Tetrahedron Vol. 29, pp. 945 to 954. Pergamon Press 1973. Printed in Great Britain

SESQUITERPENOIDS OF VETIVER OIL—I

THE STRUCTURES OF ZIZANOIC ACID AND RELATED CONSTITUENTS[1]

N. Hanayama,‡ F. Kido, R. Tanaka (née Sakuma),† H. Uda and A. Yoshikoshi*
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, Japan

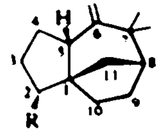
(Received in Japan 30 October 1972; Received in the UK for publication 23 November 1972)

Abstract—Two sesquiterpene carboxylic acids, *zizanoic* and *epizizanoic* acids, were isolated from the essential oil of vetiver and were assigned the structures **1a** and **2a** on the basis of chemical degradation. Although khusimol and *zizaene* (tricyclovetivene) had been assigned structures previously, the current work revealed that these sesquiterpenoids also belong to the *zizaane* group and that the formulae should be revised as **1b** and **1c**, respectively.

INTRODUCTION

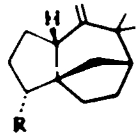
Although the acidic constituents of vetiver oils have been reported,[2] their compositions and chemical structures have not been fully examined. We have also isolated an acidic portion from the essential oil of *Vetiveria zizanioides* of Java origin and have found it to be a mixture of several sesquiterpene carboxylic acids. From Indian vetiver, Zuchi and Sadgopal[3a] have isolated a carboxylic acid named khusenic acid. Since the authentic sample of khusenic acid was not available, we could not compare our carboxylic acids with khusenic acid. To the principal carboxylic acid, therefore, a new name, *zizanoic* acid, was given, and the structure was elucidated by chemical degradation.¶ The results revealed that *zizanoic* acid belongs to a novel group of sesquiterpenoids. The structure of *zizanoic* acid and the related vetiver sesquiterpenoids assigned by the present work have been unambiguously verified by the total synthesis of *zizanoic* acid[3] and by the X-ray crystallography of khusimyl *p*-bromobenzoate.[4]

In this paper we report details of the degradative elucidation of the structure of *zizanoic* acid (**1a**) and closely related constituents, *i.e.* *epizizanoic* acid (**2a**), khusimol (**1b**), and *zizaene* (tricyclovetivene) (**1c**).§



1

a R = CO_2H
b R = CH_2OH
c R = Me
d R = CO_2Me



2

a R = CO_2H
b R = CO_2Me
c R = Me

RESULTS AND DISCUSSION

The carboxylic acids were extracted from vetiver oil with Na_2CO_3 aq and esterified with diazomethane. GLC showed the product consisting of a main component and seven minor components (Fig 1). The principal constituent, methyl *zizanoate*

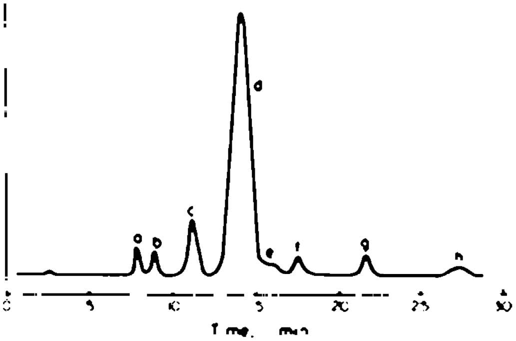


Fig 1. Gas chromatogram of the vetiver carboxylic acids esterified with diazomethane. (a) Methyl cyclocopacamphenate,[12] (b) methyl epicyclocopacamphenate,[12] (c) methyl isokhusenate (**15b**), (d) methyl *zizanoate* (**1d**), (e) unidentified, (f) methyl *epizizanoate* (**2c**), (g) methyl isovalencenate,[14] (h) unidentified. Column: 20% PEG 20M, 3 m, operated at 180°. Carrier gas: He, 66 ml/min

---

‡Present address: Yoshitomi Pharmaceutical Co., Yoshitomicho, Chikujo-gun, Fukuoka. This author is mainly concerned in *epizizanoic* acid.

†This author is mainly concerned in *zizaene*.

*Address correspondence to this author.

¶The name khusenic acid has been succeeded by Komae and Nigam and assigned to a carboxylic acid isolated from Angola vetiver oil, which was identical with *zizanoic* acid as will be mentioned later. Ref 5a.

§As other members of the *zizaane* group isolated hitherto, *zizanol* (3-hydroxy*zizaene*)[6] and isokhusimol[7] have been reported.

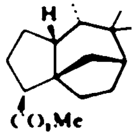
(**1d**), could be separated from the mixture by fractional distillation. Upon hydrolysis of **1d**, *zizanoic* acid (**1a**), $C_{15}H_{22}O_2$, was obtained as crystals.[*] The spectra of **1a** and **1d** demonstrated the presence of an exocyclic double bond, two tertiary Me groups, and an α-hydrogen of carboxylic (or methoxy carbonyl) group.

Exhaustive hydrogenation (Pt-EtOH) of methyl *zizanoate* (**1d**) yielded methyl dihydro*zizanoate* (**3**), demonstrating a tricyclic structure of *zizanoic* acid. LAH reduction of methyl *zizanoate* afforded the corresponding alcohol (**1b**). The spectra and other physical properties of the latter were found to be in agreement with the published data of khusimol,[6a,†] a sesquiterpene alcohol isolated first from South Indian vetiver. Tosylation of khusimol followed by LAH reduction gave an olefin, *zizaene* (**1c**), which was identical with tricyclovetivene as will be mentioned later.[‡] Attempts to obtain naphthalenic or azulenic compounds by dehydrogenation of methyl *zizanoate*, *zizanoic* acid, or *zizaene* were fruitless.

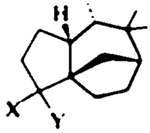
In order to investigate the carboxyl group of *zizanoic* acid, dihydro*zizanoic* acid obtained from methyl dihydro*zizanoate* (**3**) was treated with methyllithium. The resulting methylketones were submitted to peracid oxidation followed by hydrolysis to give a mixture of epimeric alcohols (**4a**), from which one of the epimers crystallized. Chromic acid oxidation of the mixture of the alcohols yielded a single ketone (**4b**), whose IR spectrum (ν_{CO} 1735 cm^{-1}) indicated a 5-membered cyclic ketone. Treatment of the ketone (**4b**) with peracid gave a δ-lactone (**5**) (ν_{CO} 1732 cm^{-1}). Since the NMR spectrum of **5** showed no signal in the magnetic field lower than 3 ppm, it was obvious that the ether oxygen of **5** is bound to a C atom bearing no hydrogen. Reported values for the degradation products (**4a**, **4b**, and **5**)[6a] of khusimol were also in good agreement with those of our compounds.

