  Bull. Chem. Soc. Jpn., 55, 1195—1201 (1982)

Synthesis of β- and α-Rotunols. Revision of the Structure of a Stress Metabolite "1-Keto-α-cyperone"[1]

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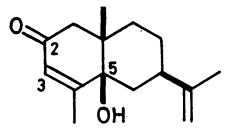
(Received September 11, 1981)

The synthesis of β- and α-rotunols, two sesquiterpene alcohols isolated from nutgrass (*Cyperus rotundus* Linne), is described. This synthetic study also involves revision of the structure of a stress metabolite "1-keto-α-cyperone" isolated from Burley and flue-cured tobaccos (*Nicotiana tabacum* L.).

The title sesquiterpene alcohols, β- and α-rotunols (**1**) and (**2**), were isolated from the crude drug "Ko-bushi," prepared from the dried rhizomes of nutgrass, *Cyperus rotundus* Linne (Cyperaceae) (Japanese name: Hamasuge) by Hikino and co-workers, and the structures were determined in 1969 on the basis of chemical and spectroscopic evidence.[2] In connection with studies on phytoalexins, we preliminarily reported that **1** has been synthesized from α-cyperone (**3**) and has played an important role as a key intermediate for the synthesis of phytuberin, one of the major phytoalexins of the genus *Solanum*.[3] We also found that the structure of a stress compound (**4**), isolated from Burley and flue-cured tobaccos and assigned a formula "1-keto-α-cyperone,"[4] should be represented by structure "2-keto-α-cyperone."[5] In the present paper we describe details of the synthesis of these sesquiterpenes **1**, **2**, and **4**.



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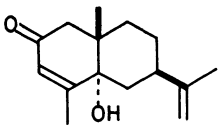

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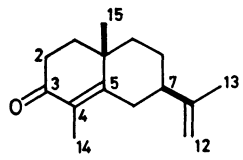

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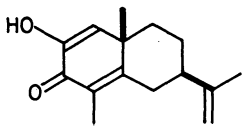

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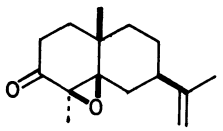

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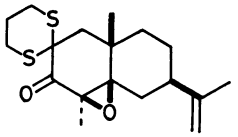

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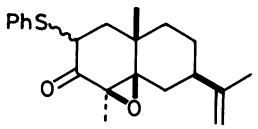

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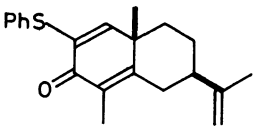

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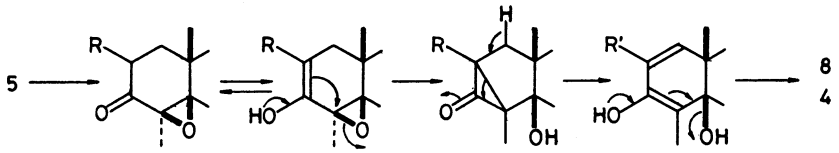
Results and Discussion

Revision of the Structure of a Stress Metabolite Named "1-Keto-α-cyperone." The synthesis of β-rotunol (**1**) from α-cyperone (**3**) required oxygenation at C-2 and C-5 as well as removal of the carbonyl group at C-3 of **3**. Thus compound **3** was first transformed into the 4β,5β-epoxy derivative[6] (**5**) in a three-step sequence [(i) reduction ($NaBH_4$ in MeOH), (ii) epoxidation (*t*-BuOOH and $VO(acac)_2$ in benzene), and (iii) oxidation (PCC in dichloromethane)] in 57% overall yield. However, attempted oxygenation reactions at C-2 of **5** under various conditions failed: namely, treatment of **5** with 1,3-propanedithiol di-*p*-toluenesulfonate and base in ethanol[7] gave a complex mixture, no expected dithiane derivative (**6**) being detected. Moreover, the epoxide (**5**), when treated with lithium diisopropylamide (LDA, 1.5 equiv.) in tetrahydrofuran (THF) and then with diphenyl disulfide[8] or benzenesulfenyl chloride, was not converted into the expected 2-phenylthio 3-ketone (**7**) and, instead, produced dienone (**8**) in 62% yield. The structure was assigned easily on the basis of the spectral data (see Experimental). Likewise, treatment of **5** with LDA (1.5 equiv.) in THF at −78 °C followed by addition of molybdenum peroxide $MoO_5 \cdot Py \cdot HMPA$ (MoOPH)[9] (1.5 equiv.) afforded 2-oxo-α-cyperone (**4**) in 75% yield. The structure of **4** was also based on the spectral data: MS, *m/e* 232 (M^+) and 189 (base); NMR, δ 1.28 (3H, s, 15-H), 1.82 (3H, s, 13-H), 1.99 (3H, s, 14-H), 4.84 (2H, s, 12-H), 6.07 (1H, s, 1-H), and 6.53 (1H, s, OH); IR (Nujol), 3400, 3120, 1660(sh), 1635, and 880 cm^{-1}. As expected, compound **8**, when treated with mercury(II) chloride in aqueous acetonitrile[10] under reflux, was converted into **4** in moderate yield (48%).

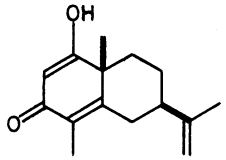
A plausible pathway for the formation of dienones **8** and **4** is depicted in Scheme 1: unstable 2-phenylthio and 2-oxomolybdenum cyclopropanone derivatives (**10** and **11**) would be formed by initial attack of the C-2 anion to the C-4 oxirane carbon, and subsequent ring cleavage caused by deprotonation at C-1 would produce the dienols (**12** and **13**), which underwent dehydration of the resultant β-hydroxy ketones to yield the dienone derivatives (**8** and **4**). This unexpected result indicated that a hydroxyl group or its equivalent would have to be introduced into C-5 after oxygenation at C-2 of α-cyperone.

Incidentally, the spectral data of the relevant 2-oxo-α-cyperone (**4**) were completely identical with those of a stress compound named "1-keto-α-cyperone," which had been isolated from Burley and flue-cured tobaccos (*Nicotiana tabacum*) by Roberts[4] in 1972 and assigned



10, R=SPh 12, R'=SPh
11, R=OMoO$_4$L$_2^-$ 13, R'=OH

Scheme 1.



