

The Chemistry of the Natural Order Cupressales

XVIII*. Nootkatene, a New Sesquiterpene Type Hydrocarbon from the Heartwood of *Chamaecyparis nootkatensis* (Lamb.) Spach.

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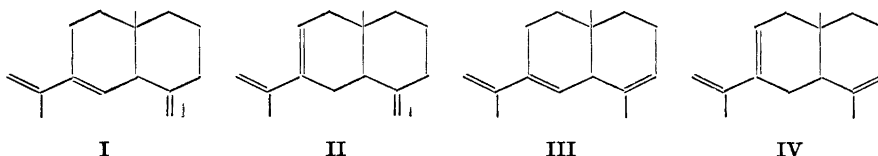
A preliminary study of the neutral constituents of the heartwood extractives of "Alaska yellow cedar" (*Chamaecyparis nootkatensis*) has been carried out. Terpenoid hydrocarbons, alcohols and carbonyl containing compounds were obtained in addition to carvacrol methyl-ether previously reported. A sesquiterpene hydrocarbon "nootkatene" was isolated in an apparently pure state. It contains three double bonds, two of which are conjugated and since it yields eudalene on dehydrogenation appears to be a dehydroselinene. The alcohol fraction similarly yielded 1-methyl-7-ethyl-naphthalene. Like the carbonyl fraction it appears to contain C_{14} -components, presumably related to nootkatene

Earlier investigations¹ have shown that the heartwood of *Chamaecyparis nootkatensis* contains a large quantity of extractable neutral material in addition to nootkatin², carvacrol¹ and chamic and chaminic acids³. A previous examination of the low boiling neutral oils revealed the presence of carvacrol methyl ether⁴.

The sesquiterpene fraction of the neutral oil has now been examined and we wish to give a preliminary account of the findings. Fractional distillation has shown the main hydrocarbon component to be a liquid b.p. 134°/11 mm, n_D^{25} 1.5222, $[\alpha]_D$ —177° ($CHCl_3$), d_{24}^{24} 0.933, $[R_L]_D$ 66.86, for which the name *nootkatene* is proposed. The carbon-hydrogen analysis corresponds to a molecular formula of $C_{15}H_{22}$ and catalytic hydrogenation revealed the presence of 3 double bonds in the molecule. Dehydrogenation with selenium gave eudalene in moderate yield, identified as the picrate. Moreover, the ultraviolet absorption spectrum of the compound shows a maximum at 235 $m\mu$, ϵ 13 500, indicative of a conjugated diene system with three or four substituents, and the infra-red absorption spectrum (very strong band at 890 cm^{-1} and strong

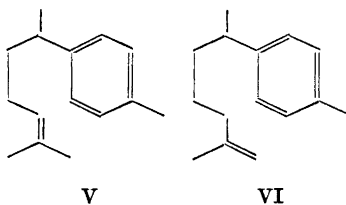
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band at 827 cm^{-1}) points to the presence of a terminal methylene group and a trisubstituted double bond. Ozonolysis afforded formaldehyde but no acetone. Hence these preliminary studies reveal that nootkatene can be regarded as a dehydroselinene, the most probable structural possibilities being I to IV although certain other structures are not rigidly excluded on the basis of the present evidence.



The conjugated double bond system as given in formulae I to IV would give on 1,4-addition a tetrasubstituted double bond which might be expected to be rather unreactive. Since catalytic hydrogenation of nootkatene using 10 % palladium charcoal in ethanol and the action of bromine in chloroform resulted in incomplete addition to the third double bond the results may be cited as evidence in favour of the position of the diene system as shown.

The only previously reported naturally occurring $\text{C}_{15}\text{H}_{22}$ sesquiterpene type hydrocarbon appears to be *ar*-curcumene⁵ (V and VI). Further studies on the structure of nootkatene are in progress.



The sesquiterpene "alcohol" fraction of *Chamaecyparis nootkatensis* has also been briefly examined. Selenium dehydrogenation yielded 1-methyl-7-ethylnaphthalene in fair yield, identified as the picrate. Chromatography of the fraction revealed the presence of a small proportion of a component or components having an α/β -unsaturated carbonyl function. Both the latter and the alcohol portion appear to be mixtures containing mainly C_{14} compounds. Efforts are now being made to find a suitable procedure for separating these compounds.

EXPERIMENTAL

Isolation of sesquiterpene components from the heartwood. Finely divided heartwood (12 kg) was extracted with acetone and the extract separated into crude acidic, phenolic and neutral fractions as described previously¹. The crude "neutral" material (294 g) thus obtained, was distilled *in vacuo* yielding 215 g of distillate b.p. $100\text{--}190^\circ/5\text{ mm}$. This oil was then subjected to careful fractional distillation *in vacuo* using a silvered, vacuum jacketed double glass spiral column. A section of the distillation data obtained is given in Table I.

