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Extractive Components from the Wood of *Taiwania cryptomerioides* Hayata: the Structures of "T-cadinol" and "T-murrolol"

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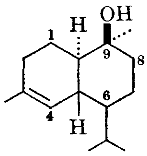
THE wood components of *Taiwania cryptomerioides* Hayata (family *Taxodiaceae*, genus *Taiwania*, monotypic), indigenous to Taiwan, have been investigated by various authors.[1] Recently, the sesquiterpene alcohol fraction was re-investigated.

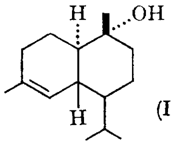
Column chromatography of the steam-volatile fraction of the acetone extract was performed on alumina. The nonpolar components were removed with n-hexane and the polar components were then eluted with the mixed solvent of n-hexane and benzene. The sesquiterpene alcohol fraction was eluted when benzene concentration reached 25%. The first fraction was a colourless oil, which was further purified by preparative gas chromatography. The gas chromatographically pure component was named "T-cadinol." The second fraction was obtained as a crystalline solid, which was separated into α-cedrol[2] and x-cadinol[3,4] by gas chromatography. The third fraction, a crystalline solid m.p. 78·5—80° (n-hexane), was named "T-murrolol." The fourth fraction was a crystalline solid, from which α- and δ-cadinol were identified as its major components.[1a] x-Cadinol, long thought to be a homogeneous substance, was recently[5] proved to be a mixture of "T-cadinol" and "T-murrolol," by comparison of the i.r. and n.m.r. spectra.

"T-Cadinol" (I), $C_{15}H_{26}O$ (*m/e* 222), colourless oil, $[\alpha]_D^{30}$ − 4·7° (*C* 4·4 in $CHCl_3$), shows peaks in i.r. spectrum at 3550 (hydroxyl group), 1670, 780 (trisubstituted double bond) and 1370, 1380 $cm.^{-1}$ (isopropyl group). The n.m.r. spectrum shows a pair of partly overlapped doublets at τ 9·21 and 9·10 [6 H, J = 7 c./sec., $-CH\cdot(CH_3)_2$], a singlet at 8·82 [3 H, $=C(OH)\cdot CH_3$], a broad singlet at 8·37 (3 H, $CH_3-C=CH$), a broad singlet at 4·51 (1 H, $CH_3-C=C-H$). "T-Cadinol" gave (−)-cadinene dihydrochloride (m.p. 117°) with HCl gas. Therefore "T-cadinol" is one of the cadinol isomers. The n.m.r. spectrum of δ-cadinol (III)[6] showed the vinyl proton as a doublet (J = 6·5 c./sec.), and for the same reason, the vinyl protons at C-8 and C-2 would be expected as a doublet. On the other hand, the n.m.r. spectrum of α-cadinol (II)[6] showed a singlet for the vinyl proton. As "T-cadinol" has one vinyl proton as a singlet, it should be represented by the structure (I).

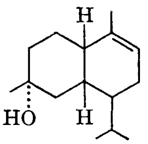
"T-Murrolol" (IV), m.p. 78·5—80° $[\alpha]_D^{23}$ − 102·9 (*c* 1·0 in $CHCl_3$), $C_{15}H_{26}O$, shows peaks in its i.r. spectrum at 3500 (hydroxyl group), 1660, 845 (trisubstituted double bond), and 1370, 1380 $cm.^{-1}$ (isopropyl group). The n.m.r. spectrum shows a pair of doublets at τ 9·17 and 9·12 [6 H, J = 7 c./sec., $-CH\cdot(CH_3)_2$], a singlet at 8·85 [3 H, $=C(OH)\cdot CH_3$], a broad singlet at 8·38 (3 H, $CH_3-C=C-H$), a doublet at 4·47 (1 H, J = 5 c./sec., $CH_3-C=C-H$). "T-murrolol" gave a crystalline dihydrochloride which were subsequently separated, by fractional recrystallization with methanol, into two components. The less-soluble major component, m.p. 87°, was identified as (+)-murrolene dihydrochloride.[7]† The more-soluble minor component, m.p. 117°, was identified as (+)-cadinene dihydrochloride. Therefore, "T-murrolol" is one of the murrolol isomers. The dehydration of "T-murrolol" by thionyl chloride in pyridine afforded a mixture of hydrocarbons which showed no terminal methylene absorption in their i.r. spectra. This result indicates that the hydroxyl group in "T-murrolol" is axial.[8] The epoxy-alcohol prepared by the action of perbenzoic acid on "T-murrolol" was treated with methylmagnesium iodide, to give the diol, which on subsequent dehydrogenation with Pd–C afforded 4-methylcadalene.[9] From this result, the structure and the absolute configuration of "T-murrolol" be represented by formula (IV).



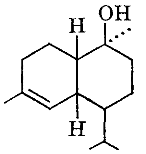
(I)



(II)



(III)



(IV)

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† The direct comparison of i.r. spectrum has been made by courtesy of Dr. Lars Westfelt, Stockholm.

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[4] The same component (x-cadinol) isolated from *Athrotaxis selaginoides* Don. was also separated into two components by Dr. Lars Westfelt, *Arkiv Kemi*, 1967, in the press.

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[6] W. G. Dauben, B. Weinstein, P. Lin, and A. B. Anderson, *Tetrahedron*, 1961, **15**, 217. The structure of δ-cadinol was shown to be the structure (III), (*cis*-junction) by Dr. Lars Westfelt, *Acta Chem. Scand.*, 1967, in the press.

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