SECTION-II

MISCELLANEOUS RELATED INVESTIGATIONS

CHAPTER-V

REEVALUATION OF NEUTRAL CONSTITUENTS OF *Cedrus deodara*.

REEVALUATION OF NEUTRAL CONSTITUENTS OF CEDRUS DEODARA

ABSTRACT

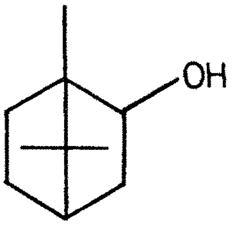
This Chapter summarises the earlier work done on the Wood of *C. deodara*. *trans*-Atlantone was isolated under very mild and nonracemising conditions but still was found to be racemic to the extent of 94.8% thereby leading to the conclusion that atlantone is racemised in the plant itself. During this study, himachalene oxide was isolated for the first time from *C. deodara*.

REEVALUATION OF THE NEUTRAL CONSTITUENTS OF *CEDRUS DEODARA*

INTRODUCTION

It can be truely said that the wood of *Cedrus deodara* is a treasurehouse of sesquiterpenoids of different skeletons. Monoterpenes and diterpenes are practically absent in the wood oil. The needles however, yield an yellow oil (0.6%) which was found to contain chiefly borneol (1), α-pinene(2), β-pinene (3), 3-carene(4), bornyl acetate (5) and ℓ-limonene (6).

The essential oil of the wood of *Cedrus deodara* has been the subject of a number of investigations(1-22). Several sesquiterpene hydrocarbons and oxygenated products have been isolated from the oil. Most of these belong to either bisabolane or himachalane skeletons, while one member each belongs to longibornane and cadinane systems. Some nor-terpenoids have also been isolated from the oil which are obviously artefacts.



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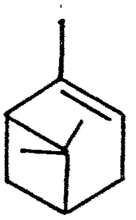

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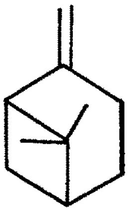

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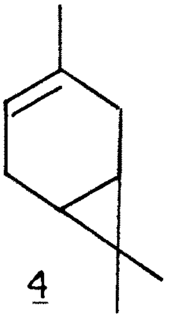

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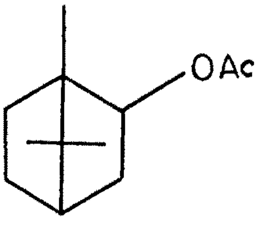

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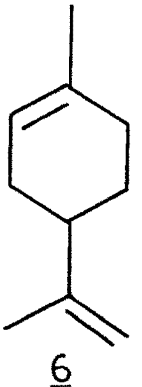

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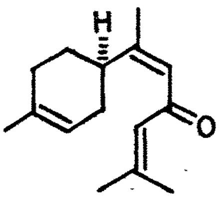
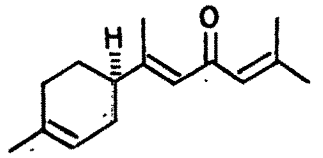
CHART 1 : CONSTITUENTS OF CEDRUS DEODARA

