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TERPENOIDS*—CVI

THE STRUCTURE OF CALARENOL

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Abstract—A new monoethynoid, tricyclic tertiary alcohol, $C_{15}H_{24}O$, named calarenol, has been isolated from the roots of *Nardostachys jatamansi.* D.C. On the basis of spectral evidences and its conversion to calarene and calarane, it has been represented by the stereoformulae I.

IN PREVIOUS communications, we have reported the isolation and characterization of a new sesquiterpenic compound, nardol[1] and also calarene[2] and valarenone[3] from *Nardostachys jatamansi.* D.C. (black brown variety). We have now isolated a new monoethynoid sesquiterpenic tertiary alcohol, $C_{15}H_{24}O$, which is represented by the structure I and named calarenol, because of its structural relation to calarene. It has been shown recently that β-gurjenene-aristolene (calarene) consists of inseparable double bond isomers represented by the structure VII; similarly the newly isolated alcohol, calarenol, is a mixture of two inseparable structural isomers I.

The neutral volatile fraction of the 'concrete' obtained from *N. jatamansi* was subjected to chromatography over neutral alumina (Grade III) and separated into pet. ether, benzene, ether, and ethanol eluted fractions. Careful rechromatography of the benzene eluted fraction yielded the new alcohol, calarenol. The IR spectrum of calarenol shows the presence of OH group (band at 3336 cm^{-1}) and a trisubstituted double bond (bands at 1665 and 847 cm^{-1}); UV spectrum: 210 $m\mu$ (ϵ 3665); NMR signals at 4·45 τ (multiplet, $-CH{=}C<$); 8·92 τ (singlet, $CH_3-\underset{|}{C}-OH$); 9·0, 9·04 τ (9H, three quarternary methyls) and 9·49 τ (multiplet, two cyclopropane protons). This is reminiscent of calarene.[2a]

Calarenol gives a positive colour test with tetranitromethane. Quantitative hydrogenation absorbs one mole of hydrogen indicating the presence of one double bond and thus establishing its tricyclic nature. Dihydrocalarenol (II), $C_{15}H_{26}O$, is a homogeneous material.

The tertiary nature of the OH group is proved on the basis of its stability towards Jones' chromic acid reagent and is further supported by its NMR spectrum (no signal between 5·6 to 7·5 τ region attributable to $-CH_2OH$ and $-CHOH$). It forms

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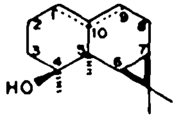
[1] S. D. Sastry, M. L. Mahaswari and S. C. Bhattacharyya, *Tetrahedron Letters* No. 10, 1035–1042 (1966).

[2] [a] G. Büchi, F. Greuter and Tokoroyama, *Tetrahedron Letters* No. 18, 827–833 (1962); [b] J. Streith, P. Pernelle, G. Ourisson, *Bull. Soc. Chim. Fr.* 518 (1963); [c] J. Vrkoč, J. Krěpinský, V. Herout and F. Šorm, *Coll. Czech. Chem. Commun.* **29**, 795 (1964).

[3] W. Klyne, S. C. Bhattacharyya, S. K. Paknikar, C. S. Narayan, K. S. Kulkarni, J. Křepinský, M. Romaňuk, V. Herout and F. Sorm, *Tetrahedron Letters* No. 23, 1443 (1964).

an acetate, $C_{17}H_{26}O_2$, only under energetic conditions; IR bands at 1746 and 1240 cm^{-1} ($-\overset{|}{\underset{|}{C}}-OAc$); NMR signals at 4·45 τ (multiplet, $-\underset{|}{C}H{=}C\langle$); 8·0 τ (7H, CH_3-OOC- and four allylic protons); 8·84 τ (singlet, $CH_3-\overset{|}{\underset{|}{C}}-OAc$); 9·0, 9·04 τ (9H, three quarternary methyls) and 9·49 τ (multiplet, two cyclopropane protons). The Me singlet ($CH_3-\overset{|}{\underset{|}{C}}-OH$) of alcohol shifts from 8·92 to 8·84 τ, when it is converted to the corresponding acetate, indicating the presence of a Me group attached to a carbon containing oxygen function.



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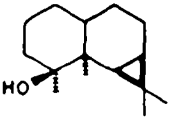

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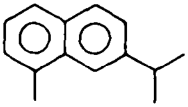

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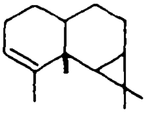

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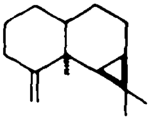

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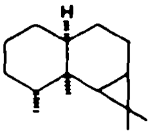

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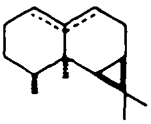

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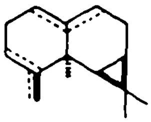

VIII

On selenium dehydrogenation calarenol gives eudalene (III), identical with an authentic specimen (Experimental).