Methyl *zizanoate* (**1d**) was ozonized to give ketoester (**6a**). A hydroxyester obtained from the latter upon $NaBH_4$ reduction was dehydrated with $POCl_3$ to an unsaturated ester (**7a**). The IR and NMR spectra of **7a** showed the presence of a trisubstituted double bond, and the pattern of the olefin proton, a narrow multiplet ($W_{1/2}$ 4 Hz), demonstrated that the splitting of the signal was due to long-range coupling only. The corresponding olefin (**7b**) was derived from the ester (**7a**) *via* alcohol **7c**. The ketoester (**6a**) was treated with LAH to afford a diol (**8**). Selective tosylation of **8** followed by treatment with LAH gave an alcohol, whose Jones oxidation gave a ketone (**6b**). The ketone was also obtained by hydroboration-oxidation of the olefin **7b**. Base catalysed deuteration of **6b** gave a monodeuterated product. These facts demonstrated that one of the carbons flanked with the exomethylene in *zizanoic* acid possesses an H atom and that another bears no hydrogen or nonenolizable hydrogen as seen in the bridgehead position.

To obtain B-seco derivatives, the oxidative cleavage of the C(5)–C(6) bond was examined. Although the ketoester (**6a**) resisted Baeyer-Villiger oxidation, the olefin (**7b**) was oxidized with OsO_4 to give

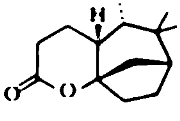


3

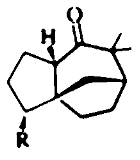


4

a X = OH, Y = H
b X, Y = O

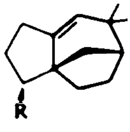


5



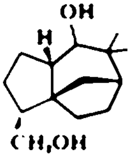
6

a R = CO_2Me
b R = Me



7

a R = CO_2Me
b R = Me
c R = CH_2OH



8

---

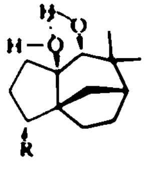
[*] Initially we reported *zizanoic* acid as an oil,[10] while Klein obtained the acid as crystals – personal communication, see also Ref. 9.

[†] The identification was made on the basis of the spectral comparison of both khusimol itself and the methyl ester of the Jones oxidation product of khusimol, *i.e.*, methyl *zizanoate*. We thank Dr. K. K. Chakravarti for providing authentic samples of these compounds.

[‡] The correlation between *zizanoic* acid, khusimol, and tricyclovetivene has also been reported by other authors, Refs. 5*b* and 5*c*.

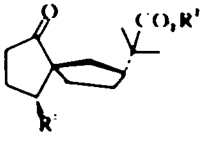
an α-glycol (**9a**) in good yield. Interestingly, the hydroxy proton and the α-proton of the sec. OH group of **9a** were observed as a pair of doublets in the NMR spectrum at 2·65 and 3·28 ppm, respectively. By the addition of D_2O the former doublet disappeared, and the latter collapsed into a singlet. This may be explained by an intramolecular H-bonding between these groups and the resulting fixation of the proton of the OH group. Treatment of **9a** with $Pb(OAc)_4$ followed by CrO_3 yielded a seco-acid (**10a**), which involves a 5-membered ketone as shown by its IR spectrum ($\nu_{C=O}$ 1732 cm^{-1}). The methyl ester (**10b**) of the seco acid showed a fragment ion (*m/e* 102) due to $[Me_2C=C(OH)OMe]^+$ in the mass spectrum as the base peak, while no ion due to $[CH_2CMe_2CO_2Me]^+$ was observed at *m/e* 115. This implied the presence of the grouping $>CHCMe_2CO_2Me$ in the ester. Derivatives (**9b** and **10c**) corresponding to **9a** and **10a** were also prepared from the unsaturated ester (**7a**) in a similar fashion (Experimental).

The location of the gem. dimethyl group presumed by the mass spectrum of **10b** was confirmed further as follows: the seco-acid (**10c**) was treated with $Pb(OAc)_4$ and LiCl in benzene to undergo decarboxylative chlorination[10] and gave a chloroester (**11**), whose gem dimethyl group was shown at 1·55 ppm in the NMR spectrum as a 6-proton singlet. On the other hand, an aldehyde obtained from the ketoester (**6a**) upon irradiation was oxidized with CrO_3, and the resulting carboxylic acid (**12**) was shown to have an isopropenyl group by its spectra.



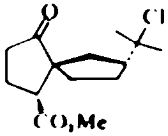
9

- **a** R = Me
- **b** R = CO_2Me
- **c** R = CO_2H

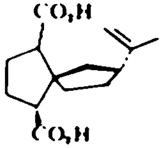


10

- **a** R' = Me, R' = H
- **b** R' = Me, R' = Me
- **c** R' = CO_2Me, R' = H



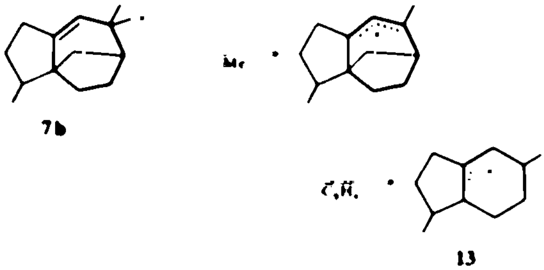
11



12

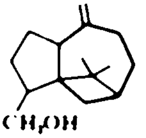
The common feature of fragmentation in the mass spectra of methyl zizanoate (**1d**), zizaene (**1c**), and the olefin (**7b**) appears to be the initial loss of an allylic Me group and subsequent elimination of ethylene as indicated by the observed metastable ions. This fragmentation may be expressed for the olefin (**7b**) by the following scheme, producing stable allylic ion (**13**).*

All of the results described support the gross formula of **1a** as the most probable structure of zizanoic acid and revised the structures **14a** or **14b** previously proposed for khusimol[4a] to the gross formula of **1b**.

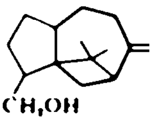


SCHEME 1

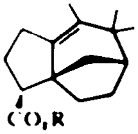
From Angola vetiver Komae and Nigam also isolated two carboxylic acids, khusenic and isokhusenic acids.[3a] They independently gave the identical structure (**1a**) and an isomeric structure (**15a**) to khusenic and isokhusenic acids, respectively, without stereochemical assignment. We also found isokhusenic acid in our essential oil.



14a



14b



15

- **a** R = H
- **b** R = Me

While the study on zizanoic acid was in progress, an olefin was isolated from the hydrocarbon fractions of the vetiver oil. By comparison of the IR spectra, the olefin was identified as tricyclovetivene,† to which the structure **16** was assigned by Chiurdoglu and Tullen.[11] Since the NMR spectrum of the olefin was incompatible with the proposed structure (**16**), we re-examined the structure.

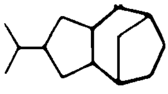
The NMR spectrum of tricyclovetivene showed the presence of a sec Me and two tertiary Me groups, and an exocyclic methylene group. Although Chiurdoglu and Tullen[11] have reported the formation of vetivazulene (**17**) and eudalene (**18**) on dehydrogenation of tricyclovetivene, numerous attempts to obtain these aromatic compounds only

---

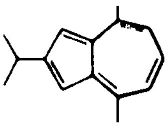
*For the fragmentation of **1d** and **1c** in the mass spectra, see Experimental.

†We are indebted to Professor V. Herout for the identification.