Table 1. Pressure 11 mm. Back pressure 15 mm. Reflux ratio 25:1. Take off rate ca. 10 ml/hour

| Fraction | Vol. of fraction (ml) | Temp.* °C | $n_D^{16.5}$ | $[\alpha]_D$ (CHCl ₃) |
|----------|-----------------------|-----------|--------------|-----------------------------------|
| a | 3 | 132.0 | 1.5171 | -41.5 |
| b | 3 | 132.5 | 1.5175 | -53 |
| c | 4 | 133.25 | 1.5298 | -82 |
| d | 3 | 133.75 | 1.5211 | -107 |
| e | 3 | 133.75 | 1.5220 | -126 |
| f | 3 | 134.0 | 1.5233 | -146 |
| g | 3 | 134.0 | 1.5240 | -160 |
| h | 3 | 134.0 | 1.5247 | -169 |
| i | 3 | 134.0 | 1.5250 | -175 |
| j | 3 | 134.0 | 1.5256 | -177 |
| k | 3 | 134.0 | 1.5256 | -166 |
| l | 3 | 141.5 | 1.5247 | -149 |

* Temperatures were taken at the end of each fraction.

Fraction (j) was analysed by the sorption method of Blohm⁶ with the following results. Sample n_D^{25} 1.5221. Fractions, as removed from silica gel column (1) n_D^{25} 1.5212 (2) n_D^{25} 1.5221 (3) n_D^{25} 1.5222 (4) n_D^{25} 1.5222 (5) n_D^{25} 1.5222 (6) n_D^{25} 1.5220. Thus this result coupled with the distillation data provides good evidence for the fact that fraction (j) is an essentially pure sample of a new sesquiterpene hydrocarbon, *nootkatene*. The physical data relating to *nootkatene* (all determined on fraction j) may then be stated as follows: b.p. 134°/11 mm; n_D^{25} 1.5222; $[\alpha]_D$ -177° (c 2.02 in CHCl₃); d_{25}^{24} 0.933; $[R_L]_D$ 66.86; ultra-violet spectrum, max 235 $m\mu$ (ϵ 13 500); infra-red spectrum, very strong band at 890 cm^{-1} and strong band at 827 cm^{-1} . (Found: C 88.60; H 10.77. C₁₅H₂₂ requires: C 89.02; H 10.96)

Nootkatene did not give a crystalline adduct on refluxing with maleic anhydride in dry xylene for 5 h nor a crystalline hydrochloride on treatment with dry hydrogen chloride in dry ether at -10° for 1 h.

Hydrogenation experiments. (a) *Nootkatene* (0.268 g) was hydrogenated in glacial acetic acid solution (25 ml) in the presence of Adams' catalyst (0.051 g) at room temperature and atmospheric pressure. Hydrogenation ceased after 108 ml (3.1 mole) of hydrogen had been absorbed in 40 min. The rate of uptake of the third mole was somewhat slower than that of the first two.

(b) A further sample of the hydrocarbon (0.202 g) in ethanol (20 ml) was reduced at atmospheric pressure and room temperature in the presence of a 10 % palladium charcoal catalyst (0.071 g). 51 ml (2 mole) of hydrogen were absorbed in 18 min. The rate of uptake then dropped noticeably and 70 % of a third mole of hydrogen was absorbed over 65 min at which point the hydrogenation ceased.

Bromine titration. To *nootkatene* (0.5111 g) in chloroform (10 ml) was added a solution of bromine in chloroform of known concentration from a burette. 39.4 ml of the bromine solution (\equiv 2 mole of bromine) was rapidly decolourised. A further 8.7 ml was then decolourised at an appreciably slower rate after which the uptake became too slow for effective measurement.

Dehydrogenation. *Nootkatene* (0.53 g) was heated with selenium powder (1 g) for 13 h at 300° ± 10°. The product was extracted with ether and after filtration the ether was evaporated and the residue distilled *in vacuo*, giving a faintly coloured oil (0.423 g), b.p. ca. 130°/7 mm, showing an ultra-violet absorption spectrum typical of a naphthalene hydrocarbon *viz.* max 227, 280, and 320 $m\mu$, ϵ 36 000, 2 000 and 240, respectively. The picrate which crystallised out on mixing concentrated warm ethanolic solutions of the hydrocarbon (0.40 g) and picric acid (0.40 g) had m.p. 93-94° (corr) and amounted to 0.110 g. The mother liquors on concentration yielded a further 0.125 g of picrate m.p. 89-91° (corr). Recrystallisation of the first picrate batch from ethanol gave pure eudalene picrate as fine needles m.p. 93.5-94.5 (corr.), undepressed on admixture with authentic eudalene picrate.

