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Stereoselectivity in Microbiological Transformation of Stereoisomers of α-Cyperone and Dihydro-α-cyperone with *Colletotrichum phomoides*[1]

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Incubation of three stereoisomers of α-cyperone (**1**, **2**, and **3**) with *Colletotrichum phomoides* resulted in two types of modification hydroxylation (C–2 and C–6) in one isomer (**2**) and dehydrogenation (C–6: C–7) in another isomer (**3**) at the nuclei and in three types of modification (hydration to an alcohol, allylic hydroxylation to an allyl alcohol, and oxidation to a 1,2-glycol) at the side chains in all the isomers in different rates. On fermentation with the same microbe of three stereoisomers of dihydro-α-cyperone (**16**, **17**, and **18**), prepared for prevention of the side chain modification, hydroxylation at the nucleus (C–1) occurred merely in one isomer (**16**), and the same types of oxidation at the side chains also took place in all the isomers as in their congeners (**1**—**3**). The stereoselectivity and the probable mechanisms of the transformations are discussed.

Microbial transformation, from its nature as enzyme-conducted reaction, is naturally predicted to show the stereoselectivity for which the following transformations may be exemplified. In the microbial hydroxylation of steroids, the positions and the configurations of introduced hydroxyls are characteristic of the microorganisms employed.[3] In the microbial reduction of alicyclic carbonyls, the configurations of newly formed hydroxyls are depending upon the conformations of the substrates.[4] Further examples in which the differences such as the yields, the stereochemistry, *etc.*, in products are found due to the enantiomerism of the substrates, are the microbial reduction of (+)- and (−)-codeinone and of (+)- and (−)-14-hydroxycodeinone by *Trametes sanguinea*.[5]

In the hope of examining the stereoselectivity of enzyme-conducted reactions effected by microorganisms, we have first tried microbial transformation of the stereoisomers of α-cyperone. The reasons for the first choice of this series are that they are readily available and also easily metabolized by certain microorganisms.

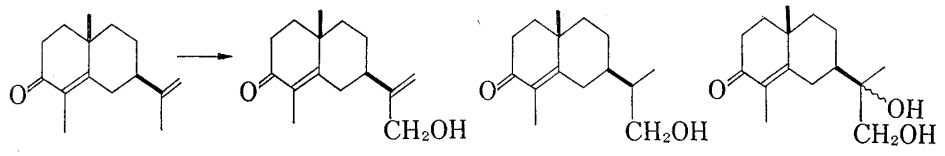
Among the four possible stereoisomers, (+)-7α(H),10β-eudesma-4,11-dien-3-one ((+)-α-cyperone, **1**), was isolated from the essential oil of nutgrass, *Cyperus rotundus* Linné (Cyperaceae), and the other (−)-7α(H),10α-eudesma-4,11-dien-3-one ((−)-10-*epi*-α-cyperone, **2**), and (+)-7β(H),10β-eudesma-4,11-dien-3-one ((+)-7-*epi*-α-cyperone, **3**), were synthesized from (+)- and (−)-carvone according to Halsall,[6] respectively.

Initial screening tests on (+)-α-cyperone using 11 species of microorganisms (see Experimental part) revealed that *Colletotrichum phomoides* and *Fusarium lini* performed the most efficient transformation of the substrate, the transformation rates by *C. phomoides*

1) This paper constitutes Part XLIX in the series on Sesquiterpenoids. Preceding paper, Part XLVIII: H. Hikino, T. Kato, and T. Takemoto, *Yakugaku Zasshi*, **95**, 243 (1975).
2) Location: *Aoba-yama, Sendai.*
3) *Cf.* H. Iizuka and A. Naito, "Microbial Transformation of Steroids and Alkaloids," University of Tokyo Press, Tokyo, 1967.
4) V. Prelog, *Pure and Applied Chem.*, **9**, 119 (1964).
5) K. Tsuda, "Chemistry of Microbial Products (6th Symposium of the Inst. Appl. Microbiology, Univ. of Tokyo)," 1964, p. 167.
6) T.G. Halsall, D.W. Theobald, and K.B. Walshaw, *J. Chem. Soc.*, **1964**, 1029.

being 60—70% in one week and 80—90% in two weeks. Therefore, *C. phomoides* was employed throughout the following experiments.

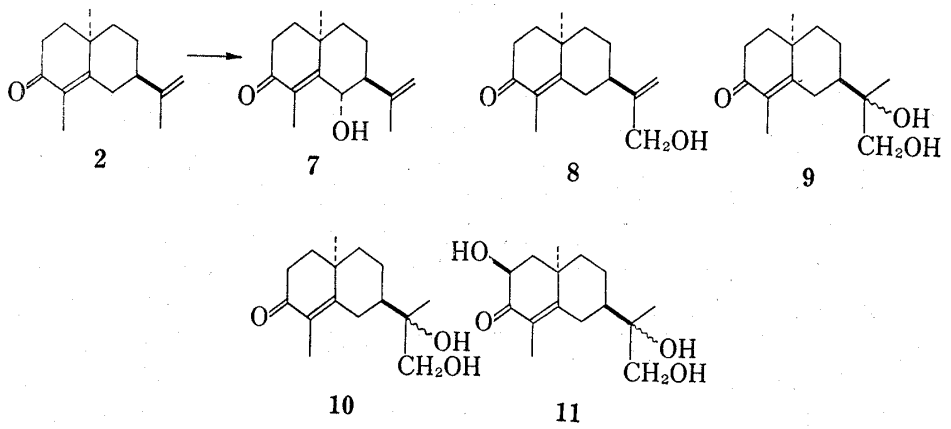
On incubation with *C. phomoides*, (+)-α-cyperone gave three main products which were separated by silica gel chromatography. The least polar product has the composition $C_{15}H_{22}O_2$ one oxygen more than the substrate. The ultraviolet (UV) and infrared (IR) spectra showed the retention of the 4-en-3-one system (λ_{max} 248 nm, ν_{max} 1653, 1607 cm^{-1}) and the vinylidene (ν_{max} 898 cm^{-1}) and the formation of a hydroxyl (ν_{max} 3380 cm^{-1}). The nuclear magnetic resonance (NMR) spectrum revealed the presence of most functional groups in the substrate but exhibited the disappearance of one of the vinyl methyls and instead the formation of a carbinyl methylene (δ 4.16 ppm). Concurrently, the vinylidene hydrogen signal, which appeared as a broad singlet (δ 4.70 ppm) in the spectrum of the substrate, was displaced downfield (δ 4.98, 5.12 ppm). Double resonance experiments disclosed the presence of the long range coupling between the methylene hydrogens and the vinylidene hydrogens. These data indicated the first product to be 13-hydroxy-derivative (**4**). The second product possesses the molecular formula $C_{15}H_{24}O_2$ two hydrogens and one oxygen more than the substrate, and was characterized also as the acetate. The UV and IR spectra of the metabolite exhibited the retention of the 4-en-3-one chromophore (λ_{max} 249 nm, ν_{max} 1650, 1609 cm^{-1}), but the disappearance of the vinylidene and instead the formation of a hydroxyl (ν_{max} 3400 cm^{-1}). In the NMR spectrum, a vinyl methyl hydrogen signal and a vinylidene hydrogen signal were absent and a carbinyl methylene multiplet (δ 3.55 ppm), a methine multiplet (δ 1.58 ppm), and a secondary methyl doublet (δ 0.99 ppm) were observed. Decoupling experiments revealed the vicinal couplings between the methylene hydrogens and the methine hydrogen and between the methine hydrogen and the methyl hydrogens, indicating that the second product is represented by formula **5**. The third and main product has the empirical formula $C_{15}H_{24}O_3$ two hydrogens and two oxygens extra than the substrate. The UV and IR spectra showed the retention of the 4-en-3-one moiety (λ_{max} 249 nm, ν_{max} 1647, 1603 cm^{-1}) but the disappearance of the vinylidene and instead the formation of hydroxyls (ν_{max} 3400 cm^{-1}). In accord with this observation, the NMR spectrum exhibited the absence of a vinyl methyl hydrogen signal and a vinylidene hydrogen signal and the occurrence of two carbinyl methylene doublets as an AB spectrum (δ 3.44, 3.60 ppm) and a tertiary methyl signal (δ 1.17 ppm). It was demonstrated by double resonance experiments that the methylene signal and the methyl signal were long range coupled each other, a fact which established the third product to be **6**.