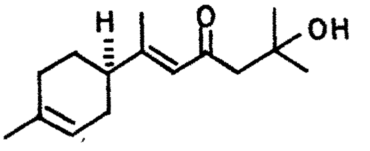
BISABOLANE TYPE



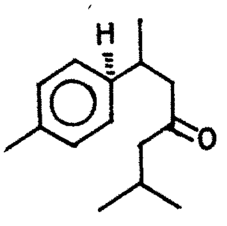
CIS - ATLANTONE 7



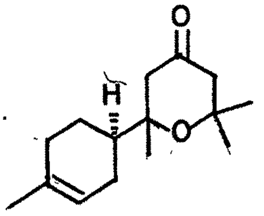
TRANS - ATLANTONE 8



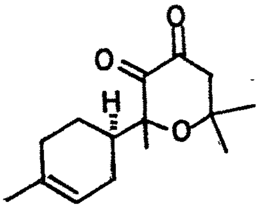
ATLANTOLONE 9



DEHYDRO-ar-TURMERONE 10

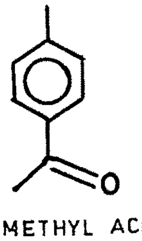


DEODARONE 11

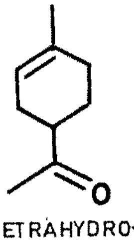


DEODARDIONE 12

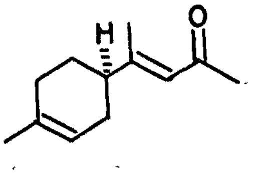
DEGRADATION PRODUCTS



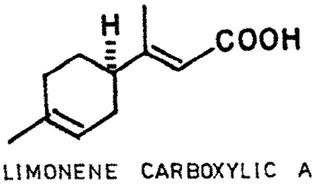
p-METHYL ACETOPHENONE 13



TETRAHYDRO-Δ^3 p-METHYL ACETOPHENONE 14



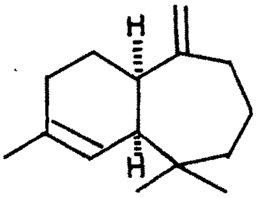
C 12-KETONE 15



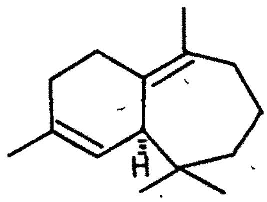
LIMONENE CARBOXYLIC ACID 16

CONSTITUENTS OF CEDRUS DEODARA LOUD (CONTD.)

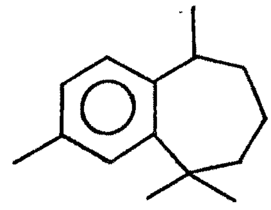
HIMACHALANE TYPE



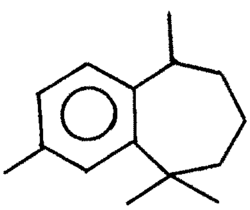
α - HIMACHALENE 17



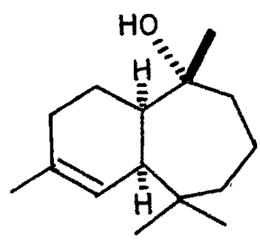
β - HIMACHALENE 18



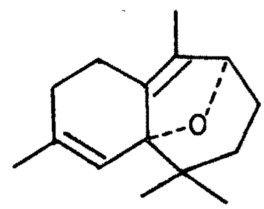
ar - HIMACHALENE 19



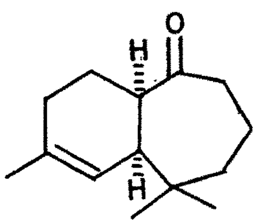
DEHYDRO-ar-HIMACHALENE 20



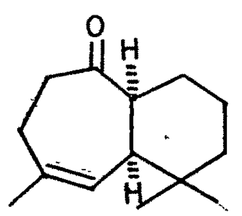
HIMACHALOL[19] 21



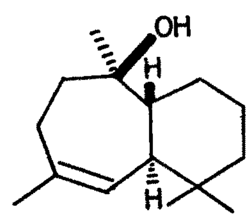
OXIDO HIMACHALENE 22



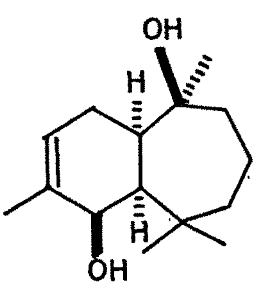
ISOHIMACHALONE 23



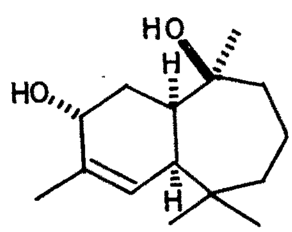
ALLOHIMACHALONE 24



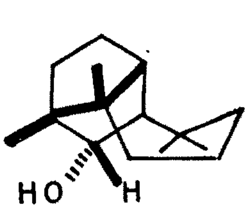
ALLOHIMACHALOL 25



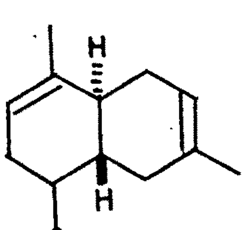
HIMADROL 26.



