

ON THE OCCURRENCE OF THE TERPENE TERPINENE
IN THE OIL OF *Eucalyptus megacarpa*.

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TERPINENE was first recognised as a definite terpene by Wallach,¹ and has, so far, been detected only in a very few essential oils. It was first discovered by Weber² in cardamom oil, and has been recorded as occurring in marjoram oil, dill oil, coriander oil, and a few others. Terpinene is thus rarely found existing naturally, and Gildemeister and Hoffmann³ have stated "that it may appear doubtful whether this terpene is really found in nature or whether it is formed by the influence of heat during the distillation from other compounds contained in the respective oils." This opinion cannot now be supported in reference to *Eucalyptus* oils, because if true the terpene would without doubt, have been detected in them before this, seeing that the oils of such a large number of species have now been determined. It must, therefore, be considered as a naturally occurring terpene in some *Eucalyptus* oils.

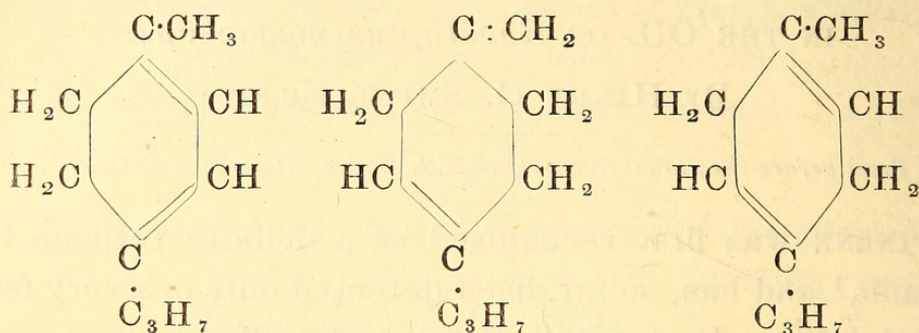
Terpinene is formed artificially by the action of alcoholic sulphuric acid on many of the terpenes and terpene derivatives, ordinary turpentine (pinene) being well adapted for the purpose. It may also be prepared by similar means from terpineol, geraniol, dihydrocarveol and cineol. This formation is interesting in this connection as, besides cineol and the terpenes pinene and limonene, geraniol appears to be present also as an ester in the oil of *Eucalyptus megacarpa*.

¹ *Ann. Chem.*, (230) 254 and 260.

² *Ann. Chem.*, 238, (1887) 107.

³ "The Volatile Oils," p. 119 (English translation, 1900).

The molecular structures which have been suggested for terpinene are the following, known as α , β , and γ -terpinenes respectively:—



Wallach¹ contends that it has been shown with sufficient clearness that terpinene is a mixture of $\triangle_{1,3}$ and $\triangle_{1,4}$ dihydrocymenes, and that it is the former which gives the characteristic nitrosite reaction. A considerable amount of work has been undertaken upon this terpene by Wallach, Semmler, Auwers and others, and both the α , and γ -forms have been synthesised during these investigations.

As terpinene has not, so far, been regenerated from its solid derivative in a pure form, its physical properties cannot be stated with precision, but from the several results obtained with the terpene formed in various ways the following range of figures may be given:—

Boiling point 171 to 181°C .; specific gravity 0.842 at 22° to 0.848 at 18° ; refractive index 1.4719 to 1.4789 .

The two reactions which largely help to distinguish terpinene from other terpenes are (a) the crystallised nitrosite $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_3$ melting at 155°C ., which is formed when the oil is treated with nitrous acid, and (b), the comparative ease with which it is destroyed when treated in the cold with Beckmann's chromic acid mixture; this reagent under such conditions has little action upon either pinene, limonene or cineol.

¹ *Ann. Chem.*, 374, 217.

The pinene in the oil of *E. megacarpa* was shown to be highly lævorotatory, as was also the limonene; dipentene appears also to be present. The cineol content was 30%. It does not appear that the terpinene in this oil can exceed 10%, judging from the results of the distillation and the amounts of other constituents determined.

Although limonene tetrabromide was formed with the oil of the fraction boiling between 170 – 190° yet the result was not altogether satisfactory, and the compound small in amount. This peculiarity naturally led to further search for the interfering constituent with the resulting detection of the terpinene.

Limonene rarely occurs in eucalyptus oils, and it may be that terpinene will be found more frequently associated with that terpene in the oils of certain species of this group. The formation of terpinene from terpineol through the terpene terpinolene is thus of special interest, because dipentene can also be formed from the same terpineol. Wallach and Kerkhoff¹ found that oxalic acid was a useful reagent by which to prepare terpinolene and then terpinene from terpineol.

E. megacarpa is a Western Australian species, and the oil was forwarded to the Technological Museum for investigation by Mr. C. E. Lane Poole, the Conservator of Forests for that State.

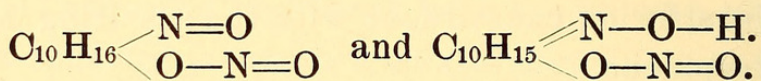
The formation of the terpinene nitrosite.

A portion of the fraction distilling between 170 – 190° C. was mixed with an equal quantity of petroleum ether and an equal bulk of a saturated solution of sodium nitrite added, and afterwards sufficient glacial acetic acid to decompose the salt. The whole was then allowed to stand on one side. After twenty-four to thirty hours

¹ *Ann. Chem.*, (275), 106.

crystals commenced to form, and increased considerably in amount after two days. The crystals were separated, pressed on porous plate to absorb the liquid products, and purified from a mixture of alcohol and chloroform. The terpinene nitrosite thus formed melted at 155°C. (corrected), and answered to the more easily applied chemical reactions for this substance.

Terpinene nitrosite, which is a more stable substance than the corresponding compound formed with phellandrene, has had two formulæ suggested for it:—



but no definite conclusion has yet been arrived at.

Treatment with Beckmann's reagent.

A portion of the fraction boiling between 170 – 190° was repeatedly treated in the cold with small quantities of Beckmann's chromic acid mixture, until the formation of the brown precipitate was less noticeable. The optical rotation of the fraction before treatment was 35·5 degrees to the left, due principally to the limonene. After the first treatment, the optical activity had increased to 36·4 degrees, and after further action reached 36·6 degrees. The substance removed in this way was evidently the inactive terpinene, while the optical activity of the limonene had apparently not been interfered with.

If Wallach's statement that the α -form produces the crystalline nitrosite is accepted, and assuming that the terpene is not a mixture of the α - and γ -forms, then the terpinene in the oil of this *Eucalyptus* species has the molecular structure *I* above.

E. megacarpa, in the sequence of species, more nearly approaches the first members of the genus, or those with the parallel feathery leaf venation, than the more recent

forms. This is also indicated by the principal chemical constituent in the oil being pinene. It is only in the oils of the more recent members of the genus that the terpene phellandrene is found, so that the peculiarity is noticed of terpinene (one of these closely agreeing terpenes) being found at that end of the genus which is more largely represented in Western Australia, while the other terpene (phellandrene) is a characteristic constituent in the oils of the members of the more recent groups of the genus, or those which occur most abundantly in the south-eastern portion of Australia.



Smith, Henry George. 1918. "On the occurrence of the terpene terpinene in the oil of *Eucalyptus megacarpa*." *Journal and proceedings of the Royal Society of New South Wales* 52, 529–533. <https://doi.org/10.5962/p.359741>.

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