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STRUCTURES OF NEW SESQUITERPENES RELATED TO PSEUDOTSUGONAL AND TODOMATUIC ACID ISOLATED FROM DOUGLAS-FIR WOOD

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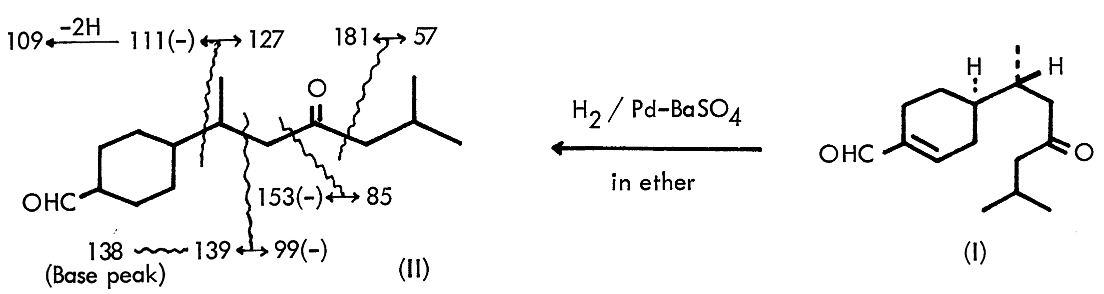
Three new sesquiterpenes related to pseudotsugonal and todomatuic acid, named dihydropseudotsugonal, dihydropseudotsugonol, and ar-todomatuic acid, have been isolated from the volatile wood oil of Douglas fir. The structures and stereochemistry of these compounds have been established.

In a previous paper,$^{1)}$ we reported the absolute configurations of methyl todomatuate, pseudotsugonal, and ar-pseudotsugonal isolated from the volatile wood oil of Douglas fir (Pseudotsuga menziesii (Mirb.) Franco). We could isolate, in the subsequent studies, additional two new sesquiterpenic compounds (II and III) related to pseudotsugonal(I) from the neutral fraction, and a new sesquiterpenic acid(VIa) together with the known todomatuic acid(IVa) and 4-(1′,5′-dimethyl-3′-oxohexyl)cyclohexane-1-carboxylic acid$^{2)}$ (Va) from the acidic fraction. In this paper we report the isolation and determination of the absolute configurations of these compounds, named dihydropseudotsugonal(II), dihydropseudotsugonol(III), and ar-todomatuic acid(VIa), from the volatile wood oil of Douglas fir grown in British Columbia, and the revisal of the sign of rotation of 4-(1′,5′-dimethyl-3′-oxohexyl)cyclohexane-1-carboxylic acid proposed by Rogers and Manville$^{2)}$ from (-)- into (+)-.

In the fraction eluted with a mixture of hexane-ether (1 : 1) from silica gel column chromatography of the neutral oil, compound(II) was found as a minor component together with pseudotsugonal, and separated by preparative GLC using OV-17 and Carbowax-20M columns. Compound(III) was succesively eluted with ether as a major component in this fraction.

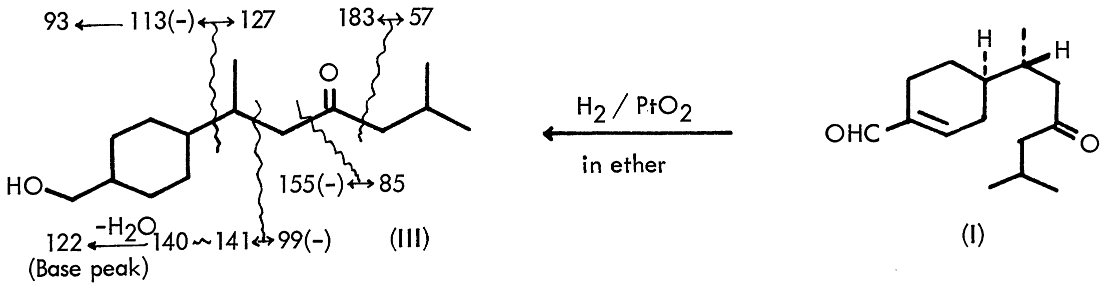
The acidic fraction (16.7%) of the oil was treated with diazomethane to give a mixture of methyl esters. From the higher boiling fraction of the methyl esters of sesquiterpenic acids, compounds Vb, VIb, and IVb were isolated in that order by means of preparative GLC using OV-17 column (200°, He 80 ml/min). It is certain that these parent acidic compounds Va, VIa, and IVa were contained in the volatile wood oil.