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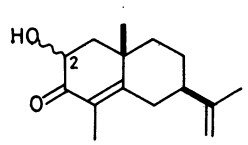
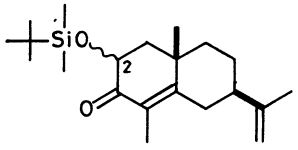
formula **9** shown by the name. It follows that this finding implies revision of the assigned structure of the stress metabolite.

Synthesis of β-Rotunol (1). Treatment of α-cyperone (**3**) with LDA (1.5 equiv.) in THF at −78 °C followed by addition of MoOPH effected oxygenation at C-2, giving a *ca.* 2 : 1 inseparable mixture (**14**) of 2β- and 2α-hydroxy-α-cyperones (**14a** and **14b**) in 62% yield, which were converted into the *t*-butyldimethylsilyl ethers (**15a** and **15b**) by treatment with *t*-butyldimethylsilyl chloride and imidazole in *N,N*-dimethylformamide.[11] The β- and α-configurations were assigned to the 2-hydroxyl groups of **14a** and **14b** on the basis of analogy of the contribution ($\Delta\delta$) of the 2-hydroxyl groups to the chemical shift of the 19-methyl protons of Δ^4-3-keto steroids in their NMR spectra:[12] δ_{obsd} 1.34 and 1.22 [total, 3H (2 : 1), each s, 15-H]; δ_{calcd} 1.32 and 1.22 for **14a** and **14b**. This assignment was confirmed by examination of the respective spectra of **14a** and **14b**, which were prepared alternatively as described later: specially, splitting patterns [**14a**, δ 4.21 (1H, dd, J=14 and 6 Hz); **14b**, δ 4.30 (1H, dd, J=12 and 6 Hz)] of the C-2 protons indicated that the A-ring of **14a** and **15a** would take a twist-boat conformation with the relevant functions at C-2 pseudo-equatorial and also with the 3- and 10-carbon atoms at bow-sprit and flag-pole positions, while that of **14b** and **15b** would adopt a half-chair form with the functions at C-2 pseudo-equatorial (Fig. 1). These conformations would probably result from hydrogen bonding between the 2-hydroxyl and 3-oxo groups in **14a** and **14b**, and from large bulkiness of the 2-alkylsilyloxyl group in **15a** and **15b**.

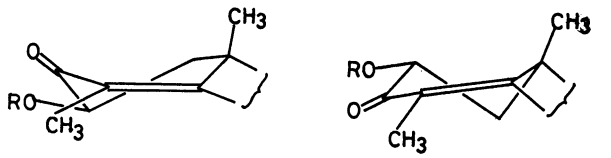


14a, 2α-H
14b, 2β-H



15a, 2α-H
15b, 2β-H

Treatment of the mixture of silyl ethers **15a** and **15b** with lithium tri-*s*-butylborohydride (L-selectride) (1 equiv.) in THF at −78 °C resulted in completely



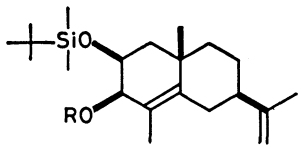
14a, R = H
15a, R = t-BuMe$_2$Si

14b, R = H
15b, R = t-BuMe$_2$Si

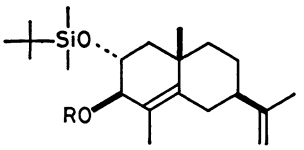
Fig. 1.

stereoselective reduction of only **15a**, giving 3β-alcohol (**16a**) in 55% yield with 29% yield of the unreacted ketone (**15b**). While reduction of the recovered one (**15b**) with sodium borohydride in methanol afforded a 3 : 1 mixture of 3β- and 3α-alcohols (**16b** and **16c**), treatment with lithium aluminium hydride (LAH) at −78 °C produced 3β-alcohol (**16b**) in 80% yield as a single product. The stereoselective formation of these 3β-alcohols (**16a** and **16b**) with the hydride reagents, specially with L-Selectride, clearly resulted from attack of the reagents to the 3-carbon atom from the less-hindered side. The resultant 3-alcohols were converted into the 3-acetates (**17a**, **17b**, and **17c**), whose NMR spectra [**17a**, δ 3.90 (1H, dt, J=10 and 4.5 Hz, 2-H) and 5.30 (1H, dd, J=4.5 and 2 Hz, 3-H); **17b**, δ 3.90 (1H, m, 2-H, and dd, J=10 and 4.5 Hz, on irradiation at 5.40) and 5.40 (1H, d, J=8 Hz, 3-H); **17c**, 3.90 (1H, dt, J=12 and 4 Hz, 2-H) and 5.28 (1H, d, J= 4 Hz, 3-H)] indicated that **17a** and **17b** would take twist-boat and half-chair conformations, respectively (Fig. 2). The conformation of **17a** was also supported by the long-range coupling (2 Hz) between the hydrogen atoms at C-1 and C-3. Then the 3β-alcohol (**16a**) was oxidized smoothly with activated manganese(IV) oxide[13] in dichloromethane to **15a** in pure state in 93% yield. Moreover, hydrolysis of **15a** and **15b** with acetic acid in aqueous THF[14] gave rise to **14a** and **14b** in pure state quantitatively, respectively.

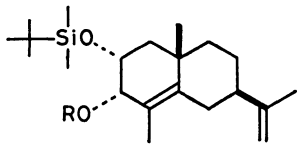
Introduction of a β-hydroxyl group into C-5 was carried out as follows. Epoxidation of 3β-alcohol **16a** with *t*-butyl hydroperoxide in the presence of bis-(acetylacetonato)oxovanadium(IV) [VO(acac)$_2$][15] in benzene produced 4β,5β-epoxy 3β-alcohol (**18a**), which was converted smoothly into the 3β-mesylate (**19a**) in 84% yield from **16a**: **19a**, δ 3.86 (1H, ddd, J=13, 5,



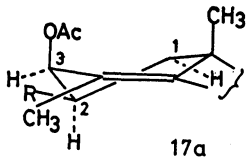
16a, R=H
17a, R=Ac



16b, R=H
17b, R=Ac

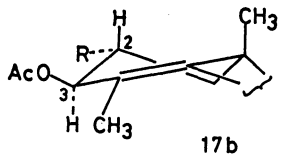


16c, R=H
17c, R=Ac



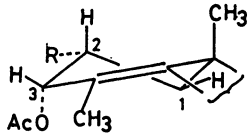
17a

J_{2-3} = 4.5 Hz
$J_{1\alpha-3}$ = 2 Hz



17b

J_{2-3} = 8 Hz

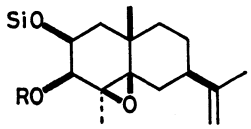


17c

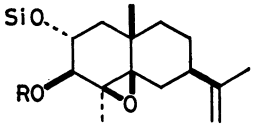
J_{2-3} = 4.5 Hz
$J_{1\beta-3}$ = 2 Hz

Fig. 2.

