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248. Hiroshi Hikino, Keitaro Aota, and Tsunematsu Takemoto*1 : Structure and Absolute Configuration of Cyperol and Isocyperol.*2

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Two sesquiterpenic alcohols, cyperol and isocyperol, have been isolated from nutgrass (*Cyperus rotundus* (Cyperaceae)) and shown to have stereostructures I and Ⅳ, respectively, by means of spectral determinations and by transformations to α-cyperone (Ⅱ) and 4β(H)-eudesman-3-one (Ⅸ), respectively.

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From the crude "Kō-bushi," the tuber of *Cyperus rotundus* LINNÉ (Cyperaceae), of Japanese origin we have hitherto isolated the sesquiterpenoids, α-cyperone, cyperotundone,[1] and cyperolone.[2] In continuation of our work on the analysis of the crude drug we have further isolated two new sesquiterpenic alcohols. Evidence for their structural assignment as shown in formulae I and Ⅳ, respectively, is presented in this paper.

The first, a crystalline alcohol, has the molecular formula $C_{15}H_{24}O$ and exhibited the following spectroscopic properties suggestive of the presence of a secondary hydroxyl (3311 cm^{-1}, 6.26τ), a tetrasubstituted ethylenic bond with a methyl on it (8.28τ, no vinyl proton signal), an isopropenyl (3106, 1645, 882 cm^{-1}, 8.28, 5.35τ), and a tertiary methyl group (9.00τ). Oxidation of the alcohol with chromium trioxide-pyridine complex gave an α,β-conjugated ketone, which was identified as α-cyperone (Ⅱ) by its physico-chemical properties including the optical rotation, and by melting point of its 2,4-dinitrophenylhydrazone. The structure and absolute stereochemistry of the alcohol were, therefore, elucidated except for the configuration at C-3. The α-configuration of the C-3 hydroxyl group was indicated by the following observations. Comparing the optically active C-3 epimers of the allylic alcohols, I and Ⅲ, one being the natural product and the other prepared from α-cyperone (Ⅱ) by hydride reduction,[3] we observed that 1) the NMR (nuclear magnetic resonance) signal of the C-3 hydrogen in the natural alcohol appeared as a single peak (band width at half height: 6 c.p.s.), while that in its synthetic counterpart (Ⅲ) occurs as a broad peak (band width at half height: 15 c.p.s.), and 2) the natural alcohol is more dextrorotatory ($\Delta[M]_D$ +251°) than its epimer (Ⅲ).[4] On the basis of the above evidence the natural alcohol is shown to be represented by stereoformula I.

Previously, Kimura, *et al.*[5] reported having isolated from the same oil an alcohol $C_{15}H_{24}O$ which they called "cyperol." However, it was obtained only by simple distillation, and was therefore probably a mixture of many substances. For this reason we propose that the name cyperol be devoted to the alcohol (I), presently isolated.

The second, an oily alcohol, also analyzed for $C_{15}H_{24}O$, and was shown by spectral data to have a secondary hydroxyl (3356 cm^{-1}, 5.83τ), a vinylidene (3106, 1647, 902 or 887 cm^{-1}, 5.51, 5.16τ), an isopropenyl (902 or 887 cm^{-1}, 8.24, 5.35τ), and a tertiary methyl