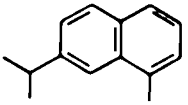
gave rise to the formation of an intractable product. OsO$_4$ oxidation of tricyclovetivene gave a crystalline glycol (**19**) in good yield, and oxidative cleavage of **19** by Pb(OAc)$_4$ afforded a single norketone (**6b**). On the other hand, ozonization of the olefin and treatment of the resulting ozonide with NaI in acetic acid yielded the same norketone (**6b**) as a mixture of the epimers. The IR spectra of both the norketones were not superimposable with that of the norketone obtained by Chiurdoglu and Tullen[11] upon ozonization of their olefin. Finally, we found that tricyclovetivene was identical with zizaene (**1c**) derived from zizanoic acid. Reported formation of vetivazulene (**17**) and eudalene (**18**) on dehydrogenation and nonidentity of their norketone with our compound in the IR spectra would be responsible for contamination with other olefins in their tricyclovetivene.



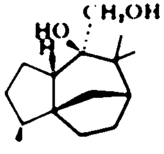
16



17



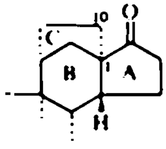
18



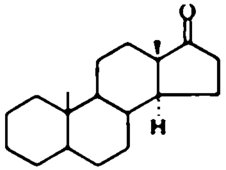
19

The stereochemistry of zizanoic acid was investigated by comparing the ORD of appropriate ketones with those of model compounds. The 5-membered ketone (**4b**; see **20**) showed a negative Cotton effect (molecular amplitude, −104) comparable to that of androstan-17-one (**21**) (molecular amplitude, +140),[12] although we could not find more suitable model compounds. A trans A/B ring fusion and the absolute stereochemistry as depicted in **20** were concluded for the ketone,* supposing that the C(1)–C(10) bond corresponding to the C(18)-methyl of androstan-17-one (**21**) constitutes a 5-membered ring (ring C) to give an insignificant effect to the conformation of ring A.

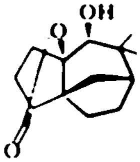
The ORD of the ketoester (**6a**) showed a strong positive Cotton effect (molecular amplitude, +133). Molecular models predicted a positive or a negative Cotton effect depending upon trans A/B (**23**) or cis A/B fusion (**24**) of the ketoester, respectively (Fig 2). The observed positive Cotton effect afforded additional evidence to the trans A/B ring fusion of



20



21

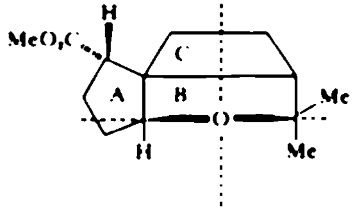


22

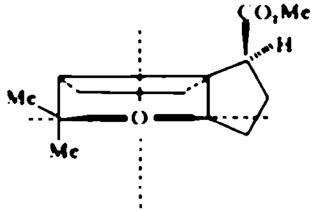
zizanoic acid. The configuration of the carboxyl group was established by the formation of the γ-lactone (**22**) from dihydroxycarboxylic acid (**9c**), obtained by mild hydrolysis of the corresponding ester (**9b**), on treatment with dicyclohexylcarbodiimide. Since the oxidizing agent would attack preferentially from the less hindered exo-face (β) of the moiety of bicyclo[3.2.1]octane ring system of the olefinic ester (**7a**), the carboxyl group of zizanoic acid was considered to have a β-orientation.

Thus the stereochemistry of zizanoic acid, khusimol, and zizaene (tricyclovetivene) could be represented as **1a-c**, respectively.

From a mixture of the methyl esters, an ester, which showed a mass spectrum resembling to that of methyl zizanoate (**1d**), was isolated by extensive silica gel column chromatography or by preparative GLC. Epizizanoic acid (**2a**), C$_{15}$H$_{22}$O$_2$, was ob-



23



24

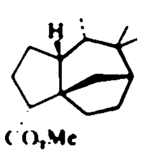
Fig 2. Octant projection for the trans A/B (upper) and cis A/B fusion (lower) of ketoester (**6a**).

---

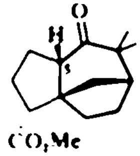
*Andersen has also reached the same stereochemical conclusion as to the A/B ring fusion by the examination of the ORD of 3-ketozizaene and its 2-epimer. Ref 6b.

tained as crystals from the above methyl ester on hydrolysis with NaOH in DMSO at room temp. The IR and NMR spectra of epizizanoic acid (**2a**) and the methyl ester (**2b**) demonstrated, like zizanoic acid, the presence of an exocyclic double bond, two tertiary Me groups, and an α-hydrogen of the carboxyl (or methoxycarbonyl) group. Methyl dihydroepizizanoate (**25**) and 2-epizizaene (**2c**) were derived from methyl epizizanoate (**2b**) by the same procedure as described for methyl zizanoate. The physical characteristics of these derivatives, especially fragmentation patterns in the mass spectra, were strikingly similar to those of the corresponding derivatives of zizanoic acid. This implied that epizizanoic acid may be an epimer of zizanoic acid.

Since there are two epimerizable centers C-2 and C-5 in the zizaane skeleton, epizizanoic acid must be an epimer regarding to either center. OsO_4 oxidation of **2b** followed by treatment with $Pb(OAc)_4$ gave the ketoester (**26**) which was not identical with the ketoester (**6a**) obtained from methyl zizanoate. Equilibration of **26** with NaOMe under mild conditions formed the C-6 epimer, and the latter, however, was also not identical with **6a**. Methyl zizanoate (**1d**) was then heated with NaOMe in methanol, and an epimer was isolated from the resulting mixture. This ester was identical with methyl epizizanoate in every respect. It was thus evidenced that epizizanoic acid is the epimer of zizanoic acid at C-2.

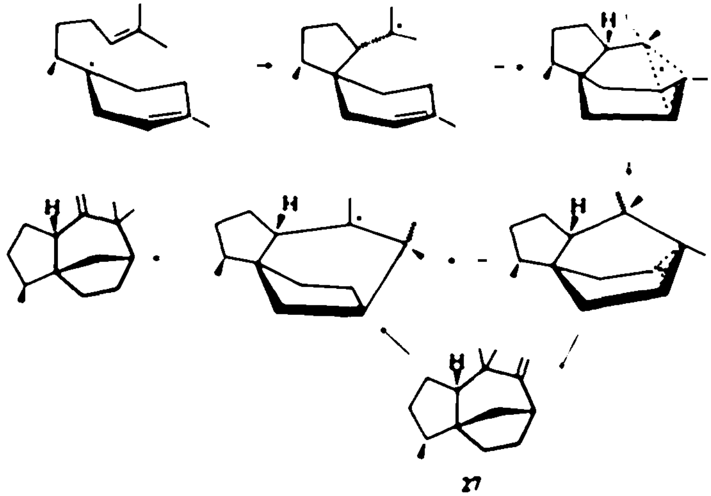


25

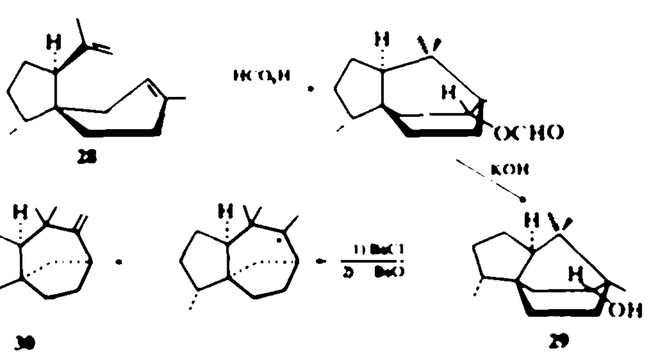


26

With regard to the biogenesis of the zizaane sesquiterpenoids a pathway, where an intermediate of zizaene genesis is also biogenetically related to cedrenes, was proposed initially.[14-16] When the relative and absolute stereochemistry of zizaene were established later,[18] it was found that zizaene is produced *via* a biogenetic pathway stereochemically different from that of cedrenes (Scheme 2).