Ozonolysis. Nootkatene (0.483 g) dissolved in a mixture of dry chloroform (8 ml) and dry carbon tetrachloride (2 ml) was ozonised until no more ozone was being taken up as indicated by iodine titration (*ca.* 30 min). The exit gases were bubbled through a trap containing a small quantity of water and after the ozonolysis was complete the water in the trap was mixed with an equal volume of concentrated aqueous dimedone solution and on scratching a small quantity of formaldehyde-dimethone separated m.p. 190–191° (*corr.*), undepressed on admixture with authentic formaldehyde-dimethone. The ozonide was obtained as a glass by evaporation of the solvent under water pump vacuum at 0°. The exient vapours during this evaporation were passed through an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride but no significant precipitate was obtained. Water was added to the ozonide and the mixture was refluxed for 30–60 min with precautions for trapping any outgoing vapours with 2,4-dinitrophenylhydrazine hydrochloride solution. However no volatile aldehydes or ketones were detected during this period. The mixture was then distilled into aqueous 2,4-dinitrophenylhydrazine hydrochloride solution whereupon an insoluble 2,4-dinitrophenylhydrazone was precipitated. After a short time this was collected by filtration and dried, m.p. 162–165° (*corr.*), undepressed on admixture with authentic formaldehyde 2,4-dinitrophenylhydrazone, m.p. 167–168° (*corr.*). The non-steam volatile product was extracted with ether and the acidic material was separated by alkali extraction and isolated as a gum by acidification and ether extraction in the usual way (0.193 g). The neutral portion, obtained as an oil, amounted to 0.083 g. Both the acidic and neutral products failed to crystallise.

Sesquiterpene "alcohol" fraction. From the continuation of the fractional distillation of the oil described in the isolation of nootkatene a considerable number of fractions, amounting in all to 50–60 ml of viscous oil, b.p. 140–150°/3 mm, $n_D^{16.5}$ 1.5179–1.5254, $[\alpha]_D +31 - +107^\circ$, were obtained. The physical constants of the various fractions showed a definite drift between the limits given but it was clear that no clear cut separation of the components had occurred. The middle fractions, which showed an appreciable absorption in the ultra-violet with a maximum at 235 $m\mu$ and ϵ values of 2 000–3 000 were further investigated as described.

Dehydrogenation. "Alcohol fraction" (1.2 g) was heated with selenium powder (2.0 g) at 290–300°. After 4 h a further 1.0 g of selenium was added and the dehydrogenation was continued for a further 18 h at the same temperature. The product was isolated by ether extraction and distilled *in vacuo* affording 0.482 g of distillate b.p. 120–160°/7 mm (bath temp) which was then passed through a short alumina column in petroleum ether (40–60°) yielding 0.334 g of purified product. The ultra-violet absorption spectrum of the product showed maxima at 228, 280 and 321 $m\mu$ typical of a naphthalene hydrocarbon. The hydrocarbon picrate prepared in the usual manner melted at 95.5–96.5° (*corr.*) after recrystallisation from ethanol (Found: C 57.03; H 4.78; N 10.54. Calc. for $C_{19}H_{17}O_7N_3$: C 56.99; H 4.28; N 10.50). Thus the analysis of the picrate suggests that the molecular formula of the hydrocarbon is $C_{13}H_{14}$. The hydrocarbon trinitrobenzene adduct prepared from the hydrocarbon and somewhat less than the theoretical quantity of 1,3,5-trinitrobenzene in methanol crystallised from methanol as yellow needles, m.p. 106.5–107.5° (*corr.*) (Found: N 11.12. $C_{19}H_{17}O_6N_3$ requires N, 10.96). The melting point of the picrate was not depressed on admixture with a synthetic specimen of 1-methyl-7-ethylnaphthalene picrate, kindly supplied by Prof. D. H. R. Barton, or with a specimen of the same compound prepared from santolin and kindly supplied by Prof. W. Cocker.

Chromatography of "Alcohol fraction". "Alcohol fraction" (1.89 g) was dissolved in a small volume of petroleum ether (40–60°) and chromatographed on a column of alumina (175 g). Elution with 15 % ether in benzene removed a component (0.317 g) having the following constants: n_D^{25} 1.5269, $[\alpha]_D +189$ (*c* 1.7 in $CHCl_3$), ultra-violet absorption spectrum: max 235 $m\mu$ (ϵ 10 900); 306 $m\mu$ (ϵ 74). (Found: C 81.50; H 10.13. $C_{14}H_{22}O$ requires C 82.30; H 9.87. $C_{14}H_{22}O$ requires C 81.30; H 10.75). The ultra-violet absorption data is compatible with the component containing an α/β -unsaturated carbonyl function which was confirmed by the preparation of a semicarbazone using semicarbazide hydrochloride and sodium acetate in aqueous ethanol. The semicarbazone crystallised in ill defined prisms from ethanol or ethyl acetate, m.p. 190–192° (*corr.*), unchanged on further recrystallisation, $[\alpha]_D +210^\circ$ (*c* 0.2 in $CHCl_3$). Ultra-violet absorption, max 268 $m\mu$ (ϵ 28 500). (Found: C 68.47; H 9.05; N 14.61; 14.77. $C_{15}H_{24}ON_3$ requires C 68.68; H 9.21; N 16.02).

The indications are that the semicarbazone is not a single compound. The chromatography did not appear to give a very good separation of the other components of the mixture.

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