Compound (II), $C_{15}H_{26}O_2$ (M^+, m/e 238, 1%), $[\alpha]_D^{24} \gtrsim 0°$, shows a carbonyl band at 1710 cm^{-1} and aldehyde bands at 2700 and 1710 cm^{-1}(overlapping). The nmr spectrum is similar to that of pseudotsugonal except for the signals due to an α,β-unsaturated aldehyde system. The nmr and mass spectra suggest the presence of 1,5-dimethyl-3-oxohexyl side chain residue (δ 0.80 ppm (3H,d,J=6 Hz) and δ 0.88 (6H,d,J=6 Hz); m/e 57(78%), 85(60%), and 127(22%)) and a dihydrophellandral residue (δ 9.55 ppm(1H,d,J=6 Hz); m/e 109(26%), 138(100%), 139(20%), and 181(21%)). These evidences indicate that it is the dihydro derivative of pseudotsugonal; for it we propose the name dihydropseudotsugonal. This structure was confirmed by comparison of its ir and mass spectra with those of the hydrogenated product from pseudotsugonal (I)(Pd-$BaSO_4$, ether).



(II) (I)

Compound (III), $C_{15}H_{28}O_2$ (M^+, m/e 240, 4%), $[\alpha]_D^{24}$ +4.3° (c 0.53, $CHCl_3$), shows a carbonyl band at 1710 cm^{-1} and a hydroxyl band at 3400 cm^{-1}. The nmr and mass spectra suggest the presence of 1,5-dimethyl-3-oxohexyl side chain residue (δ 0.80 ppm (3H,d,J=6 Hz) and δ 0.87 (6H,d,J=6 Hz); m/e 57(81%), 85(54%), and 127(78%)) and an ethylcyclohexane carbinol residue (δ 3.45 ppm (2H,d,J=6 Hz) and δ 3.53 (1H, s); m/e 122(100%), 140(48%), 141(9%), 165(21%), and 183(14%)). From the above data, compound (III) was suggested to be the corresponding saturated hydroxy ketone of II, and named dihydropseudotsugonol. This structure was also confirmed by comparison of its ir and mass spectra with those of the hydrogenated product from pseudotsugonal (I)(PtO_2, ether).

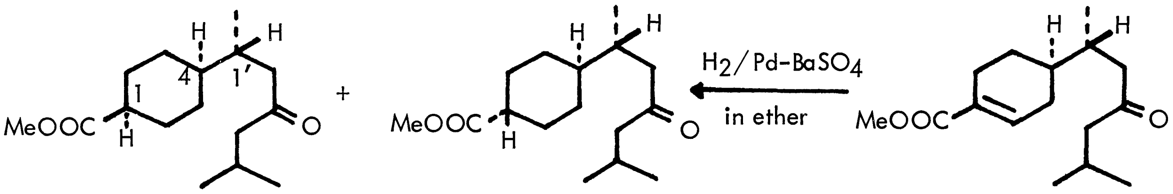


(III) (I)

Compound (IVb)(Methyl ester of compound IVa), $C_{16}H_{26}O_3$ (M^+, m/e 266, 0.4%), $[\alpha]_D^{24}$ +61.5° (c 0.51, EtOH), was identical with (+)-methyl todomatuate isolated from the neutral fraction.$^{1)}$ All the spectral data were superimposable with those of the authentic sample.

