Chemical Investigation of *Cedrus Deodara* Stem-Bark II. Isolation and Identification of Some Sesquiterpene Hydrocarbons

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Summary: G .C. M. S. studies showed that the pet.ether soluble fraction of Cedrus deodara bark has a large number of hydrocarbons. This paper describes the isolation and identification of saturated straight and branched chain hydrocarbons ranging C_{14} - C_{20} and unsaturated sesquiterpene hydrocarbons with empirical formula $C_{15}H_{24}$. Four isomers of himachalene have been found. A new isomer with double bonds in a conjugated position 4 and 10, not reported before has been identified by its I.R, U.V., N.M.R and mass spectra.

Introduction

Cedrus deodara belonging to family Pinaceae is believed to have termite repellent properties [1] and is used for making furniture. The exudate of wood obtained by heating it in the absence of air is also reported to be active against leprosy [2]. Many terpenes have been reported from the wood of this plant [2-13]. However there is no evidence in the literature of the study of isolated bark (which is a waste after using the timber) of this tree. The studies in bark alone in our laboratories reveal that besides some of the compounds which are common in wood and bark, the bark also contains some non-terpenoidal compounds [9-10]. This paper describes G. C. M. S. studies on the oil from the bark of this tree, which provide evidence for the presence of some saturated and unsaturated sesquiterpene hydrocarbons. These compounds are not reported in the bark. One of the isomers of himachalene which has been isolated by us has the two double bonds in conjugation with each other. This isomer is not reported in wood of this tree. As a matter of fact this structure is unknown in the literature. The structure is confirmed on the basis of I.R., M.M.R., U.V. and mass spectral data.

Experimental

The branches of the tree were collected from the forest of Patriata in Murree hills in October 1987. The bark was separated from the wood. It was dried at room temperature away from sunlight, powdered (3 kg) and extracted thoroughly with redistilled commercial ethanol. The solvent was evaporated in vaccuo. The residue (25 g) was triturated with pet-ether 40- 60°.The pet-ether solution was evaporated and the oily residue (2 g) was chromatographed on t.l.c. 95:5 pet-ether chloroform, silica gel HF 254. It showed ten spots. Column chromatography using the same eluants gave seven major fractions. The two least polar oily fractions were studied chromatographically and spectroscopically.

Fraction 1.

(300 mg.) R_f = 0.79 gave I.R and N.M.R. typical of saturated hydrocarbon. In the G.C.M.S. it showed 7 peaks with the following masses:

1 Retention time 6.63 min

m/z 198 (M^+ n-$C_{14}H_{30}$, 2%), 155 (0.5) 139 (1), 127 (2), 119 (2) 113 (3), 109 (2), 99 (8), 85 (30), 71 (42), 57 (100), 43 (83), 41 (50).

2 Retention 8.08 min.

m/z 212 (M^+ n-$C_{15}H_{32}$, 2%), 169 (1.5), 155 (3), 141(4), 127 (3), 113 (5), 99 (5), 97 (10), 85 (49), 71 (75), 57 (100), 43 (81), 41 (50).

Retention 9.47 min.

m/z 226 (M^+, n -$C_{16}H_{34}$, 1.5%), 157 (1.8), 155 (1.8), 141 (2), 127 (4), 113 (5), 99 (6), 85 (38), 71 (50), 57 (100), 43 (60), 41 (42).

R. Retention 10.76 min.

m/z 240 (M^+, n-$C_{17}H_{36}$, 3%), 197 (1), 183 (2), 169 (1.5), 155 (2), 141 (2.5), 127 (3),113 (9),99 (13), 85 (38), 71 (52), 57 (100), 43 (75), 41 (28).

5. Retemtopm 11.95 min.

m/z 254 (M^+, n-$C_{18}H_{38}$, 0.58%), 197 (0.5), 183 (.5), 169 (1), 155 (1.5), 141 (2.5), 127 (5), 113 (5),99 (8), 85 (30), 71 (52),57 (100), 43 (52), 41 (27).

Retention 13.10 min.

m/z 268 (M^+, n-$C_{19}H_{40}$, 0.5%), 211 (1), 197 (1.5), 183 (1.5), 169 (2), 155 (2.5), 141 (3), 127 (4), 113 (7), 99 (15), 85 (50), 71 (55), 57 (100), 43 (77), 41 (28).

7 Retention 14.16 min.

m/z 282 (M^+, n-$C_{20}H_{42}$, 0.5%), 211 (1), 197 (1), 169 (1),155 (1.5), 141 (2), 127 (4), 113 (8), 99 (10), 85 (30), 71 (50), 57 (100), 43 (70), 41 (22).

