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BIOGENETICALLY SIGNIFICANT COMPONENTS
IN VETIVER OIL

by R.Kaiser and P.Naegeli

(Givaudan-Esrolko Ltd., Research Company,
Dübendorf-Zürich, Switzerland)

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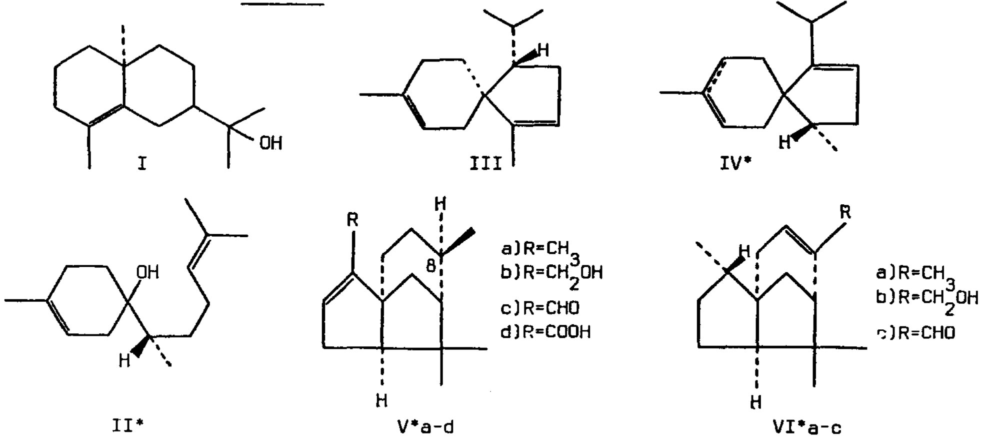
In view of recent publications on vetiver oil (1) we would like to communicate a few details of our own work in this field. During the analysis of the essential oil of Vetiveria zizanoides (Stapf) a few minor constituents of presumably biogenetic importance were isolated.

On one hand we found (-)10-epi-γ-eudesmol(I) the structure of which was confirmed through comparison with an authentic sample, synthesized according to J.A.Marshall and M.T.Pike (2). Epi-γ-eudesmol is assumed to be the precursor of the nootkatane-,α- and β-vetivane derivatives primarily occurring in the oil (1).

On the other hand we isolated β-bisabolol (II), two new acoradienes III and IV and seven new cedrane derivatives V a-d and VI a-c (see table 1).

