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Contributors

Power, Frederick B. 1853-1927.
Tutin, Frank.
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THE CONSTITUENTS OF THE ESSENTIAL OIL FROM THE FRUIT OF

PITTOSPORUM UNDULATUM

BY

FREDERICK B. POWER, PH.D.

AND

FRANK TUTIN

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THE WELLCOME CHEMICAL RESEARCH LABORATORIES
FREDERICK B. POWER, PH.D., *Director*
6, King Street, Snow Hill
LONDON, E.C.

CX.—*The Constituents of the Essential Oil from the Fruit of Pittosporum undulatum.*

By Frederick Belding Power and Frank Tutin.

Pittosporum undulatum, Ventenat, is a tree indigenous to south-eastern Australia, where it is known to the English colonists by the popular names of "Native Laurel" and "Mock Orange" (compare *Select Extra-tropical Plants*, by Baron Ferd. von Mueller, 1884, p. 284, and *Pharmacographia Indica*, Vol. 1, p. 154).

In a communication to the Royal Society of N. S. Wales, on December 4th, 1895, Professor R. Threlfall, of the University of Sydney, described the general characters of the fruit of *Pittosporum undulatum*, and particularly noted that, when bruised, it develops a fragrant odour, resembling that of the tangerine orange, although easily distinguished from the latter. The flowers of this tree are also known to possess an exquisite fragrance, which, however, is quite distinct from that of the fruit, and resembles that of orange blossoms.

In order to ascertain the nature of the odorous principle of Pittosporum fruit, Professor Threlfall subjected 50 kilograms of the entire fruit to steam distillation, and obtained therefrom about 180 c.c. of an essential oil. As the specific gravity of the latter was determined by him to be 0·848 at 24°, the yield of oil would correspond to about 0·3 per cent. of the weight of the fruit. He then submitted about 60 c.c. of the oil to a single fractional distillation, but none of these fractions were further examined, and they were subsequently sent to Professor W. A. Tilden, of the Royal College of Science, London, together with a small quantity of the original oil. Through the kindness of Professor Tilden, these specimens were placed at the disposal of one of us for further examination.

The oil distilled by Professor Threlfall was stated by him to have been dried by means of fused calcium chloride, and the portion received by us amounted to about 160 grams. After further drying with anhydrous sodium sulphate, and filtering, it was rectified by distillation. The rectified oil was pale yellow and had a pleasant odour, suggestive of the presence of a considerable proportion of limonene. Its density was 0·8638 at 15°, and its optical rotation $+82°32'$ in a 1-dcm. tube. The oil was then subjected to a preliminary examination, but, as it had evidently undergone some change on keeping, we availed ourselves of the opportunity of having a larger quantity of the oil freshly distilled for us in Australia for the purpose of its more complete investigation.

Although Professor Threlfall in his paper (*loc. cit.*) has indicated that the *Pittosporum undulatum* is common in the bush around Sydney, this appears at present not to be the case, and a supply of fruit sufficient for the distillation of the oil could only be obtained from private gardens, where the tree is cultivated on account of the fragrance of the flowers. The distillation was conducted during the months of December and January, just before the period of ripening of the fruit, and while it was still green. From 220 kilograms of the fruit, 960 grams of essential oil were obtained, corresponding to a yield of 0·44 per cent.

EXPERIMENTAL.

The investigation here described was conducted entirely with the oil which had been freshly distilled for us in Australia, and the amount employed for this purpose was 900 grams. It is pale yellow, and has a pleasant odour resembling that of orange oil. After being dried with anhydrous sodium sulphate and filtered, it had a density of 0·8615 at 15°/15°, and an optical rotation of $+74°4'$ in a 1-dcm. tube. It was insoluble in ten times its volume of 70 per cent. alcohol.

A determination of the amount of free acids and esters gave the following data: 20 grams of the oil required 0·2 c.c. of a semi-normal alcoholic solution of potassium hydroxide for the neutralisation of the free acids, and on subsequently adding an excess of alkali and boiling for thirty minutes, it was found that 4 c.c. of semi-normal alkali were required for the hydrolysis of the esters present.