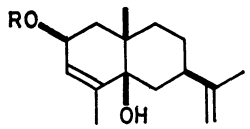
and 4 Hz, 2-H) and 4.85 (1H, dd, J=4, and 2 Hz, 3-H). These splitting patterns again indicated that compounds **18a** and **19a** would possess a twist-boat form with two β-substituents at C-2 and C-3 pseudo-equatorial and pseudo-axial, respectively. Reductive elimination of the epoxy mesylate (**19a**) with sodium in liquid ammonia and dry THF[16] afforded allyl alcohol (**20a**) in 95% yield, which was hydrolyzed in a 1 : 1 : 2 mixture of acetic acid, water, and THF to give Δ^3-2β,5β-glycol (**21a**) in 90% yield. Likewise, 3β-alcohol **16b**, an isomer of **16a**, was transformed into the corresponding Δ^3-2α,5β-glycol (**21b**) *via* the 4β,5β-epoxy 3β-alcohol (**18b**), the 3β-mesylate (**19b**), and the Δ^3-5β-alcohol (**20b**), in 50% yield from **16b**: **19b**, δ 4.01 (1H, ddd, J=10, 9, and 4 Hz, 2-H) and 4.68 (1H, d, J=9 Hz, 3-H). Oxidation of **21a** and **21b** with activated manganese(IV) oxide in dichloromethane produced the same α,β-unsaturated ketone, mp 117—119 °C, $[\alpha]_D$ +41.4° ($CHCl_3$), in 85 and 90% yields. The ketone was identified as β-rotunol (**1**), mp 118—119 °C, $[\alpha]_D$ +44.8° ($CHCl_3$), by comparison of the spectra of synthetic and natural samples. The overall yield amounted to 29.6% from (+)-α-cyperone (**3**). Since β-rotunol has been transformed into dehydrosolavetivone[2] (**22**) and then into solavetivone[17] (**23**), stress metabolites in diseased potatoes, by Hikino,[2] Anderson and co-workers,[17] respectively, the present synthesis of β-rotunol also constitutes, in a formal sence, the synthesis of the metabolites (**22**) and (**23**).



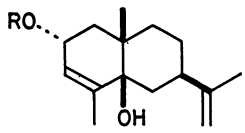
18a, R=H
19a, R=Ms



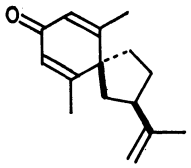
18b, R=H
19b, R=Ms



20a, R=t-BuMe$_2$Si
21a, R=H



20b, R=t-BuMe$_2$Si
21b, R=H



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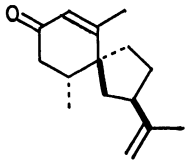

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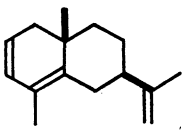
Synthesis of α-Rotunol (2). Treatment of α-cyperone (**3**) under the Shapiro conditions[18] effected reductive deoxygenation to give diene (**24**) in 73% yield, which on oxygenation with triplet oxygen in the presence of tungsten(VI) chloride in the dark at −78 °C[19] followed by treatment of the resulting peroxide (**25**) with alumina afforded α,β-unsaturated ketone, mp 102—104 °C, $[\alpha]_D$ +53°, in 88% yield. The ketone was identified as α-rotunol (**2**), mp 87.5—88.5 °C, by comparison of the spectra of synthetic and natural samples.



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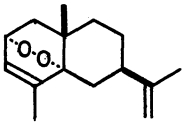

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Experimental

All the melting points were uncorrected. The homogeneity of each compound was always checked by TLC on silica gel (Wakogel B-5) with various solvent systems, the spots being developed with cerium(IV) sulfate in diluted sulfuric acid

and/or iodine. The optical rotations, UV and NMR (100 MHz) spectra were measured in chloroform, ethanol, and chloroform-*d* respectively, unless otherwise stated.

4β,5β-Epoxyeudesm-11-en-3-one (5). *i)*: To a solution of (+)-α-cyperone (100 mg) in methanol (5 ml) cooled at −50 °C was added sodium borohydride (55 mg) with stirring. After stirring for 1.5 h at −45——50 °C, the reaction was quenched by addition of acetic acid. The product was extracted with chloroform and the extracts were washed with saturated sodium hydrogencarbonate and saturated brine, dried, and evaporated to give eudesma-4,11-dien-3β-ol (95 mg) as a single product, oil; $[\alpha]_D$ +9.7°, (Ref.[6]) +10.9°); NMR, δ 4.05 (1H, br, t, W_H=15 Hz, 3α-H). The spectral data were identical with the reported data.[6]

ii): To a stirred solution of eudesma-4,11-dien-3β-ol (220 mg, 1 mmol) and $VO(acac)_2$ (4 mg, 0.014 mmol) in dry benzene (10 ml) was added dropwise *t*-butyl hydroperoxide (0.186 g, 1.5 mmol) under reflux, and the mixture was stirred under reflux for 10 min. The reaction mixture was poured into aqueous sodium hydrogensulfite. The organic layer was separated and the aqueous solution was extracted with ether. The benzene and ether solution were combined, washed with water, dried, and evaporated to leave an oil (300 mg), which was chromatographed over silica gel (9 g) with benzene–ether (5 : 1) to give 4β,5β-epoxyeudesm-11-en-3β-ol (203 mg), oil; $[\alpha]_D$ +57.6°; IR (neat), 3500, 3100, 1625, and 890 cm^{-1}; NMR, δ 1.08 (3H, s, 15-H), 1.40 (3H, s, 14-H), 1.76 (3H, s, 13-H), 3.80 (1H, br, W_H=7 Hz, 3α-H), and 4.74 (2H, s). The spectral data were identical with the corresponding reported data.[6]

iii): To a mixture of pyridinium chlorochromate (PCC, 323 mg, 1.5 mmol) in dry dichloromethane (5 ml) was added a solution of 4β,5β-epoxyeudesm-11-en-3β-ol (234 mg, 1 mmol) in dichloromethane (3 ml). The whole reaction mixture was stirred at room temperature for 2 h, diluted with dry ether (10 ml) and filtered. The filtrate was evaporated to leave an oil (230 mg), which was separated by chromatography over silica gel with benzene–ether (10 : 1). Fractions (180 mg) with high R_f value, showing a single spot on TLC, afforded **5**, oil; IR (neat), 3080, 1710, 1625, and 890 cm^{-1}; NMR, δ 1.20 (3H, s, 15-H), 1.42 (3H, s, 14-H), 1.76 (3H, s, 13-H), and 4.76 (2H, s). The spectral data were identical with the corresponding reported data.[6]