Scheme 2. Biogenesis of zizaene



Scheme 3. Formation of the enantiomer of prezizaene from β-acoradiene

Recently, Andersen and Falcone found a new tricyclic hydrocarbon prezizaene (27) in vetiver oil, and the discovery has given strong support to the biogenetic route shown in Scheme 2.[13]* Interestingly, Tomita has found that the solvolysis of the *p*-bromobenzenesulfonate of allo-cedrol (29), obtained from *β*-acoradiene (28) upon formolysis followed by alkaline hydrolysis, gave the enantiomer (3) of prezizaene (Scheme 3).[14] Ramage *et al* have proposed another biogenetic pathway where hinesol has been regarded as the precursor of zizaene,[16] but this has been criticised.[13a] Epizizanoic acid (2a) would be a biogenetic epimerization product of zizanoic acid (1a).‡

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were taken on a Hitachi EPI-S2 or a G-2 spectrophotometer. NMR spectra of CCl_4 solns (unless otherwise stated) containing TMS (δ = 0 ppm) as internal standard were taken on a Varian A-60 spectrometer and coupling constants were given in Hz. Mass spectra were obtained using a Hitachi RMU-6D spectrometer.

Isolation of methyl zizanoate (1d)

An ethereal soln of vetiver oil¶ (Java origin) was extracted with 10% Na_2CO_3 aq, and the combined extracts were acidified with dil HCl. Liberated acids were collected in ether. The ether extracts were washed and dried, and removal of the solvent left an oily mixture of the acids in about 5% yield based upon the essential oil.

An ethereal soln of the acids was esterified with ethereal diazomethane, and the resulting mixture of methyl esters was distilled *in vacuo* through a short column to separate the nonvolatile products. GLC (20% PEG-20M column, 3 mm × 3 m, column temp, 180°, He flow, 66 ml/min) showed at least eight peaks as shown in Fig 1. GLC mass spectrometry§ indicated that these peaks may be assigned to methyl esters of cyclocopacamphenic,[17] epicyclocopacamphenic,[17] isokhusenic (15a),[18] zizanoic (1a), an unidentified compound, epizizanoic (2a), and isovalencenic acids,[14] and an unidentified compound in order of elution times, respectively.

A mixture of the methyl esters was fractionally distilled *in vacuo* through a spinning band column (80 theoretical plates), and a fraction boiling at 120–121°/1·8 mm Hg was taken as methyl zizanoate. GLC showed that the fraction is practically homogeneous.

Methyl zizanoate (1d) was an oil, $[\alpha]_D$ + 39·7° (*c* 1·2 in MeOH), ν_{max} (neat) 3070, 1730, 1635, and 890 cm^{-1}, δ 1·20 and 1·23 (3H, s each), 2·58 (1H, q, *J* = 4 and 7), 3·60 (3H, s), and 4·50 and 4·70 (1H, t, *J* = 1·5 each), *m/e* 248 (M^+, 30%), 233 (M^+ − 15, 67%, m* 218·9), and 205 (M^+ − 15 − 28, 20%, m* 180·5). (Found: C, 77·95, H, 9·80. $C_{16}H_{24}O_2$ requires: C, 77·34, H, 9·74%)

The spectra of methyl zizanoate were superimposable with those of the methyl ester of a carboxylic acid obtained from khusimol on Jones oxidation.

Zizanoic acid (1a)

A soln of 310 mg of 1d in 40 ml DMSO and 3 ml of 1N NaOH was allowed to stand under N_2 at room temp. The mixture was diluted with cold water and extracted with ether. The aq layer was acidified with dil HCl using Congo red as the indicator. Liberated acid was collected in ether, and the extracts were washed and dried. Removal of the ether left crystalline residue, which was recrystallized from MeOH aq to give pure 1a, mp 80–81°, $[\alpha]_D^{22}$ + 21·8° (*c* 2·95 in $CHCl_3$), ν_{max} (KBr) ~ 2600, 1700, 1630, and 890 cm^{-1}, δ 1·07 and 1·10 (3H, s), 2·64 (1H, q, *J* = 4 and 7), and 4·58 and 4·73 (1H, t, *J* = 1·5 each) (Found: C, 77·02, H, 9·25. $C_{15}H_{22}O_2$ requires: C, 76·88, H, 9·46%)

Methyl dihydrozizanoate (3)

Methyl zizanoate 1d (6·2 g) in 90 ml EtOH was hydrogenated over 100 mg of Adams catalyst at room temp. After H_2 absorption ceased, the catalyst was filtered off, and the solvent was evaporated. The residual oil was distilled and a fraction boiling at 122–125°/1·8 mm Hg was taken as 3, ν_{max} (neat) 1730 cm^{-1} (Found: C, 76·80, H, 10·71. $C_{16}H_{26}O_2$ requires: C, 76·75, H, 10·47%)

LAH reduction of methyl zizanoate (1d)

To a suspension of excess LAH in dry ether 1d (200 mg) was added in the same solvent, and the mixture was refluxed for 1·5 hr with stirring. After quenching with dil HCl, the mixture was extracted with ether. The extracts were washed with brine and dried over $MgSO_4$. Evaporation of the solvent gave an alcohol 1b, $[\alpha]_D^{20}$ + 26·6° (*c* 1·0 in MeOH), ν_{max} (neat) 3300, 1637, and 890 cm^{-1}, δ ($CDCl_3$) 1·07 and 1·09 (3H, s each), 3·59 (1H, m), and 4·60 and 4·74 (1H, t, *J* = 1·5 each). The spectra demonstrated the alcohol to be identical with khusimol.

The 3,5-dinitrobenzoate melted at 113° (Found: C, 64·01, H, 6·15, N, 6·45. $C_{22}H_{26}O_6N_2$ requires: C, 63·75, H, 6·32, N, 6·76%)

Zizaene (1c)

A soln of 1b (2·2 g) and tosyl chloride (2·86 g) in 25 ml of dry pyridine was allowed to stand at room temp overnight. The mixture was poured into ice-water and extracted with ether. The extracts were combined and washed with dil HCl, water, and then brine. The solvent was evaporated to leave an oily tosylate, which was refluxed with an excess of LAH in dry ether for 24 hr. Work-up as usual gave 1·5 g of an oil, which was distilled at 120° (bath temp)/1·2 mm Hg to give 1c, $[\alpha]_D$ + 39·8° (*c* 4·9 in $CHCl_3$), ν_{max} (neat) 3100, 1640, and 890 cm^{-1}, δ 0·95 (3H, d, *J* = 7), 1·04 and 1·06 (3H, s each), and 4·53 and 4·68 (1H, t, *J* = 1·5 each), *m/e* 204 (M^+) (Found: C, 88·44, H, 12·11. $C_{15}H_{24}$ requires: C, 88·16, H, 11·84%).