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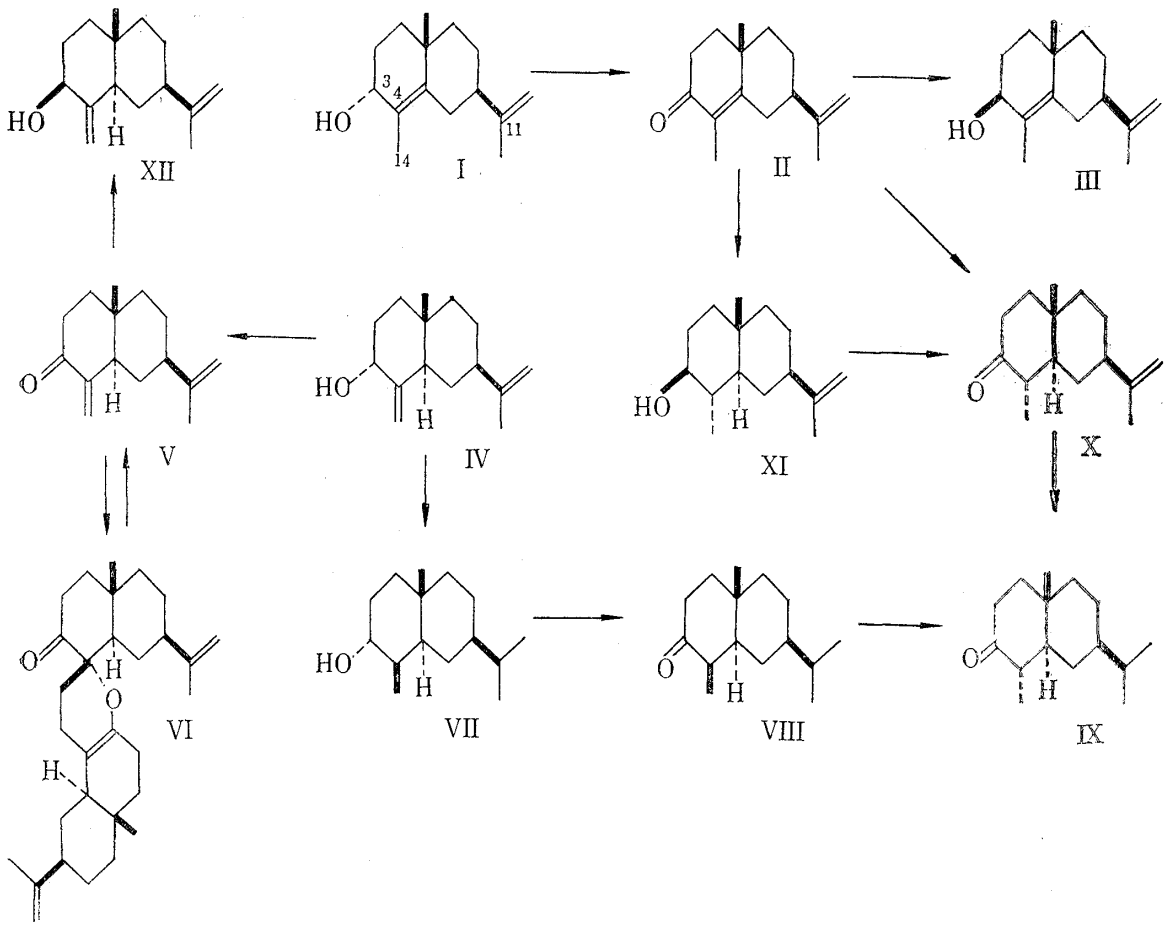
*2 This paper forms Part XVI in the series on Sesquiterpenoids. Preceding paper, Part XV, H. Hikino, Y. Takeshita, Y. Hikino, T. Takemoto: Yakugaku Zasshi, **87**, 1035 (1967).

1) H. Hikino, K. Aota, T. Takemoto: This Bulletin, **13**, 628 (1965); **14**, 890 (1966).
2) H. Hikino, K. Aota, Y. Maebayashi, T. Takemoto: *Ibid.*, **14**, 1439 (1966); **15**, 1349 (1967).
3) H. Hikino, N. Suzuki, T. Takemoto: *Ibid.*, **14**, 1441 (1966); **15**, 1395 (1967).
4) J. A. Mills: J. Chem. Soc., **1952**, 4976.
5) Y. Kimura, M. Otani: Yakugaku Zasshi, **48**, 971 (1928).