Attempted Phenylsulfenylation of 5. To a solution of diisopropylamine (0.066 ml, 0.48 mmol) in dry THF (1 ml) cooled at 0 °C was added dropwise a solution of butyllithium in hexane (0.272 ml, 0.48 mmol) under nitrogen, and the solution was stirred at 0 °C for 15 min. To the solution cooled at −78 °C was added a solution of **5** (75 mg, 0.32 mmol) in THF (2 ml). The reaction mixture, after being stirred at −78 °C for 50 min, was mixed with a solution of diphenyl disulfide (105 mg, 0.48 mmol) in dry THF (2 ml) at room temperature and stirred for 1 h at room temperature. The whole mixture was poured into ice–water, and extracted with chloroform. The chloroform solution was washed with water and saturated brine, dried, and evaporated to leave an oil (330 mg), which was separated by preparative TLC over silica gel with benzene–ether (5 : 1). Fractions (39 mg) with higher R_f value, showing a single spot on TLC, afforded the dienone derivative (**8**), gum; $[\alpha]_D$ −98.2°; MS, *m/e* 324; IR (neat), 1640, 1625, and 1065 cm^{-1}; NMR, δ 1.76 (3H, s, 13-H), 1.93 (3H, s, 14-H), 6.12 (1H, s, 1-H), and 7.08—7.56 (5H, br m, C_6H_5). Found: C, 77.70; H, 7.37%. Calcd for $C_{21}H_{24}OS$: C, 77.78; H, 7.41%. Fractions (28.5 mg) with lower R_f value afforded the unchanged starting material (**5**).

Attempted hydroxylation of 5. To a solution of LDA (*ca.* 0.64 mmol), prepared by treatment of diisopropylamine (0.0986 ml, 0.64 mmol) with butyllithium in hexane (0.37 ml, 0.64 mmol) in THF (5 ml) at 0 °C for 15 min, was added a solution of **5** (100 mg, 0.427 mmol) in THF (2 ml) at −78 °C under nitrogen. The reaction mixture, after being stirred at −78 °C for 1 h, was mixed with MoOPH (278 mg, 0.64 mmol) and stirred for 1 h at the same temperature and for 30 min at room temperature. After addition of water to quench the reaction, the mixture was concentrated *in vacuo*, and the residue was diluted with water and extracted with ether, repeatedly. The organic layers were washed with saturated sodium hydrogencarbonate, 2 M† hydrochloric acid, and water, dried, and evaporated to leave an oil (190 mg), which was separated by preparative TLC over silica gel with benzene. Fractions (37 mg) with higher R_f value, showing a single spot on TLC, afforded 2-oxo -α-cyperone (**4**), mp 76—77 °C; $[\alpha]_D$ −166°; UV_{max}, 259.5 nm (ε 18000); MS, IR, and NMR, in the text. Found: C, 77.63; H, 8.59%. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%. Fractions (49 mg) with lower R_f value afforded the unreacted starting material (**5**).

Hydrolysis of 8. A mixture of **8** (100 mg, 0.31 mmol) and mercury(II) chloride (251 mg, 0.93 mmol) in water (2 ml) and acetonitrile (8 ml) was stirred under reflux under nitrogen for 1 h. The resulting precipitates were removed by filtration through Celite and the filtrate was concentrated *in vacuo*, diluted with water, and extracted with chloroform, repeatedly. The chloroform solution was worked up as usual to leave an oil (86 mg), which was separated by preparative TLC with benzene. Fractions (32 mg) with higher R_f value afforded the unchanged starting material (**8**). Fractions (33 mg) with lower R_f value, showing a single spot on TLC, afforded 2-oxo-α-cyperone (**4**), mp 74—76 °C, $[\alpha]_D$ −171.0°, which was identical with the sample (**4**) described above in all respects.

*2-Hydroxy-α-cyperones (**14a** and **14b**).* To a solution of LDA (*ca.* 21 mmol), prepared by treatment of diisopropylamine (3.228 ml, 21 mmol) with butyllithium in hexane (11.58 ml, 21 mmol) in THF (30 ml) at 0 °C for 15 min, was added a solution of **3** (3.0 g, 13.8 mmol) in THF (20 ml) at −78 °C under nitrogen. After being stirred at −78 °C for 1 h, the mixture was mixed rapidly with MoOPH (9.12 g, 21 mmol), and stirred at −78 °C for 1.4 h and at room temperature for 30 min. After addition of water, the mixture was concentrated *in vacuo*, and the residue was diluted with water and extracted with ethyl acetate, repeatedly. The organic solutions were worked up as usual to leave an oil (3.2 g), which was chromatographed over silica gel (100 g) with benzene–ether (10 : 1). More mobile fractions (0.5 g) afforded **4**, and less mobile fractions (2.05 g) gave a 2 : 1 inseparable mixture (**14**) of 2β- and 2α-hydroxy-α-cyperones, (**14a** and **14b**), oil; MS, *m/e* 234 (M^+), 216, 190, 147, and 122; IR (neat), 3550, 3100, 1680 (br), 1615, and 890 cm^{-1}; NMR, δ 4.20 (0.67H, dd, *J*=14 and 6 Hz, 2α-H) and 4.28 (0.33H, dd, *J*=12 and 6 Hz, 2β-H).