Table 1

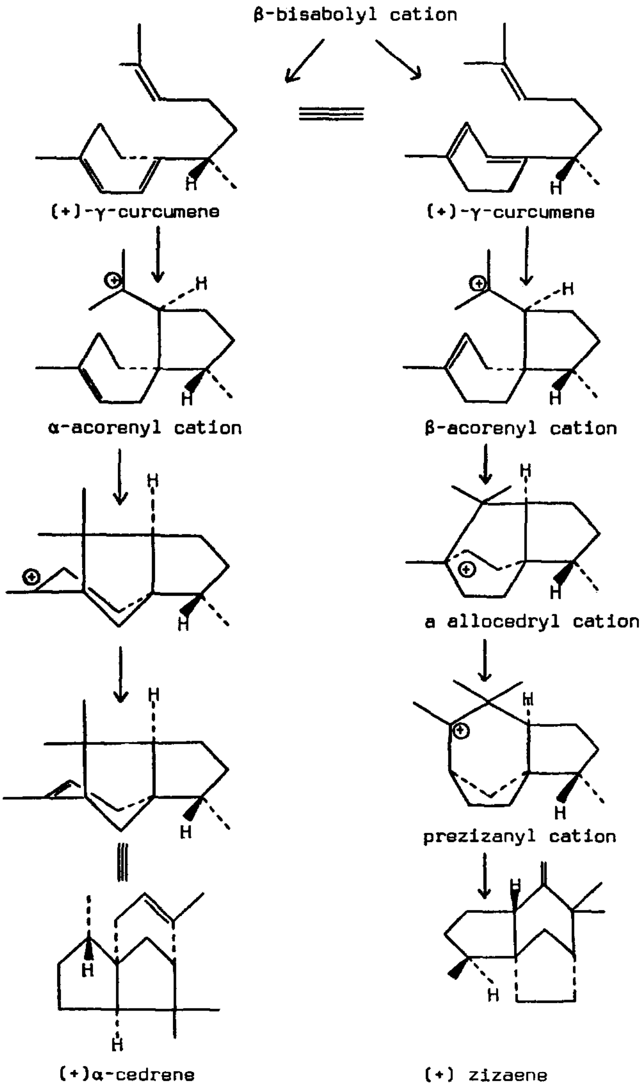


*We assign absolute configurations only on grounds of co-occurrence with (+)-α-cedrene,(+)-prezizaene and (+)-zizaene and the postulated biogenetic scheme outlined in table 2. For the stereochemistry in position 8 of formula V see (3).

N.Andersen (1) proposed a biogenetic scheme for the formation of tricyclovetivanes from (+)-γ-curcumene stressing the important role of spirofused sesquiterpenes as intermediates.

The α-cedrene we isolated from vetiver oil exhibits a positive rotation ($[\alpha]_D = +81^{\circ}$, c=0.500 in $CHCl_3$). Since it occurs together with acoradienes as well as prezizaene and zizaene we may use these facts as complementary evidence to Andersens biogenetic proposal also in the case of vetiver oil (see table 2).

Table 2



Regarding structure proof for the new substances, identification of VIa-c was clearcut while II was characterized through transformation into β-curcumene. Compounds III and Va were related to synthesized products (3). Structure IV was determined through spectroscopic comparison with III.

Physicochemical data (4)

III: $[\alpha]_D$= $-3,8^{o}$ (c=0,522 in $CHCl_3$) taken on a 95% purity sample.
ν max (liquid film): 3035/15, 1385/75/65, 1195, 1160, 1065, 1030/15/10, 955/45, 810, 807, 798 cm^{-1}.
NMR ($CDCl_3$+TMS): δ=5,40(1H,m); δ=5,30(1H,m); δ=1,70-1,50(6H,m);δ=0,91(3H,d with 6,5cps) and δ=0,80 ppm(3H,d with 6,5 cps) showing up as pseudo triplet.
MS molecular ion at $^{m}/e$: 204.
characteristic fragments at $^{m}/e$: 189, 175, 161, 145, 136, 121, 105, 94=base peak, 79/77.

IV : $[\alpha]_D$= $+34,4^{o}$ (c=0,244 in $CHCl_3$).
ν max (liquid film): 3050, 3015, 1460/55/45, 1380, 1305, 1205, 1160, 1055, 1040, 995, 965, 948, 920, 815/10, 800, 762 cm^{-1}.
NMR ($CDCl_3$+TMS): δ=5,50-5,25(2H,m); δ=1,62(3H,m); δ=1,01(6H,d with 6,5 cps); δ=0,87 ppm (3H,d with 6,5 cps).
MS molecular ion at $^{m}/e$: 204.
characteristic fragments at $^{m}/e$: 189, 161, 136=base peak, 121, 107, 93.

V a: $[\alpha]_D$= -102^{o} (c=1,176 in $CHCl_3$).
ν max (liquid film): 3030, 3000, 1460/50, 1372, 1360, 1275, 1182, 1151, 1128, 1062, 1040, 998, 910, 808, 782 cm^{-1}.
NMR ($CDCl_3$+TMS): δ=5,12(1H,m); δ=1,63(3H,m); δ=1,06(3H,s); δ=0,85(3H,s); δ=0,87 ppm (3H,d with 6,5 cps).
MS molecular ion at $^{m}/e$: 204.
characteristic fragments at $^{m}/e$: 189, 175, 161, 147, 136, 119=base peak, 105, 93, 77, 69.

The MS of Va is practically indistinguishable from the MS of 2-epi-cedrene XV (cf.(3)) and from the MS of α-cedrene.