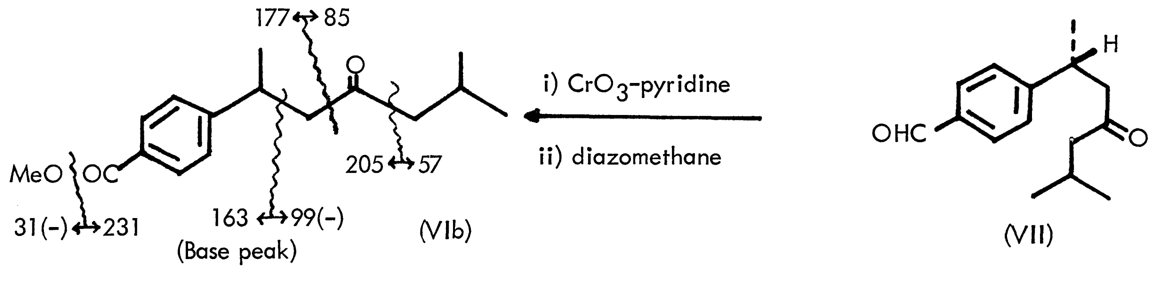
Compound (Vb)(Methyl ester of compound Va), $C_{16}H_{28}O_3$ (M^+, m/e 268, 1%), $[\alpha]_D^{24}$ +2.7° (c 0.70, EtOH), shows a carbonyl band at 1710 cm^{-1} and a methoxy carbonyl band at 1725 cm^{-1}. The ir, nmr, and mass spectra of compound (Vb) were in accord with the data except for optical rotation of (-)-cis-(1'R)-4-(1',5'-dimethyl-3'-oxohexyl)cyclohexane-1-carboxylic acid methyl ester isolated from the wood of a British Columbia Interior variety of Douglas fir (Pseudotsuga menziesii var. glauca (Beissn.) Franco) by Rogers and Manville.[2)] Furthermore, the ir and mass spectra of compound (Vb) were superimposable on those of the more volatile component of two saturated keto esters (1 : 1) obtained by hydrogenation of the known (+)-methyl todomatuate over $Pd\text{-}BaSO_4$ in ether. The above evidences, therefore, confirm that compound (Vb) is (+)-methyl dihydrotodomatuate, (+)-cis-4-(1',5'-dimethyl-3'-oxohexyl)cyclohexane-1-carboxylic acid methyl ester.

Natural (+)-methyl dihydrotodomatuate was found in the neutral fraction by means of GC-MS measurement.



(Vb) cis-isomer trans-isomer (IVb)

Compound (VIb)(Methyl ester of compound VIa), $C_{16}H_{22}O_3$ (M^+, m/e 262, 34%), $[\alpha]_D^{24}$ -18.8° (c 0.32, EtOH), shows a carbonyl band at 1715 cm^{-1}, a carbonyl band of benzoate at 1700 cm^{-1}, and aromatic bands at 1600, 855, 830, 735, and 710 cm^{-1}. The ir spectrum is closely similar to that of methyl cuminate. The nmr and mass spectra suggest the presence of an isobutyl ketone group (δ 0.83 ppm (6H,d,J=6 Hz); m/e 57 (62%), 85(68%), and 205(22%)) and a methyl cuminate residue (δ 1.23 ppm (3H,d,J=7 Hz), δ 3.82 (3H,s), and δ 7.18 and 7.86 (4H, AB d, each J=8.5 Hz); m/e 163(100%), 177(13%), and 178(13%). Thus, it is concluded that compound (VIb) is the aromatized derivative of todomatuate, p-(1,5-dimethyl-3-oxohexyl) benzoic acid methyl ester, and named ar-todomatuic acid methyl ester. This structure could be further confirmed by the following procedures : oxidation of ar-pseudotsugonal (VII)[1)] with CrO_3-pyridine complex followed by esterification with diazomethane afforded the corresponding benzoate, which was identical with compound VIb.



(VIb) (VII)

The Absolute Configurations of Dihydropseudotsugonal, Dihydropseudotsugonol, and ar-Todomatuic Acid.