*2-(t-Butyldimethylsilyloxy)-α-cyperones (**15a** and **15b**).* A mixture of **14** (250 mg, 1 mmol), imidazole (170 mg, 2.5 mmol), and *t*-butyldimethylsilyl chloride (180 mg, 1.2 mmol) in dry dimethylformamide (0.5 ml) was heated at 35—40 °C for 10 h with stirring under nitrogen. The reaction mixture was poured into ice–water and extracted with ether, repeatedly. The organic solutions were washed with water, dried, and evaporated to leave an oil (396 mg), which was chromatographed over silica gel (10 g) with benzene to give **15** (350 mg) as an 2 : 1 inseparable mixture (**15**) of 2β- and 2α-(*t*-butyldimethylsilyloxy)-α-cyperones (**15a** and **15b**), oil; MS, *m/e* 348 (M^+), 333 (base), and 291; IR (neat), 3080, 1695, 1650, 1620, and 895 cm^{-1}; NMR, δ 4.23 (0.67H, dd, *J*=10

† 1 M=1 mol dm^{-3}.

and 7 Hz, 2α-H), 4.35 (0.33H, dd, J=12 and 7 Hz, 2β-H).

*2α-(t-Butyldimethylsilyloxy)eudesma-4,11-dien-3-one (**15b**) and 2β-(t-butyldimethylsilyloxy)eudesma-4,11-dien-3β-ol (**16a**).* To a stirred solution of **15** (430 mg, 1.24 mmol) in THF (10 ml) was added L-Selectride (1 ml, 1.24 mmol) at −78 °C during 1 h under nitrogen. The solution was stirred at −78 °C for 1 h under nitrogen. After dropwise addition of water (1 ml) to decompose the reagent, the reaction mixture was stirred with 10% aqueous potassium hydroxide and 30% aqueous hydrogen peroxide at room temperature for 30 min and then treated with 5% aqueous sodium thiosulfate (10 ml) under cooling to decompose the hydrogen peroxide, and concentrated *in vacuo*. The residue was diluted with water and extracted with chloroform. The chloroform solution was worked up as usual to leave an oil (452 mg), which was chromatographed over silica gel (13 g) with benzene. Fractions (123 mg) with higher higher R_f value, showing a single spot on TLC, afforded **15b**, oil, $[\alpha]_D$ +50.0°; MS, *m/e* 348 (M^+), 333, and 291 (base); IR (neat), 3100, 1690, 1650, 1618, 1145, and 885 cm^{-1}; NMR, δ 0.09 (3H, s), 0.17 (3H, s), 0.92 [9H, s, $(CH_3)_3C$–], 1.31 (3H, s, 15-H), 1.78 (3H, s, 14-H), 1.80 (3H, s, 12-H), 4.34 (1H, dd, J=12 and 7 Hz, 2β-H), and 4.77 (2H, s). Found: C, 71.97; H, 10.33%. Calcd for $C_{21}H_{36}O_2Si$: C, 72.41; H, 10.34%. Fractions (236 mg) with lower R_f value, showing a single spot, afforded **16a**, mp 72—73 °C; $[\alpha]_D$ −79.4°; MS, *m/e* no M^+, 332, 293, 275, and 117; IR (neat), 3560, 3070, 1645, 1080, and 895 cm^{-1}; NMR, δ 0.09 (6H, s), 0.91 [9H, s, $(CH_3)_3C$–], 1.12 (3H, s, 15-H), 1.76 and 1.82 (each 3H, each s, 13- and 14-H), 3.76—3.86 (total 2H, m), and 4.74 (2H, s). Found: C, 71.99; H, 10.30%. Calcd for $C_{21}H_{38}O_2Si$: C, 72.00; H, 10.34%.

*Reduction of **15b** with Sodium Borohydride.* Compound **15b** (530 mg) was treated with sodium borohydride (200 mg) in methanol (10 ml) at −40—−50 °C for 1 h. After being quenched by addition of acetic acid, the reaction mixture was concentrated and extracted with ether. The ether solution was worked up as mentioned above to leave an oil (540 mg), showing two spots on TLC. The oil was separated into two fractions by column chromatography over silica gel (15 g) with benzene–hexane (1 : 1). Fractions (380 mg) with higher R_f value afforded **16b**, oil, $[\alpha]_D$ −9.4°; MS, *m/e* no M^+, 332 ($M^+ - H_2O$), 293 [$M^+ - C(CH_3)_3$], and 117; IR (neat), 3540 (br), 3090, 1645, 1090, and 885 cm^{-1}; NMR, 0.12 (6H, s), 0.92 [9H, s, $(CH_3)_3C$], 1.15 (3H, s, 15-H), 1.74 and 1.76 (each 3H, each s, 13- and 14-H), 3.72—4.04 (2H, m), and 4.74 (2H, s). Found: C, 71.88; H, 9.98%. Calcd for $C_{21}H_{38}O_2Si$: C, 72.00; H, 10.34%. Fractions (104 mg) with lower R_f value gave **16c**, oil; $[\alpha]_D$ +60.8°; MS, *m/e* no M^+, 332, 293, and 117; IR (neat), 3620, 3550 (br), 3110, 1650, 1080, 895, and 885 cm^{-1}; NMR, δ 0.11 (6H, s), 0.92 [9H, s, $C(CH_3)_3$], 1.10 (3H, s, 15-H). 1.76 and 1.82 (each 3H, each s, 13- and 14-H), 3.76—4.04 (2H, m), and 4.74 (2H, s). Found: C, 71.48; H, 10.71%. Calcd for $C_{21}H_{38}O_2Si$: C, 72.00, H, 10.34%.

*Reduction of **15a** with LAH.* To a stirred solution of **15b** (500 mg) in dry THF (30 ml) was added dropwise a suspension (2 ml) of LAH (100 mg) in dry THF (5 ml) at −78 °C during 5 min. The mixture was stirred at the same temperature for 20 min and, after addition of water (0.5 ml) and 1% aqueous potassium hydroxide (0.5 ml), was filtered. The filtrate was dried and evaporated to leave an oil (519 mg), which was chromatographed over silica gel (15 g) with benzene–hexane (2 : 3). Fractions (145 mg) with higher R_f value, showing a single spot on TLC, afforded the unreacted starting material (**15b**). Fractions (280 mg) with lower R_f value, showing a single spot on TLC, gave **16b** in pure state.

