

SEMPERVIRIOL, A NOVEL TYPE OF DITERPENE PHENOL

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The acidic fraction of the resin from *Cupressus sempervirens* has been investigated and the occurrence of a number of diterpenes has previously been reported (1). From the non-acidic fraction we have now isolated totarel (2), manool (3), ferruginol (4), torulesal (5), torulosol (5), agathadiol (5), "agatholal" (6) and in very small amount a new diterpene phenol, sempervirol.

Oily sempervirol has been characterized as crystalline acetate  $C_{22}H_{32}O_2$  (Ia) m.p. 92-93°<sup>(+)</sup>,  $[\alpha]_D +51^\circ$  (in  $CHCl_3$ ), M.W. (mass spectrometry) 328,  $\nu_{max}^{CCl_4}$  1770  $cm^{-1}$ ,  $\lambda_{max}^{EtOH}$  276  $\mu$  ( $\epsilon$  1230), 267  $\mu$  ( $\epsilon$  1140).

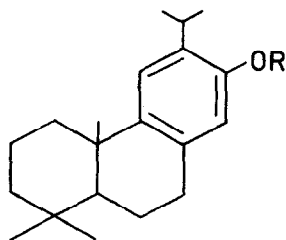
The NMR spectrum of acetate (Ia) showed the presence of two para aromatic protons [singlets (1 proton) at 2.82  $\tau$  and 3.35 $\tau$ ], of an aromatic isopropyl group [doublets (3 protons;  $J$  7 c/s) at 8.76  $\tau$  and 8.74  $\tau$ ; quintuplet (1 proton;  $J$  7 c/s) at 6.92 $\tau$ ] and of three methyl groups with no  $\alpha$ -hydrogens [sharp peaks at 9.13  $\tau$  (6 protons) and at 8.88  $\tau$  (3 protons)].

Chromic oxidation of acetate (Ia) gave a ketoacetate  $C_{22}H_{30}O_3$  (IIa)

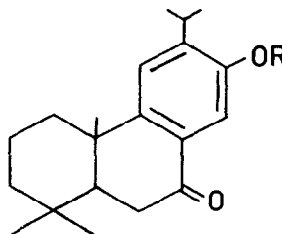
(+) Melting points were determined on a Kefler block and have not been corrected. NMR spectrum was determined on a Varian A60 spectrometer in deuteriochloroform (in the range 2-5 $\tau$ ) and in benzene (in the range 5-10  $\tau$ ) using tetramethylsilane as internal reference.

m.p. 162-163.5°,  $\nu_{\text{max}}^{\text{CCl}_4}$  1770, 1695  $\text{cm}^{-1}$ , indicating that sempervirol has the usual A/B trans junction (7). When hydrolysed, ketoacetate (IIa) afforded a ketophenol  $\text{C}_{20}\text{H}_{28}\text{O}_2$  (IIb) m.p. 180-181°, whose UV spectrum [ $\lambda_{\text{max}}^{\text{EtOH}}$  327  $\mu$  ( $\epsilon$  3600), 266  $\mu$  ( $\epsilon$  11500)], very similar to the spectrum of 7-oxo-totarol (8), showed that the phenolic hydroxyl must be placed meta to the carbonyl group.

The above-mentioned chemical and spectroscopic data strongly suggested structure (Ib) for sempervirol.



(Ia) R = COCH<sub>3</sub>  
(Ib) R = H



(IIa) R = COCH<sub>3</sub>  
(IIb) R = H

The correctness of such a structure was eventually proved by total synthesis of racemic sempervirol. Synthetic and natural acetates showed identical IR, UV and NMR spectra.

Sempervirol therefore, like totarol, contains a modified abietane skeleton with the isopropyl group in a wrong position.

In terms of biogenesis, the occurrence of sempervirol beside ferruginol and totarol in the resin from *Cupressus sempervirens* suggests that sempervirol may be originated from a ferruginol type precursor through an acid-catalyzed process like that proposed by E. Wenkert and B.G. Jackson for totarol (9).

Full details of this work and synthesis of ( $\pm$ ) sempervirol will be published in *Gazzetta Chimica Italiana*.

## REFERENCES

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