Chemistry. — *The Essential Oil from Gastrochilus panduratum Ridl.* By A. J. ULTÉE. (Communicated by P. VAN ROMBURGH.)

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The rhizome of this plant, which belongs to the Zingiberaceae family, is characterised by the presence of an essential oil possessing a fresh, pleasant aroma, resembling to some extent the smell of Esdragon and Basicilum oil.

As this rhizome constitutes an ingredient of an Indian rice dish, it is obtainable at the so-called "pasars" (under the Malayan name *Temoe koentji*) but only in small amounts, so that considerable patience was required to collect sufficient material for the examination of this hitherto uninvestigated oil.

The yield of the essential oil is also very small, and varied from only 0.06 % (by weight) in the young fresh rhizomes, to 0.32 % in older material, which however contained much less water.

The specific gravity of the freshly distilled oil varied according to the different methods of extraction, from 0.8636 at 25° (young material) to 0.8731 at 31°. If the oil is allowed to remain exposed to the air, its consistency and specific gravity rapidly increase, a result that would almost certainly be caused by the oxidation of an olefinic terpene present in the oil. After some months preservation in a bottle which was repeatedly opened, the specific gravity had already risen to fully 0.9.

The oil was of a faint yellow colour and showed a dextro-rotation ; in a tube 10 cm. long, different preparations showed rotations from +10°30′ at 27° (young material) to +12°56′ at 32°.

The oil had a neutral reaction ; the presence of esters was determined by boiling the oil with alcoholic potash and subsequent back titration with sulphuric acid.

2.2460 grams oil required 1.20 cm³ 0.5 n alcoholic potash.
1.7950 ,, ,, ,, 0.99 ,, ,, ,, ,,

If one assumes that the methyl ester of cinnamic acid (see below) is the only ester present, it is thus contained in the oil to an extent of 4.32 and 4.46 % respectively.

Since this ester has been isolated by previous investigators, amongst others VAN ROMBURGH, from several members of the Zingiberaceae, the oil was examined first for this ester. Methyl cinnamate is characterised by its extremely slow rate of distillation when distilled with steam.

100 cm³ of the oil were thus steam distilled until the residue (10 cm³) had about the same specific gravity as water. Upon fractionation of this

residue, the temperature rose at once to 220°, the greater part (3 cm^3) distilling between 250—270°. A thick brown residue remained in the flask and could not be further distilled without undergoing decomposition.

After repeated distillation, a small amount of distillate was obtained which boiled between 255—260° and which solidified upon cooling. It melted at ± 33°.

These properties agree with those of methyl cinnamate, so that it is practically certain that this compound is present in the oil.

The oil that had passed over during the steam distillation, was distilled at ordinary pressure, it distilled mainly between 160—220°, the greater part being collected between 180—200°. The specific gravity of the portion that first collected amounted to 0.8553 at 28°.

A resinous residue remained in the flask, and probably represented the oxidation product of an olefinic terpene, consequently during the further examination of the oil, the distillations were carried out under reduced pressure.

The fraction that boiled between 180—200° possessed a distinct smell of cineol, and since this compound is known to occur in various members of the Zingiberaceae, the oil was examined for it. The oil was shaken out with a 50 % solution of resorcinol, separated from the unabsorbed portion and steam distilled. In this way I obtained a liquid that floated upon the aqueous distillate, which after drying was distilled from sodium.

The liquid thus obtained had the following properties :

1. Boiling point : 176—177° ;
2. Specific gravity at 25° : 0.9226 ;
3. The addition product formed with iodol melted at ± 112°.

These properties show that cineol is undoubtedly present.

In order to obtain an idea as to the amount actually present, 5 cm^3 of the original oil were shaken out with the resorcinol solution, whereby 1.6 cm^3 were absorbed, corresponding to a cineol content of 32 %.

Since in this determination, oxygenated compounds, and thus methyl cinnamate, can influence the result, the figure obtained is probably on the high side.

In the fraction distilling over below 200°, and thus probably on the low side, 26.4 % of cineol was found.

During the vacuum distillation (35 mm) of the original oil, at 120° some crystals collected in the condenser. The fraction distilling between 120—140° was now distilled once more at ordinary pressure, up to 215°, and after strongly cooling the distillate, crystallisation took place. After suction filtration, pressing between filter paper, and sublimation, the crystals, which possessed a strong camphoraceous smell, melted at 175°.

When mixed with pure camphor, the melting point rose to 177°.

When thrown upon water, the crystals showed the typical phenomenon of camphor.

The occurrence of camphor in this essential oil is thus proven. The

content is however very small and probably amounts to not more than a few percent.

The lower boiling fractions from the vacuum distillation, which had been freed from cineol by shaking out with resorcinol solution, and which contained the supposed olefinic terpene, were repeatedly distilled from sodium in an atmosphere of carbon dioxide in order to prevent resinification, this however, could not be completely avoided.

Finally, a very mobile oil having the following constants was obtained :

1. Boiling point at 13 mm 62—64° ;
2. Specific gravity at 17° 0.8253 ;
3. Refractive index $n_D^{12} = 1.4843$;
4. Optical rotation $\alpha_D^{12} = 11°.42'$.

The boiling point at ordinary pressure (in an atmosphere of carbon dioxide) was 174° at 753 mm, but it altered quickly.

A boiling test carried out in conformity with the method employed by ENKLAAR (see thesis) for ocimene, gave the following results :

At the commencement			the boiling point		was	174°
After	2	minutes	,,	,,	,,	175
,,	3	,,	,,	,,	,,	176
,,	5	,,	,,	,,	,,	177.5
,,	10	,,	,,	,,	,,	178.5
,,	25	,,	,,	,,	,,	180
,,	60	,,	,,	,,	,,	183

The course followed is thus different from that of ocimene.

By distillation in vacuum (at 13 mm to 80°) a liquid having a specific gravity of 0.8349 at 24° was obtained.

The olefinic terpene was reduced with sodium and alcohol according to the method of ENKLAAR. After steam distillation it was distilled at ordinary pressure from sodium. A fraction was obtained that boiled between 168—169° at 754 mm. *It possessed a smell similar to that of hydromyrcene.*

Optical rotation : $\alpha_D^{12} = 12°54'$.

Specific gravity at 14° 0.805. Refractive index $n_D^{12} = 1.4553$.

The olefinic terpene (in cooled acetic acid) was treated with bromine in acetic acid solution. Hydrogen bromide was evolved and the liquid became coloured, but no solid compound was obtained.

In conclusion it may be mentioned, that the lower fractions obtained from the distillation of the olefinic terpene had a turpentine like smell and a higher specific gravity, so it is probable that another terpene is also present in this essential oil.