1 4 5 6

Incubation of (—)-10-*epi*-α-cyperone (**2**) with *C. phomoides* afforded five products. The least polar product possesses the composition $C_{15}H_{22}O_2$ one oxygen more than the substrate. The UV, IR, and NMR spectra indicated the retention of all the functional groups present in the substrate and further disclosed the introduction of a secondary hydroxyl (ν_{max} 3460 cm^{-1}, δ 4.40 ppm). The findings that the carbinyl hydrogen signal appeared as a singlet, though somewhat broadened, showing the carbon next to this carbinyl group bears only one hydrogen and the dihedral angle between these two hydrogens to be nearly 90°, and that the C-15 methyl hydrogen signal and the C-12 vinylidene hydrogen signal showed downfield shifts ($\Delta\delta$ —0.18 and —0.15 ppm, respectively) relative to the corresponding signals in the spectrum of the substrate, demonstrated a hydroxyl to be introduced to the 6α-position. The first product is thus concluded to be **7**. The second product has the empirical formula $C_{15}H_{22}O_2$ one oxygen more than the substrate. From its spectral properties, it was revealed that most of the func-

tional groups in the substrate were retained but one of the vinyl methyl disappeared and instead a carbinyl methylene formed (δ 3.95 ppm). The downfield shifts of the C-12 vinylidene hydrogens caused by the introduction of a hydroxyl ($\Delta\delta$ −0.20 and −0.34 ppm) were observed, showing that a hydroxyl was introduced into the C-13 vinyl methyl. In confirmation of this conclusion, double resonance experiments indicated that the carbinyl methylene hydrogens and the vinylidene hydrogens are long range coupled each other. The structure of the second product as **8** is thus elucidated. The third and main product possesses the composition $C_{15}H_{24}O_3$ two hydrogens and two oxygens more than the substrate. The UV, IR, and NMR spectra showed that the isopropenyl group disappeared and instead an isolated carbinyl methylene (δ 3.37, 3.50 ppm) and a tertiary methyl (δ 1.04 ppm) formed. These data point to the third product to have the structure **9**. The fourth product has the same molecular formula $C_{15}H_{24}O_3$ as the third product. The spectral properties of both the products showed remarkable resemblance, demonstrating that the functional groups present are also identical. Based on the above evidence, the fourth product is concluded to be the epimer (**10**) of the third product with regard to C-11. The most polar product has the composition $C_{15}H_{24}O_4$ two hydrogens and three oxygens extra relative to the substrate. The UV, IR, and NMR spectra were very similar to those of the third and fourth products but exhibited the presence of an extra secondary hydroxyl (δ 4.09 ppm), suggesting that the fifth product was formed by the further introduction of a hydroxyl to a methylene in the third or fourth product. The observation that the carbinyl hydrogen signal in question occurred as a doublet of doublets (J=6, 13 Hz), showing it to be an X part of an ABX system, indicated the location of the hydroxyl at C-1, C-2, or C-9. Further, the coupling constants involved the one due to an axial-axial spin coupling, a fact which demonstrated the hydroxyl to be equatorially oriented. Although paucity of material prevented further chemical work, the deshielded line position of the carbinyl hydrogen signal indicated that the carbinyl group is adjacent to the C-3 carbonyl. Accumulated data lead to the conclusion that the last product is represented by formula **11**.

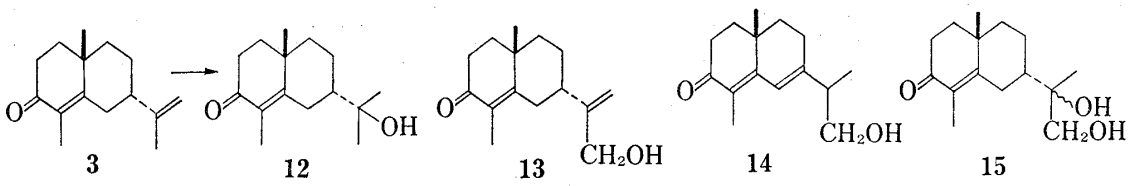


2 7 8 9

10 11

Incubation of (+)-7-*epi*-α-cyperone (**3**) with *C. phomoides* and separation of the fermentation product by silica gel chromatography gave rise the isolation of four metabolites. The least polar metabolite has the molecular formula $C_{15}H_{24}O_2$ two hydrogens and one oxygen more than the substrate. The UV, IR, and NMR spectra indicated that the isopropenyl group disappeared and instead two tertiary methyls formed (δ 1.20 ppm), establishing that the vinylidene in the substrate was hydrated to generate the first metabolite (**12**). The second metabolite has the empirical formula $C_{15}H_{22}O_2$ one oxygen more than the substrate. As verified from its spectral properties, most of functional groups in the substrate were still retained but one of the vinyl methyls was replaced by a methylene carriyng a hydroxyl (δ 3.95 ppm). The downfield shifts of the C-12 vinylidene hydrogen signals caused by the introduction of a hydroxyl were observed ($\Delta\delta$ −0.20 and −0.34 ppm). On the basis of the above evidence,