Alcohol (4a)

Methyl dihydrozizanoate 3 (1·00 g) was hydrolyzed by refluxing in 20 ml 10% ethanolic KOH for 3 hr. The mixture was concentrated *in vacuo* and diluted with water. After the soln was extracted with ether, dil HCl was added to acidify. The liberated acid was extracted with

---

*Very recently, on the basis of their chemical simulation experiments, Andersen and Syrdal have proposed a hypothetical biogenetic pathway from (−) nerolidyl pyrophosphate to prezizaene, Ref 15.

‡Andersen has also presumed similarly. Personal communication.

¶The vetiver was cultivated in Amami, Japan. The essential oil was gifted by courtesy of Ogawa Perfumery Co.

§The GLC mass spectra were measured by courtesy of Hasegawa Perfumery Co.

ether, and the extracts were washed and dried. Evaporation of the ether left 840 mg of an oily acid.

To a soln of MeLi, prepared from 0·42 g Li and 4·26 g MeI in dry ether, 0·7 g of the above-mentioned carboxylic acid in 10 ml dry ether was added at room temp over 30 min, and the mixture was refluxed for 9 hr. Water was added, and the organic layer was separated. Work-up afforded an oil (0·68 g), which was then submitted to silica gel column chromatography. Chloroform eluted 0·41 g of a methylketone, ν_{max} (neat) 1710 cm^{-1}, δ 2·02 (s, 3H), which was a mixture of the epimers as shown by TLC. The methylketone (120 mg) was added to a chloroform soln containing 330 mg perbenzoic acid. After the soln was allowed to stand at room temp for 5 days, the mixture was washed successively with Na_2CO_3 aq and brine. Work-up gave 120 mg of an oily product, 30 mg of which was heated with 10% ethanolic KOH to yield 28 mg of an oil. One of the epimers crystallized from the oil on standing. Recrystallization from light petroleum gave crystals, mp 135–136°, ν_{max} (KBr) 3300 cm^{-1}, δ 3·85 (1H, d, $J = 5$) (Found: C, 80·48; H, 11·59. $C_{14}H_{24}O$ requires: C, 80·71; H, 11·61%).

5-Membered ketone (**4b**)

A mixture of the epimers of **4a** (30 mg) was dissolved in 3 ml acetone, and excess of Jones reagent was added with cooling in an ice bath. The mixture was vigorously shaken for 3 min and diluted with water. The product was extracted with ether, and the combined extracts were washed with Na_2CO_3 aq, water, and then brine. Removal of the solvent left 30 mg of **4b**, an oil, ν_{max} (neat) 1733 cm^{-1}, ORD $[\phi]$[illegible] +5200° (peak) and $[\phi]$[illegible] −5200° (trough) (*c* 0·06 in MeOH).

δ-Lactone (**5**)

To a chloroform soln of **4b** (30 mg), excess perbenzoic acid (chloroform soln) was added. The mixture was allowed to react at room temp overnight. A crystalline residue (26 mg) was obtained. Recrystallization from light petroleum and subsequent vacuum sublimation gave the pure δ-lactone **5**, mp 104·5–105·5°, ν_{max} (KBr) 1735 cm^{-1} (Found: C, 75·33; H, 9·72. $C_{14}H_{22}O_2$ requires: C, 75·63; H, 9·97%).

Ketoester (**6a**)

A soln of **1d** (4·5 g) in 100 ml AcOEt was ozonized in an ice bath. The resulting ozonide soln was hydrogenated over Pd–C. The catalyst was filtered off, and the soln was washed with $NaHCO_3$ aq, water, and then brine, and dried. Removal of the solvent left a semisolid residue, from which crystals were separated by filtration. Recrystallization of the crystals from MeOH or light petroleum afforded 1·2 g of pure **6a**, mp 102–103·5°, $[\alpha]_D$ +129·8° (*c* 1·0 in dioxane), ν_{max} ($CHCl_3$) 1720 and 1705 cm^{-1}, δ 0·99 and 1·16 (3H, s each), and 3·63 (3H, s), ORD* $[\phi]$[illegible] −6100° (trough) and $[\phi]$[illegible] +7200° (peak) (*c* 0·04 in MeOH) (Found: C, 71·69; H, 8·69. $C_{15}H_{22}O_3$ requires: C, 71·97; H, 8·86%).

Unsaturated ester (**7a**)

$NaBH_4$ (0·3 g) in MeOH was added to a methanolic soln of **6a** (1·0 g), and the mixture was allowed to react at room temp for 24 hr. Dil HCl was added and the product was extracted with ether. An oily alcohol (1·01 g), ν_{max} (neat) 3550 and 1720 cm^{-1}, was obtained from the extracts. The alcohol (110 mg), without purification, was refluxed with 1 ml of $POCl_3$ in 5 ml dry pyridine for 6·5 hr. The mixture was poured into ice-water and extracted with ether. Work-up gave 70 mg of a crystalline product, which on recrystallization from MeOH gave colorless prisms, mp 65–66°, ν_{max} (KBr) 1725 and 840 cm^{-1}, δ 0·95 (6H, s), 3·60 (3H, s), and 4·82 (1H, q, $J = 2$ and 3) (Found: C, 76·59; H, 9·41. $C_{15}H_{22}O_2$ requires: C, 76·88; H, 9·46%).

Unsaturated alcohol (**7c**)

The ester **7a** (600 mg) was refluxed with 150 mg LAH in dry ether for 2 hr and treated in a usual manner, giving 520 mg of **7c**, ν_{max} (neat) 3350 and 845 cm^{-1}, δ 0·92 (6H, s), 3·45 (2H, m), and 4·77 (1H, q, $J = 2$ and 3) (Found: C, 81·91; H, 11·09. $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75%).

Olefin (**7b**)

A soln of **7c** (480 mg) and 573 mg tosyl chloride in 5 ml dry pyridine was allowed to stand at room temp overnight. Work-up as usual gave an oily tosylate, which was then refluxed with 170 mg LAH in 10 ml dry ether for 24 hr. The reaction was quenched by the addition of water, yielding 410 mg of an oily olefin, ν_{max} (neat) 850 and 845 cm^{-1}, δ 0·93 (6H, s), and 4·81 (1H, q, $J = 2$ and 2), *m/e* 190 (M^+, 21%), 175 ($M^+ - 15$, 100%, m* 161·2), and 147 ($M^+ - 15 - 28$, 42%, m* 123·5), was obtained on treatment in a customary manner (Found: C, 88·07; H, 11·43. $C_{14}H_{22}$ requires: C, 88·35; H, 11·65%).

