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α-Vetivone[1]

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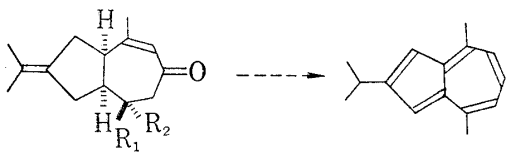
The structure of α-vetivone, one of the major odoriferous principles of vetiver oil had previously been accepted as being represented by Ia. Air oxidation of α-vetivone in the presence of 1N *t*-butoxide yielded, after treatment with *p*-toluenesulphonic acid, a conjugated dienedione VII. The enantiomeric compound was prepared, by oxidation, from the structurally well-established eremophilone XII, thus requiring that the structure of α-vetivone be revised to II. Some interesting observations were made with regards ORD and CD measurements in comparison with curves obtained from cholest-4-en-3-one. Biogenetic relationships between some related compounds are also discussed.

The similarity in physical properties of α- and β-vetivone, together with some parallel in chemical behaviour, and, more particularly, their occurrence in the same plant, led to the suggestion that these substances were stereoisomeric. Based on chemical studies of β-vetivone a hydrovetivazulene skeleton was suggested, specifically Ia and Ib for α- and β-vetivone respectively.[3]

The evidence for the functional groups in β-vetivone appeared good and the selection of the vetivazulene framework, determined by the obtention of vetivazulene by the dehydrogenation of both ketones,[3] reasonable. The sum of the evidence appeared persuasive and the structure remained unchallenged.



Ia : R_1=H, R_2=Me
Ib : R_1=Me, R_2=H

XVII

Chart 1

In connection with other work we wished to be certain of the stereochemistry of these substances. From the inspection of models (Dreiding) a curious fact emerged. The ultraviolet absorption maximum is recorded[3,4] as being at 240 mμ for both vetivones with an absorption of ε=16000. This extinction represents close to the maximum found for this type of system, and the wavelength is normal, but the models revealed that with a *cis* fusion of the rings considerable distortion of the chromophore was involved, which should have resulted in a modified absorption spectrum. Since the *cis* fusion seemed one of the most reliable of the available facts the matter was perplexing. It seemed, however, that the hypothesis of a *cis* fusion was capable of being tested since the models revealed that ready isomerisation to a *trans* fusion should occur. A specimen of α-vetivone was accordingly isolated. The NMR-spectrum, discussed in the following paragraph, clearly indicated that the structure Ia was incorrect, and so attention was then directed to the elucidation of the structure and stereochemistry of the compound.[5]

1) Terpenoids part 15. Part of the following has been reported in preliminary form.[5] Part 14 of this series: J. J. Dugan, P. de Mayo, M. Nisbet, J. R. Robinson and M. Anchel, *J. Am. Chem. Soc.*, **88**, 2838 (1966).
2) Location: *London, Ontario, Canada.*
3) For a discussion of the earlier work see J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, Cambridge, 1952, p. 224 *et seq.*
4) Y. R. Naves, *Bull. Soc. Chim. France*, **1951**, 369.
5) K. Endo and P. de Mayo, *Chem. Commun.*, **1967**, 89.

The NMR-spectrum of α-vetivone provided, together with the earlier data,[3] almost sufficient information to establish the new structure II. The existance of an isopropylidene group had earlier been proven by ozonolysis to give acetone: the relevant methyl groups were now seen as a broad singlet at 1.73 ppm. Only one vinylic proton signal was observed and this, because of its deshielded position (5.62 ppm) was to be placed α to the carbonyl group. Two methyl signals were detected (at 0.97 and 1.00 ppm), one of which was a doublet (J=6 cps) and the other a singlet. Neither, obviously, could be assigned to a methyl group on an sp^2 carbon, and this fact alone was sufficient to exclude structure Ia.

Further evidence for the environment of the functional groups was obtained in the following way. Acetylation of α-vetivone with either isopropenyl acetate, acetic anhydride–sodium acetate, or acetyl chloride gave a mixture of isomeric enol acetates, III and IV,[6] which was extremely air-sensitive. The major product, III, which represented about ninety percent of the mixture, showed maximal absorption at 238 mμ. Two vinylic proton signals could be observed in its NMR-spectrum, at 5.31 (apparent triplet) and at 5.59 ppm (singlet). These values are close to those observed for the enol acetate of cholest-4-en-3-one, which had λ_{max} 237 mμ and signals at 5.27 and 5.55 ppm under the same condition.

The minor component showed quadruple maxima, at 297, 312, 324 and 341 mμ, and the values observed were close to those recorded for the 3-acetate of cholest-3,5,7-triene[7] (λ_{max} 305, 316 and 330 mμ in ethanol).