ISOCENTDROL 27



LONGIBORNEOL 28



α -CADINENE 29

RESULTS AND DISCUSSION

i) Optical purity of (+)-7(E)-atlantone

All bisabolane-based sesquiterpenoids isolated from the essential oil of Cedrus deodara are either partially or extensively racemised. This would become clear from Table 1.

Table 1: Optical activity of some bisabolane-based sesquiterpenoids.

Compound	Structure	$CHCl_3$ $[\alpha]_D$	Reported for synthetic sample	Racemisation
Limonene carboxylic acid[17,26]	(16)	+25.6°	+79°*	67.6%
Deodarone[14]	(11)	+6.3°	-	-
trans-Atlantone[12,26]	(8)	+1.2°	+77°*	98.45%
Deodardione[17,26]	(12)	+5.2°	-	-
Atlantolone[14,26]	(9)	+2.87°	-	-

* Reported in ethanol solution.

This loss in the optical activity raised serious doubts about the earlier methodology of isolation. All the bisabolane-based compounds have a very labile C-6 proton due to functionalised C-7 carbon atom and therefore prone to racemisation even under moderate conditions. Earlier isolation procedures[12,15] have involved steam distillation as the mode of obtaining the essential oil and therefore, it can be argued that such thermal treatment in the presence of acidic components present in wood could lead to the partial/complete racemisation as observed in the isolated compounds.

The present investigation was directed towards isolating one such compound under mildest possible conditions involving strict temperature control for optical activity study. (+)-trans-Atlantone (8) the major bisabolane-based constituent of essential oil of *Cedrus deodara*[12] was considered ideal for this investigation.

Cold percolation (30°C) of the powdered wood of *C. deodara* with acetone gave an extract (18%) which after solvent stripping (36-38°C) was mixed thoroughly with celite. Cold percolation of this celite-extract mixture with petroleum ether gave petroleum ether solubles (73%). Removal of acids by sodium carbonate wash left the neutral fraction which was chromatographed on neutral silica gel (IVA). The fourth fraction which eluted with 5% ether/petroleum ether was essentially a mixture of two compounds with RRT 1.0 and 1.20 (10% SE-30, 200^{o}C). The two were isolated by preparative GLC (5% carbowax, 180^{o}C).

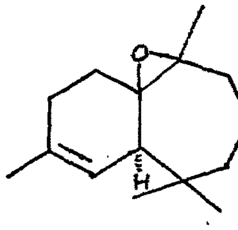
The compound with RRT 1.20 was found identical with (+)-<u>trans</u>-atlantone (<u>8</u>) on the basis of physical and spectroscopic data. Its specific rotation was found to be +4^{o} ($CHCl_3$, C.2%). Thus, isolation of essentially the racemic product indicates that the racemisation probably occurs in the plant itself!

ii) <u>Isolation of himachalene epoxide</u>

The second compound having the RRT 1.00 showed in its IR spectrum (Fig: V-I) the presence of an oxirane ring-1072, 862 cm^{-1} ($-\overset{O}{C-C}-$) 2920 cm^{-1}, 895 cm^{-1}, 910 cm^{-1}.

Its PMR (Fig: V-2) shows following features: $C\underline{H}_3-C-C\underline{H}_3$ (3H, s, 0.84 ppm; 3H, s, 0.94 ppm); $C\underline{H}_3-C=C-$(3H, s, 1.74 ppm); $C\underline{H}_3-C-O$ (3H, s, 1.27 ppm); $C\underline{H}_3-C=C\underline{H}$ (1H, bs, 5.37 ppm).

Comparison of the electron induced fragmentation pattern of this compound with that of synthetic himachalene epoxide clinched the structure as shown in (<u>30</u>). Epimeric



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himachalene epoxides have been isolated earlier by Cookson and his co-workers[23] from Cedrus atlantica. Both of them show the same PMR, IR, UV and Mass fragmentation pattern. They however, differ in their GLC RRT.