Compounds **16a**, **16b**, and **16c** were converted almost quantiatively into the respective monoacetates (**17a**, **17b**, and **17c**) by treatment with acetic anhydride and pyridine at room temperature, which had the following properties: **17a**, oil; $[\alpha]_D$ −135.8°; MS, *m/e* no M^+, 335, 332, and 117 (base); IR (neat), 3100, 1748, 1657, 1240, 1085, and 885 cm^{-1}; NMR, δ 0.08 (6H, s), 0.86 [9H, s, $C(CH_3)_3$], 1.13 (3H, s, 15-H), 1.68 and 1.76 (each 3H, each s, 13- and 14-H), 2.08 (3H, s, $OCOCH_3$), 3.90 (1H, dt, J=10 and 4.5 Hz, 2α-H), 4.74 (2H, s), and 5.30 (1H, dd, J=4.5 and 2 Hz, 3α-H): **17b**, mp 102—104 °C (from ether); $[\alpha]_D$ −45.6°; MS, *m/e* no M^+, 335, 332, and 117 (base); IR (Nujol), 3100, 1743, 1642, 1240, 1080 and 880 cm^{-1}; NMR, δ 0.04 (6H, s), 0.84 [9H, s, $C(CH_3)_3$], 1.12 (3H, s, 15-H), 1.51 and 1.72 (each 3H, each s, 13- and 14-H), 2.06 (3H, s, $OCOCH_3$), 3.76—4.04 (1H, m, and dd, J=10 and 4.5 Hz on irradiation at 5.40, 2β-H), 4.69 (2H, s), and 5.40 (1H, d, J=8 Hz, 3α-H): **17c**, oil; $[\alpha]_D$ +95.2°; MS, *m/e* no M^+, 335, 332, and 117 (base); IR (neat), 3100, 1743, 1657, 1243, 1110, and 890 cm^{-1}; NMR, δ 0.06 (3H, s), 0.10 (3H, s), 0.88 [9H, s, $C(CH_3)_3$], 1.12 (3H, s, 15-H), 1.63 and 1.74 (each 3H, each s, 13- and 14-H), 2.06 (3H, s, $OCOCH_3$), 3.90 (1H, dt, J=12 and 4 Hz, 2μ-H), 4.72 (2H, s), and 5.28 (1H, dd, J=4 and 2 Hz, 3β-H).

*Transformation of **15b** and **16a** into **14a** and **14b**.* Compound **15b** (150 mg) was stirred with acetic acid (1 ml) in water (1 ml) and THF (1.5 ml) at room temperature for 16 h under nitrogen. The mixture was worked up as usual to leave an oily residue (159 mg), showing a single spot on TLC, which was purified by preparative TLC over silica gel with benzene–ether (10 : 1) to yield **14b** in pure state (92 mg), oil; $[\alpha]_D$ +99.1°; MS, *m/e* 234 (M^+), 216, 190 (base), 147, and 122; IR (neat), 3550, 3100, 1676, 1658, 1615, and 890 cm^{-1}; NMR, δ 1.33 (3H, s, 15-H), 1.77 and 1.83 (each 3H, each s, 13- and 14-H), 4.30 (1H, dd, J=12 and 6 Hz, 2β-H), and 4.78 (2H, s). Found: C, 76.91; H, 9.38%. Calcd for $C_{15}H_{22}O_2$: C, 76.92; H, 9.40%.

Compound **16a** (110 mg) was stirred with activated manganese(IV) oxide (500 mg) in dry dichloromethane (10 ml) at room temperature for 24 h. The mixture was worked up as usual to leave an oily residue (120 mg), showing a single spot on TLC, which was purified by preparative TLC over silica gel with benzene to give **15a** (102 mg), oil; $[\alpha]_D$ −162.6°; MS, *m/e* 348 (M^+), 333, and 291; IR (neat), 3100, 1695, 1655, 1620, 1170, and 895 cm^{-1}; NMR, δ 0.10 (3H, s), 0.14 (3H, s), 0.91 (9H, s), 1.77 and 1.80 (each 3H, each s, 13- and 14-H), 1.25 (3H, s, 15-H), 4.22 (1H, dd, J=7 and 10 Hz, 2-H), and 4.79 (2H, s). Found: C, 72.77; H, 10.23%. Calcd for $C_{21}H_{36}O_2Si$: C, 72.41; H, 10.34%.

Compound **15a** (50 mg) was stirred with acetic acid (1 ml) in water (1 ml) and THF (1.5 ml) at room temperature for 16 h under nitrogen. The mixture was worked up as usual to leave an oily residue (61 mg), showing a single spot, which was purified by preparative TLC over silica gel to yield **14a** (43 mg), oil; $[\alpha]_D$ −217.8°; MS, *m/e* 234 (M^+), 216, 190, 147, and 122; IR (neat), 3550, 3105, 1690, 1657 (sh), 1622, and 895 cm^{-1}; NMR, δ 1.23 (3H, s, 15-H), 1.75 and 1.83 (each 3H, each s, 13- and 14-H), 4.21 (1H, dd, J=14 and 6 Hz, 2α-H), 4.76 (2H, s). Found: C, 76.85; H, 9.38%. Calcd for $C_{15}H_{22}O_2$: C, 76.92; H, 9.40%.

*2β-(t-Butyldimethylsilyloxy)-4β,5β-epoxyeudesm-11-en-3β-ol (**18a**) and Its 2α-Epimer (**18b**).* *i)*: To a refluxing green-colored solution of **16a** (1.1 g) in dry benzene (30 ml) containing $VO(acac)_2$ (20 mg) was added rapidly *t*-butyl hydroperoxide (72%, 2 ml), when the solution became red-colored. The solution was further refluxed for 10 min and cooled. The resulting yellow mixture was washed with saturated aqueous sodium thiosulfate, 5% aqueous sodium hydrogencarbonate and water, dried, and evaporated to

leave an oil (1.22 g), showing a single spot on TLC, which was purified by column chromatography over neutral alumina (1 g) with benzene to give **18a** (1.0 g), unstable oil; $[\alpha]_D$ −14.3°; MS, *m/e* 366 (M^+), 351, 291, 217, and 131; IR (neat), 3520, 3060, 1640, 1075, and 900 cm^{-1}; NMR, δ 0.09 (3H, s), 0.11 (3H, s), 0.92 [9H, s, $C(CH_3)_3$], 1.12 (3H, s, 15-H), 1.48 (3H, s, 14-H), 1.76 (3H, s, 13-H), 3.52—3.86 (2H, m, 2α- and 3α-H), and 4.72 (2H, s).

ii): A solution of **16b** (360 mg) in benzene (15 ml) was refluxed with *t*-butyl hydroperoxide (0.6 ml) in the presence of $VO(acac)_2$ (6 mg) for 15 min. The reaction mixture was worked up in the same manner as that of **16a** to leave an oil (405 mg), showing a single spot on TLC, which was purified by column chromatography over neutral alumina (500 mg) with benzene to give **18b** (340 mg), unstable oil; $[\alpha]_D$ −14.2°; MS, *m/e* 366 (M^+), 351, 291, 217, and 131; IR (neat), 3510, 3100, 1651, 1100, 1075, and 895 cm^{-1}; NMR, δ 0.09 (3H, s), 0.11 (3H, s), 0.92 [9H, s, $C(CH_3)_3$], 1.11 (3H, s, 15-H), 1.50 (3H, s, 14-H), 1.75 (3H, s, 13-H), 3.52—3.86 (2H, m), 4.74 (2H, s).

