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CYCLOSATIVENE - A TETRACYCLIC SESQUITERPENE FROM ABIES MAGNIFICA MURRAY.*

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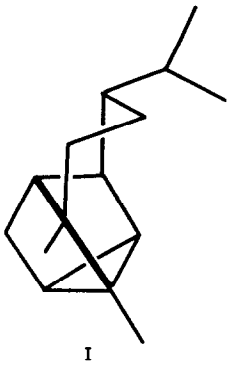
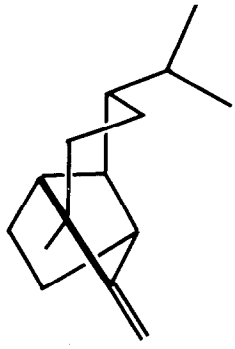
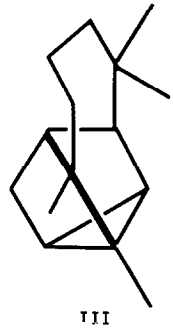
Our investigations of the cortical turpentine of California red fir (Abies magnifica Murray) have revealed the presence of a tetracyclic sesquiterpene, cyclosativene (I) related to sativene (II) (1) as longicyclene (III) is to longifolene (IV) (2).



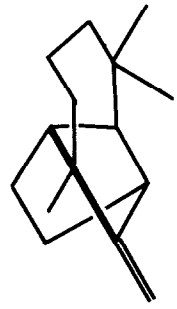
I



II



III



IV

Upon chromatography of the lowest boiling sesquiterpene fraction on silver nitrate-silica gel with light petroleum as solvent, two components were eluted with the front. The mixture could be separated by gas liquid chromatography using a Carbowax 20M column (1% on Chromosorb G 100-120 mesh, 53' x 1/4", 150°C) yielding longicyclene (III) $[\alpha]_D$ + 33.3, c 0.5 ($CHCl_3$) and cyclosativene (I) $[\alpha]_D$ + 94.1, c 0.5 ($CHCl_3$).

The mass spectra (3) of the two compounds were superimposable except for the intensities of the peaks at m/e 204, 189 (M-15) and 161 (M-43) which were 84, 41 and 7% and 100, 16 and 61% for longicyclene and cyclosativene, respectively. The infrared spectrum of cyclosativene (I) (in CCl_4/CS_2) showed no absorption in the double bond region but did show characteristic bands at

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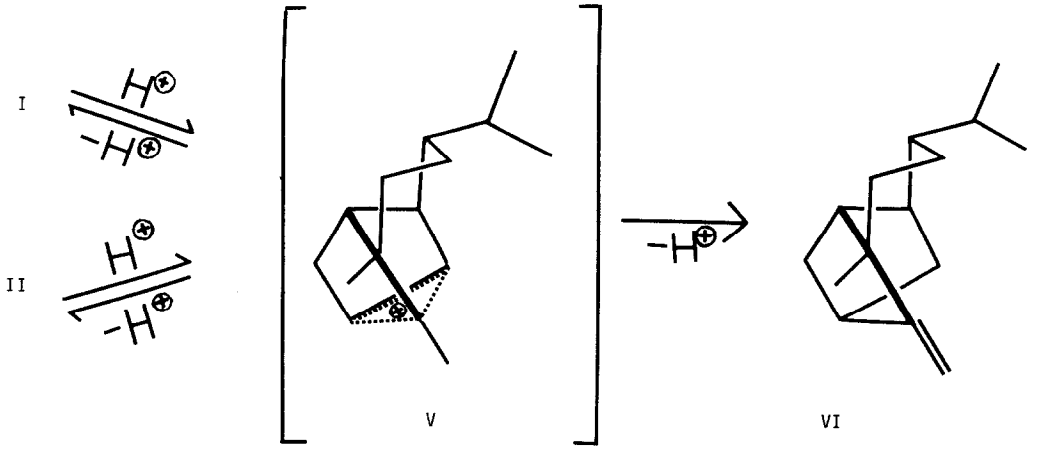
3050, 859 and 840 cm^{-1}, the latter being assigned to a tricyclene structure (2,4). The presence of a tetrasubstituted double bond was excluded by Raman spectroscopy (5) and by the absence of absorption above 200 mμ in the ultraviolet.

The nmr spectrum (6) verified the proposed structure (I): two quaternary methyls τ 9.01 (3 H, s.) and 9.23 (3 H, s.); one isopropyl group 9.12 (3 H, d. J 6.0 cps) and 9.09 (3 H, d. J 6.0 cps); two cyclopropane protons 9.34 (1 H, d. J 5.5 cps) and 9.22 (1 H, partly unresolved).

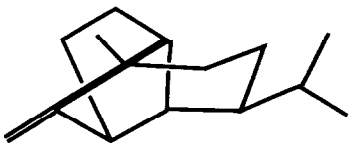
In analogy with the structural elucidation of longicyclene (2) cyclosativene (I) was treated with cupric acetate in acetic acid (110°C). Within one hour the formation of sativene (II) reached its maximum value of 7%, although 90% of the cyclosativene was unchanged. Gas liquid chromatography showed the presence of a third peak which, in contrast to that of sativene, increased with prolonged treatment and reached a value of 60% after 72 hrs. The nmr spectrum (6) suggested structure (VI) with one exocyclic methylene τ 5.54 (1 H, s.) and 5.26 (1 H, s.), one quaternary methyl 9.01 (3 H, s.), one isopropyl 9.11 (6 H, broad d. J 6.0 cps) and one allylic proton 7.38 (1 H, broad d.). The sativene formed in the reaction was isolated by glc (900' x 0.03", SF-96(50), 150°C) and identified by micro infrared and mass spectroscopy.

Treatment of sativene (II) (7) for 72 hrs under the same conditions as above gave the same mixture as cyclosativene (I) viz. 33% cyclosativene, 6% sativene and 61% of VI, indicating a reaction mechanism via carbonium ion V or its classical counterparts. Thus, interconversion of cyclosativene (I) and sativene (II) must be kinetically controlled whereas VI is favoured thermodynamically.



Similarly longifolene (IV) upon cupric acetate-acetic acid treatment for five days gave a mixture of longicyclene (III) 17%, isolongifolene 30% and 53% unchanged.

The fact that sativene (II) and not copacamphene (VII) (8) was an isomerisation product of cyclosativene clearly demonstrates the configuration assigned to the isopropyl group.



VII

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