This is therefore, the first reported case of isolation of himachalene epoxide (30) from Cedrus deodara.

EXPERIMENTAL

For general remarks see Chapter II, Experimental.

Ether refers to diethyl ether. Preparative GLC analysis was carried out on Al. columns (144" x 3/8" O.D), packed with 5% carbowax 20M on chromosorb W 45-60 (mesh) at 180°C.

Neutral fraction obtained after sodium carbonate (page62) wash was used for present study.

Chromatography of neutral extract

Chromatogram

Silica gel (IV-A): 100 gms; Column: 47 x 2.5 cm.

Material charged: 5.5 gms

Fr. No.	Eluent	Eluate (ml)	Weight/gms.
1.	Pet. ether	1 x 100	-
2.	Pet. ether	5 x 100	1.6415
3.	5% ether/pet. ether	2 x 100	0.4155
4.	5% ether/pet. ether	4 x 100	0.8085
5.	50% ether/pet.ether	4 x 100	1.3986
6.	Acetone	5 x 100	1.0508
		Total	5.3149

Fr. 4 comprising of two components with RRT 1.0 and 1.20 was purified by preparative GLC.

The compound with RRT of 1.20 was identical with trans-atlantone (8). b.p.: 140-145^{o}(bath)/1 mm. n_D^{30} 1.5344. $[\alpha]_D$: +4^{o} ($CHCl_3$.C. 2%).

Himachalene epoxide RRT 1.0, n_D^{25} 1.5038.
Mass: m/e^+. 220(55.3%); 110(100%); 95(52.7%), 151(34%); 69(32.4%); 131(25.3%); 202(21.3%); 159(20.7%); 105, 132(20.3%); 137 (19.7%).