These results suggested that the ketone (II) has methylene groups at the γ and δ position, and that the isopropylidene group was attached at the ε position, the latter being required to account for the migration of this double bond into conjugation under, for instance, the action of sodium acetate–acetic anhydride. In agreement, the signals for the doubly allylic methylene protons, the AB part of an ABX were observed between 2.5—3.0 ppm. Further,

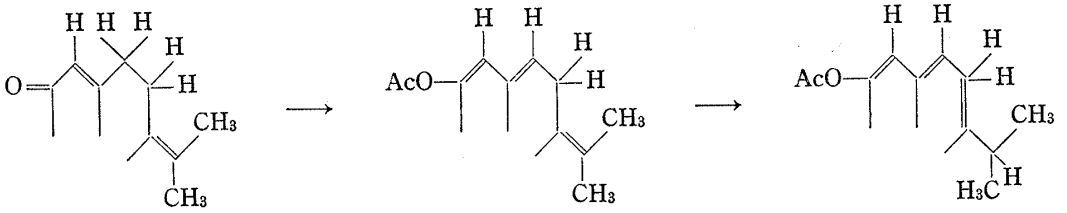


Chart 2

in the conversion of II to III there was a chemical shift of 13 cps to higher fields of the singlet methyl protons. A similar change (18 cps) was observed in the acetylation of cholest-4-en-3-one.

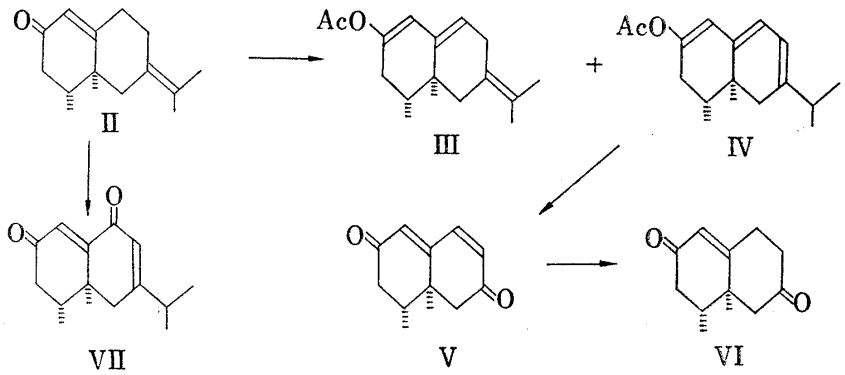


Chart 3

6) The structures finally arrived at are used for simplicity of presentation.
7) W. G. Dauben, J. F. Eastham and R. A. Micheli, *J. Am. Chem. Soc.*, 73, 4496 (1951).

Oxidation of the isomeric enol acetates, III and IV, with chromic acid in acetic acid gave a *trisnor*-dione, V (ν_{max} 1667 cm^{-1}). Reduction of this diketone with zinc in acetic acid gave a dihydro derivative, VI. The latter showed absorption in the infrared at 1671 and 1718 cm^{-1} indicating that the two cabocyclic rings in VI, and hence in II were six-membered.

The genesis of V may be rationalised in a number of ways. Perhaps the most plausible involves the epoxidation (or equivalent) of the tetrasubstituted ethylenic linkage followed by opening and dealdolisation.

Since the location of the quaternary methyl group was restricted to a single position the only uncertainty remaining was that of the methyl group giving rise to the doublet in the NMR-spectrum. It seemed highly probable that α-vetivone was an eremophilanoid substance, and the simplest way to resolve the problem of structure, stereochemistry and absolute configuration seemed by direct interrelation with a member of the eremophilane group.

Base catalysed air oxidation[8] of α-vetivone in *t*-butyl alcohol at room temperature gave a complex mixture of products which was chromatographically separated and then treated with *p*-toluenesulphonic acid to convert the hydroperoxides to ketones. From this mixture VII was isolated in poor yield. An accompanying substance tentatively assigned the structure VIII or IX, and presumably formed by allylic oxidation of the enol, was also isolated. It was characterised as the enol acetate X or XI.