2β-(t-Butyldimethylsilyloxy)-4β,5β-epoxyeudesm-11-ene-3β-ol Mesylate (19a) and Its 2α-Epimer (19b). *i)*: To a solution of **18a** (270 mg) in dry pyridine (1.5 ml) was added methanesulfonyl chloride (0.15 ml). The reaction mixture was stirred at room temperature for 2 h, and then poured into ice–water and extracted with chloroform, repeatedly. The chloroform solution was worked up as usual to leave an oil (320 mg), showing a single spot on TLC, which was purified by chromatography over silica gel (4 g) with benzene to give **19a** (292 mg), solid, $[\alpha]_D$ −28.0°; MS, *m/e* no M^+, 387 [$(M^+ - C(CH_3)_3$], 349, and 313; IR (neat), 3080, 1640, 1180, 1100, and 875 cm^{-1}; NMR, δ 0.12 (6H, s), 0.90 [9H, s, $C(CH_3)_3$], 1.12 (3H, s, 15-H), 1.50 (3H, s, 14-H), 1.72 (3H, s, 13-H), 3.12 (3H, s, OSO_2CH_3), 3.86 (1H, ddd, J=13, 5, and 4 Hz, 2α-H), 4.72 (2H, s), and 4.85 (1H, dd, J=4 and 2 Hz, 3α-H). Found: C, 59.80; H, 9.39%. Calcd for $C_{22}H_{40}O_5SSi$: C, 59.46; H, 9.01%.

ii): A mixture of **18b** (1.1 g) and methanesulfonyl chloride (0.61 ml) in dry pyridine (6.1 ml) was stirred at room temperature for 3 h. The reaction mixture was worked up in the same manner as that of **18a** to leave crude crystals (1.4 g). showing a single spot on TLC, which were purified by simple column chromatography over silica gel (10 g) with benzene to yield **19b** (1.09 g), mp 105—107 °C (from ether–hexane); $[\alpha]_D$ −38.8°; MS, *m/e* no M^+, 387, 349, and 313; IR (Nujol), 3090, 1655, 1090, 1075, and 895 cm^{-1}; NMR, δ 0.09 (6H, s), 0.89 [9H, s, $C(CH_3)_3$], 1.12 (3H, s, 15-H], 1.49 (3H, s, 14-H), 1.73 (3H, s, 13-H), 4.05 (1H, ddd, J=10, 9, and 4 Hz, 2β-H), 4.68 (1H, d, J=9 Hz, 3α-H), and 4.73 (2H, s). Found: C, 59.91; H, 9.19%. Calcd for $C_{22}H_{40}O_5SSi$: C, 59.46; H, 9.01%.

2β-(t-Butyldimethylsilyloxy)eudesma-3,11-dien-5β-ol (20a) and Its 2α-Epimer (20b). *i)*: To a mixture of **19a** (200 mg) in ammonia (10 ml) and dry THF (4 ml) was added sodium (40 mg, 4-fold excess) at −50 °C (bath temp), when the blue color appeared. The reaction mixture was stirred for 5 min, and then ammonium chloride was added until the blue color disappered. After removal of ammonia and THF, the residue was diluted with cold-water and extracted with chloroform. The chloroform solution was worked up as usual to leave an oil (171 mg), showing a single spot on TLC, which was purified by simple column chromatography over silica gel (2 g) with chloroform to give **20a** (140 mg), oil; $[\alpha]_D$ +9.0°; MS, *m/e* 350 (M^+), 332, 293, and 131; IR (neat), 3450, 3060, 1637, 1060, and 880 cm^{-1}; NMR, δ 0.08 (6H, s), 0.90 [9H, s, $C(CH_3)_3$], 1.02, 1.70, and 1.72 (each 3H, each s, 15-, 13-, and 14-H), 4.30 (1H, br m, 2α-H), 4.65 (2H, s), and 5.44 (1H, br, W_H=6 Hz, 3-H). Found: C, 72.33; H, 10.93%. Calcd for $C_{21}H_{38}O_2Si$: C, 72.00; H, 10.86%.

ii): Compound **19b** (72 mg) was reduced under the same Birch conditions (sodium, 15 mg, THF, 3 ml, and ammonia, 8 ml) as described above to give **20b** (45 mg), oil; $[\alpha]_D$ +71.7°; MS, *m/e* 350 (M^+), 332, 293, and 131; IR (neat), 3500, 3095, 1650, 1055, and 890 cm^{-1}; NMR, δ 0.08 (6H, s), 0.91 [9H, s, $C(CH_3)_3$], 1.05, 1.76, and 1.78 (each 3H, each s, 15-, 13-, and 14-H), 4.18 (1H, br, W_H=12 Hz, 2β-H), 4.76 (2H, s), and 5.56 (1H, br, W_H=12 Hz, 3-H). Found: C, 72.29; H, 11.24%. Calcd for $C_{21}H_{38}O_2Si$: C, 72.00; H, 10.86%.