The proof for the basic skeleton was obtained by pyrolysis of the acetate of the dihydroalcohol (II) when a mixture of two hydrocarbons(IV, V) was obtained (TLC). The IR spectrum of the mixture shows the presence of hydrocarbons containing trisubstituted and methylenic double bonds. The trisubstituted hydrocarbon (IV), $C_{15}H_{24}$, which constitutes about 75% of the hydrocarbon mixture, was obtained in the pure form by preparative TLC using silver nitrate (25%)-impregnated silica gel. Catalytic hydrogenation of the above mixture yields the pure saturated hydrocarbon, calarene, $C_{15}H_{26}$ (VI). Its IR spectrum is superimposable with that of an authentic sample of calarane and both the samples have same retention times in GLC. On the basis of the above data structure II has been assigned to dihydrocalarenol and IV–V to the corresponding hydrocarbons.

The evidence for the location of the double bond is obtained by pyrolysis of calarenol acetate, when a mixture of hydrocarbons (VIII) is obtained. The presence of the trisubstituted hydrocarbons and hydrocarbons having a methylenic double bond is indicated in the IR spectrum. The hydrocarbons could not be separated by preparative TLC on silvernitrate-impregnated silica gel as they undergo decomposition during the process. The mixture was catalytically hydrogenated so as to reduce the methylenic double bond. The product shows four spots (TLC, silvernitrate-impregnated silica gel) of which spot I corresponds to calarane (VI), and spot II to calarene (VII). Spot II is separated by preparative TLC and its IR spectrum is superimposable on that of an authentic sample of calarene. Hence calarenol can be assigned the structure I, it being a mixture of two inseparable double bond isomers.

Dihydrocalarenol (II) on dehydration[4] with thionyl chloride in pyridine furnishes mainly the trisubstituted hydrocarbon, IV. The mode of dehydration supports the axial nature of the OH group at C_4 position. The stereochemistry[2a] of calarene is well established and it has the C_4, C_5 methyls α-oriented and the cyclopropane ring β-oriented at C_{6-7}. On the basis of the above evidences presented in this paper calarenol can be represented by the stereoformulae I.

EXPERIMENTAL

Rotations were determined in chf. IR spectra were recorded as liquid films or in nujol suspension on a Perkin-Elmer Infracord spectrophotometer, model No. 137-B. UV spectra were measured in EtOH solns on a Beckman ratio recording spectrophotometer, model DK-2. NMR spectra were recorded with a Varian A-60 spectrometer operating at 60 mc. TLC of $AgNO_3$—impregnated silica gel was done according to method of Sukh Dev and Gupta.[6] GLC analysis was done on polyester column.

Calarenol (I). The neutral volatile fraction from the 'concrete' was chromatographed over grade III neutral alumina, and separated into pet. ether, benzene, ether and EtOH eluted fractions. Careful rechromatography of the benzene eluted fraction yielded the new alcohol, nardol,[1] in the initial fractions and calarenol (TLC/GLC) in the latter fractions. It has the following properties, b.p. 120–125° (bath)/0·1 mm; n_D^{30} 1·5143, $[\alpha]_D^{30}$ +47·9° (*c*, 3·0). IR spectrum: bands at 3336, 2959, 1665, 1460, 1379, 1316, 1282, 1242, 1241, 1188, 1149, 1131, 1089, 1055, 1020, 980, 965, 890, 847, 787, 769 cm^{-1}. (Found: C, 81·98; H, 10·65; $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%.)

Dihydrocalarenol (II). To prereduced Adams catalyst (0·024 g) in glacial AcOH (10 ml) was added calarenol (0·198 g) in glacial AcOH (1 ml). Hydrogenation stopped after it absorbed one mole equivalent of H. After removal of the catalyst, the filtrate afforded dihydrocalarenol (0·185 g) which was purified by chromatography on grade II alumina (3 g) followed by distillation. TLC showed single spot and GLC indicated single peak, b.p. 120–125° (bath)/0·1 mm; n_D^{30} 1·4996; $[\alpha]_D^{30}$ −16·83° (*c*, 2·5). (Found: C, 81·27; H, 12·18; $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%.)

Selenium dehydrogenation of calarenol (I). Alcohol (0·298 g) and Se metal (0·282 g) were placed in the dehydrogenation flask fitted with an air condenser. The mixture was heated at (295–310°) in an electrical furnace under N atm. The reaction mixture was cooled, extracted with pet. ether and the product purified by chromatography on grade I alumina (3 g) and eluting with pet. ether, a mixture of hydrocarbons and an aromatic hydrocarbon was obtained. This was identified as eudalene (III) by comparing with an authentic sample in GLC analysis (RT of dehydrogenation product 3′·29″, authentic eudalene 3′·30″). UV spectrum: λ_{max}^{EtOH} 222, 278, 290 mμ (ε 7711, 788, 560 respectively).