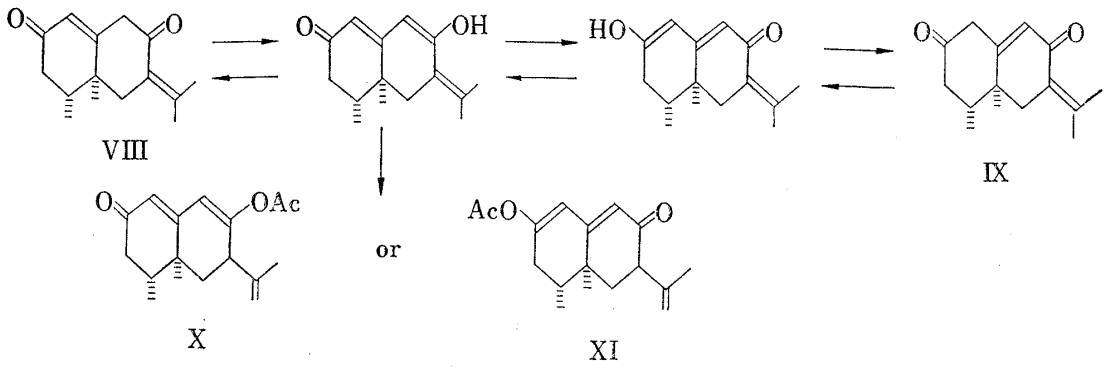


Chart 4

Acetylation of eremophilone XII gave a mixture of isomeric enol acetates, XIII and XIV. One, XIV, was isolated chromatographically and oxidised with sodium dichromate in acetic acid to yield the partially conjugated diene dione XV (ν_{max} 1680 and 1697 cm^{-1}) as the major product. The migration of the isolated double-bond into conjugation was achieved by treatment with Claisen's alkali. The product, XVI, was also detected as a minor product of the oxidation of XIV.

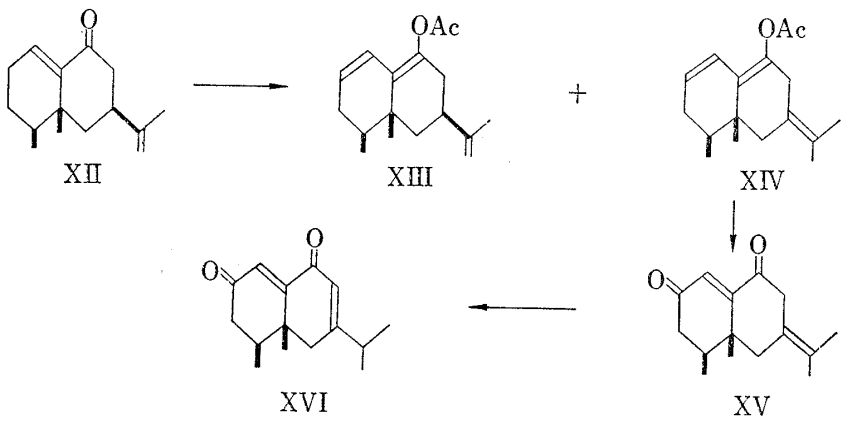


Chart 5

8) R Howe and F. J. McQuillin, *J. Chem. Soc.*, **1958**, 1513.

The diones VII (from α-vetivone) and XVI (from eremophilone) were indistinguishable from each other in all properties except optical rotatory power. In this they were antipodal, as indicated by their ORD-curves (Figure 1).

With the structure of α-vetivone established it was clear that the formation of vetivazulene, XVII, was a consequence of a

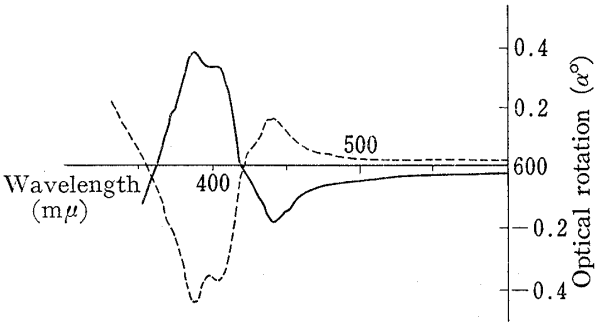


Fig. 1. Optical Rotatory Dispersion Curves of Enantiomeric Diones VII (——) and XVI (------)