Diol (**8**)

To a suspension of 500 mg LAH in 50 ml dry ether, a soln of **6a** (1·9 g) in 20 ml dry ether was added dropwise. The mixture was refluxed for 9 hr with stirring. Work-up afforded 1·15 g of a crystalline product, which was recrystallized from MeOH to give **8** as colorless prisms, mp 162·5–164°, ν_{max} (KBr) 3350 cm^{-1} (Found: C, 74·74; H, 10·53. $C_{14}H_{24}O_2$ requires: C, 74·95; H, 10·78%).

Ketone (**6b**)

(a) *From the olefin* **7b**. To a soln of **7b** (190 mg) and 140 mg of BF_3-etherate in 7 ml dry ether, a suspension of 57 mg of LAH in 7 ml dry ether was added with stirring under N_2. The mixture was stirred for 3 hr at room temp. A small amount of acetone and sat Na_2SO_4 aq were added, and then Na_2SO_4 was added to separate the organic layer. Evaporation of the ether gave a resinous residue, which was stirred at 70° with 130 mg NaOH and 0·4 ml of 20% H_2O_2 in 5 ml EtOH. Water was added to the mixture, and the product was extracted with ether. 210 mg of resinous product obtained from the extracts was dissolved in 5 ml acetone, and excess 8N Jones reagent was added at ice bath temp. After the mixture was shaken for 8 min, a usual work-up afforded 105 mg of crude **6b**. The pure ketone, ν_{max} (neat) 1710 cm^{-1}, *m/e* 206 (M^+), was obtained upon silica gel column chromatography using chloroform as the eluting solvent. The ketone showed two closely neighboring spots in TLC demonstrating to be a mixture of the epimers. (Found: C, 81·96; H, 10·97. $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75%).

(b) *From the diol* **8**. A soln of **8** (1 g) and 1·02 g tosyl chloride in 9 ml pyridine was allowed to react at room temp overnight. Work-up gave the crude monotosylate. The tosylate was refluxed with 0·4 g LAH in dry ether for 24 hr and worked up to give 0·9 g of an oil. An acetone soln of the oil was treated with excess 8N Jones reagent in an ice bath for several min. Work-up gave 820 mg of **6b**,

---

*We thank Dr H. Minato (Shionogi Laboratories) for the measurement.

which on comparison of the IR spectra was identical with the ketone obtained from **7b**.

Deuteration of the ketone (**6b**)

The ketone **6b** (60 mg) was added to a NaOMe soln prepared by dissolving 20 mg Na in 2 ml MeOD, and the mixture was refluxed for 30 min. The solvent was removed by evaporation *in vacuo*. MeOD (2 ml) was added to the residue and refluxed for 30 min. D_2O was added and the product was extracted with dry ether 3 times. The combined extracts were washed with D_2O and dried over $MgSO_4$. Removal of the ether gave 52 mg of the deuterated ketone, whose molecular ion was shown at *m/e* 207 ($C_{14}H_{21}OD$) in the mass spectrum.

α-Glycol (**9a**)

A soln of **7b** (1·0 g) and 1·4 g OsO_4 in 12 ml pyridine was allowed to stand in the dark for 91 hr. The resulting osmate soln was treated with $NaHSO_3$ aq, and the mixture was extracted with ether. Crystals were obtained from the extracts, and recrystallization from light petroleum gave pure **9a**, mp 94°, ν_{max} (KBr) 3400 cm^{-1}, δ ($CDCl_3$) 0·87 (1H, d, $J = 6·5$), 1·01 (6H, s), 2·50 (1H, s, OH), 2·65 (1H, d, $J = 5$, OH), and 3·28 (1H, d, $J = 5$) (Found: C, 74·80; H, 10·46. $C_{14}H_{24}O_2$ requires: C, 74·95; H, 10·78%).

Dihydroxyester (**9b**)

A soln of **7a** (234 mg) and 280 mg OsO_4 in 7 ml pyridine was treated as described for **9a** giving 246 mg crystals. Recrystallization from ligroin gave pure **9b**, mp 89·5–90°, ν_{max} (KBr) 3400 and 1725 cm^{-1}, δ ($CDCl_3$) 1·02 (6H, s), 2·68 (1H, d, $J = 5$, OH), 3·15 (1H, s, OH), 3·30 (1H, d, $J = 5$), and 3·65 (3H, s) (Found: C, 67·41; H, 8·78. $C_{15}H_{24}O_4$ requires: C, 67·13; H, 9·02%).

seco-Keto acid (**10a**)

$Pb(OAc)_4$ (1·7 g) was dissolved in a soln of **9a** (800 mg) in 20 ml dry benzene, and the mixture was stirred at room temp for 20 hr. The mixture was filtered and washed with $NaHCO_3$ aq and water, and dried. The solvent was evaporated to leave an oil. The oil was dissolved in 7 ml acetone, and excess Jones reagent was added. After stirring overnight, water was added, and the product was extracted with ether. The combined extracts were washed with $NaHCO_3$ aq, and the aq layer was acidified with dil HCl to give crystals. Recrystallization from light petroleum afforded pure **10a**, mp 72–73°, ν_{max} ($CHCl_3$) 2600, 1730, and 1700 cm^{-1}, δ ($CDCl_3$) 0·99 (3H, d, $J = 6$), 1·16 (6H, s), and 5·70 (1H, br s) (Found: C, 81·96; H, 10·97. $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75%).

Methyl ester (**10b**) was obtained from **10a** on treatment with diazomethane.

seco-Keto acid (**10c**)

Excess 8N Jones reagent was added to a soln of **9b** (134 mg) in 18 ml acetone, and the mixture was stirred at room temp overnight. Similar treatment afforded a resinous acid, which was chromatographed on a silica gel column. $CHCl_3$ eluted **10c**, and recrystallization from light petroleum gave an analytical sample, mp 80–81°, ν_{max} ($CHCl_3$) 2600, 1735, and 1700 cm^{-1}, δ ($CDCl_3$) 1·17 (6H, s), 3·36 (3H, s), and 11·28 (1H, br s) (Found: C, 67·55; H, 8·24. $C_{15}H_{22}O_4$ requires: C, 67·64; H, 8·33%).

Chloroester (**11**)

A mixture of **10c** (50 mg), 640 mg $Pb(OAc)_4$, 52 mg LiCl, and 3·5 ml dry benzene was stirred at 83–86° for 1 hr. The mixture was filtered and washed with $NaHCO_3$ aq, and then water. Evaporation of the solvent left an oil, which was purified on a silica gel column using chloroform as the eluting solvent to give 30 mg of **11**, an oil, ν_{max} (neat) 1730 cm^{-1}, δ ($CDCl_3$) 1·54 (6H, s), and 3·70 (3H, s) (Found: C, 61·69; H, 7·93. $C_{14}H_{21}O_3Cl$ requires: C, 61·59; H, 7·70%).