The absolute configuration of ar-todomatuic acid methyl ester was established as the R configuration since it had a negative optical rotation and coexisted with ar-pseudotsugonal having the R configuration.$^{1)}$

The ord spectrum of (+)-methyl dihydrotodomatuate (Vb) agreed with that published for (-)-cis-(1'R)-4-(1',5'-dimethyl-3'-oxohexyl)cyclohexane-1-carboxylic acid methyl ester.$^{2)}$ All the spectral data (ir, ms, nmr, ord, and cd) of (+)-methyl dihydrotodomatuate were also superimposable on those of the cis-isomer obtained from the reduction products of the known (+)-methyl todomatuate. Thus, (+)-methyl dihydrotodomatuate and dihydrotodomatuic acid must possess the cis configuration at C-1 and C-4, and the R configuration at C-1'.

The ord and cd spectra (shown in Figures 1 and 2) of dihydropseudotsugonal (II), dihydropseudotsugonol (III), and the oxidation product (V'a) of dihydropseudotsugonol with CrO_3, were quite similar to those of (+)-methyl dihydrotodomatuate (Vb), showing a negative maximum at λ 310 nm in the ord spectra and a negative maximum at λ 284 nm in the cd spectra respectively. From these results, therefore, dihydropseudotsugonal, dihydropseudotsugonol, and dihydrotodomatuic acid must also possess the cis configuration at C-1 and C-4, and the R configuration at C-1',

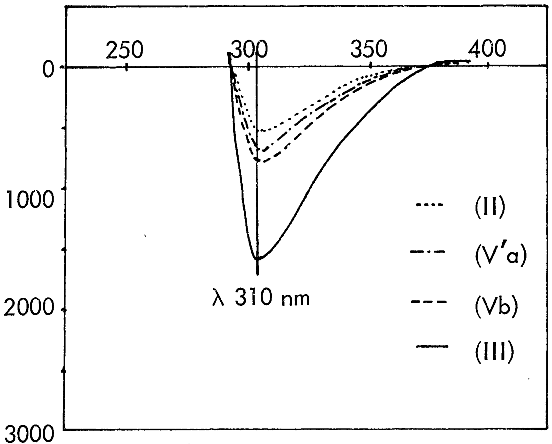


Fig. 1 The ord spectra

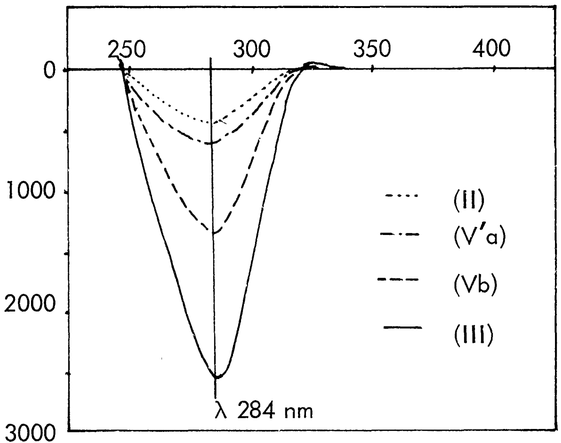
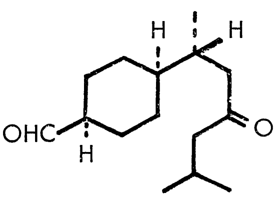
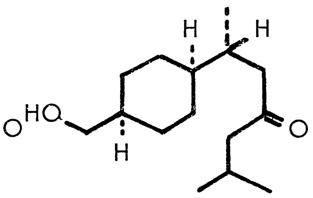


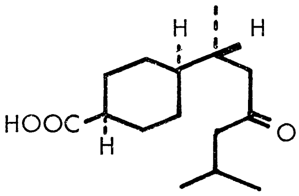
Fig. 2 The cd spectra



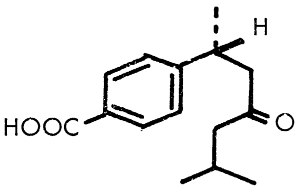
(II)



(III)



(Va)



(VIa)

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