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TERPENOIDS LXXXVII. THE STRUCTURE OF NARDOL*

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IN continuation of our earlier work[1,2] on *Nardostachys jatamansi* D.C. (greyish brown variety), we are also examining the constituents of the dark brown variety. In this communication, we wish to report in brief the isolation of some of the constituents of the dark brown variety and the constitution of a new sesquiterpene alcohol, which we propose to name as nardol.=

The concrete (4.38%) obtained from the roots by employing low temperature solvent extraction procedur is separated in the usual way into acidic (2.2%) and neutral fraction (97.8%). The volatile fraction obtained by high vacuum distillation of the latter, on chromatography over alumina (gr.III, 25 times) and elution with

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= Details of this work will be published elsewhere.

pet.ether, benzene, ether and ethanol yields in the pet. ether fraction, calarene[3] (I; 4.5%), aristolene[4] (II; 4.5%), valeranone[5] (III; 0.48%) and several other unidentified constituents.

Careful rechromatography of the benzene fraction on grade II alumina has yielded a new alcohol (0.36%), nardol (GLC/TLC pure), b.p.120-125° (bath)/0.5 mm., n_D^{26} 1.5005; $(\alpha)_D^{27}$ - 10.17° (c, 2.36; $CHCl_3$); IR spectrum bands at: 3500, 2950, 1648, 1468, 1385, 1310, 1225, 1120, 982, 950, 940, 907 and 895 cm^{-1}; UV spectrum: end absorption (ϵ 220^{560}), which analyses for $C_{15}H_{26}O$ (Found: C, 80.71; H, 11.92. $C_{15}H_{26}O$ requires: C, 81.02; H, 11.79%).

It gives a positive color test with tetranitromethane and contains only one double bond (quantitative hydrogenation; PtO_2/AcOH-EtOH) and is therefore bicyclic in nature.

The hydroxyl group is found to be tertiary on the basis of its stability towards Jones' chromic acid reagent. Selenium dehydrogenation (13 hr) gives Se-guaiazulene (IV; 14%; m.p. and mixed m.p. of TNB adduct 148-9°) and traces of naphthalenic bodies. Sulphur dehydrogenation (12 hr) gives S-guaiazulene (V; 5%; m.p. and mixed m.p. of TNB adduct 147-8°). On prolonging the time of dehydrogenation (48 hr), mainly a mixture of the naphthalenic hydrocarbons, eudalene and cadalene (25%; 40:60, GLC) is isolated. These results indicate that nardol contains the basic azulenic skeleton (VI).

The nature of the olefinic linkage is methylenic, as shown by its IR spectrum (bands at 1648 and 895 cm^{-1}) and the NMR spectrum* (Fig.1; a doublet at τ = 5.45, 2H). Position of the methylenic double bond is proved to be exocyclic by ozonisation, which furnishes a keto alcohol having a carbonyl function on a seven membered ring (IR band at 1712 cm^{-1}). The possibility of the olefinic linkage being at C_{11-12} is excluded on the basis that the ozonization product does not give a haloform test and the NMR spectrum of nardol does not indicate the presence of any methyl group on a double bond.

The tertiary nature of the hydroxyl function is also supported by its NMR spectrum (no absorption between τ = 5.6 to 7.5 region). The NMR spectrum of nardol in the methyl absorption region shows the presence of an isopropyl grouping (two doublets at τ = 9.15 and 9.18, J = 7 c/s, 6H) and a quaternary methyl (a singlet at τ = 8.89, 3H), which seems to be attached to a carbon carrying an oxygen function. This is further supported by the NMR spectrum of dihydronardol, which shows the presence of one methyl on a carbon carrying an oxygen function (a singlet at τ = 8.6, 3H) and three secondary methyls (signals at τ = 8.95, 9.06, 9.15

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* All NMR measurements were carried out at 60 Mc/sec. for CCl_4 solution. Chemical shifts are expressed in τ units, while coupling constants (J) are in c/s.

and 9.17; 9H). On the basis of these findings, structures VII, VIII and IX can be assigned for nardol, dihydronardol and the ketoalcohol respectively.

The position of the hydroxyl group at C_4 is further confirmed by pyrolysis of the benzoate of the dihydroalcohol (VIII), which furnishes a mixture of epimeric hydrocarbons. The IR spectrum of the mixture shows the presence of a hydrocarbon having trisubstituted double bond (band at 803 cm^{-1}) and only traces of a hydrocarbon having methylenic double bond(very weak bands at 1650 and 892 cm^{-1}). Two main components of this hydrocarbon mixture are separated by preparative TLC, using silver nitrate (25%) impregnated silica gel.

The NMR spectrum of the hydfocarbon obtained from the top moving spot of the above TLC shows the presence of trisubstituted olefinic linkage (a broad signal at τ = 4.9, 1H), a methyl group present on an olefinic linkage (doublet at τ = 8.39, 3H, J = 2 c/s, coupling with olefinic proton) and the presence of three secondary methyls (signals at τ = 9.05, 9.11 and 9.14, 9H).