Unsaturated acid (**12**)

A soln of **6a** (500 mg) in 400 ml dry ether was irradiated with a 400 W high pressure mercury lamp for 1 hr and then washed with $NaHCO_3$ aq and brine. An oily residue obtained from the ethereal soln showed IR absorptions due to formyl group at 2750 cm^{-1}. The oil was dissolved in 300 ml acetone, and excess 8N Jones reagent was added. After stirring at room temp for 5 min, work-up gave 180 mg of an acidic product, which was chromatographed on a silica gel column. Chloroform eluted 50 mg of **12**, an oil, ν_{max} ($CHCl_3$) 2600, 1725, 1705, 1645, and 890 cm^{-1}, δ 1·69 (3H, br s), 3·64 (3H, s), 4·65 (2H, br s), and 11·57 (1H, br s) (Found: C, 67·37; H, 8·00. $C_{15}H_{22}O_4$ requires: C, 67·64; H, 8·33%).

γ-Lactone (**22**)

The dihydroxyester (**9b**) was hydrolyzed with 5% methanolic KOH by allowing to stand at room temp overnight. No epimerization of the carboxyl group during the hydrolysis was observed as indicated by the fact that the hydrolysis product was esterified with diazomethane to yield the original **9b**. A soln of 56 mg hydrolysis product and 46 mg dicyclohexylcarbodiimide in 2·5 ml dichloroethane was stirred at room temp for 4 hr and filtered. Evaporation of the solvent gave 72 mg of an oil, which was chromatographed on a silica gel column to give 18 mg of **22**, mp 82·7–83° (recrystallized from ligroin), ν_{max} ($CHCl_3$) 3550 and 1780 cm^{-1}, δ 1·08 and 1·13 (3H, s each), and 3·62 (1H, s). (Found: C, 71·30; H, 8·31. $C_{14}H_{20}O_3$ requires: C, 71·16; H, 8·53%).

Isolation of zizaene (tricyclovetivene) (**1c**) *from the essential oil*

Vetiver oil was distilled with a Widmer column, and a fraction boiling 100–120°/5 mm Hg was taken. The fraction (100 g) was poured onto a column containing 1·9 kg active alumina and eluted with n-hexane to give 72·5 g of a mixture of olefins. The olefin mixture was carefully fractionated through a spinning-band column (80 theoretical plates), and a fraction boiling 115–117°/3 mm Hg was obtained in 15% yield of the olefin mixture. The fraction (400 mg) was submitted to inverted column chromatography using a column packed with 100 g of $AgNO_3$-impregnated silica gel. A mixture of n-hexane-benzene (16 : 1) was used for development. The middle part of the column contained 195 mg of a pure olefin, which was extracted with ether and distilled *in vacuo*. The olefin, $[\alpha]_D$ + 40·4° (*c* 5·2 in $CHCl_3$), showed a peak at the retention time of 12·3 min in GLC (column, 25% PEG 20M, 3 mm × 2·5 m, column temp, 169°, He flow, 71 ml/min), and the IR, NMR, and mass spectra were totally identical with those of zizaene derived from zizanoic acid. On the other hand, the IR spectra showed the olefin to be also identical with tricyclovetivene, *m/e* 204 (M^+, 10%), 189 (M^+ − 15, 20%, m* 175·1), and 161 (M^+ − 15 − 28, 20%, m* 137·1) (Found: C, 87·84; H, 11·54. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%).

OsO_4 *Oxidation of zizaene*

A soln of **1c** (200 mg) and 274 mg OsO_4 in 5 ml dry pyridine was allowed to stand at room temp for 6 days. An aq soln of 3 g $NaHSO_3$ was added, and the mixture was stirred for 5 hr. The product was extracted with ether, and the extracts were washed successively with water, dil HCl, water, $NaHCO_3$ aq, and brine. Removal of the solvent gave **19** as crystals quantitatively. An analytical sample was obtained by recrystallization from light petroleum, mp 84–84.5°, ν_{max} ($CHCl_3$) 3500 cm^{-1}, δ 0.90 (3H, s), 0.91 (3H, d, J = 6.5), 1.00 (3H, s), and 3.65 (2H, s) (Found C, 75.67, H, 10.66. $C_{15}H_{26}O_2$ requires C, 75.58, H, 11.00%).

$Pb(OAc)_4$ *Oxidation of the glycol* (**19**)

A soln of **19** (50 mg) and 142 mg $Pb(OAc)_4$ in 2 ml dry benzene was allowed to react at room temp for 20 hr. Water was added, and the organic layer was separated and washed with $NaHCO_3$ aq and brine. Evaporation of the solvent left 41 mg of an oil, which was distilled *in vacuo* (bath temp, 90–115°/2 mm Hg) to give **6b**, ν_{max} (neat) 1708 cm^{-1}, δ 0.98 (3H, d, J = 7), 0.99 (3H, s), and 1.17 (3H, s), ORD $[\phi]$[illegible] −5950° (trough) and $[\phi]$[illegible] +6100° (Peak) (c 0.06 in MeOH). The ketone showed a single spot in TLC (Found C, 81.23, H, 10.52. $C_{14}H_{22}O$ requires C, 81.50, H, 10.75%).

Ozonization of zizaene

Ozonized air was passed through a soln of 1.0 g *zizaene* in 20 ml EtOAc at −50 – −70°. 3.3 g NaI in 11 ml AcOH was added to the ozonide soln, and the mixture was allowed to stand overnight. After neutralizing with NaOH aq, the mixture was extracted with EtOAc. The extracts were washed with $Na_2S_2O_3$ aq, water, and then brine. The solvent was removed to leave 850 mg of an oil. The oil was purified by silica gel column chromatography, and 291 mg of the ketone was eluted with light petroleum–ether (20:1). The ketone, ν_{max} (neat) 1709 cm^{-1}, showed two neighboring spots in TLC, and the NMR spectrum indicated that the ketone is a mixture of **6b** and its C-5 epimer.

Isolation of methyl epizizanoate (**2b**)

A fraction (13 g) boiling at a temp higher than methyl *zizanoate* was redistilled through a spinning-band column (80 theoretical plates). The distillate (10 g) boiling in the range of 128–137°/1 mm Hg was divided into 10 fractions. GLC showed that the fifth and sixth fractions contained **2b** as the main component. The fifth fraction (1.0 g) was poured onto a silica gel column (60 g SiO_2) and eluted with n-hexane–chloroform (1:2) to give 139 mg of pure methyl epizizanoate, an oil, ν_{max} (neat) 1736, 1640, and 890 cm^{-1}, δ 1.07 and 1.10 (3H, s each), 3.60 (3H, s), and 4.55 and 4.75 (1H, q, J = 1.5 and 2 each) (Found C, 77.64, H, 9.57. $C_{16}H_{24}O_2$ requires C, 77.37, H, 9.74%).

Preparative GLC (PEG 20M column) also provided pure methyl epizizanoate.

