

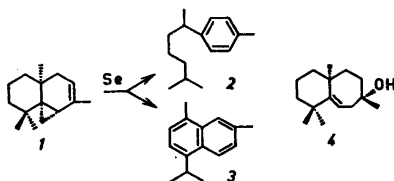
Selenium Dehydrogenation of Thujopsene

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The main constituents from a selenium dehydrogenation of thujopsene (*1*) have been isolated. Two of them have been identified as dihydroarcurcumene (*2*) and 1,7-dimethyl-4-isopropyl-naphthalene ("isocadalene") (*3*). These compounds, respectively, constitute about 20 % and 15 % of the reaction mixture.

Selenium dehydrogenation was used in the early stages of our work on the structure of thujopsene. The results obtained, however, were confusing and other methods were used for the elucidation of the structure of this tricyclic sesquiterpene.¹⁻³ However, in the light of the known structure of thujopsene (*1*) the puzzling results of the dehydrogenation experiments may be of some interest and will be discussed in this communication.



Thujopsene (*1*) was dehydrogenated with selenium in the usual way and the volatile part of the reaction mixture was subjected to chromatography on alumina. One of the main components (25 % of the crude mixture) was found to be a gas chromatographically pure saturated hydrocarbon ("X") which analysed for C₁₅H₂₆ but was not further investigated. A considerable amount (20 %) of dihydroarcurcumene (*2*) was present in the dehydrogenation mixture. This compound was identified by direct comparison with a synthetic sample.⁴ A small amount of an unknown *p*-substituted benzenoid hydrocarbon ("Y") was also isolated and, like dihydroarcurcumene (*2*), it gave terephthalic acid on oxidation with dilute nitric acid. Compound "Y" exhibited a vapour phase chromatographic behaviour similar to that of cuparene⁵ but the spectroscopic data were different.

About 15 % of the reaction mixture consisted of 1,7-dimethyl-4-isopropyl-naphthalene ("isocadalene") (*3*) (*cf.* also Refs. 1, 6). This compound was

identified by direct comparison with an authentic sample.^{7,8} The same compound has also been obtained⁸ from a selenium dehydrogenation of the sesquiterpene alcohol widdrol (4)⁹ and this led us at an early stage to suspect a structural relationship between thujopsene and widdrol both of which frequently occur together in Cupressales.

The extensive rearrangements which must have taken place during the dehydrogenation of thujopsene are remarkable. Any interpretation of the formation of the identified products must be very speculative and this problem will therefore not be discussed at present.

EXPERIMENTAL

Light petroleum refers to a fraction of b.p. 40–60°. Alumina used for chromatography was of standard quality (Brockmann activity I). Vapour phase chromatographic (VPC) examinations were made on a "PYE Argon Chromatograph", column length 1.2 m; internal column diameter 5 mm. Three different types of columns were used. Column "A": 100–115 mesh Silocel C22 brick powder impregnated with 2,4-dinitrophenyl-2-naphthyl ether (15 %) and dibenzylpyridine (a mixture of 2,4- and 2,6-isomers, 0.75 %);¹⁰ column temperature 150°. Column "B": 100–115 mesh Silocel C22 brick powder impregnated with "Apiezon M" (5 %); column temperature 150°. Column "C": 100–120 mesh "Gas-Chrom P" impregnated with silicone rubber gum (1 % "E301"); column temperature 100°.

Selenium dehydrogenation. Thujopsene (1) (20 g; $[\alpha]_D - 110^\circ$, $n_D^{25} 1.5031$)¹ and selenium (20 g) were refluxed at about 290° under nitrogen. After 24 h additional amounts of selenium (20 g) were added and heating continued for 48 h. The reaction mixture was distilled under reduced pressure (about 15 mm Hg) to yield an oil (14.5 g) which was analysed by VPC. The figures for the relative amounts of the various constituents, discussed above, were estimated from the relative areas of the corresponding peaks in the chromatograms.