Calarenol acetate. A mixture of Ac_2O (20 ml) and calarenol (8·0 g) in pyridine (40 ml) was kept overnight. The mixture was heated on a water bath. (7 hr) and worked up to yield a mixture of hydrocarbons, acetate and the unreacted alcohol. The product on chromatography over grade I alumina (160 g) yielded the pure acetate (TLC). b.p. 117–122° (bath)/1 mm; n_D^{30} 1·4971; $[\alpha]_D^{30}$ +51·57° (*c*, 2·6); IR bands at 1746 and 1240 cm^{-1} (>C—OAc). (Found: C, 77·94; H, 9·93; $C_{17}H_{26}O_2$ requires: C, 77·82; H, 9·99%.)

Pyrolysis of dihydrocalarenol acetate, hydrocarbon (IV). Dihydrocalarenol acetate (2·53 g) was taken in a pyrolysis flask with a test tube receiver cooled in ice. The flask was heated (290–300°)

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[4] D. H. R. Barton, A. Das, Campos-Naves and R. C. Cookson, *J. Chem. Soc.* 3500 (1956).

[6] Sukh Dev and A. S. Gupta, *J. Chromatog.* 12, 189 (1963).

in an electrical furnace. After completion of pyrolysis, the product was extracted with pet. ether and washed with 10% $NaHCO_3$aq and water. The crude product was further purified by chromatography over grade I alumina (60 g). The pet. ether eluted fraction yielded the hydrocarbon mixture (IV, V). IR bands at 1665, 833 and 1645, 892 cm^{-1} indicate the presence of trisubstituted and methylenic double bonds.

Trisubstituted hydrocarbon which constituted more than 75% of the mixture was purified by preparative thin layer $AgNO_3$ (25%)-impregnated silica gel (15% benzene in pet. ether). The hydrocarbon IV (GLC/TLC) showed the following properties: b.p. 125–130° (bath)/9 mm; n_D^{24} 1·5081; $[\alpha]_D^{28}$ $-63{\cdot}9°$ (*c*, 2·2); IR bands at 1665 and 833 cm^{-1} due to the trisubstituted double bond. (Found: C, 88·31; H, 12·02; $C_{15}H_{24}$ requires: C, 88·11; H, 11·84%.)

Calarane (VI). A soln of the hydrocarbon mixture IV and V (0·245 g) in glacial AcOH (15 ml) was hydrogenated over PtO_2 (0·052 g). The product obtained was purified by chromatography over grade I alumina (4 g). Pet. ether eluted fraction was distilled over Na, b.p. 120–125° (bath)/8 mm; n_D^{24} 1·4946; $[\alpha]_D^{28}$ $-46{\cdot}41°$; IR bands at 3145, 2941, 2717, 1447, 1374, 1307, 1250, 1218, 1183, 1160, 1145, 1124, 1078, 1033, 996, 955, 930, 892, 855, 845, 839, 782, 740 cm^{-1}. IR spectrum is superimposable on the IR spectrum of an authentic sample of calarane. (Found: C, 87·14; H, 13·03; $C_{15}H_{26}$ requires: C, 87·30; H, 12·7%.) Retention times (1′·41″) of saturated hydrocarbon and authentic sample of calarane and their physical constants prove their identity.

Pyrolysis of calarenol acetate, hydrocarbons (VIII). On pyrolysis, calarenol acetate (3·25 g) yielded a mixture of hydrocarbons (VIII) (Four spots, $AgNO_3$ (25%) impregnated silica gel). IR bands at 1665, 1645, 890 and 840 cm^{-1}.

Calarene (VII). Hydrocarbon VIII (2·13 g) in EtOH (120 ml) was hydrogenated over PtO_2 (0·21 g). Hydrogenation was stopped when it absorbed 0·2 mole equiv of H. The product showed 4 spots in TLC ($AgNO_3$ (25%) impregnated silica gel) of which spot I corresponded to VI and spot II to VII. The product from spot II was separated by preparative TLC (15% benzene in pet. ether) and gave VII. It showed the following properties; b.p. 120–125° (bath)/8 mm; n_D^{24} 1·5020; $[\alpha]_D^{28}$ $+38{\cdot}9°$. IR spectrum bands at 3140, 2950, 1665, 1449, 1370, 1235, 1198, 1129, 1063, 1039, 995, 943, 899, 847, 807, 775, 744, 695 cm^{-1}. (Found: C, 88·26; H, 11·92; $C_{15}H_{24}$ requires: C, 88·11; H, 11·84%.)

Hydrocarbon (IV). To a soln of dihydrocalarenol (0·21 g) in pyridine (3 ml), $SOCl_2$ (1 ml) was slowly added with stirring at ice cold temp. Stirring was continued at room temp for 4 hr. The product poured in water and extracted with ether. Combined extracts washed with 10% tartaric acid soln and finally with water, dried over Na_2SO_4 and solvent removed. The crude product was chromatographed over grade I alumina (4 g). Pet. ether eluted fraction yielded the hydrocarbon (0·92 g). IR bands at 1665 and 833 cm^{-1} which are characteristic of trisubstituted double bond. It was found to be IV by its physical constants and TLC comparisons with an authentic sample. (Found: C, 88·02; H, 11·85; $C_{15}H_{24}$ requires: C, 88·11; H, 11·84%.)