Fraction II

(300 mg) gave four separate G.C.M.S. spectra with the same fragmentation pattern but different relative intensities at masses as follows:

m/z 204, 1877 (M^+, $C_{15}H_{24}$), 189,161, 147, 133, 121, 119, 101, 93, 91, 81, 79, 67, 57, 55.

Preparative T.L.C. on silica gel HF 254, pet ether, chloroform 95:5 yielded two compounds in workable quantiteis.

(1) Soluble in pet ether, chloroform acetone but insoluble in methanol.

ν_{max} 2960, 2850, 1650, 1450, 1370, 1020, 89, 730 cm^{-1} λ_{max} (hexane) 242 nm. ($CDCl_2$ - 600 MHz) δ: 0.66-10.1 (4 Signals 9H), 1.67 (s, 3H, 1.2-2.76 (m, 11H), 5.40 (bs, 1H). m/z 204.1877 ($C_{15}H_{24}$, 30%) 189 (12), 175 (4), 161 (18), 147 (10), 133 (24), 121 (22),119 (48), 109 (34), 94 (42), 83 (42), 79 (22), 71 (48) 57 (100), 55 (54).

(2)Solubility like (1)

ν_{max} 2970, 2860, 1720, 1450, 1370, 1270, 1170, 1040,750 cm^{-1} (60 MHz, $CDCl_3$) 0.73, 1 (2 singlet s 6H), 1.70 (s, 3H,), 12.76 (bm, 12H), 5.70 (bm, 3H).

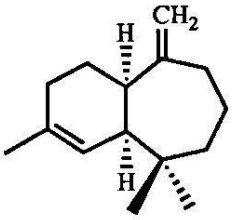
m/z 204.1887 (M^+, $C_{15}H_{24}$, 100%), 189 (22), 161 (30), 147 (25),133 (60),121 (30), 119 (90), 101 (57), 93 (88), 91 (70), 81 (40), 79 (35), 69 (15), 67 (16), 57 (70), 55 (40).

Mass spectral analyses were done at HEJ Research Institute of Chemistry, University of Karachi. G.C.M.S spectra were recorded at Centre of Excellence in Physical Chemistry, University of Peshawar. The I.R spectra were recorded on Unicam SP-1000. The u.v. spectra were recorded on Hitachi Model 10050 and 60 MHz N.M.R spectra were recorded on Jeol PMX-60 instruments.

Results and Discussion

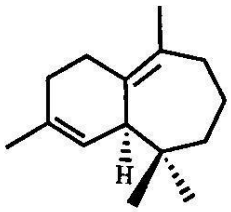
The spectral data of Fraction 1 was in excellent agreement with the saturated hydrocarbons. There were also some traces of branched chain hydrocarbons in some cases.

Fraction II gave four peaks in G.C.M.S. with the same fragmentation pattern but different retention times at m/z 204. 1877 corresponding to empirical formula $C_{15}H_{24}$. The fragmentation pattern confirmed the sesquiterpene himachalene. The four spectra were attributed to four different isomers of himachlaene. Three of the isomers have been reported in the literature [14,15,16] as α, β and γ himachalene. In order to confirm the isomeric structures various chromatographic techniques were tried. Preparative G.L.C. proved to be unsuccessful perhaps due to interconversion of the isomers at elevated temperatures of the injector and column oven. Repeated preparative T.L.C. on silica gel HF 254, thick layer plates using pet-ether chloroform 95:5 gave four bands but only two of these could be separated in a workable quantity. One of these gave spectral data in good agreement with γ-himachalene i.e. 1720 cm^{-1} str. vibration for exocyclic methylene, and the N.M.R signals were also in agreement with literature. The second band gave a U.V. absorption at λ_{max} 242. Applying Wood Wards rules a heteroannular diene should absorb at about 244 which is very near to the value obtained experimentally. Moreover the N.M.R. also gave resonances for three saturated and one unsaturated methyl groups. There was just one proton corresponding to olefinic proton. The mass spectrum gave molecular ion at 204.1788 for $C_{15}H_{24}$ and a fragmentation similar to himachalene. Therefore structure (D) was assigned to the new isomer of himachalene and it was named δ-himachalene.



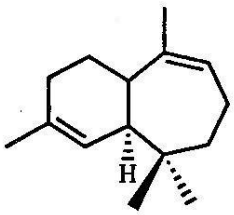
α-himachalene

(A)



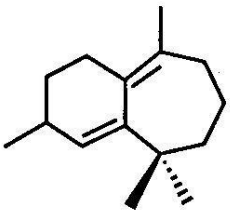
β-himachalene

(B)



γ-himachalene

(C)



δ-himachalene

(D)

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