

The Occurrence of a Diterpene-camphor in Scots Fir (*Pinus silvestris* L)

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The different role which each class of chemical compounds: hydrocarbons, camphors, acids etc. plays among the monoterpenes, the sesqui-, di- and polyterpenes is a remarkable peculiarity in terpene chemistry.

The monoterpenes exhibit the most splendid variations in isoprene-hydrocarbons accompanied by a lot of alcohols, aldehydes and ketones, or camphors as we are accustomed to designate them. Apart from citronellic-, geranic- and teresantallic acid, carbonic acids are very scarce.

In the sesquiterpene group hydrocarbons and camphors again play the most important role, but in the plant family of the *Compositae* some interesting lactones (the alantolactones), keto-lactones (the santonins) and hydroxy-keto-lactones (artemisin) have been found.

The diterpenes on the contrary are overwhelmingly represented through unsubstituted carbonic acids: the resin acids make up the greater part of all wood resins. Diterpenehydrocarbons are scarce, in the camphor group the only pure representative is the aliphatic alcohol phytol, this compound being of quite outstanding importance. The investigation of Ruzicka¹ have proved sclareol of Salvia-oil to be a diterpenglycol. Three oxides *viz.* dicitronell-oxide,² manoyloxide³ and the oxide $C_{20}H_{34}O$ from *Olearia paniculata*⁴ are described in literature, besides manoyloxide keto-manoyloxide and a trihydroxy-diterpeneoxide were found.

The one of us (T. B.) has for some years studied the alterations in the terpenes of fir-stumps from Norwegian moors. To check the results we wished to convince ourselves that the supposed degradation products of the terpenes were all absent in living fir. For this purpose resinrich pine-material as the twig-roots and resinified trunks were distilled with superheated steam. The

resin acids were extracted from the ethereal solution of the distillate with very diluted sodium hydroxide. By fractionating the neutral material we got some fractions b. p. 180—220° at 7 mm (140—175° at 0.2 mm) having the composition of diterpenes with 1 and 2 O-atoms. The experiments were very much facilitated as it turned out that one of these compounds gave a semicarbazone sparingly soluble in methanol or benzene. After recrystallisation the semicarbazone melted at 223—224° and analysis gave $C_{21}H_{33}ON_3$ (+ H_2 ?) corresponding to a carbonyl compound $C_{20}H_{30}O$ (+ H_2 ?). The new diterpene-camphor ought to be a keto-diterpene as the very characteristic semicarbazone could be isolated even if the raw-fraction was treated with silver nitrate and alkali according to the excellent procedure of Curtius.⁵ The free camphor was prepared by splitting the semicarbazone with oxalic acid according to Ruzicka.⁶ The free diterpene-camphor distilled at 0.1 mm and bath temperature 160—165°, and crystallised in the recipient after short standing, m. p. 50—52°. Titration with perbenzoic acid: after 2 days 2.03 /⁻, after 10 days 2.53 /⁻. Only 1 /⁻ was readily hydrogenated with Pd or Pt-catalysts which do not reduce the carbonyl group of ordinary camphor. We therefore suppose that the new diterpene-camphor, for which we propose the name *cryptopione*, is a tricyclic diterpene-ketone with one hindered ethylene bond. Work on its constitution is in progress.

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