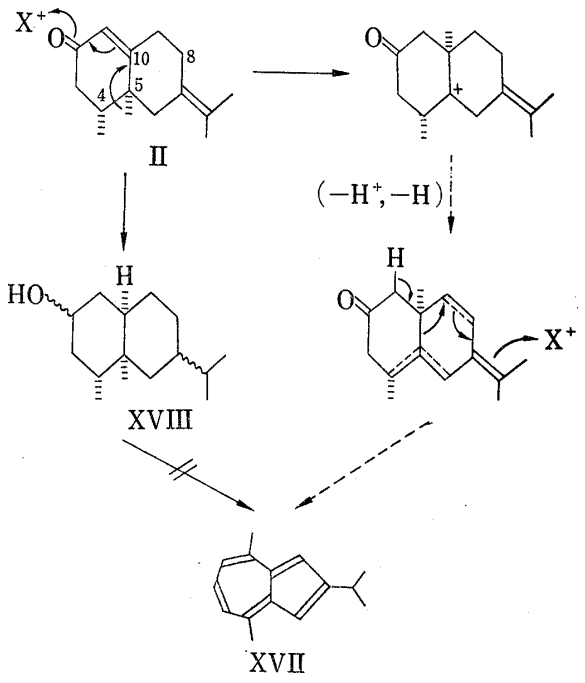


Chart 6

rearrangement during dehydrogenation. In this rearrangement a bond is formed from C_5 to C_9 and the bond between C_5 and C_{10} cleaved. Further, the conjugated system present appeared necessary for the generation of a positive charge at C_{10} to enable the required methyl migration to occur. Removal of this feature should inhibit the formation of XVII. It is noteworthy that eremophilone, itself, in which these requirements would be met with difficulty, gives no azulenic compounds on dehydrogenation. That the conjugated system (or its equivalent) for vetivazulene formation was indeed necessary was shown when it was found that dehydrogenation of tetrahydro-α-vetivanol,[3] XVIII, gave no azulene. A possible scheme, which should be regarded as a formalism, by which the azulene may be generated is indicated in the Chart 6.

An interesting observation was made with regards ORD and CD measurements (Figures 2 and 3). α-Vetivone has the same functionality as ring A of cholest-4-en-3-one and hence the Cotton effects were expected to be similar. However, as shown in Figure 2, α-vetivone has a weak positive Cotton effect whereas the steroid has a large negative curve. The differences may be attributed to multiple Cotton effects together with a difference in the population of conformers.[9] A weak positive Cotton effect at a slightly longer wavelength and a major effect with a negative sign are opposed in the case of II, and reinforcing each other in the steroid. This situation is clarified by inspection of the CD-curves (Figure 3).

This revistion of the structure of α-vetivone requires the like revision of the structures of α-vetivenene[10] and bicyclovetivenol[11] which have been based on a relationship with II.

It seems probable that this less common, antipodal, form of the eremophilane skeleton is derived from a selinane type precursor.[12] Recently, an enantiomeric form of a selinenol,

9) R. E. Ballard, S. F. Mason and G. W. Vane, *Discussions Faraday Soc.*, **35**, 43 (1963).
10) M. Romaňuk and V. Herout, *Collection Czech. Chem. Commun.*, **25**, 2540 (1960).
11) G. Chiurdoglu and J. Decot, *Tetrahedron*, **4**, 1 (1958).
12) H. Ishii, T. Tozyo and H. Minato, *J. Chem. Soc.*, **1966**, 1545.

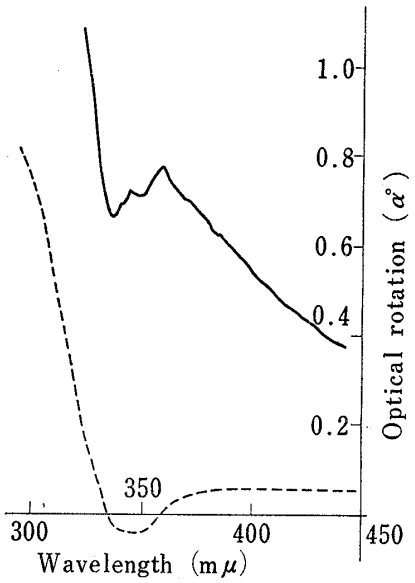


Fig. 2. Optical Rotatory Dispersion Curves of α-Vetivone (——) and Cholest-4-en-3-one (------)

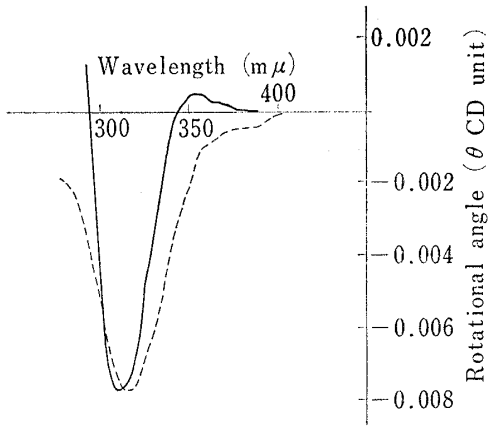


Fig. 3. Circular Dichroism Curves of α-Vetivone (——) and Cholest-4-en-3-one (------)

laevo-junenol XIX, has been isolated from a vetiver oil[13] of Indian origin in which antipodal cadinenoids were also found.[14]

