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A NEW SYNTHETIC APPROACH TO THE

ACORANE-, DAUCANE- AND CEDRANE SKELETON

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In the preceding communication (1) we reported the presence of several new acorane- and cedrane derivatives in vetiver oil.For the structure determination of the acoradiene III and Δ 2-cedrene (Va) we used the following synthetic approach:

The known ketone IX (2) was prepared by heating racemic dehydrolinalool in an autoclave to 200°C to give epimeric alcohols VIII practically quantitatively (3). Alcohols VIII were treated at 150°C in an autoclave with 3 equivalents of methyl-isopropenyl ether (4) in the presence of a trace of phosphoric acid to form IX in 75% yield. Reaction of IX with vinyl magnesium bromide in tetrahydrofurane at 50°C furnished after distillation in 90% yield the tertiary allylic alcohol XII with the following physicochemical data:

bp: 98°C/0,1 mmHg (5).

n_D^{20}: 1,4921.

ν max (liquid film): 3420, 3090, 1642, 1370, 1110, 1000, 925, 892, 740 cm^{-1}.

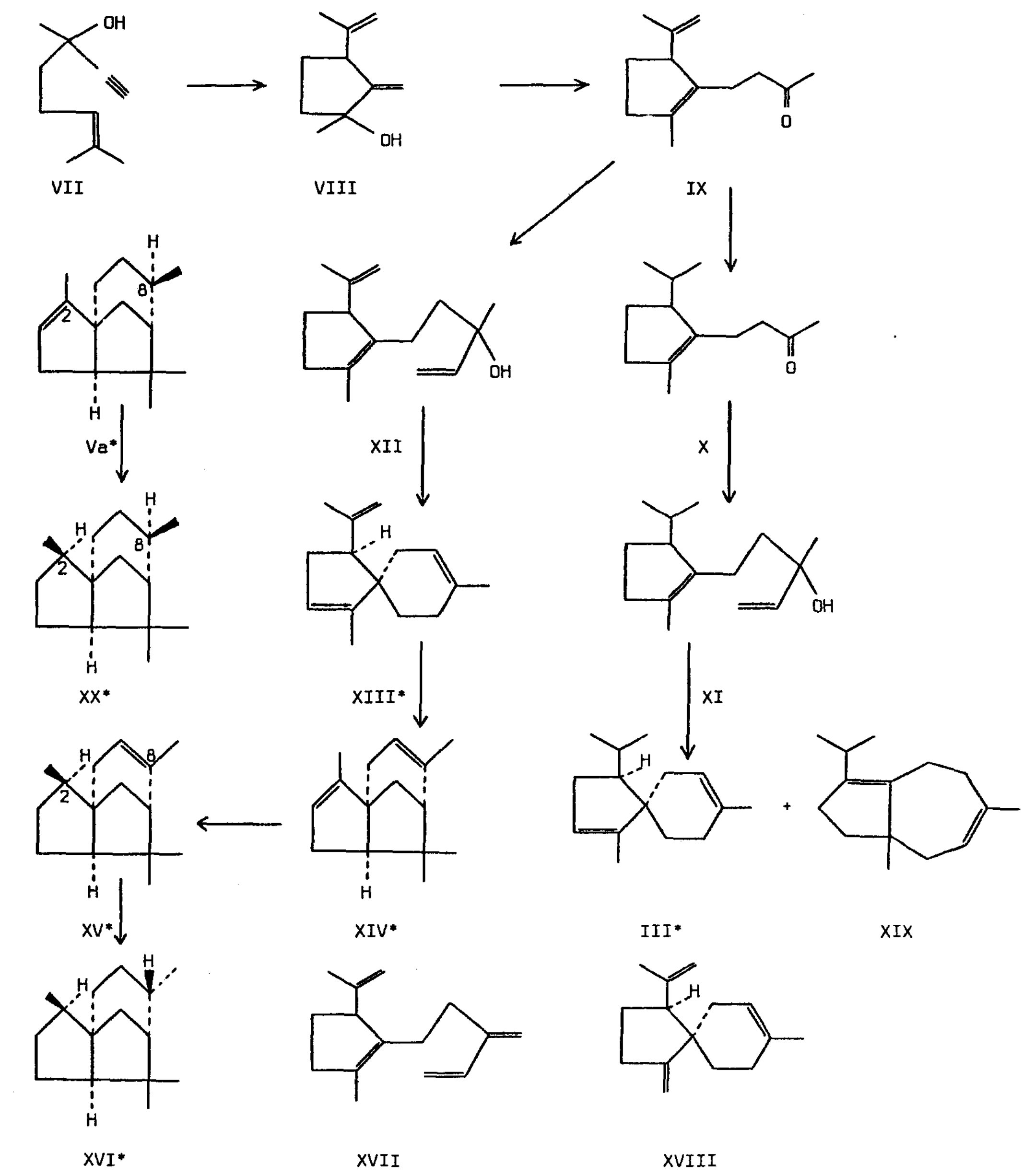
NMR ($CDCl_3$+TMS): δ=5,94(1H,dd with 17,5 and 10 cps); δ=5,38-4,90(2H,m); δ=4,70(2H,narrow dd; δ=3,32(1H,broad m); δ=1,63(3H,broad s); δ=1,55(3H,narrow dd); δ=1,25 ppm(3H,s).