The entire oil was then shaken several times successively with small portions of 20 per cent. sulphuric acid, and afterwards washed well with water. The acid aqueous liquid was freed from adhering oil by shaking with ether, then made alkaline with potassium hydroxide, and again shaken with ether. After washing the ethereal liquid and drying it by means of potassium carbonate, the ether was removed, but only a trace of brown, resinous matter was obtained, thus indicating the absence of any basic substance such as methyl anthranilate.

About 20 c.c. of the oil were shaken for four hours with a saturated solution of sodium bisulphite, but it yielded no solid compound, nor did the aqueous bisulphite liquid contain any aldehyde or ketone.

As the amount of free acids contained in the oil was so very small, it was, after treatment with the dilute sulphuric acid, directly extracted several times successively with a 5 per cent. solution of potassium hydroxide, and subsequently washed with water. The alkaline aqueous liquid, after being freed from adhering oil, was acidified with sulphuric acid and extracted with ether, the ethereal solution being subsequently shaken with a solution of sodium carbonate to remove any acids, and finally washed with water. On removing the ether, a very small brown residue was obtained, which had an odour resembling that of eugenol and gave a brown colour with ferric chloride, but no definite benzoyl derivative could be prepared from it.

The sodium carbonate liquid, which contained the acids from the preceding extraction with potassium hydroxide, was acidified with sulphuric acid and extracted with ether. On removing the ether, a very small quantity of a brown oil was obtained, which had a strong odour of valeric acid and gave an intense violet coloration with ferric chloride. This violet coloration was apparently due to the presence of a trace of salicylic acid. The oily liquid, after standing some time, deposited crystals which, after several crystallisations from alcohol, melted at 62°, and evidently consisted of palmitic acid, since the melting point was not changed on mixing the substance with an equal amount of pure palmitic acid.

Preliminary Examination of the Terpenes.

As a preliminary test for the presence of an olefinic or other unstable terpene, the oil, which had previously been treated with dilute sulphuric acid and with alkali, as above described, was dried with anhydrous sodium sulphate, and then distilled under 60 mm. pressure. The portion which boiled below 110° was collected, and, after submitting this to several fractionations under a pressure of 20 mm., the density of a fraction boiling below 70° was determined, and found to be 0·8466 at 15°/15°, which proved the absence of any olefinic terpene. These liquids were then distilled under the ordinary pressure, and the following fractions collected: below 165°; 165—170°; 170—172°. The density of the fraction 165—170° was found to be 0·8471 at 15°/15°, thus confirming the absence of myrcene. The fraction 170—172° was specially tested for phellandrene, but with a negative result.

Hydrolysis of the Oil.

All the oil boiling above 190° under the ordinary pressure was hydrolysed by boiling with an alcoholic solution of 7 grams of potassium hydroxide for about half an hour in a flask provided with a reflux condenser. After being allowed to cool, water was added, and the separated oil collected, washed, and dried with anhydrous sodium sulphate. It was then distilled under 60 mm. pressure, which removed a small amount of non-volatile, resinous matter.

Fractional Distillation of the Oil.

The hydrolysed oil, together with the portion which had previously been separated under diminished pressure, was then submitted to repeated distillation under the ordinary pressure, when the following fractions were ultimately obtained: below 165°; 165—169°; 169—173°; 173—180°; 180—185°; 185—195°; 195—205°; 205—215°; 215—225°; 225—235°; 235—245°; 245—255°; 255—270°; 270°+. The last-mentioned fraction was a viscid, green oil, and amounted to only 3·8 grams.

Identification of Pinene.

Fraction below 165°.—This was a colourless, limpid liquid, which commenced to boil at about 157° and had an odour of pinene. It was nearly insoluble in 70 per cent. alcohol, and amounted to 23 grams.

0·1077 gave 0·3444 CO_2 and 0·1141 H_2O. C = 87·2; H = 11·8.

$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

d15°/15° = 0·8515; α_D +61°50′ in a 1-dcm. tube.

This fraction evidently consisted of a hydrocarbon, and was found to contain pinene, as it yielded a small amount of a crystalline nitrosochloride, from which the corresponding nitrolbenzylamine, melting at

123°, was prepared. The fraction was also examined for camphene, but with a negative result.

Fraction 165—169°.—The weight of this fraction was 18 grams.

0·1324 gave 0·4274 CO_2 and 0·1401 H_2O. C = 88·0 ; H = 11·8.
d15°/15° = 0·8494 ; α_D + 73°50′ in a 1-dcm. tube.