Eudesma-3,11-diene-2β,5β-diol (21a) and Its 2α-Epimer (21b). *i)*: Compound **20a** (150 mg) was stirred with acetic acid (1 ml) in water (1 ml) and THF (2 ml) at room temperature for 16 h. The mixture was worked up as usual to leave crude crystals (120 mg), showing a single spot on TLC, which were purified by preparative TLC over silica gel with etheyl acetate–hexane (3 : 1) to give **21a** (90 mg), mp 170—171 °C (from ether); $[\alpha]_D$ +48.3°; MS, *m/e* 236 (M^+), 218, and 200; IR (Nujol), 3500, 1635, and 885 cm^{-1}; δ 1.24, 1.70, and 1.76 (each 3H, each s, 15-, 13-, and 14-H), 4.18 (1H, br dd, J=10 and 6 Hz, 2α-H), 4.68 (2H, s), and 5.52 (1H, br s, W_H=5 Hz, 3-H). Found: C, 75.93; H, 10.16%. Calcd for $C_{15}H_{24}O_2$: C, 76.27; H, 10.17%.

ii): Compound **29b** (50 mg) was stirred with acetic acid (0.5 ml) in water (0.5 ml) and THF (1 ml) at room temperature for 19 h. The mixture was worked up as uaual to leave a gum (45 mg), showing a single spot on TLC, which was purified by preparative TLC over silica gel with ethyl acetate–hexane (3 : 1) to give **21b** (27 mg), gum, $[\alpha]_D$ +108.4°; MS, *m/e* 236 (M^+), 218, and 200; IR (neat), 3450 (br), 3110, 1650, and 890 cm^{-1}; NMR, δ 1.07, 1.75, and 1.83 (each 3H, each s, 15-, 13-, and 14-H), 4.30 (1H, br, W_H=16 Hz, 2β-H), 4.76 (2H, s), and 5.72 (1H, br, W_H=7.5 Hz, 3-H). Found: C, 75.81; H, 10.21%. Calcd for $C_{15}H_{24}O_2$: C, 76.27; H, 10.17%.

Conversion of 21a and 21b into (+)-β-Rotunol (1). *i)*: Compound **21a** (1 g) was stirred with activated mangnanese(IV) oxide (4.8 g) in dry dichloromethane (85 ml) at room temperature for 16 h. The reaction mixture was filtered through a Celite column. The filtrate was evaporated to leave crude crystals (1.1 g), showing a single spot on TLC, which were purified by preparative TLC with ethyl acetate–hexane (1 : 2) to give **1** (844 mg), mp 117—119 °C (needles from ether); $[\alpha]_D$ +41.4°; MS, *m/e* 234 (M^+), 216, 173, and 111; IR (Nujol), 3450, 3090, 1625 (sh), and 890 cm^{-1}; NMR, δ 1.15, 1.75, and 2.00 (each 3H, each s, 15-, 13-, and 14-H), 2.08 and 2.72 (each 1H, ABq, J=17 Hz, 1-H), 4.74 (2H, s), and 5.88 (1H, br s, W_H=4 Hz, 3-H).

ii): Compound **21b** (35 mg) was stirred with activated manganese(IV) oxide (300 mg) in dry dichloromethane (5 ml) at room temperature for 16 h. The reaction mixture was worked up in the same manner as that of **21a** to give **1** (29 mg), mp 116—118 °C (needles from ether), whose spectral data ($[\alpha]_D$, MS, IR, NMR) were identical with those obtained from **21a**. These synthetic samples of β-rotunol (**1**) were completely identical with a sample of the natural compound in the spectral data: natural sample, mp 118—119 °C (needles); $[\alpha]_D$ +44.8° ($CHCl_3$); MS, *m/e* 234, 216, 173, and 111; IR (Nujol), 3450, 3100, 1640, and 890 cm^{-1}; NMR, δ 1.15 (3H, s, 15-H), 1.74 (3H, t, J=1 Hz, 13-H), 1.99 (3H, d, J=1 Hz, 14-H), 2.07 and 2.71 (each 1H, ABq, J=17 Hz, 1-H), 4.75 (2H, q, J=1 Hz, 12-H), and 5.89 (1H, q, J=1 Hz, 3-H).

Eudesma-2,4,11-triene (24). A solution of **3** (248 mg, 1 mmol) in THF (5 ml) containing tosylhydrazine (186 mg, 1 mmol) and concd hydrochloric acid (one drop) was heated under reflux for 7 h. After addition of benzene (10 ml), the mixture was evaporated to remove THF, until the boiling

point became 80 °C, and cooled with an ice-bath. To the benzene solution was added methyllithium [0.7 M in ether (3.2 ml), 2.24 mmol], when nitrogen gas was evolved. The reaction was continued by stirring at room temperature for 30 min and ceased by addition of water. The whole mixture was extracted with hexane (3×20 ml), washed with water, dried, and evaporated to leave oily residue (260 mg), which was purified by column chromatography over silica gel with hexane–ethyl acetate (9 : 1) to give **24** (170 mg), oil; $[\alpha]_D$ +170.2°; MS, *m/e* 202 (M^+), 187, and 131 (base); UV_{max}, 266 nm (log ε 3.79) and 208 (3.78); IR (neat), 3100, 3050, 1650, 1590, 890, and 720 cm^{-1}; NMR, δ 0.93 and 1.71 (each 3H, s, 15- and 13-H), 1.76 (3H, t, J=2, 14-H), 4.72 (2H, s, 12-H), and 5.67 (2H, s, 2- and 3-H). Found: C, 88.89; H, 10.88%. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96%.

*Transformation of **24** into α-Rotunol (**2**).* To a solution of **24** (50 mg, 0.216 mmol) in dichloromethane (25 ml) cooled at −78 °C was added rapidly tungsten(VI) chloride (17 mg, 0.043 mmol) under nitrogen. Into the mixture was passed oxygen gas under vigorous stirring in the dark for 2 h. The reaction mixture was then kept at room temperature for 10 min, mixed with water, and extracted with ether (3× 20 ml). The ether solution was washed, dried and evaporated to leave oily crude peroxide (**25**), (64 mg), which without further purification was treated with alumina (Merck, activ basisch, Type E, Activitätsstufe I, 1.6 g) in ether at room temperature for 16 h. The mixture was filtered and the insoluble alumina was washed with ether repeatedly. The combined ether solutions were dried and evaporated to give crude **2** (60 mg), which was purified by preparative TLC over silica gel with hexane–ethyl acetate (3 : 1) to afford **2** (51 mg) in pure state, mp 102—104 °C (from ethyl acetate–hexane); $[\alpha]_D$ +53°; UV_{max} 235 nm (log ε 4.20); IR ($CHCl_3$), 3480, 3100, 1660, 1630 (sh), and 890 cm^{-1}; NMR, δ 1.04 and 1.77 (each 3H, each s, 15- and 13-H), 1.96 (3H, d, J=11 Hz, 14-H), 2.72 (1H, d, J=17 Hz, 1-H), 4.77 (2H, s, 12-H), and 5.81 (1H, s, 3-H).

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