group (9.29τ). On oxidation with chromium trioxide-pyridine complex the alcohol gave the ketone (V). The α,β-conjugated system in an S-*cis* conformation was demonstrated by the following evidence: 1) the infrared spectrum disclosed bands at 1690 and 1613 cm^{-1}, 2) the NMR spectrum showed the methylene proton signals at 5.02 and 4.29τ (1H triplet each), and 3) the enone on standing at room temperature gave a dimer of the molecular formula $C_{30}H_{48}O_2$. The infrared and NMR spectra of the dimer indicated the presence of a carbonyl in a six-membered ring and with α-equatorial oxygen substitution (1723 cm^{-1}), a tetrasubstituted ethylenic linkage with an oxygen on it (1676 cm^{-1}, no vinyl proton signal), two tertiary methyls (9.21, 8.83τ), and two isopropenyls (3028, 1641, 891 cm^{-1}, 8.33, 8.26, 5.41, 5.33τ). However, no indication was found, in the appropriate region of the NMR spectrum, of the presence of a methylene attached to oxide linkage. This spectral evidence suggests the structure VI for the dimer, formed by Diels-Alder type dimerization of the monomer (V). This type of dimerization has ample precedence, *e.g.*, 2-vinylidenecyclohexanone,[6] and pinocarvone.[7] In confirmation, pyrolysis of the dimer (VI) reconverted to the monomer (V) by reverse Diels-Alder reaction. Hydrogenation of the second natural alcohol over Adams' catalyst in methanol proceeded with consumption of two moles of hydrogen to afford the tetrahydro-derivative (VII) whose infrared and NMR spectra revealed the disappearance of the vinylidene and the isopropenyl group, and the formation of three secondary methyl groups during hydrogenation. Oxidation of the tetrahydro-alcohol (VII) with chromic acid yielded the ketone (VIII). The assignment of the configuration of the methyl group vicinal to the carbonyl in the ketone (VIII) was deduced from the observation that the methyl proton resonance suffered an upfield

6) C. Mannich: Ber., **74**, 557 (1941).
7) T. Takemoto, T. Nakajima: Yakugaku Zasshi, **77**, 1157 (1957).

shift on passing from carbon tetrachloride to benzene solution indicating the methyl to be oriented in an axial configuration.[8] Treatment of the ketone (Ⅷ) with alkali furnished an isomerized ketone. That epimerization of the methyl group on carbon adjacent to the carbonyl from the less stable axial configuration to the more stable equatorial one occurred during alkali treatment was indicated by increase of the positive Cotton effect (Δa+38). The isomerized ketone was identical in its physico-chemical properties with 4β(H)-eudesman-3-one (Ⅸ) obtained by hydrogenation of the ketone (Ⅹ), 4β(H)-eudesm-11-en-3-one, which was prepared from α-cyperone (Ⅱ) by reduction with lithium and ammonia,[9] or by reduction with sodium and ethanol[10] to 4β(H)-eudesm-11-en-3β-ol (Ⅺ) followed by oxidation with chromic acid. It may be worthy to present the evidence for the β-configuration of the C-3 hydroxyl group of the alcohol (Ⅺ). Thus, the NMR spectrum of the alcohol (Ⅺ) showed the C-3 hydrogen signal as a broad peak (band width at half height : 19 c.p.s.) indicating that it was in an axial configuration. Hence the C-3 hydroxyl group must be equatorial as expected on mechanistic grounds, and therefore in the β-configuration provided that the ring fusion is *trans*. The above identification of both the ketones thus established the carbon skeleton of the second natural alcohol. The remaining problem to be solved was the configuration of the C-3 hydroxyl group. Reduction of the unsaturated ketone (Ⅴ) with lithium aluminum hydride gave the alcohol (Ⅻ). The NMR signal of the C-3 hydrogen in the natural alcohol appeared as a single peak (band width at half height : 6 c.p.s.) showing that the C-3 hydroxyl was axially disposed, whereas in the epimer (Ⅻ) the peak was broader (band width at half height : 19 c.p.s.) demonstrating that the C-3 hydroxyl was equatorially situated. With the stereochemistry of the carbon skeleton in mind, the C-3 hydroxyl of the natural alcohol was, therefore, shown to be in the α-configuration. Combination of the above evidence leads to the conclusion that the second natural alcohol has the stereostructure Ⅳ.

The isolation of an alcohol $C_{15}H_{24}O$, having the eudesmane skeleton and named "isocyperol," has been reported,[11] but judging from the purification procedure described, it cannot be considered as a pure substance. Therefore, we propose that the name isocyperol be given to the alcohol (Ⅳ), presently isolated.

Cyperol (Ⅰ) must biosynthetically be derived from eudesma-4,11-diene and is certainly an immediate precursor of α-cyperone (Ⅱ), while isocyperol (Ⅳ) must be biosynthesized from β-selinene, eudesma-4(14),11-diene. However, the corresponding ketone (Ⅴ), an unstable substance, has not been found in the oil.