MS molecular ion at $^m/e$: 220. characteristic fragments at $^m/e$: 202, 187, 173,$\underline{147}$=base peak, 133/34, 119, 105, 93, 79.

When the alcohol XII was dissolved in benzene-ether (5 to 1) and treated with 1,5 molar equivalents of stannic chloride at 0°C, a hydrocarbon mixture consisting of 75 to 80% β-acoratriene XIII could be obtained in 65% yield. Chromatography on silicagel impregnated with silver nitrate easily allowed its purification.

The cyclization of said alcohol XII requires some comment in so far as it is remarkably stereospecific. The isopropenyl group seems to direct the approach of the end of the side chain to the unhindered side of the cyclopentene ring. There could not be isolated any isomeric α-acoratriene nor any doubly cyclized product such as XIV. The two main by-products formed are the olefins XVII and XVIII.

Table 3



*We assign absolute stereochemistry to these compounds only on grounds of co-occurrence with (+)-α-cedrene, (+)-prezizaene and (+)-zizaene in vetiver oil (cf.(1)).

Short treatment of XIII with a catalytic amount of para toluene sulfonic acid in refluxing benzene furnished, after distillation, in 60% yield a hydrocarbon mixture, containing about 50% cedradiene XIV (cf. also (6)). Chromatography on silver nitrate impregnated silicagel allowed separation of the pure product, showing the following data:

bp: ~50°C/0,08 mmHg. n_D^{20}: 1,5068.

ν max (liquid film): 3030,1655,1382/80,1362,1153,1106,1040,1025,1008,940/30,910,811,800, 782 cm^{-1}.

NMR ($CDCl_3$+TMS): δ=5,25(1H,m); δ=5,15(1H,m); δ=1,75(3H,narrow m); δ=1,60(3H,narrow m); δ=1,08(3H,s); δ=0,96 ppm(3H,s).

MS molecular ion at $^m/e$: 202. characteristic fragments at $^m/e$: 187,173,159=base peak with same intensity as molecular peak, 145,131,119,115,109,105,91,77,67/65.

Partial hydrogenation of cedradiene XIV with palladium on charcoal in ethyl acetate furnished 2-epi-α-cedrene (XV) exhibiting the following spectra (cf. also (6)):

ν max (liquid film): 3020,1460,1377,1362,1283,1250,1240,1230,1185,1140,1100,1055,1025, 1010,930,915,830,800 cm^{-1}.

NMR ($CDCl_3$+TMS): δ=5,22(1H,m); δ=1,71(3H,narrow m); δ=1,01(3H,s); δ=0,92(3H,s); δ=0,89 ppm(3H,d with 5,5 cps).

MS molecular ion at $^m/e$: 204. characteristic fragments at $^m/e$: 189,161,147,136,119=base peak,105,93,77,69. In contrary to IR,NMR and GLC-retention time the MS is practically indistinguishable from the MS of α-cedrene or of the natural Δ2-cedrene Va.

Hydrogenation of XV under the same conditions or with platinum in acetic acid gave 2-epi-cedrane (XVI) under the reasonable assumption that the hydrogenation of XV leads to the same stereochemistry in position 8 as the hydrogenation of α-cedrene to cedrane. Data of XVI:

ν max (liquid film): 1475,1460,1438,1383,1375,1362,1248,1225,1100,1064,1010,997,972,948, 938,905,897 cm^{-1}.