Fraction 169—173°.—The weight of this fraction was 27 grams.

0·1352 gave 0·4345 CO_2 and 0·1428 H_2O. C = 87·6 ; H = 11·7.
d15°/15° = 0·8482 ; α_D + 79°36′ in a 1-dcm. tube.

Both this fraction and that immediately preceding it were colourless, limpid liquids, and evidently consisted of a mixture of pinene with the constituent of the following fraction.

Identification of Limonene.

Fraction 173—180°.—This fraction represented by far the largest portion of the oil, and amounted to 485 grams. It was a colourless, highly refractive liquid, having the characteristic odour of limonene, and on analysis was found to consist entirely of a hydrocarbon.

0·1140 gave 0·3679 CO_2 and 0·1214 H_2O. C = 88·0 ; H = 11·8.
$C_{10}H_{16}$ requires C = 88·2 ; H = 11·8 per cent.
d15°/15° = 0·8488 ; α_D + 89°10′ in a 1-dcm. tube.

It was readily identified as *d*-limonene by the formation of the tetrabromide, which, after recrystallisation from ethyl acetate, melted at 104°.

Fraction 180—185°.—The weight of this fraction was 46 grams.

0·1161 gave 0·3657 CO_2 and 0·1211 H_2O. C = 85·9 ; H = 11·6.
d15°/15° = 0·8588 ; α_D + 82°42′ in a 1-dcm. tube.

This fraction evidently also consisted to a large extent of *d*-limonene.

Fraction 185—195°.—The weight of this fraction was only 4·8 grams.

0·1083 gave 0·3347 CO_2 and 0·1128 H_2O. C = 84·3 ; H = 11·6.
d15°/15° = 0·8727 ; α_D + 66°48′ in a 1-dcm. tube.

It was evidently a mixture of the hydrocarbon contained in the preceding fractions with the oxygenated substance contained in the succeeding ones.

Fraction 195—205°.—This fraction, which was very pale yellow, amounted to only 4·1 grams.

0·1251 gave 0·3736 CO_2 and 0·1293 H_2O. C = 81·4 ; H = 11·5.
d15°/15° = 0·8938 ; α_D + 46°32′ in a 1-dcm. tube.

It was specially tested for linalool, but with a negative result.

Fraction 205—215°.—The weight of this fraction was 5·9 grams. It was light yellow, and possessed a pleasant, somewhat camphoraceous and rose-like odour.

0·1287 gave 0·3720 CO_2 and 0·1328 H_2O. C = 78·8; H = 11·5.
$d15°/15° = 0{\cdot}9179$; α_D +27°8′ in a 1-dcm. tube.

As this fraction was very small, it was further examined in connection with the following one.

Fraction 215—225°.—This fraction resembled the immediately preceding one in odour, and amounted to 8·2 grams.

0·1018 gave 0·2964 CO_2 and 0·1057 H_2O. C = 79·4; H = 11·5.
$d15°/15° = 0{\cdot}9242$; α_D + 17°0′ in a 1-dcm. tube.

This fraction and the preceding one evidently contained the greater proportion of the oxygenated constituent of the oil, and as their total weights amounted to only 14 grams, they were mixed together for the purpose of further examination.

A portion of the mixed liquid was treated with semicarbazide, but no semicarbazone could be obtained from it. The remainder of the liquid was therefore carefully oxidised by adding it slowly to a mixture of eight times its weight of potassium bichromate and twelve times its weight of sulphuric acid, the latter having been previously diluted with three times its volume of water. After the first action had ceased, the mixture was gently heated on a water-bath, with frequent shaking, for half an hour, then cooled, and repeatedly extracted with ether, which removed a yellow, oily substance. The latter was subjected to steam distillation, when nearly all passed over. The non-volatile portion was examined for the oxidation products of terpineol, but with a negative result. The oil contained in the distillate, which had a somewhat coumarin-like odour, was extracted with ether, the ethereal liquid freed from a trace of acid by shaking with a solution of sodium carbonate, washed, dried, and the ether removed. The oil thus obtained was treated in methyl alcohol solution with semicarbazide hydrochloride and sodium acetate, and allowed to stand overnight. On the addition of water, a rather viscid oil was precipitated, which did not become crystalline, and steam was therefore passed through the mixture in order to remove any uncombined oil, after which the semicarbazone solidified on cooling. It was accompanied by a considerable amount of gummy matter, but, after being dried and then recrystallised several times from alcohol, it was obtained in tufts of small needles, which melted at 174°. It was analysed with the following result:

0·0775 gave 0·1739 CO_2 and 0·0591 H_2O. C = 61·2 ; H = 8·5.
$C_{10}H_{17}ON_3$ requires C = 61·5 ; H = 8·7 per cent.