the second metabolite is concluded to be **13**. In support of this conclusion, the behaviors on thin-layer chromatography (TLC) and vapar phase chromatography (VPC), and IR and NMR spectra were identical with those of the ketol (**8**) above obtained from fermentation of (—)-10-*epi*-α-cyperone (**2**), indicating both ketols to be enantiomers each other. The third metabolite possesses the composition $C_{15}H_{22}O_2$ one oxygen extra than the substrate. The UV and IR spectra indicated the formation of an α,β,γ,δ-unsaturated carbonyl (λ_{max} 298 nm, ν_{max} 1642, 1608 cm^{-1}). The NMR signal attributed to a vinyl hydrogen appeared as a broadened singlet, coupled with the above observation, demonstrated the introduction of an extended ethylene bond at C-6: C-7. Further, the NMR spectrum indicated that, during the fermentation, the isopropenyl group disappeared and instead a methylene bearing a hydroxyl (δ 3.45, 3.56 ppm) and a secondary methyl (δ 1.07 ppm) occurred. These data showed the structure of the third metabolite to be **14**. The most polar metabolite has the molecular formula $C_{15}H_{24}O_3$ two hydrogens and two oxygens more than the substrate. The IR spectrum exhibited the retention of the 4-en-3-one chromophore (ν_{max} 1640, 1612 cm^{-1}), the disappearance of the vinylidene, and the formation of a hydroxyl (ν_{max} 3380 cm^{-1}). From the NMR spectrum, it was evident that the isopropenyl was replaced by an insulated methylene carrying a hydroxyl (δ 3.37, 3.51 ppm) and a tertiary methyl (δ 1.05 ppm). The splitting pattern of the methylene and the methyl, along with their deshielded line positions, indicated the introduction of a hydroxyl also at C-11. Based on the above evidence, the final product is concluded as **15**. Upon this conclusion, the keto-diol (**15**) was compared with the two diastereoisomers formed from fermentation of (—)-10-*epi*-α-cyperone (**2**) and revealed to be the antipode of one (**10**) of them.



3 12 13 14 15

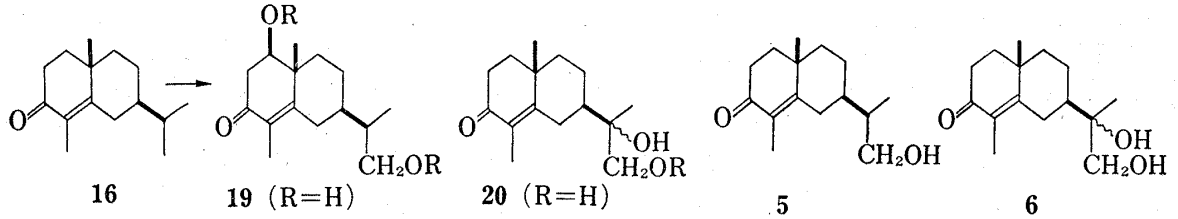
Judged from the structures of the metabolites obtained from three stereoisomers of (+)-α-cyperone by fermentation of *C. phomoides*, the transformations by this microbe can be classified into two types of reactions, *i.e.*, modification (introduction of hydroxyls and dehydrogenation) of the nucleus and modification (hydration, hydroxylation, and oxidation) of the side chains, in which, however, the latter is predominant. The reason for this preference of the reactions at the side chain may be the presence of the chemically reactive vinylidene groups at the ends of the substrate molecules. There is distinct difference in the modification at the nuclei, *i.e.*, only 10-*epi*-α-cyperone (**2**) was hydroxylated at C-2 and C-6 and 7-*epi*-α-cyperone (**3**) was dehydrogenated at C-6: C-7. Concerning the modification of the side chains, it may be classified into three types: conversion of the isopropenyl group into the 1- or 2-hydroxyisopropyl, that into the hydroxyisopropenyl, and that into 1,2-dihydroxyisopropyl. The distinct differences in the types and the yields of the reactions are observed depending upon the stereochemistry of the substrates. The mechanism for the conversion of the substrates into their 11- or 12-hydroxyderivatives will be discussed later. Introduction of a hydroxyl at C-13 is common to all the three substrates employed, which may be rationalized by the explanation that the methyls, situated at the ends of the substrate molecules, are most difficult to be influenced by the stereoisomerism. This may most probably be effected by direct hydroxylation of the allylic methyl, though the possibility that the reaction proceeds by conversion of the vinylidene into the 1,2-glycol followed by dehydration of the resulting tertiary hydroxyl cannot be excluded. The transformation of the substrates to their 11,12-dihydroxy-derivatives is also common to all the substrates. Although the conversion of the vinylidene into the 1,2-glycol is considered to occur most probably *via* direct oxidation or less likely *via* epoxidation

and the subsequent cleavage of the resultant epoxides, an alternative pathway is later revealed to be also possible (*vide infra*).

Since the above substrates, the α-cyperones, possess the reactive double bonds at their side chains which might give rise to the preferential modification, our next endeavor was directed towards the microbial transformation of the corresponding dihydro-derivatives of the previous substrates, the dihydro-α-cyperones, which no longer have double bonds in the side chains and consequently must be much more inactive for microbial transformation.

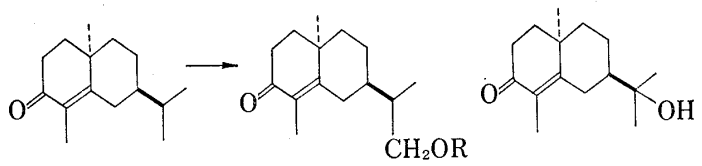
The substrates, the dihydro-α-cyperones (**16**, **17**, and **18**) were prepared from the corresponding α-cyperones (**1**, **2**, and **3**) by partial catalytic hydrogenation.