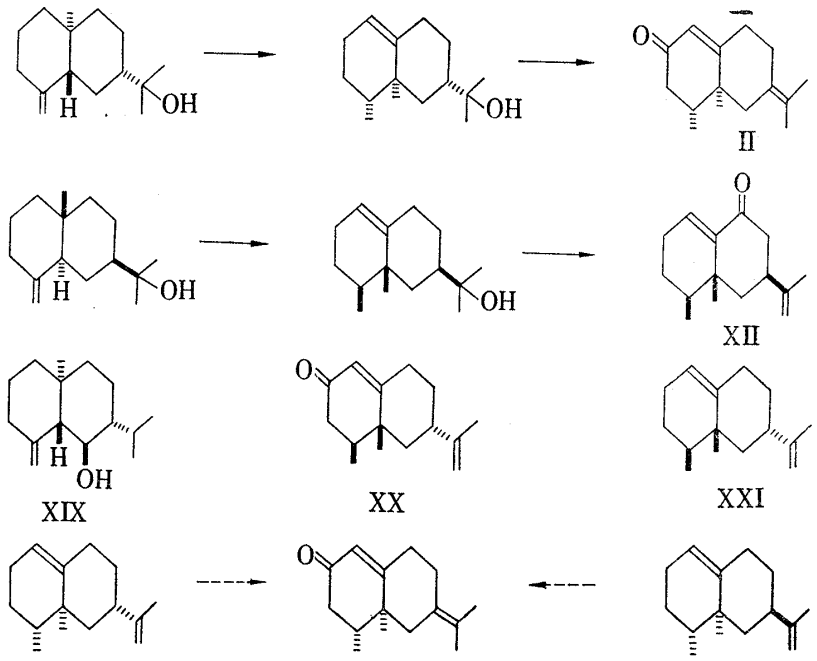


Chart 7

Recently the term "isonootkatone" was suggested[15] for the substance known as α-vetivone because of its relationship to nootkatone (XX), a sesquiterpenoid, which belongs to the valencane group. Since, however, the distinguishing feature between the valencene,

13) S. C. Bhattacharyya, A. S. Rao and A. M. Shaligram, *Chem. Ind.* (London), **1960**, 469; *idem*, *Tetrahedron*, **18**, 969 (1962).

14) C. C. Kartha, P. S. Kalsi, A. M. Shaligram, K. K. Chakravarti and S. C. Bahttacharyya, *Tetrahedron*, **19**, 241 (1963); K. K. Chakravarti, *Indian J. Chem.*, 3, 324 (1965); R, Seshadri, P. S. Kalsi, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron*, 23, 1267 (1967).

XXI, and eremophilane type, that is the configuration of the isopropenyl group, is absent in the vetivone the naming of α-vetivone by relationship to nootkatone, a valencane substance, may be biogenetically misleading.

Experimental

All melting points were determined on the Reichert hot stage and are corrected. Optical rotations were measured with Rudolph polarimeter, model 80. Infrared spectra were recorded with a Beckman IR-10, and ultraviolet spectra with a Cary recording spectrophotomether, model 14. Nuclear magnetic resonance spectra were recorded with a Varian A-60 spectrometer in carbon tetrachloride solutions, with tetramethylsilane as an internal standard. Optical rotatory dispersion and circular dichroism curves were obtained with a Jasco optical rotatory dispersion recorder model ORD/UV-5. Analytical, as well as preparative vapour phase chromatography (VPC) was achieved using a column with a stationary phase of diethyleneglycol adipate (5%) on 60—80 mesh Chromosorb.

α-Vetivone and β-Vetivone——The neutral portion of vetiver oil (Fritzsche and Co., Reunion vetiver oil) (183 g) was dissolved in ethanol (350 ml) followed by addition of Girard's T reagent (30 g). The mixture was then warmed to reflux for one hour and left at room temperature overnight. The solvent (*ca.* 200 ml) was removed by distillation. The residue was diluted with water (1200 ml) and the non-ketonic compounds (154 g) extracted with ether. The partial decomposition of the water soluble components with formalin[18] (10 ml each of 36% formalin) regenerated crude α-vetivone (19 g). This was combined with a similar fraction (27 g) and distilled (bp 129—133°, 0.8 mmHg) and the distillate again treated with the Girard's reagent. The regenerated α-vetivone fraction (9.6 g) was recrystallised from light petroleum ether yielding colourless prisms, mp 50—51°. $[\alpha]_D^{25°}$ +225° (EtOH, c=4.91). UV $\lambda_{max}^{cyclohexane}$ mμ (ε): 233 (15900). NMR δ: 0.97 (3H, singlet), 1.00 (3H, doublet, J=6 cps), 1.73 (6H, broad singlet), 5.62 (1H, singlet). ORD (c=0.092, MeOH) [Φ] (mμ): +451° (589), +1269° (400), +1803° (358), +1672° (348), +1696° (344), +1541° (337), +2383° (325). CD (c=0.51, MeOH) [θ] (mμ): 0° (380), +172° (352), −2720° (310), −350° (296). Infrared spectra were superimposable with those of α-vetivone published authentically.[19] Two 2,4-dinitrophenylhydrazones were obtained, mp 150—151° and 183—184° respectively.