The selenium dehydrogenation product (14 g) was chromatographed on alumina (700 g). Elution with the solvents indicated gave following fractions: (a-d) light petroleum (L.p.) (1200 ml), 5.75 g; (e) L.p. (300 ml) 2.92 g; (f) L.p. (300 ml), 0.71 g; (g-k) L.p. (1500 ml) 1.92 g; (l) 10 % benzene in L.p. (3000 ml), 0.54 g; (m) ether (2000 ml) 0.16 g.

Fractions (a–d) dissolved in methylene chloride (50 ml) were treated with ozone at –70° until excess ozone was present. Water (10 ml) was added and the methylene chloride evaporated under reduced pressure. The residue was refluxed with hydrogen peroxide (30 %, 2 ml) and aqueous potassium hydroxide (10 %, 10 ml) for 5 min. The organic phase (4.01 g) of the reaction mixture was chromatographed on alumina (700 g). Light petroleum eluted in the earlier fractions the hydrocarbon "X" (2.42 g). (Found: C 86.9; H 12.9. $C_{15}H_{26}$ requires C 87.3; H 12.7). The later fractions (0.80 g) were rechromatographed and yielded dihydroarcurumene (2), having UV and IR spectra identical with those of an authentic sample.⁴ Furthermore, the product gave terephthalic acid on treatment with aqueous nitric acid (30 %) in a sealed tube at 170° (cf. Refs. 5, 11).

Fraction (e) was absorbed on alumina (400 g). Light petroleum first eluted dihydroarcurumene (1.6 g) and later the hydrocarbon "Y" in an almost gas-chromatographically pure state. Hydrocarbon "Y" exhibited infrared characteristics similar to those of *p*-substituted benzenoid hydrocarbons and gave terephthalic acid on nitric acid oxidation according to the above procedure.

Fraction (f) consisted mainly of 1,7-dimethyl-4-isopropyl-naphthalene (3).

Fractions (g–k) were crystalline 1,7-dimethyl-4-isopropyl-naphthalene, m.p. and mixed m.p. 59–60°, IR and UV spectra identical with those of an authentic sample;^{7,8} picrate, m.p. and mixed m.p. 90–91°.

Fraction (l) was a complex bluish mixture of mainly naphthalenoid compounds and azulenes as indicated by UV data. This fraction like fraction (m) has not been investigated.

Retention times. The relative retention times for the compounds isolated were as follows (dihydroarcurcumene taken as 1): aliphatic hydrocarbon "X", 1.06, 1.58, and 1.04 on columns "A", "B" and "C", respectively; aromatic hydrocarbon "Y", 2.00, 1.07, and 1.61; 1,7-dimethyl-4-isopropyl-naphthalene ("isocadalene"), 10.2, 3.95, and 3.52.

Acknowledgements. I thank Professor H. Erdtman for his interest in this work. A grant from the *Swedish Technical Research Council* is gratefully acknowledged.

REFERENCES

1. Norin, T. *Acta Chem. Scand.* **15** (1961) 1676.
2. Norin, T. *Acta Chem. Scand.* **17** (1963) 738.
3. Dauben, W. G. and Ashcraft, A. C. *J. Am. Chem. Soc.* **85** (1963) 3673.
4. Ruzicka, L. and van Veen, A. G. *Ann.* **468** (1929) 143.
5. Enzell, C. and Erdtman, H. *Tetrahedron* **4** (1958) 361.
6. Kubayashi, H., Nagahama, S. and Akiyoshi, S. *Bull. Chem. Soc. Japan* **34** (1961) 1123.
7. Sýkora, V., Novotný, L. and Šorm, F. *Tetrahedron Letters* **1959** No. 14, 24.
8. Erdtman, H. and Thomas, B. R. *Acta Chem. Scand.* **12** (1958) 267.
9. Enzell, C. *Acta Chem. Scand.* **16** (1962) 1553.
10. Groth, A. B. *Svensk Papperstid.* **61** (1958) 315.
11. Runeberg, J. *Acta Chem. Scand.* **14** (1960) 1288.

Received April 29, 1965.