Incubation of (+)-dihydro-α-cyperone (**16**) with *C. phomoides* gave four products which were separated by silica gel chromatography and, in the two less polar ones, by combination of acetylation and chromatography. The first product was isolated as an acetate $C_{17}H_{28}O_5$. The IR and NMR spectra of the acetate showed the presence of the 4-en-3-one system (ν_{max} 1673, 1613 cm^{-1}) and two acetoxyls (ν_{max} 1740, 1225 cm^{-1}, δ 1.98, 2.01 ppm). The NMR spectrum, when compared with that of the substrate, further revealed the disappearance of one of the two secondary methyls and instead the formation of a carbinyl methylene (δ 3.95 ppm), demonstrating the hydroxylation at a β-position of the isopropyl. Further the occurrence of a carbinyl hydrogen signal (δ 4.96 ppm) as a doublet of doublets constituting an X part of an ABX system was observed, a fact which indicated the introduction of a hydroxyl at C-1, C-2, or C-9 during the fermentation. Attempted hydrolysis of the acetate with alkali under mild conditions yielded no hydrolysis product but the dehydration product (**24**) whose UV and NMR spectra showed the presence of the 1,4-dien-3-one chromophore (λ_{max} 240, 264 nm, δ 6.10, 6.62 ppm). Facile dehydration upon treatment with alkali indicates the first product to have a β-ketol moiety, and the splittings of the carbinyl hydrogen signal in question (J=6, 10 Hz) deduce the equatorial nature of the C-1 hydroxyl. From these data, the first product is concluded to be as **19** (R=H). The second product was also isolated as an acetate $C_{17}H_{26}O_4$. The spectral properties of the acetate exhibited the existence of the 4-en-3-one moiety, a hydroxyl (ν_{max} 3400 cm^{-1}), and an acetoxyl (ν_{max} 1730, 1220 cm^{-1}, δ 2.05 ppm). Comparison of the NMR spectrum of the acetate with that of the substrate indicated the conversion of the two methyls in the isopropyl into an isolated carbinyl methylene (δ 3.98 ppm) and a tertiary methyl (δ 1.17 ppm), showing that both C-11 and C-12 positions were hydroxylated. The formulation **20** (R=H) was thus allotted to the second product. The third and main product has the composition $C_{15}H_{24}O_2$. The UV, IR, and NMR spectra indicated the retention of most of the functional groups present in the substrate but the disappearance of a secondary methyl and instead the formation of a carbinyl methylene next to a methine. Based on the above evidence, the third product was compared with the product (**5**) obtained from (+)-α-cyperone (**1**) by the previous fermentation to reveal the identity. The fourth product possesses the molecular formula $C_{15}H_{24}O_3$ two oxygens more than the substrate. The UV, IR, and NMR spectra demonstrated the transformation of the isopropyl to 1,2-dihydroxyisopropyl as evidenced by the disappearance of two secondary methyls and the formation of an insulated carbinyl methylene (δ 3.44, 3.60 ppm) and a tertiary methyl (δ 1.16 ppm). These data pointed to the identity of the fourth product with the product (**6**) previously obtained from (+)-α-cyperone (**1**) which was confirmed by direct comparison. This product is consequently to be an stereoisomer of the second product (**20**: R=H).



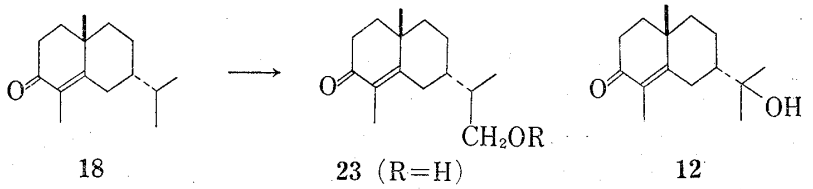
16 **19** (R=H) **20** (R=H) **5** **6**

On incubation with *C. phomoides*, (−)-dihydro-10-*epi*-α-cyperone (**17**) afforded two products. Since these products were difficult to be separated by liquid chromatography, these were treated with acetic anhydride in pyridine under controlled conditions to yield an acetate of the first product and the unchanged second product. The spectral properties of the acetate $C_{17}H_{26}O_3$ showed the introduction of a hydroxyl at C-12 as substantiated by the conversion of a secondary methyls into a carbinyl methylene adjacent to a tertiary carbon (δ 4.00 ppm). The structure of the first product was thus elucidated as shown in formula **21** (R=H). The second product has the composition $C_{15}H_{24}O_2$ one oxygen more than the substrate. The UV, IR, and NMR spectra indicated the disappearance of two secondary methyls and instead the formation of two methyls on quaternary carbon bearing a hydroxyl (ν_{max} 3450 cm^{-1}, δ 1.20 ppm). These data showed the second product to be represented by formula **22**, the antipode of the metabolite (**12**) previously obtained from (+)-7-*epi*-α-cyperone (**3**), which was confirmed by direct comparison.



17 21 (R=H) 22

Next, fermentation of (+)-dihydro-7-*epi*-α-cyperone (**18**) with *C. phomoides* was performed to form two products. Since these products were hardly separable by liquid chromatography, the mixture was treated with acetic anhydride in pyridine under controlled conditions to afford an acetate of the first product and the intact second product. The spectral properties of the acetate exhibited disappearance of one of the two secondary methyls in the isopropyl and instead occurrence of a carbinyl methylene next to a tertiary carbon, indicating that a hydroxyl was introduced into C-12. In confirmation of this conclusion, the acetate showed the same behaviors on chromatography and gave the identical spectra as the keto-diol acetate (**21**: R=Ac) above yielded from (−)-dihydro-10-*epi*-α-cyperone (**17**). The second product was shown by the spectral properties to have the same functional groups as the substrate (**18**) except that the two secondary methyls in the latter were replaced in the former by two tertiary methyls on a hydroxyl-bearing carbon (ν_{max} 3450 cm^{-1}, δ 1.20 ppm), a fact which indicated that the second product has the structure **12**. In fact, direct comparison of the chromatographic behaviors and the IR and NMR spectra revealed the identity of the second product with the ketol (**22**) above formed as a metabolite of (−)-dihydro-10-*epi*-α-cyperone (**17**).



18 23 (R=H) 12

As has been discussed before, previous incubation of the α-cyperones with *C. phomoides*, led to the principal attack at the side chains of enzymes induced in the microbe which was considered to be due to mainly the reactivity of the double bonds at C-11: C-12. Therefore, the second series of incubation was performed on the substrates whose C-7 side chain are saturated in order to prevent facile attack of the microbe at the side chains. Nevertheless, as judged from the structures of the metabolites, fermentation of the dihydro-α-cyperones with the microorganism resulted mainly in the introduction of hydroxyls into the C-7 side chain and the modification of the nucleus, which was originally more desired to occur for the evaluation of the stereoselectivity, took place merely partly. However, modification (hy-

droxylation at C-1) of the nucleus was observed only in dihydro-α-cyperone (**16**). demonstrating that the stereoselectivity is still effective in the microbial transformation of the stereoisomers of dihydro-α-cyperone. An interesting fact is that transformation of a pair of enantiomers (**17** and **18**) gave two sets of antipodes (**21** (R=H) and **22**, and **23** (R=H) and **12**, respectively), their conversion rated being nearly identical.