Experimental*3

Isolation of Cyperol and Isocyperol——The crude drug "Kō-bushi', the dried rhizomes of *Cyperus rotundus* Linné (Japanese name : Hama-suge), was steam-distilled to give the essential oil as a pale brown liquid in 0.6% yield.[1]

The oil was chromatographed over alumina. After percolation with benzene of ketone fractions followed by acetate fractions, successive elution with the same solvent afforded alcohol fractions which, upon combination, were submitted to rechromatography on silica gel coated with $AgNO_3$(10%).

Elution with benzene followed by crystallization from light petroleum gave cyperol (Ⅰ) as colorless needles, m.p. 111.5~112°, $[\alpha]_D$ +131.4°(c=6.2), *Anal.* Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found : C, 81.97;

*3 Melting points are uncorrected. Rotations were measured in $CHCl_3$ solution. NMR spectra were recorded at 60 Mc.p.s. in CCl_4 solution using $(CH_3)_4Si$ as internal standard unless otherwise indicated. Chemical shifts are given in τ-units and coupling constants (J) in c.p.s.

8) N. S. Bhacca, D. H. Williams : "Application of NMR Spectroscopy in Organic Chemistry," 159 (1964). Holden-Day, Inc., San Francisco.
9) R. Howe, F. J. McQuillin : J. Chem. Soc., **1956**, 2670.
10) A. E. Bradfield, B. H. Hegde, B. S. Rao, J. L. Simonsen : *Ibid.*, **1936**, 667.
11) B. J. Hegde, B. S. Rao : J. Soc. Chem. Ind., **54**, 388 (1935).

H, 10.82. IR (KBr) cm^{-1} : 3311 (hydroxyl), 3106, 1645, 882 (vinylidene), NMR : singlet (3H) at 9.00 τ ($C\underline{H}_3$-C$\leqslant$), singlet (6H) at 8.28 τ ($C\underline{H}_3$-C=C$\langle$), single peak with fine splittings (1H) at 6.26 τ (band width at half height : 6 c.p.s., -CH_2-C$\underline{H}$(OH)-C=C$\langle$), singlet (2H) at 5.35 τ (unresolved, $C\underline{H}_2$=C-CH_3).

Successive elution with benzene-AcOEt (5:1) and distillation under diminished pressure yielded isocyperol (Ⅳ) as a colorless oil, $[\alpha]_D$ −5.4°(c=4.5), *Anal.* Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found : C, 81.82; H, 11.05. IR (liquid) cm^{-1} : 3356 (hydroxyl), 3106, 1647, 902, 887 (vinylidene), NMR : singlet (3H) at 9.29 τ ($C\underline{H}_3$-C$\leqslant$), singlet (3H) at 8.24 τ ($C\underline{H}_3$-C=CH_2), single peak with fine splittings (1H) at 5.83 τ (band width at half height : 6 c.p.s., -CH_2-C$\underline{H}$(OH)-C=CH_2), two triplets (1H each) at 5.51, 5.16 τ (J=1.7, $C\underline{H}_2$=C-CH(OH)-), singlet (2H) at 5.35 τ ($C\underline{H}_2$=C-CH_3).

Oxidation of Cyperol with Chromium Trioxide-Pyridine Complex——Cyperol (50 mg.) in pyridine (0.8 ml.) was added to CrO_3 (62 mg.) in pyridine (0.5 ml.) and set aside at room temperature overnight. Extraction in the usual manner afforded a product (50 mg.) which was distilled under reduced pressure to give α-cyperone (Ⅱ) as a colorless oil, $[\alpha]_D$ +95.6°(c=4.5), identified by comparison of IR and NMR spectra.

The 2,4-dinitrophenylhydrazone, prepared in the customary way ($NH_2NHC_6H_3(NO_2)_2$-H_2SO_4-EtOH), crystallized from AcOEt as red needles, m.p. 208~208.5°, which showed no m.p. depression on admixture with an authentic sample.

