

A CONTRIBUTION TO THE CHEMISTRY OF THE PHELLANDRENES.

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IN the course of his well-known investigations on the phellandrenes, Wallach established the complete chemical and physical identity of the dextro-gyrate phellandrene of elemi oil with the dextro-gyrate phellandrene of bitter fennel oil. Further, the lævo-gyrate phellandrene of the essential oil of the so-called *Eucalyptus amygdalina* was characterised by him as the optical antipode of the first-named phellandrene. These phellandrenes were accordingly named *d*- α -phellandrene and *l*- α -phellandrene, respectively, whilst the dextro-gyrate phellandrene of water fennel oil was named *d*- β -phellandrene (Annalen, 1904, 336, 9; "Terpene und Campher," 1914, 486).

The characterisation of these very closely related terpenes was accomplished largely by a study of their nitrites: these are well defined crystalline derivatives, easily obtained by the action of nitrous anhydride upon solutions of the hydrocarbons in light petroleum at 0°. Schreiner (Pharm. Arch., 1901, 90; Chem. Soc. Abstracts, 1901, 80, i, 600) showed that the *l*- α -phellandrene of eucalyptus oils yielded in this way a mixture of two nitrites having distinct melting points and optical rotatory powers. In confirming Schreiner's observation, Wallach isolated an α -nitrite, melting at 113–114° and a β -nitrite, melting at 105°, from the lævo-gyrate α -phellandrene of eucalyptus oil. The melting point recorded by Schreiner for the less soluble α -nitrite was, however, 120–121°; so that a considerable

discrepancy exists between the two temperatures quoted for the melting point of this substance.

Wallach states (*loc. cit.*, p. 16) that although mixtures of the α - and β -nitrite show little change in melting point, as compared with the pure substances, it is nevertheless easy to discriminate between the two individual substances and their mixtures by observations of optical rotatory power. According to Wallach, the α -nitrite of *l*- α -phellandrene (from eucalyptus oil) in chloroform solution gave $[\alpha]_D +142.6^\circ$ and $[\alpha]_D +135.93^\circ$, whilst Schreiner obtained the value $[\alpha]_D +123.5^\circ$. Similarly, for the corresponding β -nitrite Wallach recorded the values $[\alpha]_D -40.817^\circ$ and $[\alpha]_D -40.287^\circ$, whilst Schreiner obtained $[\alpha]_D -36^\circ$ for a preparation melting at $100-101^\circ$. Values closely corresponding in magnitude were recorded for the two nitrites prepared from the *d*- α -phellandrene of bitter fennel oil, the sense of the optical rotation being, of course, reversed.

The extremely important role of the nitrites, in a study of the chemistry of the phellandrenes, need not be elaborated further for the purposes of the present paper.

During investigations on components of the essential oil of *Eucalyptus dives* we were led to prepare specimens of the nitrites of the *l*- α -phellandrene of which this oil is so notable a source. As a consequence, it was found possible to isolate without difficulty specimens of *l*-phellandrene α -nitrite melting at $121-122^\circ$, with decomposition. Such specimens, when dissolved in chloroform to form solutions of the approximate concentration indicated by Wallach, and submitted without delay to polarimetric examination, yielded results agreeing satisfactorily with the values quoted above. It was noticed, however, that the originally colourless solutions became pale yellow and finally brown, or reddish-brown, when kept. Polarimetric examination showed that the change in colour was in all instances

accompanied by remarkable changes in the magnitude, and even the sense, of the optical rotatory power. The following selection from an extensive series of observations is sufficient to indicate the pronounced mutarotation which occurs not only in chloroform solution but also when the substance is dissolved in other organic solvents:—

1. *l*- α -Phellandrene α -nitrite (m.p. 121–122°): 0.7517 gram dissolved in chloroform and made up to 30.0 c.c. at 20°.

Time	$[\alpha]_D^{20}$	Time	$[\alpha]_D^{20}$
8 mins.	+137.7°	4 hours	+81.0°
14 „	+136.9	25 „	–23.5
20 „	+135.1	48 „	–24.0
57 „	+125.3	121 „	–70.0
158 „	+99.8	144 „	–70.0

2. *l*- α -Phellandrene α -nitrite (m.p. 121–122°): 0.3762 gram dissolved in benzene and made up to 30.0 c.c. at 20°.

Time	$[\alpha]_D^{20}$	Time	$[\alpha]_D^{20}$
5 mins.	+234.4°	23 hours	+65.8°
6 „	+232.9	95 „	–42.7
20 „	+220.9	167 „	–87.3
40 „	+209.7	333 „	–103.3
75 „	+189.0	355 „	–103.3

3. *l*- α -Phellandrene α -nitrite (m.p. 121–122°): 0.5014 gram dissolved in acetone and made up to 30.0 c.c. at 20°.

Time	$[\alpha]_D^{20}$	Time	$[\alpha]_D^{20}$
8 mins.	+165.3°	21 hours	+67.0°
14 „	+164.1	70 „	+12.2
20 „	+162.7	98 „	–7.0
60 „	+154.8	335 „	–38.1
90 „	+150.8	359 „	–38.1

Thus, with all three solvents optical inversion occurred with lapse of time. These observations have, therefore, an important bearing upon the application of the nitrite

reaction for the diagnosis of phellandrenes in essential oils, as well as possessing a much more general interest in connection with the chemistry of the terpenes concerned.

It may be added in this place that certain physical and chemical agencies have been found to exert a pronounced acceleration on the velocity of mutarotation. Further, the β -nitrite of *l*- α -phellandrene appears to exhibit somewhat similar changes. The enquiry is also being extended to nitro- α -phellandrene. These observations will be recorded fully in subsequent publications, together with the results of a comparative physical and chemical examination of phellandrenes obtained from other sources, including various species of *Eucalyptus* and allied Australian genera.

We are continuing the detailed investigation of the whole field of work indicated in this paper.



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