On warming a small quantity of this semicarbazone with dilute sulphuric acid, the regenerated substance was observed to possess a strong coumarin-like odour.

From the analytical figures it would appear that the semicarbazone is derived from a ketone (or aldehyde) having the formula $C_9H_{14}O$, and as no substance reacting with semicarbazide was originally present in the fractions oxidised, it is probable that these contained an alcohol of the formula $C_9H_{16}O$. This view is also in accordance with the low percentage of hydrogen found in the respective fractions, for $C_9H_{16}O$ requires H = 11·4 per cent., whereas an alcohol of the formula $C_{10}H_{18}O$ requires H = 11·7 per cent.

The semicarbazone described above does not appear to be identical with any heretofore obtained, but as the amount of substance was so very small, it was not possible to pursue its investigation further.

Fraction 225—235°.—The weight of this fraction was 5·2 grams. It was pale yellow and had a distinctly rose-like odour.

0·1323 gave 0·3907 CO_2 and 0·1361 H_2O. C = 80·5 ; H = 11·4.
d15°/15° = 0·9236 ; α_D + 11°56′ in a 1-dcm. tube.

The properties of this fraction indicated that it might contain some geraniol or a similar alcohol of rose-like odour. An attempt was therefore made to prepare the corresponding diphenylurethane, and also to isolate the alcohol by means of its conversion into the acid phthalic ester, but the amount of material was so exceedingly small that we were unable definitely to identify any constituent of it.

Fraction 235—245°.—The amount of this fraction was only 2·7 grams.

0·1087 gave 0·3287 CO_2 and 0·1130 H_2O. C = 82·5 ; H = 11·6.
d15°/15° = 0·9238 ; α_D + 6°32′ in a 1-dcm. tube.

Fraction 245—255°.—The weight of this fraction was 5·3 grams.

0·1183 gave 0·3757 CO_2 and 0·1239 H_2O. C = 86·6 ; H = 11·6.
d15°/15° = 0·9138 ; α_D + 0°56′ in a 1-dcm. tube.

This fraction and that immediately preceding it also possessed a rose-like odour, and they evidently consisted of a mixture of some of the oxygenated constituent of a preceding fraction with the constituent of the following one.

Isolation of a New Sesquiterpene.

Fraction 255—270°.—This was a relatively large fraction, amounting to 83·2 grams. It was a yellow, slightly viscous liquid, having a decidedly fragrant odour. It was almost insoluble in 70 per cent. alcohol.

0·1205 gave 0·3855 CO_2 and 0·1264 H_2O. C = 87·2; H = 11·7.
$d15°/15° = 0·9169$; $\alpha_D + 0°8'$ in a 1-dcm. tube.

The analysis and physical constants of this fraction indicated that it consisted of a nearly pure, optically inactive sesquiterpene. It distilled almost entirely between 260° and 265°, and for the most part between 263° and 264°. For its further purification it was twice distilled over metallic sodium under 60 mm. pressure, when it almost entirely passed over between 167° and 171°.

The substance thus obtained was a slightly viscid liquid, having a pale straw colour and a delicate rose-like fragrance. It was again analysed and its constants determined with the following result.

0·1210 gave 0·3896 CO_2 and 0·1276 H_2O. C = 87·8; H = 11·7.
$C_{15}H_{24}$ requires C = 88·2; H = 11·8 per cent.
$d15°/15° = 0·9100$; optically inactive; $n_D^{20°} = 1·5030$.
Molecular refraction 66·22.

When to a solution of a drop of the sesquiterpene in 5 c.c. of glacial acetic acid a drop of concentrated sulphuric acid is added, a purplish-red coloration is produced, which gradually increases in intensity.