Oxidation of Isocyperol with Chromium Trioxide-Pyridine Complex——Isocyperol (141 mg.) in pyridine (1.0 ml.) was added to CrO_3 (145 mg.) in pyridine (0.8 ml.) and let stand at room temperature for 1 day. The product (126 mg.), isolated in the usual manner, was shown by VPC (silicone SE 30) to be a mixture of the starting alcohol (Ⅳ) and an oxidation product in the approximate ratio 6:5. Chromatography over silica gel (5 g.) and elution with light petroleum-benzene (1:1) followed by distillation under reduced pressure gave eudesma-4(14), 11-dien-3-one (Ⅴ) as a colorless oil, IR (CCl_4) cm^{-1} : 3053, 1642, 889 (vinylidene), 1690, 1613 (α-vinylidene-cyclohexanone), 1415 (methylene adjacent to carbonyl), NMR : singlet (3H) at 9.11 τ ($C\underline{H}_3$-C$\leqslant$), singlet (3H) at 8.23 τ ($C\underline{H}_3$-C=CH_2), singlet (2H) at 5.28 τ ($C\underline{H}_2$=C-CH_3), two triplets (1H each) at 5.02, 4.29 τ (J=1.7, $C\underline{H}_2$=C-CO-).

Dimerization and Dedimerization of Eudesma-4(14),11-dien-3-one——The unsaturated ketone (Ⅴ) on standing at room temperature was dimerized to deposite crystals which were crystallized from ether to give the dimer (Ⅵ) as colorless needles, m.p. 172~173°, MS (m/e) : 436 (M^+), IR (CCl_4) cm^{-1} : 3028, 1641, 891 (vinylidene), 1723 (cyclohexanone with α-oxygen substitution), 1676 (ethylene bond with oxygen on it), NMR : singlet (3H) at 9.21 τ ($C\underline{H}_3$-C$\leqslant$), singlet (3H) at 8.83 τ ($C\underline{H}_3$-C$\leqslant$), unresolved singlets (3H each) at 8.33, 8.26 τ ($C\underline{H}_3$-C=CH_2), unresolved band (4H) around 5.35 τ ($C\underline{H}_2$=C-CH_3).

The dimer (Ⅵ) (5 mg.) was heated at 160~165° under reduced pressure (2 mm. Hg) to distill the monomer, eudesma-4(14),11-dien-3-one (Ⅴ), as a colorless oil, identified by TLC (silica gel, benzene), VPC (silicone SE 30), and the IR spectrum.

Hydrogenation of Isocyperol over Adams' Catalyst in Methanol——Isocyperol (93 mg.) was hydrogenated in MeOH (8 ml.) over PtO_2 (45 mg.) at room temperature. After the consumption of about 2 moles of H_2, the catalyst was filtered off and the solution evaporated to give the product (90 mg.) which was chromatographed over silica gel (5 g.). Elution with light petroleum-benzene (1:1) yielded an oil (74 mg.) which on distillation under diminished pressure gave tetrahydroisocyperol, eudesman-3α-ol (Ⅶ) as a colorless oil, $[\alpha]_D$ +4.9° (c=4.1), *Anal.* Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found : C, 80.08; H, 12.44. IR (liquid) cm^{-1} : 3344 (hydroxyl). NMR : singlet (3H) at 9.14 τ ($C\underline{H}_3$-C$\leqslant$), doublet (9H) at 9.10 τ (J=6, $C\underline{H}_3$-CH$\langle$), single peak with fine splittings (1H) at 6.28 τ (band width at half height : 6 c.p.s., $\underline{H}$-C$\leqslant$OH).

Oxidation of Eudesman-3α-ol with Chromic Acid——To a stirred solution of the tetrahydroisocyperol (Ⅶ) (85 mg.) in ether (8 ml.) was added $Na_2Cr_2O_7 \cdot 2H_2O$ (83 mg.) in dil. H_2SO_4 (1:3, 1 ml.) and the stirring was continued for 7 hr. at room temperature. The product (58 mg.) was isolated by ether extraction and chromatographed on silica gel (5 g.). The eluate with light petroleum-benzene (1:1) was distilled under reduced pressure to yield eudesman-3-one (Ⅷ) as a colorless oil, $[\alpha]_D$ −11.3° (c=3.9), ORD (c=0.109, MeOH) : $[\alpha]_{306}^{peak}$ +590°, $[\alpha]_{259}^{trough}$ −940°, *Anal.* Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found : C, 80.88; H, 11.56. IR (liquid) cm^{-1} : 1712 (cyclohexanone), 1425 (methylene next to carbonyl). NMR : doublet (6H) at 9.12 τ (J=6, $(C\underline{H}_3)_2$-CH-), doublet (3H) at 8.98 τ (J=7, $C\underline{H}_3$-CH$\langle$), singlet (3H) at 8.94 τ ($C\underline{H}_3$-C$\leqslant$). NMR (C_6H_6) : singlet (3H) at 9.21 τ' ($C\underline{H}_3$-C$\leqslant$), doublet (6H) at 9.15 τ' (J=6, $C\underline{H}_3$-CH$\langle$), doublet (3H) at 9.07 τ' (J=6, $C\underline{H}_3$-CH$\langle$).