V b: ν max (liquid film): 3320, 1375, 1362, 1152, 1145, 1098, 1060, 1045, 1020, 1008, 995, 910, 810, 785 cm^{-1}.
NMR ($CDCl_3$+TMS): δ=5,41(1H,m); δ=3,95(2H,dd with J=4 and 2 cps); δ=1,095(3H,s); δ=0,835 (3H,s); δ=0,89 ppm(3H,d with 7 cps).
MS molecular ion at $^{m}/e$: 220.
characteristic fragments at $^{m}/e$: 205, 202, 189, 177, 159, 147, 135=base peak, 121, 105, 91, 79, 69. (5)

V c: ν max (liquid film): 2800, 2700, 1682, 1644, 1410, 1375, 1362, 1280, 1224, 1179, 1155, 1100, 1020, 940, 922, 798, 750 cm^{-1}.
NMR ($CDCl_3$+TMS): δ=9,30(1H,s); δ=6,55(1H,m); δ=3,06 and 2,48 and 2,29 ppm (each 1H,d with 4 cps); δ=1,12(3H,s); δ=0,65(3H,s); δ=0,91 ppm(3H,d with 6,5 cps).
MS molecular ion at $^{m}/e$: 218.
characteristic fragments at $^{m}/e$: 203, 189, 175, 162, 147, 133=base peak, 123, 105, 91, 79, 69. (5)

V d: (as methyl ester): ν max (liquid film): 1712, 1650, 1375, 1362, 1248, 1220, 1100, 1078, 778, 740 cm^{-1}.

NMR ($CDCl_3$+TMS): δ=6,72(1H,m); δ=3,72(3H,s); δ=3,0(1H,d with 4,5 cps); δ=1,12(3H,s); δ=0,75(3H,s); δ=0,91 ppm(3H,d with 6,5 cps).

MS molecular ion at $^{m}/e$: 248.
characteristic fragments at $^{m}/e$: 233, 217, 205, 189, 173, $\underline{163}$=base peak, 147, 136/37, 121, 105, 91, 81, 69. (5)

VIb: ν max (liquid film): 3340, 1382/75/62, 1120, 1095, 1072, 1045, 1005, 950, 912, 820 cm^{-1}.

NMR ($CDCl_3$+TMS): δ=5,50(1H,m); δ=3,97(2H,s); δ=0,97(3H,s); δ=0,95(3H,s); δ=0,86(3H,d with 6,5 cps).

MS molecular ion at $^{m}/e$: 220.
characteristic fragments at $^{m}/e$: 202, 189, 177, 159, 147, $\underline{135}$=base peak, 121, 105, 91, 79, 69.

VIc: ν max (liquid film): 2805, 2705, 1685, 1631, 1418, 1385/75/63, 1172, 1132/22, 992, 968, 918, 820, 808, 798, 785 cm^{-1}.

NMR ($CDCl_3$+TMS): δ=9,53(1H,s); δ=6,72(1H,pseudo t with 3,5 cps); δ=2,69(1H,broad d with 4 cps); δ=2,39(2H,m as pseudo dd); δ=1,06(3H,s); δ=0,88(3H,s); δ=0,95(3H,d with 6,5 cps).

MS molecular ion at $^{m}/e$: 218.
characteristic fragments at $^{m}/e$: 203, 189, 175/76, 162, 147, 133, 105, $\underline{91}$=base peak, 77/79, 69.

Literature references:

(1) N.H.Andersen and M.S.Falcone, Chemistry and Industry 62 (1971) and all references cited there.

(2) J.A.Marshall and M.T.Pike, J.Org.Chem. 33, 435 (1968)

(3) P.Naegeli and R.Kaiser, This journal. see following communication

(4) IR spectra were taken on PE 157 or 257 spectrometers, NMR spectra on a Varian A 60 A instrument and mass spectra at 70 eV on a double focussing CEC 21-110 B instrument with an all glass inlet system (temperature 150°C).

(5) Compounds Vb, Vc and Vd have been transformed into Va.

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