Comparison of the fermentation products from the α-cyperones and those from the dihydro-α-cyperones reveals that the certain metabolites are identical though generated from the different substrates. Taking this fact in mind, mechanistic considerations suggest that *C. phomoides* may have the capacity to reduce the isopropenyl to the isopropyl though the dihydro-α-cyperones themselves were not obtained by fermentation of the α-cyperones. Thus, the conversion of the isopropenyl into the 1- or 2-hydroxyisopropyl possibly occurs by hydration of the double bond, but an alternative pathway through reduction to the isopropyl followed by hydroxylation or allylic hydroxylation followed by reduction of the vinylidene may not be eliminated, because the metabolite (**5**) from α-cyperone were also obtained by the fermentation of dihydro-α-cyperone, and the metabolite (**12**) from 7-*epi*-α-cyperone was also formed by incubation of dihydro-7-*epi*-α-cyperone. Likewise, the transformation of the isopropenyl to the 1,2-hydroxyisopropyl may be considered to occur *via* reduction to the isopropyl followed by hydroxylation at both C-11 and C-12 positions as well as by direct oxidation of the double bond (or epoxidation of the double bond followed by cleavage of the resulting epoxide), since the metabolite (**6**) produced from α-cyperone was also yielded from dihydro-α-cyperone. The reaction mechanism that the isopropenyl is once reduced to the isopropyl which is further oxidized by the microbe may be the one which well rationalizes the fact that the two different series of substrates, the α-cyperones and dihydro-α-cyperones, give the same metabolites, though the yields were not consistent. There was found an interesting fact concerning the stereoselectivity in the transformation of enantiomers. Thus, the antipodes (**2** and **3**) gave the antipodal products (**8** and **13**, respectively), and further one (**2**) afforded the 6-hydroxylated derivative (**7**) while the other (**3**) furnished the dienone (**14**) which is possibly derived *via* a 6-hydroxy intermediate, though the relative yields were not compatible in this case. The striking observation was that the other pair of enantiomers (**17** and **18**) produced the antipodal metabolites (**21** (R=H) and **22**, and **23** (R=H) and **12**, respectively) and furthermore the relative yields coincided remarkably in this case, a fact which provides one of the unique examples of the stereochemically non-selective reaction conducted by microbes.

It is interesting to note that, as is seen from the fermentation products, with *C. phomoides*, presently performed, the modifications occur principally in the side chain which is the property characterizing this microorganism.

Experimental[7]

Screening Procedure for Microbial Transformation of α-Cyperone——A 500 ml flask was charged with a *Corticium* synthetic medium[8] (100 ml). The pH of the medium was adjusted to 6.8—7.0 with 1 N NaOH, and the vessel and medium was sterilized at 120° for 20 min. After cooling to room temperature, the flask was inoculated with mycelia of *Aspergillus ochraceus*, *Aspergillus flavus*, *Colletotrichum phomoides*, *Corticium sasaki*, *Cunninghamella blakesleeana*, *Curvularia lunata*, *Fusarium lini*, *Fusarium solani*, *Penicillium adametzioides*, *Penicillium chrysogenum*, or *Penicillium notatum*. The culture was shaken at 27° for a period of 4 days. A solution of α-cyperone (20 mg) in EtOH (1 ml) was added to each flask and the fermentation was continued for 1 or 2 weeks.

7) All mps are uncorrected. NMR spectra were measured at 60 MHz unless otherwise specified. Chemical shifts are expressed in ppm from tetramethylsilane as internal reference and coupling constants (*J*) in Hz. Abbreviations: s=singlet, d=doublet, dd=doublet of doublets, m=multiplet, br=broad peak.

8) H. Hikino, T. Tokuoka, and T. Takemoto, *Tetrahedron*, **24**, 3147 (1968).

The mycelia and the filtrate of the culture broth was then extracted with AcOEt and the extract was evaporated to give a fermentation product which was subject to TLC and VPC.

Fermentation of (+)-7α(H),10β-Eudesma-4,11-dien-3-one with *Colletotrichum phomoides*——The harvested fermentation product (0.10 g from the mycelia and 0.44 g from the cultured broth) obtained from (+)-α-cyperone (**1**) (450 mg) by action of *C. phomoides* for 2 weeks, was chromatographed over silica gel.

Elution with benzene–AcOEt (10: 1) gave (+)-7α(H),10β-eudesma-4,11-dien-3-on-13-ol (**4**) as a colorless oil (67 mg). ORD (optical rotatory dispersion) (*c* 0.115, MeOH): $[\phi]_{380}$ +280, $[\phi]_{339}$ −620, $[\phi]_{278}$ +9790; CD (circular dichroism) (*c* 0.115, MeOH): $[\theta]_{356}$ +76, $[\theta]_{311}$ −2400. Mass Spectrum *m/e*: 234 (M^+). UV λ_{max}^{EtOH} nm (log ε): 248 (4.67); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380 (hydroxyl), 1653, 1607 (enone), 898 (vinylidene); NMR ($CDCl_3$, 100 MHz): 3H, s, at 1.23 ($C_{(15)}$ $\underline{H}_3$), 3H, d, at 1.76 (J=1.0, $C_{(14)}$ $\underline{H}_3$), 2H, br, at 4.16 ($C_{(13)}$ $\underline{H}_2$), two 1H, br's, at 4.98, 5.12 ($C_{(12)}$ $\underline{H}_2$).

Elution with benzene–AcOEt (5: 1) afforded (+)-7α(H),10β-eudesm-4-en-3-on-12-ol (**5**) as a colorless oil (31 mg). ORD (*c* 0.114, MeOH): $[\phi]_{362}$ +1260, $[\phi]_{336}$ +467, $[\phi]_{280}$ +12900; CD (*c* 0.114, MeOH): $[\theta]_{354}$ +173, $[\theta]_{309}$ −2700. Mass Spectrum *m/e*: 236 (M^+). UV λ_{max}^{EtOH} nm (log ε): 249 (4.64); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (hydroxyl), 1650, 1609 (enone); NMR ($CDCl_3$, 100 MHz): 3H, d, at 0.99 (J=6, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.20 ($C_{(15)}$ $\underline{H}_3$), 1H, m, at 1.58 ($C_{(11)}$ $\underline{H}$), 3H, d, at 1.75 (J=1, $C_{(14)}$ $\underline{H}_3$), 2H, m, at 3.55 ($C_{(12)}$ $\underline{H}_2$).