The 2,4-dinitrophenylhydrazone, prepared in the usual way ($NH_2NHC_6H_3(NO_2)_2$-H_2SO_4-EtOH), crystallized from AcOEt as orange needles, m.p. 148.5~150°, *Anal.* Calcd. for $C_{21}H_{30}O_4N_4$: 13.92. Found : N, 13.64.

Epimerization of Eudesman-3-one with Alkali——Eudesman-3-one (Ⅷ) (28 mg.) was refluxed with 1% ethanolic NaOH (1.0 ml.) under N_2 for 1.5 hr. The product (26 mg.) was isolated by ether extraction and distilled under reduced pressure to furnish 4β(H)-eudesman-3-one (Ⅸ) as a colorless oil, $[\alpha]_D$ −16.5°(c=3.9), ORD (c=0.118, MeOH) : $[\alpha]_{303}^{peak}$ +1210°, $[\alpha]_{260}^{trough}$ −2050°, *Anal.* Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found : C, 80.89; H, 11.62. IR (liquid) cm^{-1} : 1712 (cyclohexanone), 1425 (methylene adjacent to carbonyl). NMR : doublet (6H) at 9.11 τ (J=6, $C\underline{H}_3$-CH$\langle$), doublet (3H) at 9.08 τ (J=7, $C\underline{H}_3$-CH$\langle$), singlet (3H) at 8.95 τ ($C\underline{H}_3$-C$\leqslant$). The identity with the authentic sample, which was derived from α-cyperone (Ⅱ) by means of 4β(H)-eudesm-11-en-3-one (Ⅹ) (*vide infra*), was confirmed by identical behaviors on TLC (silica gel, benzene) and VPC (silicone SE 30) and by identical IR and NMR spectra.

Reduction of α-Cyperone with Lithium and Liquid Ammonia——α-Cyperone (II) was reduced with Li and liquid NH_3 by the known method[9] to give 4β(H)-eudesm-11-en-3-one (X) as a colorless oil, $[\alpha]_D$ −23.9° (c=4.4). IR (liquid) cm^{-1}: 3106, 1645, 886 (vinylidene), 1712 (cyclohexanone), 1427 (methylene adjacent to carbonyl). NMR: doublet (3H) at 9.07 τ (J=7, $C\underline{H}_3$-CH<), singlet (3H) at 8.91 τ ($C\underline{H}_3$-C≤), singlet (3H) at 8.29 τ ($C\underline{H}_3$-C=CH_2), singlet (2H) at 5.36 τ ($C\underline{H}_2$=C-CH_3).

Reduction of α-Cyperone with Sodium and Ethanol——To a refluxed solution of α-cyperone (II) (159 mg.) in EtOH (8 ml.), metallic Na (0.4 g.) was gradually added. The mixture was refluxed for 5 hr. and concentrated by distillation of the solvent. After addition of H_2O, the residue was extracted with ether. The product (160 mg.) was submitted to chromatography over silica gel (5 g.). Light petroleum-benzene (1:1) eluted an oil (94 mg.) which was distilled under reduced pressure to give 4β(H)-eudesm-11-en-3β-ol (XI) as a colorless oil, $[\alpha]_D$ +8.9°(c=4.5). IR (liquid) cm^{-1}: 3344 (hydroxyl), 3096, 1645, 886 (vinylidene). NMR: singlet (3H) at 9.14 τ ($C\underline{H}_3$-C≤), doublet (3H) at 9.11 τ (J=6, $C\underline{H}_3$-CH<), singlet (3H) at 8.27 τ ($C\underline{H}_3$-C=CH_2), broad peak (1H) at 7.07 τ (band width at half height: 19 c.p.s., $\underline{H}$-C≤OH), singlet (2H) at 5.38 τ (unresolved, $C\underline{H}_2$=C-CH_3).