A β-vetivone rich fraction was purified by VPC and recrystallised from light petroleum ether to yield colourless prisms, mp 39—40°. $[\alpha]_D^{25°}$ −43.0° (c=0.1, MeOH). UV $\lambda_{max}^{cyclohexane}$ mμ: 233. NMR δ: 0.97 (3H, doublet, J=6 cps), 1.66 (6H, broad singlet), 1.88 (3H, broad singlet), 5.67 (1H, singlet). IR: all the patterns were the same as those of authentic β-vetivone.[19] Two 2,4-dinitrophenylhydrazones, mp 192° and 143—144°.

Acetylation of α-Vetivone——A mixture of α-vetivone (300 mg) and acetyl chloride (2 ml) was diluted with cyclohexane (2 ml) and heated to reflux for two hours under a slow stream of nitrogen. On removal of the solvent and the excess reagent under reduced pressure an air-sensitive oily residue (312 mg) was obtained. A thin-layer chromatogram (10% ethereal benzene) indicated the presence of a very small amount of II. The residue was then dissolved in cyclohexane and chromatographed on silica gel (BDH silica gel for chromatography, 20 g). Elution with benzene afforded the acetates III and IV, bp 110° (0.2 mmHg). UV $\lambda_{max}^{cyclohexane}$ mμ (ε): 238 (16800), 297, 312, 324 and 341 (*ca.* 3000 each). IR ν_{max}^{liquid} cm^{-1}: 1757, 1669, 1369, 1127. NMR δ: 0.74 (3H, singlet), 0.96 (3H, doublet, J=6 cps), 1.69 (6H, broad singlet), 2.04 (3H, singlet), 5.31 (1H, triplet, J=3.5 cps), 5.59 (1H, singlet). Although the intensities of maxima in the 300 mμ region were slightly variable depending on the conditions, almost the same results were obtained on acetylation with acetyl chloride-acetic anhydride, or with acetic anhydride-sodium acetate. The acetates III and IV were not isolated in the pure state, because of extreme instability with regards air oxidation, but by reaction with dilute sodium hydroxide solution the starting ketone was regenerated, which was identified by IR and NMR as well as VPC: their structures are therefore unambiguously established.

Dichromate Oxidation of α-Vetivenyl Acetate——The α-vetivenyl acetates (III and IV) (400 mg) in acetic acid (20 ml) was allowed to stand with sodium dichromate (250 mg) for ten minutes at room temperature. Dilution of the reaction mixture with water, after neutralization with sodium bicarbonate, followed by extraction with ether yielded, on evaporation of the solvent, a residue (357 mg). Isolation of the major

15) Very shortly after our preliminary communication appeared a further communication[16] was published in which professor Marshall has reported independent arrival at identical conclusion with regrads the structure of α-vetivone. A later communication[17] revised the structure for β-vetivone to that a spirane.
16) J. A. Marshall and N. H. Andersen, *Tetrahedron letters*, **1967**, 1611.
17) J. A. Marshall and P. C. Johnson, *J. Am. Chem. Soc.*, **89**, 2750 (1967).
18) I. C. Nigam and L. Levi, *Anal. Chem.*, **35**, 1087 (1963).
19) J. Pliva, M. Horák, V. Herout and F. Šorm, "Terpenspektren," Akademie-Verlag, Berlin, 1960, S-164 and S-170.

product by thin-layer chromatography (33% ethereal benzene) afforded a yellow compound (67 mg), which was recrystallised from petroleum ether and then from ether to give yellow needles, V, mp 95°. $[\alpha]_D$ +230° (c=3.1, EtOH). *Anal.* Calcd. for $C_{12}H_{16}O_2$ (192.25): C, 75.92; H, 7.40. Found: C, 75.76; H, 7.42. UV λ_{max}^{MeOH} mμ (ε): 287 (23200). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1667. NMR δ: 1.04 (3H, doublet, J=6 cps), 1.18 (3H, singlet), 5.98 (1H, singlet), 6.12 and 7.03 (1H each, AB type quartet, J=10 cps).

Zinc Reduction of Dione V——The crude dione V in acetic acid (64 mg in 5 ml) was warmed with powdered zinc (300 mg) for half an hour at 40°. This was then diluted with water and the mixture was extracted with ether. The organic layer was washed with aqueous sodium bicarbonate, dried and concentrated to yield an oily residue (62 mg). The major component of the product was isolated by thin-layer chromatography (33% ethereal benzene) followed by microdistillation, as a colourless oil (22 mg), VI. UV $\lambda_{max}^{Cyclohexane}$ mμ: 225. IR $\nu_{max}^{CCl_4}$: 1718 (isolated C=O), 1671 (conjugated C=O), 1622 (conjugated C=C). NMR δ: 1.00 (3H, doublet, J=6 cps), 1.10 (3H, singlet), 5.80 (1H, singlet).