NMR ($CDCl_3$+TMS): δ=1,11(3H,s); δ=0,91 ppm(3H,s); secondary methyls not clearly discernible.

MS molecular ion at $^m/e$: 206. characteristic fragments at $^m/e$: 191,177,163,150,135, 121,107,95,82=base peak,69.

Hydrogenation of the natural Δ-2-cedrene Va ex vetiver oil with palladium on charcoal in ethyl acetate or with platinum in acetic acid gave yet another cedrane (XX), exhibiting the following physicochemical data:

$[\alpha]_D$= +0,5° (c=2,24 in $CHCl_3$)

ν max (liquid film): 3000,1460,1375,1361,1180,1132,1088,1045,1020,980,973,885 cm^{-1}.

NMR ($CDCl_3$+TMS) on a Varian HA 100 spectrometer: δ=1,15(3H,s); δ=1,04(3H,s); δ=0,99(3H, d with 7 cps); δ=0,80 ppm(3H,d with 7 cps).

MS molecular ion at $^m/e$: 206. characteristic fragments at $^m/e$: 191,177,163,150,135, 121,107,95,82=base peak,69. In contrary to IR,NMR and GLC-retention time the MS is practically indistinguishable from the MS of cedrane or of 2-epi-cedrane XVI.

8-epi-cedrane has been described in the literature exhibiting a NMR-shift difference of the geminal methyl groups of 5,5 cps (7). Neither of the new cedranes described above shows this feature. Thus the hydrogenation product of Va can be assigned the structure of 2-epi, 8-epi-cedrane (XX) and the new natural products Va-c (1) would be Δ 2,8-epi-cedrenes.

When ketone X, prepared by catalytic hydrogenation with palladium on calcium carbonate in ethylacetate, was treated in analogy to ketone IX, one obtained the tertiary allylic alcohol XI, which was cyclized in the same manner as XII. The cyclization product consisted essentially of two compounds. After separation by preparative GLC the main component (70%) showed the following physicochemical data, consistent with structure XIX.

ν max (liquid film): 1460,1445,1380/75/66/60,1330,1300,1200,1110,1025,1010,986,978,828 cm^{-1}.

NMR ($CDCl_3$+TMS): δ=5,44(1H,broad t with 6,5 cps); δ=1,75(3H,broad s); δ=1,00(3H,d with 6,5 cps); δ=0,92(3H,d with 6,5 cps); δ=0,91 ppm(3H,s).

MS molecular ion at $^{m}/e$: 204. characteristic fragments at $^{m}/e$: 189,175/6,161=base peak,147/8,134,121,105,91,77,67. IR,NMR and MS as well as the GLC-retention time were identical with the ones of daucene, prepared by dehydration ($SOCl_2$,Py in ether at room temperature) of natural carotol.

The minor constituent (20%) of the cyclization reaction showed the same IR,NMR and MS as well as GLC-retention time as the natural product III, isolated from vetiver oil (1). (For the physicochemical data see preceding article).

Literature references:

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(2) G.Saucy et al., Helv.Chim.Acta 41, 160 (1958)
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(4) G.Saucy and R.Marbet, Helv.Chim.Acta 50, 2091 (1967)
(5) IR spectra were taken on PE 157 or 257 spectrometers, NMR spectra on a Varian A 60 A instrument and MS at 70 eV on a double focussing CEC 21-110 B instrument with an all glass inlet system (temperature 150°C).
(6) E.Demole et al., Helv.Chim.Acta 54, 1845 (1971)
(7) P.Teisseire et al., G.Ourisson et al., Bull.Soc.Chim.France, 2749 (1966)

P.S.: Physicochemical data of XIII:

n_D^{20}: 1,5091.

ν max (liquid film): 3070,3040,3010,1638,1375,1315,1155,1065,1018,958/48,892,805,800 cm^{-1}.

NMR ($CDCl_3$+TMS): δ=5,31(2H,m); δ=4,72(2H,split d with 1,5 cps); δ=1,70-1,50 ppm(9H, several split s).

MS molecular ion at $^{m}/e$: 202. characteristic fragments at $^{m}/e$: 187,173,159,145,134, 119=base peak, 105,91,77,65,53.

All spectral data correspond with the recently published ones for β-acoratriene (6).