Elution with benzene–AcOEt (2: 1) and crystallization from AcOEt yielded (+)-7α(H),10β-eudesm-4-en-3-one-11,12-diol (**6**) as colorless plates (96 mg), mp 146—147°. ORD (*c* 0.120, MeOH): $[\phi]_{360}$ +1360, $[\phi]_{338}$ +611, $[\phi]_{280}$ +14800; CD (*c* 0.120, MeOH): $[\theta]_{355}$ +271, $[\theta]_{309}$ −2830. Mass Spectrum *m/e*: 234 (M^+−18). UV λ_{max}^{EtOH} nm (log ε): 249 (4.66); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (hydroxyl), 1647, 1603 (enone); NMR ($CDCl_3$, 100 MHz): 3H, s, at 1.17 ($C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.20 ($C_{(15)}$ $\underline{H}_3$), 3H, br, at 1.77 ($C_{(14)}$ $\underline{H}_3$), two 1H, d's, at 3.44, 3.60 (J=11, $C_{(12)}$ $\underline{H}_2$).

Acetylation of 7α(H),10β-Eudesm-4-en-3-on-12-ol with Acetic Anhydride in Pyridine——The ketol (**5**) (30 mg) in Ac_2O (0.2 ml) and pyridine (0.4 ml) was left standing at room temperature overnight. After isolation in the usual manner, the product was chromatographed over silica gel. Elution with benzene–AcOEt (10: 1) gave 7α(H),10β-eudesm-4-en-3-on-12-ol acetate as a colorless oil (14 mg). Mass Spectrum *m/e*: 278 (M^+). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1220 (acetoxyl), 1667, 1613 (enone); NMR (CCl_4): 3H, d, at 0.98 (J=6, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.20 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.70 ($C_{(14)}$ $\underline{H}_3$), 3H, s, at 2.00 ($C\underline{H}_3COO$–), 2H, br, at 3.96 ($C_{(12)}$ $\underline{H}_2$).

Fermentation of (−)-7α(H),10α-Eudesma-4,11-dien-3-one with *Colletotrichum phomoides*——The harvested fermentation product (0.84 g from the mycelia and 0.70 g from the cultured broth) obtained from (−)-10-*epi*-α-cyperone (**2**) (1.50 g) by action of *C. phomoides* for 2 weeks, was chromatographed over silica gel.

Elution with benzene furnished (−)-7α(H),10α-eudesma-4,11-dien-3-on-6α-ol (**7**) as a colorless oil (10 mg). ORD (*c* 0.083, MeOH): $[\phi]_{354}$ −3120, $[\phi]_{281}$ +8560; CD (*c* 0.083, MeOH): $[\theta]_{324}$ −1670, $[\theta]_{269}$ +1390. Mass Spectrum *m/e*: 216 (M^+−18). UV λ_{max}^{EtOH} nm (log ε): 249 (4.59); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460 (hydroxyl), 1648, 1603 (enone); NMR ($CDCl_3$, 100 MHz): 3H, s, at 1.40 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.75 ($C_{(14)}$ $\underline{H}_3$), 3H, br, at 1.88 ($C_{(13)}$ $\underline{H}_3$), 1H, s, at 4.40 ($C_{(6)}$ $\underline{H}$), two 1H, br's, at 4.81, 4.90 ($C_{(12)}$ $\underline{H}_2$).

Elution with benzene–AcOEt (30: 1) gave (−)-7α(H),10α-eudesma-4,11-dien-3-on-13-ol (**8**) as a colorless oil (18 mg). ORD (*c* 0.198, MeOH): $[\phi]_{358}$ −1650, $[\phi]_{311}$ +1180; CD (*c* 0.198, MeOH): $[\theta]_{335}$ −1450. Mass Spectrum *m/e*: 234 (M^+). UV λ_{max}^{EtOH} nm (log ε): 251 (4.49); IR $\nu_{max}^{CHCl_3}$: 3450 (hydroxyl), 1657, 1605 (enone), 892 (vinylidene); NMR ($CDCl_3$, 100 MHz): 3H, s, at 1.23 ($C_{(15)}$ $\underline{H}_3$), 3H, br, at 1.74 ($C_{(14)}$ $\underline{H}_3$), 2H, br, at 3.95 ($C_{(13)}$ $\underline{H}_2$), two 1H, br's, at 4.75, 5.05 ($C_{(12)}$ $\underline{H}_2$).

Elution with benzene–AcOEt (5: 1) afford (−)-7α(H), 10α-eudesm-4-en-3-one-11,12-diol (**9**) as a colorless oil (260 mg). ORD (*c* 0.087, MeOH): $[\phi]_{366}$ −2180, $[\phi]_{278}$ +5170; CD (*c* 0.087, MeOH): $[\theta]_{334}$ −2630, $[\theta]_{275}$ +1430. Mass Spectrum *m/e*: 252 (M^+). UV λ_{max}^{EtOH} nm (log ε): 252 (4.55); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (hydroxyl), 1658, 1605 (enone); NMR ($CDCl_3$, 100 MHz): 3H, s, at 1.04 ($C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.21 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.77 ($C_{(14)}$ $\underline{H}_3$), two 1H, d's, at 3.37, 3.50 (J=10, $C_{(12)}$ $\underline{H}_2$).

Elution with benzene–AcOEt (4: 1) yielded (−)-7α(H),10α-eudesm-4-en-3-one-11,12-diol (**10**) as a colorless oil (8 mg). Mass Spectrum *m/e*: 252 (M^+). UV λ_{max}^{EtOH} nm (log ε): 252 (4.52); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380 (hydroxyl), 1640, 1612 (enone); NMR ($CDCl_3$, 100 MHz): 3H, s, at 1.05 ($C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.20 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.78 ($C_{(14)}$ $\underline{H}_3$), two 1H, d's, at 3.37, 3.51 (J=10.5, $C_{(12)}$ $\underline{H}_2$).