No solid nitrosate or nitrosite could be obtained from this sesquiterpene. The attempts to prepare a nitrosochloride, both by Tilden's method, as employed by Chapman in the case of humulene (Trans., 1895, **67**, 61), and the method adopted by Schreiner and Kremers (*Pharm. Arch.*, 1899, **2**, 293) were equally unsuccessful. On treatment with bromine in chloroform it yielded an intensely violet coloured liquid, but this evolved much hydrogen bromide, and no solid compound could be obtained from it. The hydrochloride was prepared by saturating an ethereal solution of the sesquiterpene with dry hydrogen chloride at −5°, and allowing it to stand for twenty four hours, but on removing the solvent a brown, heavy oil was obtained, which could not be crystallised even when cooled to −15°.

Although it was impossible to obtain any solid derivative of this sesquiterpene, and thereby definitely characterise it, it is evident that it is not identical with either of the two previously known optically inactive sesquiterpenes, as will be seen from the following comparison of their properties :

	Humulene.	Limene.	Sesquiterpene from Pittosporum oil.
Boiling point (ordinary pressure)	263—266° (corr.)	262—263° (uncorr.)	263—264° (corr.)
Density, 15°/15°	0·9001	0·873	0·9100
Refractive index, $n_D^{20°}$	1·5021	1·4910	1·5030
Hydrochloride	Liquid	Crystals, m. p. 79—80°	Liquid.
Nitrosochloride	M. p. 164—165°	"Unsatisfactory"	Could not be obtained.
Nitrosite	,, 120—121	,,	,,
Nitrosate	,, 162—163	—	,,

The sesquiterpene obtained from the essential oil of the fruit of *Pittosporum undulatum* may thus be regarded as a compound which has not hitherto been described. Its molecular refraction indicates that it belongs to the group of dicyclic sesquiterpenes with two ethylenic linkings, which also includes humulene (Trans., 1895, **67**, 60, 780), whereas the other known optically inactive sesquiterpene, limene, evidently belongs to the group of monocyclic compounds with three ethylenic linkings (Trans., 1904, **85**, 416 ; *Ber.*, 1906, **39**, 657).

Acids obtained by the Hydrolysis of the Oil.

The strongly alkaline aqueous liquid which was separated from the hydrolysed oil, as previously described, was freed from adhering oil by shaking with ether. It was then acidified with sulphuric acid and again extracted with ether, the ethereal liquid well washed with water, dried, and the ether removed. A brown, oily liquid was thus obtained, which possessed a strong odour of valeric acid, and amounted to about 2 grams. The acids contained in this liquid were converted into the potassium salts, from which, by the addition of silver nitrate, the corresponding silver salts were precipitated in eight fractions. These were washed, dried in a vacuum over sulphuric acid, and analysed :

Fraction I. 0·1570 of silver salt gave 0·0700 Ag. Ag = 44·58.
,, II. 0·2372 ,, ,, ,, 0·1170 Ag. Ag = 49·32.
,, III. 0·2210 ,, ,, ,, 0·1132 Ag. Ag = 51·22.
,, IV. 0·2073 ,, ,, ,, 0·1064 Ag. Ag = 51·33.
,, V. 0·1746 ,, ,, ,, 0·0900 Ag. Ag = 51·54.
,, VI. 0·1112 ,, ,, ,, 0·0577 Ag. Ag = 51·89.
,, VII. 0·1435 ,, ,, ,, 0·0748 Ag. Ag = 52·13.
,, VIII. 0·1173 ,, ,, ,, 0·0615 Ag. Ag = 52·43.

$C_5H_9O_2Ag$ requires Ag = 51·67 per cent.

It is evident, therefore, that these acids consisted for the most part of valeric acid, together with very small amounts of acids of a lower and higher molecular weight.

The aqueous liquid, from which these acids had been removed by means of ether, contained a very small amount of formic acid.

Summary.

The results of this investigation have shown that the essential oil of *Pittosporum undulatum* contains the following substances:

d-Pinene, about 4 per cent.

d-Limonene, about 75 per cent.

Esters of valeric, formic, and other acids, a small amount.

An optically inactive *sesquiterpene*, about 15 per cent.

Palmitic acid and an undetermined phenol, in very small amount, and apparently a trace of salicylic acid.

In conclusion, the authors desire to express their thanks to Professor W. A. Tilden for having brought this oil under their notice, and for kindly placing at their disposal the specimen of it in his possession.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

R. CLAY AND SONS, LTD., BREAD STREET HILL, E.C., AND BUNGAY, SUFFOLK.