

The Azulene from Oil of Elemi

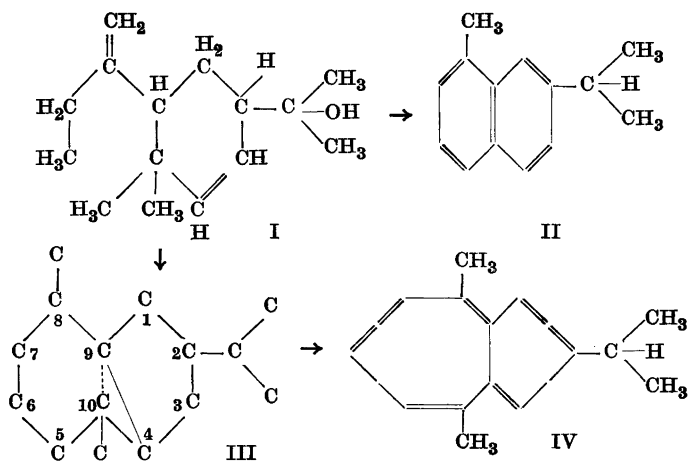
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The dehydrogenation of terpenes and camphors with sulphur or selenium to aromatic hydrocarbons has rendered most valuable information as to the constitution of the parent compounds. Of course the yields of the dehydrogenation products are frequently very small, and in some instances a definite homogeneous terpene gives rise to at least two different dehydrogenation products, say a naphthalene hydrocarbon and an azulene. So the results must be handled with some care; but on the other side a lucid connection between the two dehydrogenation products and the supposed constitutional formula may be of value.

Investigations in this laboratory on some Norwegian essential oils which gave azulene as well as naphthalene hydrocarbons on dehydrogenation gave rise to some experiments on azulene-donating terpenes, among them elemol.

In spite of the fact that elemol is an easily crystallizing sesquiterpene alcohol, Ruzicka¹, have gained degradation results difficult to connect with a single constitutional formula. Mainly, however, Ruzicka supposes elemol to possess the structure (I)



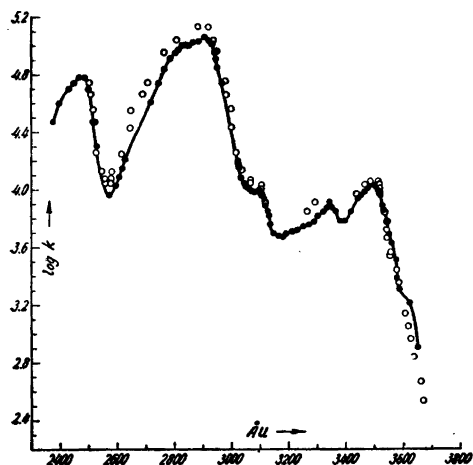


Fig. 1. Ultraviolet absorption of elemazulene and vetivazulene in hexan.

○ Vetivazulene, Susz, Pfau and Plattner⁴.
● Elemazulene, present investigation.

$$(k = \frac{\ln I_0/I}{c \cdot d}, c \text{ in Mol/l, } d = \text{cm}).$$

Although a monocyclic alcohol, elemol on dehydrogenation with Se gives bicyclic hydrocarbons. Ruzicka got eudalene (II) (1-methyl-7-isopropyl-naphthalene) in 15% yield besides quite small amounts (about 1%) of a violet azulene. Ruzicka and Haagen-Smit² found this azulene different from the known ones and named it elemazulene. Its constitution remained unknown.

✂ Pfau and Plattner³, who in 1936 brilliantly elucidated the constitution of the azulene skeleton and some of the natural azulenes and in addition cleared away some insufficiently characterized azulenes, described another violet azulene, vetivazulene with properties similar to elemazulene. Owing to the difference in the m. p. of the picrate: elemazulene 110°, vetivazulene 122°, these two azulenes have so far been considered different.

The revision of the data of the elemazulene compounds which we have carried out puts this supposition to an end. As will be seen from the table the corrected values agree completely with the data of Pfau and Plattner on vetivazulene.

✂ As is seen from Fig. 1, the ultraviolet absorption spectrum of our preparation of elemazulene is identical with the measurements of Susz, Pfau and Plattner⁴. As is known, vetivazulene does not give sharp maxima in visible light, but according to the curves given by Susz *et al.*⁴ vetivazulene differs markedly in ultraviolet light from S-guajazulene and azulene.

Although abnormal, the formation of eudalene from Ruzicka's elemol is a very simple process of ring closure. To explain the simultaneous formation of vetivazulene it is necessary to suppose that the ring closure is followed either by a migration of the 9—10 bond to 4—10 or rather more likely by a formation

Table 1. Melting points of the azulene compounds.

M. p.	Vetivazulene Pfau-Plattner ⁷	Elemazulene	
		Ruzicka ²	Present investigation
Azulene	32 — 33°	—	31.5— 32°
» picrate	122°	110°	122.5°
» trotylate	80.5— 81°	—	78.5— 79.5°
» trinitrobenzenate	151.5— 152°	—	154 — 155°
» styphnate	—	87°	95 — 96.7°

of a tricyclic skeleton. Both intermediates (III) will generate vetivazulene (IV) in a simple way, well known from the analogous reactions: Ledum camphor \rightarrow S-guajazulene ⁵, aromadendrene \rightarrow S-guajazulene ⁶.

The bond-formation from 9 to 4 ought to have been favoured through the double bond in 3—4. A bond formation 5—9 would give rise to S-guajazulene as dehydrogenation product.

We suggest that the name elemazulene ought to be dropped. Of course elemazulene was described 7 years before vetivazulene, but these first preparations can not have been quite pure. Further we find it important that vetivazulene has the real skeleton of the dominating sesquiterpene compounds of vetiver oil, α - and β -vetivon ⁸, whereas elemazulene is rather irregularly related to elemol and elemene.

SUMMARY

Reinvestigations of the azulene from oil of elemi prove this azulene to be vetivazulene.

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