Elution with benzene–AcOEt (3: 1) gave (−)-7α(H),10α-eudesm-4-en-3-one-2β,11,12-triol (**11**) as a colorless oil (13 mg). ORD (*c* 0.101, MeOH): $[\phi]_{326}$ −660; CD (*c* 0.101, MeOH): $[\theta]_{292}$ −4720. Mass Spectrum *m/e*: 250 (M^+−18). UV λ_{max}^{EtOH} nm (log ε): 252 (4.41); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (hydroxyl), 1658, 1608 (enone); NMR ($CDCl_3$): 3H, s, at 1.08 ($C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.25 ($C_{(15)}$ $\underline{H}_3$), 3H, br, at 1.87 ($C_{(14)}$ $\underline{H}_3$), two 1H, d's, at 3.38, 3.52 (J=11, $C_{(12)}$ $\underline{H}_2$), 1H, dd, at 4.09 (J=6, 13, $C_{(2)}$ $\underline{H}$).

Fermentation of (+)-7β(H),10β-Eudesma-4,11-dien-3-one with *Colletotrichum phomoides*——The harvested fermentation product (0.22 g from the mycelia and 0.33 g from the cultured broth) obtained from (+)-7-*epi*-α-cyperone (**3**) (400 mg) by action of *C. phomoides* for 2 weeks, was chromatographed over silica gel.

Elution with benzene–AcOEt (50: 1) gave 7β(H),10β-eudesm-4-en-3-on-11-ol (**12**) as a colorless oil (36 mg). Mass Spectrum *m/e*: 236 (M^+). UV λ_{max}^{EtOH} nm (log ε): 252 (4.53); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450 (hydroxyl), 1663, 1613 (enone); NMR (CCl_4): 3H, s, at 1.12 ($C_{(15)}$ $\underline{H}_3$), 6H, s, at 1.20 ($C_{(12)}$ $\underline{H}_3$, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.72 ($C_{(14)}$ $\underline{H}_3$).

Elution with benzene–AcOEt (30: 1) afforded 7β(H),10β-eudesma-4,11-dien-3-on-13-ol (**13**) as a colorless oil (41 mg). UV λ_{max}^{EtOH} nm (log ε): 250 (4.49); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (hydroxyl), 1657, 1605 (enone), 892 (vinylidene); NMR ($CDCl_3$): 3H, s, at 1.23 ($C_{(15)}$ $\underline{H}_3$), 3H, br, at 1.74 ($C_{(14)}$ $\underline{H}_3$), 2H, br, at 3.95 ($C_{(13)}$ $\underline{H}_2$), two 1H, br's, at 4.75, 5.05 ($C_{(12)}$ $\underline{H}_2$). Identification with the ketol (**8**) was carried out by comparison of TLC, VPC, and IR and NMR spectra.

Elution with benzene–AcOEt (20: 1) yielded 7β(H),10β-eudesma-4,6-dien-3-on-12-ol (**14**) as a colorless oil (26 mg). Mass Spectrum *m/e*: 234 (M^+). UV λ_{max}^{EtOH} nm (log ε): 298 (4.62); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (hydroxyl), 1642, 1608 (dienone); NMR ($CDCl_3$, 100 MHz): 3H, d, at 1.07 (J=6, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.23 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.74 ($C_{(14)}$ $\underline{H}_3$), two 1H, m's, at 3.45, 3.56 ($C_{(12)}$ $\underline{H}_2$), 1H, br, at 6.25 ($C_{(6)}$ $\underline{H}$).

Elution with benzene–AcOEt (4: 1) furnished 7β(H),10β-eudesm-4-en-3-one-11,12-diol (**15**) as a colorless oil (20 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380 (hydroxyl), 1640, 1612 (enone); NMR ($CDCl_3$): 3H, s, at 1.05 ($C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.20 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.78 ($C_{(14)}$ $\underline{H}_3$), two 1H, d's, at 3.37, 3.51 (J=11, $C_{(12)}$ $\underline{H}_2$). Identification with the keto-diol (**10**) obtained from fermentation of (−)-7α(H),10α-eudesma-4,11-dien-3-one (**2**) was carried out by comparison of TLC and VPC, and IR and NMR spectra.

Fermentation of (+)-7α(H),10β-Eudesm-4-en-3-one with *Colletotrichum phomoides*——The harvested fermentation product (1.92 g) obtained from (+)-dihydro-α-cyperone (**16**) (2.10 g) by action of *C. phomoides* for 9 days, was subjected to silica gel chromatography.

Elution with benzene–AcOEt (5: 1) gave a mixture (0.20 g) which was rechromatographed over alumina. Fractions eluted with benzene–AcOEt (1: 1) were combined and acetylated with Ac_2O (0.2 ml) and pyridine (0.4 ml). The mixture of acetates were chromatographed over silica gel. Elution with benzene–AcOEt (2: 1) gave 7α(H), 10β-eudesm-4-en-3-one-1β,12-diol diacetate (**19**: R=Ac) as a colorless oil (29 mg). Mass Spectrum *m/e*: 276 (M^+−60). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1225 (acetoxyl), 1673, 1613 (enone); NMR (CCl_4): 3H, d, at 0.96 (J=6, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.19 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.72 ($C_{(14)}$ $\underline{H}_3$), two 3H, s's, at 1.98, 2.01 (2× $C\underline{H}_3COO$–), 2H, br, at 3.95 ($C_{(12)}$ $\underline{H}_2$), 1H, dd, at 4.96 (J=6, 10, $C_{(1)}$ $\underline{H}$). Further elution with benzene–AcOEt (1: 1) furnished 7α(H),10β-eudesm-4-en-3-one-11,12-diol 12-acetate (**20**: R=Ac) as a colorless oil (39 mg). Mass Spectrum *m/e*: 276 (M^+−18). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (hydroxyl), 1730, 1220 (acetoxyl), 1655, 1603 (enone); NMR (CCl_4): 3H, s, at 1.17 ($C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.21 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.70 ($C_{(14)}$ $\underline{H}_3$), 3H, s, at 2.05 ($C\underline{H}_3COO$–), 2H, s, at 3.98 ($C_{(12)}$ $\underline{H}_2$).

Elution with benzene–AcOEt (2: 1) yielded 7α(H),10β-eudesm-4-en-3-on-12-ol (**5**) as a colorless oil (236 mg). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (hydroxyl), 1665, 1613 (enone); NMR (CCl_4): 3H, d, at 0.94 (J=6, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.20 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.71 ($C_{(14)}$ $\underline{H}_3$), 2H, d, at 3.52 (J=5, $C_{(12)}$ $\underline{H}_2$). Identification with the ketol (**5**) obtained by fermentation of (+)-7α(H),10β-eudesma-4,11-dien-3-one was performed by comparison of TLC, IR and NMR spectra.