Epizizanoic acid (**2a**)

A soln of 310 mg of **2b** in a mixture of 3 ml 1N NaOH and 40 ml DMSO was allowed to stand under N_2 overnight. The mixture was poured onto ice-water and extracted with ether. The aq layer was acidified (Congo red) with dil HCl and extracted with ether. The combined extracts were washed and evaporated to leave 300 mg of crude epizizanoic acid. Recrystallization from aq MeOH gave crystals, mp 109–110.5°, $[\alpha]_D^{21}$ 2.2° (c 2.75 in $CHCl_3$), ν_{max} (KBr) 2600, 1700, 1640, and 890 cm^{-1}, δ 1.07 and 1.09 (3H, s each), 4.55 and 4.75 (1H, m each), and 11.0 (1H, br s) (Found C, 76.61, H, 9.46. $C_{15}H_{22}O_2$ requires C, 76.88, H, 9.46%).

Hydrogenation of methyl epizizanoate (**2b**)

Methyl epizizanoate **2b** (125 mg) in 5 ml EtOH was hydrogenated over 20 mg of Adams catalyst. Work up gave an oil, which was dissolved in ether and washed with water and brine. The solvent was removed to leave crystals. Recrystallization from MeOH gave an analytical sample of **25**, mp 79°, ν_{max} (CCl_4) 1730 cm^{-1}, as colorless needles (M, 250.1942. Calcd for $C_{16}H_{26}O_2$ M 250.1934).*

Ketoester (**26**)

A soln of **2b** (50 mg) and 51.2 mg OsO_4 in 2.5 ml pyridine was allowed to stand for 12 hr. $NaHSO_3$ aq was added to the resulting osmate soln, and the mixture was stirred at room temp for 4 hr. The mixture was diluted with water and extracted with ether. The extracts were washed with dil HCl, water, and brine, and evaporated to afford 54 mg of an oil. The oil (50 mg) was dissolved in dry benzene, and an excess of $Pb(OAc)_4$ was added. After stirring at room temp overnight, the mixture was filtered. The filtrate was washed with dil HCl, Na_2CO_3 aq, and water. Removal of the solvent gave 34 mg of crystals, which was recrystallized from MeOH to give **26**, mp 77.5–78.5°, ν_{max} (CCl_4) 1740 and 1710 cm^{-1}, δ 1.00 and 1.17 (3H, s each), and 3.64 (3H, s) (Found C, 72.08, H, 8.46. $C_{15}H_{22}O_3$ requires C, 71.96, H, 8.86%).

The ketoester (100 mg) was dissolved in a soln prepared from 30 mg Na and 2 ml dry MeOH, and the mixture was allowed to stand at room temp overnight. Work up gave an oil, which was shown to be a mixture of **26** and the epimer in TLC and GLC. The epimer, however, was not identical with **6a** as indicated by TLC and GLC.

Epizizaene (**2c**)

Methyl epizizanoate (74 mg) was treated with excess LAH in ether in a usual manner giving 57 mg of an alcohol, ν_{max} (neat) 3300, 3060, 1640, and 890 cm^{-1} (Found C, 81.58, H, 10.93. $C_{15}H_{24}O$ requires C, 81.76, H, 10.98%). The alcohol (55 mg) was tosylated with 100 mg tosyl chloride in pyridine on standing at room temp for 18 hr. The crude tosylate (62 mg) was refluxed with 125 mg LAH in ether for 18 hr. Work-up gave **2c**, ν_{max} (neat) 3090, 1640, and 890 cm^{-1}, δ 0.85 (3H, d, J = 6), 1.08 (6H, s), and 4.53 and 4.73 (1H, q, J = 1.5 and 2.5 each) (Found C, 87.98, H, 12.04. $C_{15}H_{24}$ requires C, 88.16, H, 11.84%).

Base-catalyzed equilibration of methyl zizanoate (**1d**)

Methyl *zizanoate* **1d** (100 mg) was refluxed for 24 hr in a soln obtained by dissolving 50 mg Na in 7 ml dry MeOH. The mixture was diluted with water and extracted with ether. Removal of the ether left 90 mg of an oil, which was shown to be a mixture of **1d** and **2b** in the ratio of 2:1. The mixture was separated by preparative GLC, and both components were identified on comparison of the IR spectra.

---

* The high resolution mass spectrum was taken with a JEOL JMS-01SG mass spectrometer by courtesy of Japan Electron Optics Laboratory.

REFERENCES

[1] Preliminary reports [a]F. Kido, H. Uda, and A Yoshikoshi, *Tetrahedron Letters* 2815 (1967). [b]*Ibid* 1247 (1968). [c]R Sakuma and A Yoshikoshi, *Chem Comm* 41 (1968). [d]N Hanayama, F Kido, R Sakuma, H Uda, and A Yoshikoshi, *Tetrahedron Letters* 6099 (1968)

[2a] L Ruzicka, E Capato, and H Huyser, *Rec Trav Chim* **47**, 370 (1928). [b]N I Zuchi and Sadgopal, *Perfumery Essent Oil Record* **48**, 333 (1957). [c]N F Novotel'nova and R Ya Rafanova, *Khim Nauka i Prom* 3, 539 (1958), *Chem Abstr* **53**, 4336f (1959)

[3] F Kido, H Uda, and A Yoshikoshi, *Chem Comm* 195 (1969), J C S Perk I 1755 (1972). D F McSweeney and R. Ramage, *Tetrahedron* 27, 1481 (1971)

[4] R M Coates, R F Farney, S. M Johnson, and J. C Paul, *Chem Comm* 999 (1969)

[5a] H. Komae and I C Nigam, *J Org Chem* **33**, 1771 (1968) and refs cited. [b]I C Nigam, H Komae, G A Neville, C Redecka, and S K Paknikar, *Tetrahedron Letters* 2497 (1968). [c]I C Nigam, C Redecka, and H Komae, *J Pharm Sci* **57**, 1029 (1968)

[6a] A Homma, M. Kato, M-D Wu, and A Yoshikoshi, *Tetrahedron Letters* 231 (1970). [b]N H Andersen, *Ibid* 1755 (1970)

[7] D C Umarani, K. G Gore, and K. K. Chakravarti, *Perfumery Essent Oil Record* **60**, 314 (1969).

[8a] D C. Umarani, K G Gore, and K. K. Chakravarti, *Tetrahedron Letters* 1255 (1966). [b]*Perfumery Essent Oil Record* **60**, 307 (1969).

[9] E Klein, R Siewerdt, and W Rojahn, *Dragoco Rept* **2**, 23 (1969), *Chem Abstr* 71, 102045b (1969)

[10] J K Kochi, *J Org Chem* **30**, 3265 (1965)

[11] G Chiurdoglu and P Tullen, *Bull Soc Chim Belges* **66**, 169 (1957)

[12] C Djerassi, R. Riniker, and B Riniker, *J Am Chem Soc* **78**, 6377 (1956)

[13a] N H Andersen and M S Falcone, *Chem Ind* 62 (1971). [b]N H Andersen and D D Syrdal, *Tetrahedron Letters* 899 (1972)

[14] B Tomita, *15th Symposium on Terpenes, Essential Oils, and Aromatic Chemicals* Osaka, October (1971)

[15] N H Andersen and D D Syrdal, *Tetrahedron Letters* 2455 (1972)

[16] D F McSweeney, R Ramage, and A Statter, *Ibid* 557 (1970).

[17] F Kido, R Sakuma, H Uda, and A Yoshikoshi, *Ibid* 3169 (1969).