Oxidation of 4β(H)-Eudesm-11-en-3β-ol with Chromic Acid——4β(H)-Eudesm-11-en-3β-ol (XI) (82 mg.) in ether (8 ml.) was stirred with $Na_2Cr_2O_7 \cdot 2H_2O$ (88 mg.) in dil. H_2SO_4 (1:3, 0.5 ml.) at room temperature for 3.5 hr. The mixture was worked up in the customary manner and the product (82 mg.) was chromatographed over silica gel (5 g.). Elution with light petroleum-benzene (1:1) afforded an oil (64 mg.) which on distillation under reduced pressure furnished 4β(H)-eudesm-11-en-3-one (X) as a colorless oil, $[\alpha]_D$ −18.4° (c=4.3). IR (liquid) cm^{-1}: 3106, 1645, 886 (vinylidene), 1712 (cyclohexanone), 1427 (methylene α to carbonyl), NMR: doublet (3H) at 9.07 τ (J=7, $C\underline{H}_3$-CH<), singlet (3H) at 8.91 τ ($C\underline{H}_3$-C≤), singlet (3H) at 8.29 τ ($C\underline{H}_3$-C=CH_2), singlet (2H) at 5.36 τ ($C\underline{H}_2$=C-CH_3). Identification with the authentic sample, obtained from α-cyperone (II) by reduction with Li and liquid NH_3 (*vide supra*), was performed by TLC (silica gel, benzene) and VPC (silicone SE 30) analyses and by IR and NMR comparison.

Hydrogenation of 4β(H)-Eudesm-11-en-3-one with Palladized Charcoal in Ethanol——4β(H)-eudesm-11-en-3-one (X) (98 mg.) was hydrogenated in EtOH (8 ml.) in the presence of Pd-C (10%, 100 mg.) at room temperature. Distillation of the product (92 mg.) gave 4β(H)-eudesman-3-one (IX) as a colorless oil, $[\alpha]_D$ −16.4°(c=4.2), *Anal.* Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.93; H, 11.71. IR (liquid) cm^{-1}: 1712 (cyclohexanone), 1425 (methylene next to carbonyl). NMR: doublet (6H) at 9.11 τ (J=6, $C\underline{H}_3$-CH<), doublet (3H) at 9.08 τ (J=7, $C\underline{H}_3$-CH<), singlet (3H) at 8.95 τ ($C\underline{H}_3$-C≤).

The 2,4-dinitrophenylhydrazone, prepared in the usual manner ($NH_2NHC_6H_3(NO_2)_2$-H_2SO_4-EtOH), crystallized from EtOH as orange needles, m.p. 155~155.5°, *Anal.* Calcd. for $C_{21}H_{30}O_4N_4$: N, 13.92. Found: N, 13.64.

Reduction of Eudesma-4(14),11-dien-3-one with Lithium Aluminum Hydride——Eudesma-4(14),11-dien-3-one (V) (18 mg.) was stirred with $LiAlH_4$ (12 mg.) in ether (5 ml.) at room temperature for 1 hr. After worked up in the usual way, the product (19 mg.) was distilled under reduced pressure to yield eudesma-4(14),11-dien-3β-ol (XII) as a colorless oil, $[\alpha]_D$ +34.8°(c=3.1). IR (CCl_4) cm^{-1}: 3630, 3450 (hydroxyl), 3090, 1644, 885 (vinylidene). NMR: singlet (3H) at 9.27 τ ($C\underline{H}_3$-C≤), singlet (3H) at 8.27 τ ($C\underline{H}_3$-C=CH_2), broad peak (1H) at 6.10 τ (band width at half height: 20 c.p.s., $\underline{H}$-C≤OH), single peak with fine splittings (2H) at 5.35 τ ($C\underline{H}_2$=C-CH_3), two singlets (1H each) at 5.44, 5.01 τ (unresolved, $C\underline{H}_2$=C<).

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