Air Oxidation of α-Vetivone——α-Vetivone (2.0 g) in 1 N potassium *t*-butoxide in *t*-butanol (30 ml) was shaken in the presence of one litre of air at room temperature. The reaction mixture was then cooled with ice, acidified with acetic acid and diluted with water followed by extraction with ether. The organic layer was washed with aqueous sodium bicarbonate, dried over anhydrous sodium sulphate and concentrated to leave a dark brown oil (2.2 g), which was chromatographed on silica gel (60 g). Benzene eluted a reddish brown oil (245 mg), followed by a yellow crystalline compound (290 mg) which was quickly destroyed on exposure to air. Recrystallisation of the compound either from ether or methanol gave yellow needles of VIII or IX, mp 122°. *Anal.* Calcd. for $C_{15}H_{20}O_2$ (232.31): C, 77.55; H, 8.68. Found: C, 77.14; H, 8.68. UV λ_{max}^{MeOH} mμ (ε): 251 (4320), 364 (27400), these maxima were shifted to 267 and 396 mμ respectively by addition of a drop of Claisen's alkali. IR $\nu_{max}^{CS_2}$ cm^{-1}: 3400, 1653, 1608, 802. NMR δ: 0.90 (3H, singlet), 1.02 (3H, doublet, J=6 cps), 1.85 and 1.89 (3H each, broad singlet), 6.16 (1H, singlet, exchangeable with D_2O), 6.49 and 6.65 (1H each, AB type quartet, J=10 cps). Acetylation (acetic anhydride–sodium acetate) gave an acetate X or XI. UV λ_{max}^{MeOH} mμ: 286. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1677, 1641, 1619, 1200, 1085, 898. NMR δ: 1.00 (3H, doublet, J=6 cps), 1.13 (3H, singlet), 1.75 (3H, broad singlet), 2.18 (3H, singlet), 4.82 (2H, multiplet), 6.12 and 6.30 (1H each, AB type quartet).

Continued eluation with 15% ethereal benzene gave a complicated oily mixture (497 mg) and methanol washed out polar components, (837 mg). Treatment of this fraction (750 mg) with *p*-toluenesulphonic acid (300 mg) in boiling benzene (25 ml) for three hours yielded, after neutralization with sodium bicarbonate and extracted with benzene, a dark brown oil (550 mg). One of the major components (*ca.* 50 mg) was separated by thin-layer chromatography (30% ethyl acetate–petroleum ether) to afford a yellow crystalline compound, which was recrystallised from ether to give yellow plates, VII, mp 75—76°. A mixed specimen with the antipodal compound derived from eremophilone (mp 77°, see the corresponding paragraph) melted at 74°. UV λ_{max}^{MeOH} mμ (ε): 274 (16700). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1664, 1634, 1608, 1261, 877. NMR δ: 1.03, 1.08 and 1.08 (3H each, all doublet, J=6 cps), 1.12 (3H, singlet), 5.97 (1H, broad singlet), 6.43 (1H, singlet). ORD (c=0.15, MeOH) [Φ] (mμ): −30.6° (590), −316° (440), −30.6° (420), +649° (403), +636° (396), +737° (387), +383° (345).

Eremophilone——Crude eremophilone fraction[20] (50 g) of *Eremophila Michelli* was fractionated through a twenty inches spinning band distillation column. The semi-crystalline distillate (boiling range 120—130°, 0.8 mmHg) (34 g) was recrystallised from petroleum ether (bp 40°) yielding colourless prisms (20 g), mp 41°. $[\alpha]_D^{25°}$ −159° (c=0.99, EtOH). NMR δ: 0.94 (3H, doublet, J=6 cps), 0.95 (3H, singlet), 1.73 (3H, broad singlet), 4.71 (2H, broad singlet), 6.43 (1H, triplet, J=4 cps).

Eremophilenyl Acetates——Eremophilone (1.0 g) was heated with acetic anhydride and acetyl chloride (1:1 mixture, 10 ml) for ninety minutes under nitrogen. Acetyl chloride was then removed under reduced pressure, and the residue cooled to room temperature. Into this solution, sodium dichromate (500 mg) and acetic acid (5 ml) were added with stirring, and the stirring continued for one hour. The mixture was then diluted with water, neutralized with sodium bicarbonate, and the ether extract of the neutral solution yielded, on concentration, a colourless oil (976 mg), which was chromatographed on silica gel (30 g). This afforded the crude enol acetate XIV (490 mg) on elution with benzene. UV $\lambda_{max}^{cyclohexane}$ mμ: 237. IR ν_{max}^{liquid} cm^{-1}: 1750, 1366, 1211. NMR δ: 0.92 (3H, doublet, J=6 cps), 0.96 (3H, singlet), 1.54 and 1.57 (3H each, broad singlet), 2.08 (3H, singlet), 5.54 and 6.12 (1H each, AB type quartet, J=10 cps).