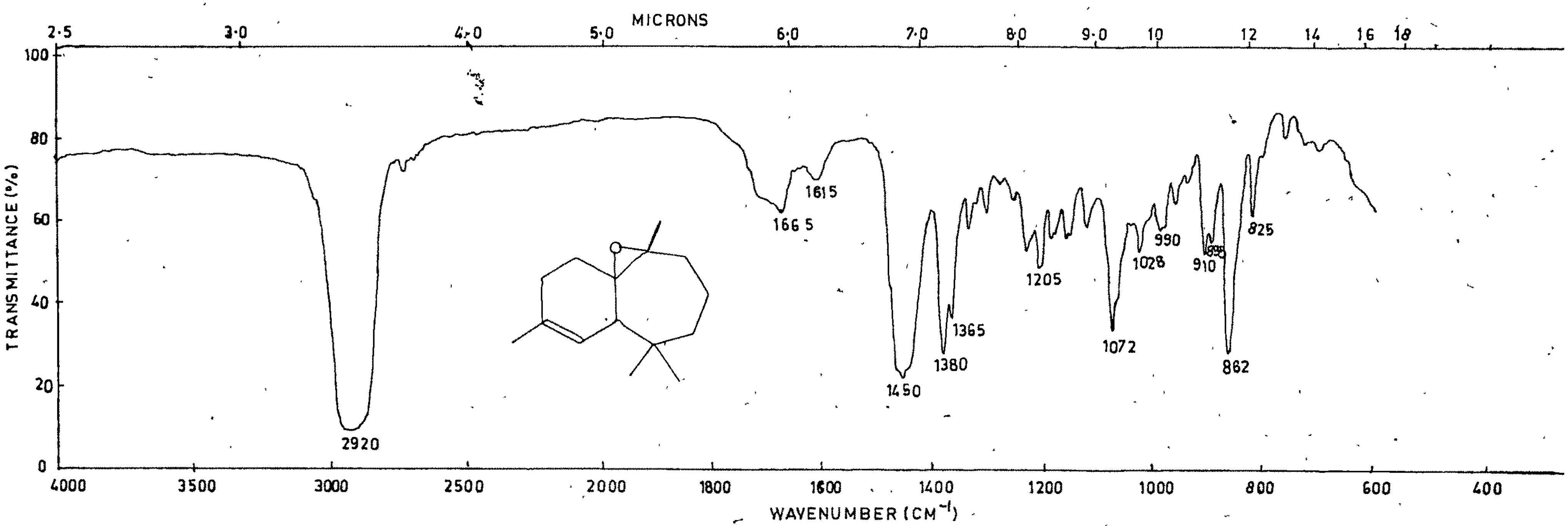

FIG V-1: IR SPECTRUM OF HIMACHALENE EPOXIDE

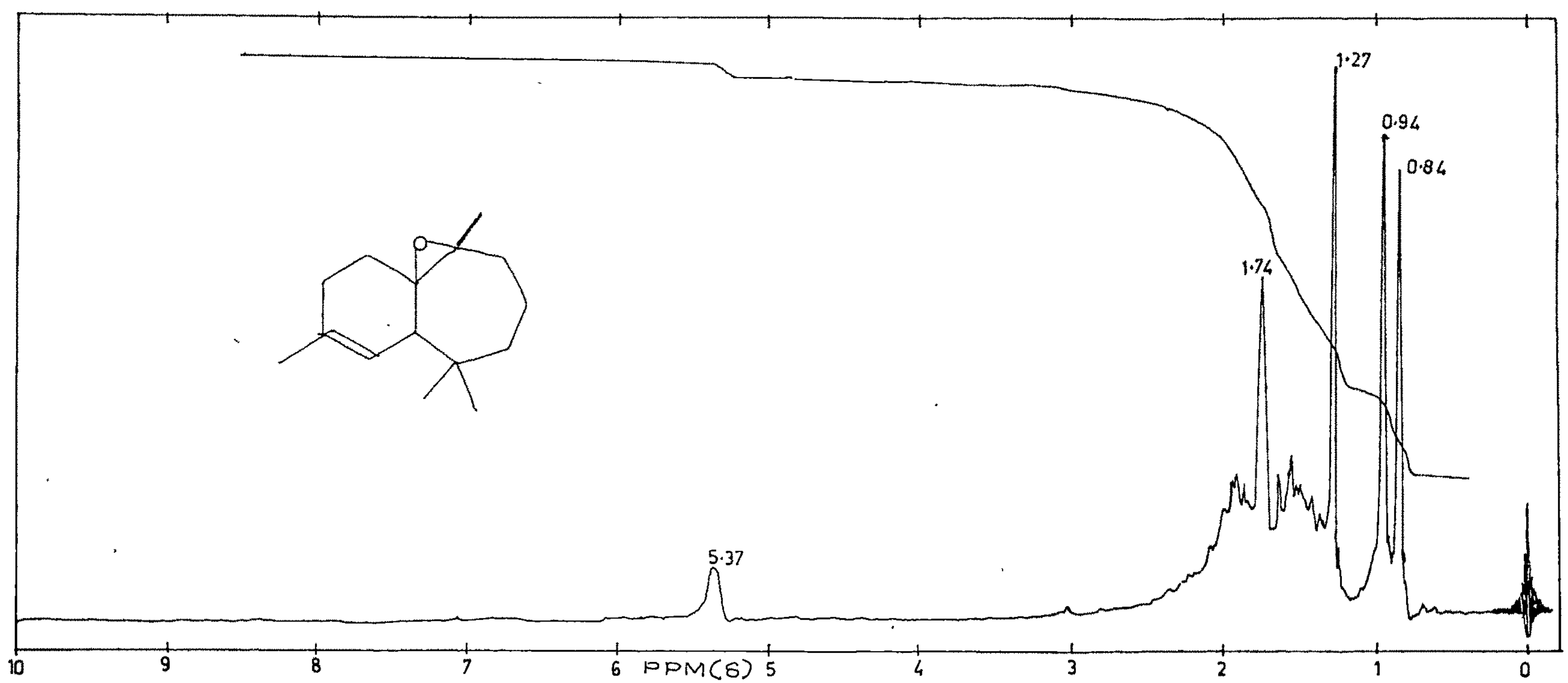

FIG V-2: PMR SPECTRUM OF HIMACHALENE EPOXIDE

R E F E R E N C E S

1. S.S. Choudhary, B.N. Nazir and K.L. Handa, Ind. Oil. Soap. J. 25, 306 (1960).

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