—1·00

#### *Identification of Linalool.*

*Fraction (1).*—The odour of this fraction indicated the presence of some terpene which had not been removed by the earlier treatment; it also possessed a fragrance similar to that of linalool. Five grams of it were added gradually to a solution containing 30 grams of potassium dichromate, 15 grams of sulphuric acid, and 100 c.c. of water, the mixture being kept cool and well shaken. After an hour it was warmed for a short time on the water-bath and then distilled with steam. The distillate contained about 2 grams of an oily liquid, which had an intensely lemon-like odour, due to the presence of citral. The citral was identified by conversion into  $\alpha$ -citryl- $\beta$ -naphthacinchonic acid. The oil from the distillate, after being dried with calcium chloride, was dissolved in dry alcohol; a small quantity of an alcoholic solution of  $\beta$ -naphthylamine and a drop or two of pyruvic acid were added, and the mixture was heated in a flask attached to a reflux condenser for about an hour. On cooling, minute, lemon-yellow plates separated, which were collected and drained on a porous tile. In order to purify this substance, it was dissolved in dilute ammonia and reprecipitated by the addition of acetic acid, was washed with water and recrystallised from hot alcohol; it now melted at 196—198°, and agreed in its general characters with a specimen of the  $\beta$ -naphthacinchonic acid prepared from citral. It is evident, therefore, that this fraction contained linalool. A careful search was made for camphor or borneol in this and the next fraction, but neither could be detected.

#### *Identification of Safrole.*

*Fraction (2).*—When this fraction was oxidised with chromic acid by the method just described, the product was found to contain citral

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and piperonal, which were separated by the method described in the following paragraph.

*Fraction (3).*—The products of the oxidation with chromic acid of 8 grams of this fraction were extracted by shaking the mixture with successive portions of ether. The ethereal solution was washed with a little water, then with solution of sodium carbonate, and again with water. The residue obtained after the removal of the ether by distillation had an odour of citral and piperonal; it was treated with solution of sodium hydrogen sulphite, and a bisulphite compound separated in small, glistening plates. This compound was warmed in contact with the solution for about half an hour in order to free the piperonal compound from that of citral, the latter being redissolved under these conditions with formation of sodium citralsulphonate,  $C_9H_{17}(SO_3Na)_2 \cdot CHO$ , as has been shown by Tiemann and Semmler (*Ber.*, 1893, 26, 2710). The bisulphite compound was now collected and decomposed with solution of sodium carbonate; piperonal separated and was transferred to a filter paper and washed with water. The product possessed the characteristic odour and general properties of piperonal, and after recrystallisation from warm light petroleum melted at  $37^\circ$ . On analysis:

0.2186 gave 0.5116  $CO_2$  and 0.0767  $H_2O$ .  $C = 63.83$ ;  $H = 3.84$ .

$C_8H_6O_3$  requires  $C = 64.00$ ;  $H = 4.00$  per cent.

The formation of piperonal by the oxidation of the oil indicated the presence of safrole, and this was confirmed by the preparation of its nitrosite by the method described by Angeli and Rimini (*Gazzetta*, 1893, 25, ii, 200). About 6 grams of the oil, from fractions (4) and (6), were dissolved in 20 c.c. of light petroleum, and the solution was poured into a flask containing an aqueous solution of sodium nitrite. Dilute sulphuric acid was added slowly, drop by drop, when an opaque, yellowish-brown substance gradually separated at the junction of the liquids. This product was transferred to a filter paper and washed with water, dilute potassium hydroxide, again with water, then with alcohol, and finally with ether. Safrole  $\alpha$ -nitrosite was thus obtained as a pale yellow powder which melted with effervescence at  $129-130^\circ$ , and corresponded in all its characters with a specimen of the nitrosite prepared from safrole. On analysis:

0.1916 gave 0.3538  $CO_2$  and 0.0764  $H_2O$ .  $C = 50.36$ ;  $H = 4.43$ .

$C_{10}H_{10}O_5N_2$  requires  $C = 50.42$ ;  $H = 4.20$  per cent.

In order to test for the presence of terpineol in fraction (3), a portion of it was treated with hydriodic acid of specific gravity 1.95; nothing separated, although an artificial mixture of terpineol with safrole, when treated in the same way, readily furnished the crystalline



dipentene dihydriodide; hence it must be concluded that terpineol is absent.

*Fraction (4).*—This fraction, on oxidation with chromic acid, yielded piperonal, together with a small quantity of citral.

*Fraction (5).*—By the oxidation of this fraction with potassium permanganate according to the method described by Tiemann (*Ber.*, 1891, 24, 2883), a small quantity of piperonylic acid was obtained, which melted at 226° (uncorr.), and agreed in its general characters with a specimen of piperonylic acid obtained by oxidising safrole in the same way.

When this fraction was oxidised with chromic acid mixture, piperonal and a little citral were produced. An attempt to detect the presence of geraniol by means of the formation of its diphenylurethane gave a negative result.

### Summary.

This investigation has shown that the chief constituents of the oil are as follows:

- (i) A *terpene*,  $C_{10}H_{16}$ .
- (ii) *Linalool*.
- (iii) *Safrole*.
- (iv) *Eugenol*.
- (v) *Eugenol methyl ether* (?).

The quantitative composition (as far as can be judged from the small sample of oil available for examination) is roughly as follows:

Terpene .....	15—20 per cent.
Alcohols (wholly, or in part, linalool) .....	30    „
Esters.....	1·5    „
Safrole .....	40—50    „
Eugenol .....	1    „
Eugenol methyl ether (?) .....	3    „

In conclusion, I desire to express my warmest thanks to Professor Dunstan, both for the suggestion that I should undertake this inquiry and for the encouragement which he has given during the course of the work.

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