Elution with benzene–AcOEt (1: 1) and crystallization from AcOEt afforded 7α(H),10β-eudesm-4-en-3-one-11,12-diol (**6**) as colorless plates (140 mg), mp 138—140°. *Anal.* Calcd. $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.08; H, 9.69. Mass Spectrum *m/e*: 234 (M^+−18). IR ν_{max}^{KBr} cm^{-1}: 3440, 3350 (hydroxyl), 1638, 1608 (enone); NMR ($CHCl_3$): 3H, s, at 1.16 ($C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.20 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.77 ($C_{(14)}$ $\underline{H}_3$), two 1H, d's, at 3.44, 3.60 (J=11, $C_{(12)}$ $\underline{H}_2$). The identity with the keto-diol (**6**) obtained by fermentation of (+)-7α(H),10β-eudesma-4,11-dien-3-one was confirmed by mixed melting point and comparison of TLC, and IR and NMR spectra.

Alkaline Hydrolysis of 7α(H),10β-Eudesm-4-en-3-one-1β,12-diol Diacetate——The keto-diol diacetate (**19**: R=Ac) (18 mg) in 5% methanolic K_2CO_3 (1 ml) was set aside at room temperature under N_2 for 1.5 hr. Aftet working up in the customary manner, the product was purified by preparative TLC (silica gel, AcOEt) to give 7α(H),10β-eudesma-1,4-dien-3-on-12-ol (**24**) as a colorless oil (2 mg). UV λ_{max}^{EtOH} nm (log ε): 240 (3.70), 264 (3.56, inf.); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (hydroxyl), 1660 (dienone); NMR ($CDCl_3$, 100 MHz): 3H, d, at 1.10 (J= 7, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.10 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.79 ($C_{(14)}$ $\underline{H}_3$), 2H, m, at 3.50 ($C_{(12)}$ $\underline{H}_2$), 1H, d, at 6.10 (J= 10, $C_{(2)}$ $\underline{H}$), 1H, d, at 6.62 (J=10, $C_{(1)}$ $\underline{H}$).

Fermentation of (−)-7α(H),10α-Eudesm-4-en-3-one with *Colletotrichum phomoides*——The harvested fermentation product (2.44 g) obtained from (−)-dihydro-10-*epi*-α-cyperone (**17**) (2.10 g) by action of *C. phomoides* for 12 days, was submitted to silica gel chromatography. From a fraction (830 mg) eluted with benzene–AcOEt (2: 1), a part (110 mg) was taken and acetylated with Ac_2O (5.5 ml) and pyridine (11 ml) at 0° for 10 min to afforded a mixture which was chromatographed over silica gel.

Elution with benzene–AcOEt (10: 1) afforded 7α(H),10α-eudesm-4-en-3-on-12-ol acetate (**21**: R=Ac) as a colorless oil (45 mg). Mass Spectrum *m/e*: 278 (M^+). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735, 1220 (acetoxyl), 1660, 1610 (enone); NMR (CCl_4): 3H, d, at 1.02 (J=5, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.26 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.74 ($C_{(14)}$ $\underline{H}_3$), 3H, s, at 2.00 ($C\underline{H}_3COO$–), 2H, br, at 4.00 ($C_{(12)}$ $\underline{H}_2$).

Further elution with benzene–AcOEt (5: 1) furnished 7α(H),10α-eudesm-4-en-3-on-11-ol (**22**) as a colorless oil (22 mg). Mass Spectrum *m/e*: 236 (M^+). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450 (hydroxyl), 1663, 1613 (enone); NMR

(CCl_4): 3H, s, at 1.12 ($C_{(15)}$ $\underline{H}_3$), 6H, s, at 1.20 ($C_{(12)}$ $\underline{H}_3$, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.72 ($C_{(14)}$ $\underline{H}_3$). Identification with the ketol (**12**) obtained from fermentation of (+)-7β(H),10β-eudesma-4,11-dien-3-one (**3**) was confirmed by comparison of TLC, IR, and NMR spectra.

Alkaline Hydrolysis of 7α(H),10α-Eudesm-4-en-3-on-12-ol Acetate——7α(H),10α-eudesm-4-en-3-on-12-ol acetate (**21**: R=Ac) (40 mg) was made to react with 5% methanolic K_2CO_3 (3 ml) under N_2 at room temperature for 4 days. After isolation in the customary way, the product was subjected to preparative TLC (silica gel, benzene–AcOEt (2: 1)) to give 7α(H),10α-eudesm-4-en-3-on-12-ol (**21**: R=H) as a colorless oil (18 mg). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420 (hydroxyl), 1659 (enone).

Fermentation of (+)-7β(H),10β-Eudesm-4-en-3-one with *Colletotrichum phomoides*——The harvested fermentation product (1.37 g) obtained from (+)-dihydro-7-*epi*-α-cyperone (**18**) (0.73 g) by action of *C. phomoides* for 10 days, was chromatographed over silica gel.

Elution with benzene–AcOEt (2: 1) gave a mixture (300 mg) which was acetylated with Ac_2O (11 ml) and pyridine (22 ml) at 0° for 4 hr to give a mixture, which was chromatographed over silica gel.

Elution with benzene–AcOEt (10: 1) afforded 7β(H),10β-eudesm-4-en-3-on-12-ol acetate (**23**: R=Ac) as a colorless oil (78 mg). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735, 1220 (acetoxyl), 1660, 1610 (enone); NMR (CCl_4): 3H, d, at 1.03 (J=5, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.26 ($C_{(15)}$ $\underline{H}_3$), 3H, s, at 1.74 ($C_{(14)}$ $\underline{H}_3$), 3H, s, at 2.00 ($C\underline{H}_3COO$–), 2H, br, at 4.00 ($C_{(12)}$ $\underline{H}_2$). Identification with the ketol acetate (**21**: R=Ac) obtained from fermentation of (−)-7α(H),10α-eudesm-4-en-3-one (**17**) was carried out by comparison of TLC and VPC, and IR and NMR spectra.

Successive elution with benzene–AcOEt (5: 1) furnished 7α(H),10α-eudesm-4-en-3-on-11-ol (**12**) as a colorless oil (43 mg). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450 (hydroxyl), 1663, 1613 (enone); NMR (CCl_4): 3H, s, at 1.12 ($C_{(15)}$ $\underline{H}_3$), 6H, s, at 1.20 ($C_{(12)}$ $\underline{H}_3$, $C_{(13)}$ $\underline{H}_3$), 3H, s, at 1.72 ($C_{(14)}$ $\underline{H}_3$). The identity with the ketol (**22**) obtained from fermentation of (−)-7α(H),10α-eudesm-4-en-3-one (**17**) was substantiated by comparison of TLC and VPC, and IR and NMR spectra.