The NMR spectrum of the hydrocarbon from the next spot also shows the presence of one trisubstituted olefinic linkage (a broad signal at τ = 4.67, 1H), a methyl group present on an olefinic linkage (doublet at τ = 8.19, J=2 c/s, 3H) and three secondary methyl groups (a broad strong doublet at $\tau = 9.13$, $J = 6$ c/s, 9H).

On the basis of the above evidences, the two hydrocarbons can be represented by X or XI.

Dihydronardol (VIII; a mixture of C_{10} epimers) on dehydration with thionyl chloride in pyridine furnishes the same mixture of hydrocarbons (X and XI; compared by GLC analysis and IR spectra). The mode of dehydration suggests the axial nature of the hydroxyl group.[6]

The catalytic hydrogenation of the mixture of hydrocarbons formed as a result of pyrolysis of the benzoate of dihydronardol (VIII), furnishes a mixture of saturated hydrocarbons (no coloration with tetranitromethane, $(\alpha)_D^{27}$ - 31.06°). This is found to be a mixture of three epimers (65:25:10 as revealed by GLC analysis). The retention time of the major constituent of this mixture is identical with that of guaiane (XII), prepared from guaiol (XIII)* but the possibility of the <u>trans</u>-ring junctures also cannot be ruled out due to non-availability of samples of the latter.

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* The sample of guaiane (XII) has been supplied by Mr. M.V. Kadival of this Laboratory.

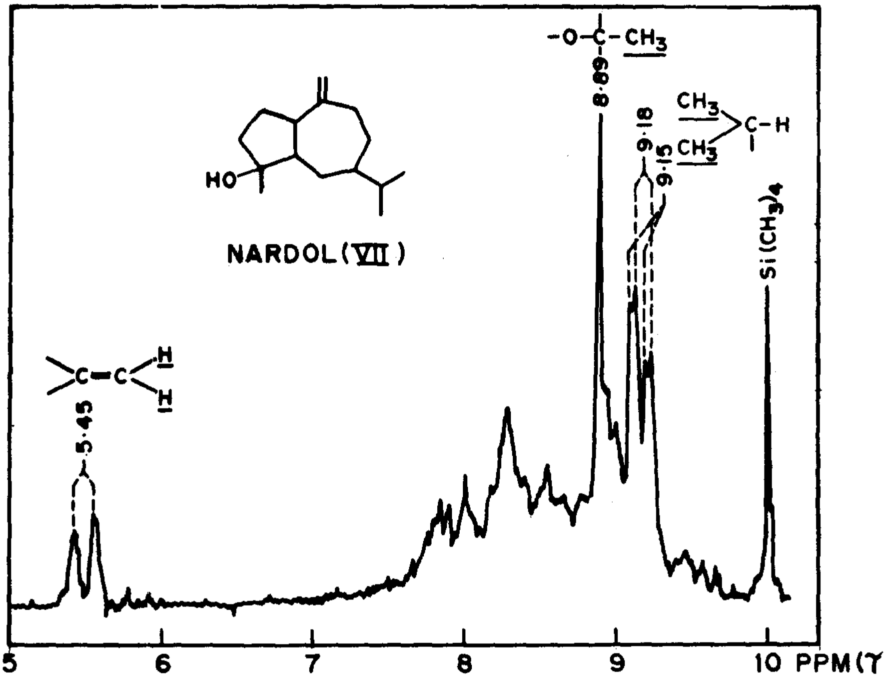
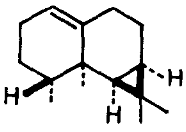

-O-C-CH3
8·89
CH3
CH3 >C-H
9·18
9·15
Si(CH3)4
HO
NARDOL(VII)
>C=C< H H
5·45
5
6
7
8
9
10 PPM(τ

FIG. 1.



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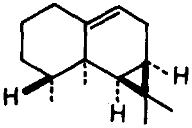

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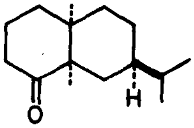

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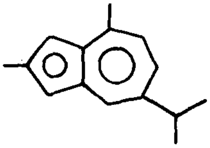

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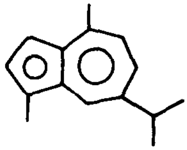

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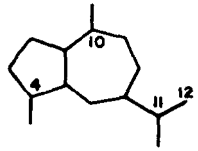

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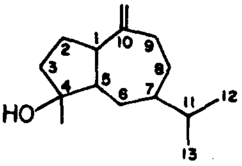

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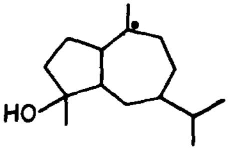
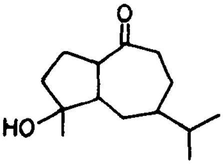


VIII



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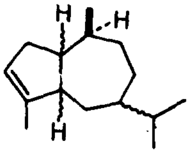
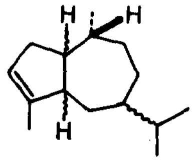


X



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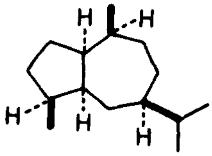
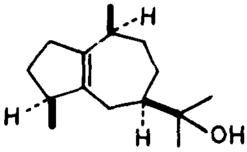


XII



XIII

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