Some earlier fraction of the benzene eluate exhibited a band at 893 cm^{-1} in thier infrared spectra (and also at 4.76 ppm in the NMR) which are attributed to the isomer XIII.

Eremophilendione XV——Acetate XIV (536 mg) in acetic acid (10 ml) was oxidised with sodium dichromate (500 mg) on a steam bath for ninety minutes, and worked up in the usual way, to yield an oily residue (247 mg). The major component was then separated by thin-layer chromatography (30% ethyl acetate-petroleum ether) afforded the crude ketone XV (91 mg), which was recrystallised from petroleum ether to give pale yellow needles, mp 108°. $[\alpha]_D^{25°}$ −172° (c=0.93, EtOH). *Anal.* Calcd. for $C_{15}H_{20}O_2$ (232.31):

20) This was kindly supplied by Dr. R. A. Massy-Westropp (Adelaide), to whom we express our gratitude.

C, 77.55; H, 8.68. Found: C, 67.19; H, 7.69, and C, 66.34; H, 5.36. Mass Spectrum m/e: 232 (M^+).[21] UV λ_{max}^{MeOH} mμ (ε): 248 (9890). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1697, 1680. NMR δ: 1.08 (3H, doublet, J=6 cps), 1.12 (3H, singlet), 1.56 and 1.59 (3H each, singlet), 6.02 (1H, singlet).

Dienedione XVI——The dione XV (80 mg) in methanol (1 ml) was mixed with Claisen's alkali[22] (10 ml) and the resulting solution was left to stand for one hour at room temperature. Then cooled solution was acidified with diluted hydrochloric acid, and extracted with ether to give a yellow oil (62 mg), which was purified by thin-layer chromatography. Recrystallisation from ether yielded yellow plates, mp 77°. *Anal.* Calcd. for $C_{15}H_{20}O_2$ (232.31): C, 77.55; H, 8 68 Found: C, 77.59; H, 8.41. UV λ_{max}^{MeOH} mμ (ε): 274 (15500). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1664, 1634, 1608, 1261, 877. NMR δ: 1.03, 1.08 and 1.08 (3H each, all doublet, J=6 cps), 1.08 (3H, singlet), 5.98 (1H, broad singlet), 6.39 (1H, singlet). ORD (c=0.13, MeOH) [Φ] (mμ): +30° (590), +329° (440), +54° (421), −762° (402), −717° (397), −908° (386), +258° (340).

Hydrogenation and Dehydrogenation of the Vetivones——α-Vetivone II (100 mg) in acetic acid (10 ml) was hydrogenated with Adams' catalyst (40 mg) for three hours at room temperature. The hydrogen uptake was 37 ml (32 ml expected). The catalyst was removed by filtration, and the filtrate diluted with water, neutralized with sodium bicarbonate, and extracted with ether to yield a viscous oil (110 mg). No carbonyl nor vinylic hydrogen was detected spectroscopically. The alcohol, XVIII, (60 mg) was heated with selenium (40 mg) at 265° for ten hours under nitrogen. The mixture was then diluted with cyclohexane and passed through a column of silica gel (1.0 g) to remove selenium. The pale yellow eluate was again diluted to 80 ml with the same solvent and the UV-absorption spectra were recorded: λ_{max} mμ ($E_{1\,cm}$) 278 (0.89), 322 (0.27), 337 (0.23). The estimated eudalene (λ_{max} at 228, 282 and 320 mμ in EtOH) yield was 23 mg.

A β-vetivone fraction (150 mg) was hydrogenated similarly though for a longer time (total 15 hours) and the products were chromatographed yielding an alcohol fraction (90 mg), with no vinylic hydrogen absorption in its NMR-spectrum. Dehydrogenation of this oil with selenium (60 mg) under the same condition yielded after passing through a silica gel column (1.0 g), a purple cyclohexane solution, which was diluted to 500 ml for UV observation. UV λ_{max} mμ ($E_{1\,cm}$): 282 (1.48), 292 (1.58), 320 (0.23), 334 (0.19), 351 (0.18). The estimated yield of vetivazulene XVII (λ_{max} at 248, 284, 292, 309, 336 and 350 mμ in EtOH) was 3.2 mg.

21) The authors wish to thank Professor S. Itô (Tohoku University, Sendai,) for obtaining this molecular weight for us.

22) L. Claisen, *Ann.*, **418**, 96 (1915).