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SYNTHESIS AND ABSOLUTE CONFIGURATION OF BOTH THE ENANTIOMERS OF LINEATIN

THE PHEROMONE OF *TRYPODENDRON LINEATUM*†

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Abstract—A new synthesis of (±)-, (+)- and (−)-lineatin (3,3,7 - trimethyl - 2,9 - dioxatricyclo[3.3.1.0^{4,7}]nonane) **1** was achieved. The stereochemistry of (+)-lineatin was established as (1*R*, 4*S*, 5*R*, 7*R*) by an X-ray crystallographic analysis of an intermediate **15**.

The striped ambrosia beetle, *Trypodendron lineatum* Olivier, is an important pest to forests both in Europe and in North America by boring tunnels into the sapwood of a number of coniferous species. The females initiate the attack and produce frass containing a pheromone named lineatin which is attractive to both sexes.[1] The structure of lineatin was first proposed by MacConnell *et al.* to be one of the two isomeric tricyclic acetals, **1** or **2**, without assignment of the absolute configuration.[2] An unambiguous synthesis of both (±)-**1** and (±)-**2** enabled us to compare the spectral data of these two racemates[3] with those of the natural pheromone published in the literature,[2] thus establishing the correct structure of lineatin to be **1**.[3]§ Almost simultaneously Borden *et al.* came to the same conclusion by synthesizing (±)-**1** in microgram-quantities whose pheromone activity was confirmed by field tests.[5] The absolute configuration of lineatin **1**, however, remained ambiguous in spite of the two low-yield syntheses of (+)- and (−)-**1** by the optical resolution of the intermediates.[6,7] Here we describe in detail a new and more efficient synthesis of (±)-, (+)- and (−)-lineatin together with the result of a single-crystal X-ray analysis of an optically active intermediate **15**. This crystallographic analysis enables us to assign (1*R*, 4*S*, 5*R*, 7*R*)-stereochemistry to (+)-lineatin **1**,[8] the bioactive enantiomer.[9] The present stereochemical assignment suggests a close biogenetical relationship between (+)-lineatin **1** and (+)-grandisol **3**, the boll weevil pheromone.

Our retrosynthetic analysis is shown in Fig. 1. A hydroxy lactone **A** seems to be an ideal candidate for optical resolution. A hydroxy ketone **B**, which serves as the precursor of **A**, should be obtainable from a cyclobutanone **C** by aldol condensation with acetone. The symmetrical cyclobutanone **C** is to be synthesized by the cycloaddition of dichloroketene **D** to isoprene **E**. With this strategy we can avoid the use of photocycloaddition as the key reaction to construct the cyclobutane ring. Our experience in the previous lineatin synthesis[3,6] demanded this, because the photo-reaction was not adequate for a large-scale preparation of the starting material.

Synthesis of racemic lineatin

The synthesis of (±)-lineatin was executed as shown in Fig. 2. Dehalogenation of Cl_3CCOCl with Zn–Cu couple in the presence of isoprene **5** and $POCl_3$ according to Hassner's general procedure[10] resulted in the smooth cycloaddition of dichloroketene **4** to **5** to give an unstable mixture of **6** and **7**, in which the desired isomer **6** was predominating (3.3:1) as judged by its GLC and NMR analyses. A major peak due to CH_3 of **6** (δ 1.44) and a minor peak due to that of **7** (δ 1.90) were observed in the NMR spectrum of the mixture. This desirable regioselectivity was not unexpected in view of the reported regioselectivity (**ii**:**iii** = 1.5:1 ~ 7:3) in the case of the cycloaddition of diphenylketene **i** to isoprene **5**.[11,12] The mixture of chloroketones **6** and **7** was immediately reduced with Zn–AcOH to give a mixture of cyclobutanones **8** and **9**. It was separable by spinning-band distillation affording the desired ketone **8** in 39% yield from Cl_3CCOCl. The isomer **9** was also obtained pure in 15% yield from Cl_3CCOCl.¶ Aldol condensation between a carbanion derived from **8** and acetone at −74° yielded, when quenched at −74°, an aldol product **10** as a crude stereoisomeric mixture. A dehydrated α,β-unsaturated ketone **iv** was also generated, if the reaction temp was allowed to raise to room temp before quenching. Although the hydroxy ketone **10** was obtained as a 1:1 mixture of the *cis*- and *trans*-isomers as revealed by GLC analysis, no effort was made to separate them because the separation at a later stage (e.g. a mixture of

†Pheromone Synthesis-57. Dedicated to the memory of the late Prof. F. Šorm in admiration of his works on isoprenoids and juvenile hormones. This work was presented by K. M. as a part of his lecture at Rattanakosin Bicentennial Seminar on Chemistry of Natural Products, Bangkok (Aug. 1982). Part 56, S. Senda and K. Mori, *Agric. Biol. Chem.* in press.

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§The ^{1}H-NMR spectrum of (±)-**1** at 100 MHz was distinctly different from that of (±)-**2**, although MacKay *et al.* recently reported that the ^{1}H-NMR spectral data at 100 MHz was not sufficient evidence to differentiate **1** and **2**.[4]

¶Utilization of the isomer **9** for another synthetic project will be reported in due course.

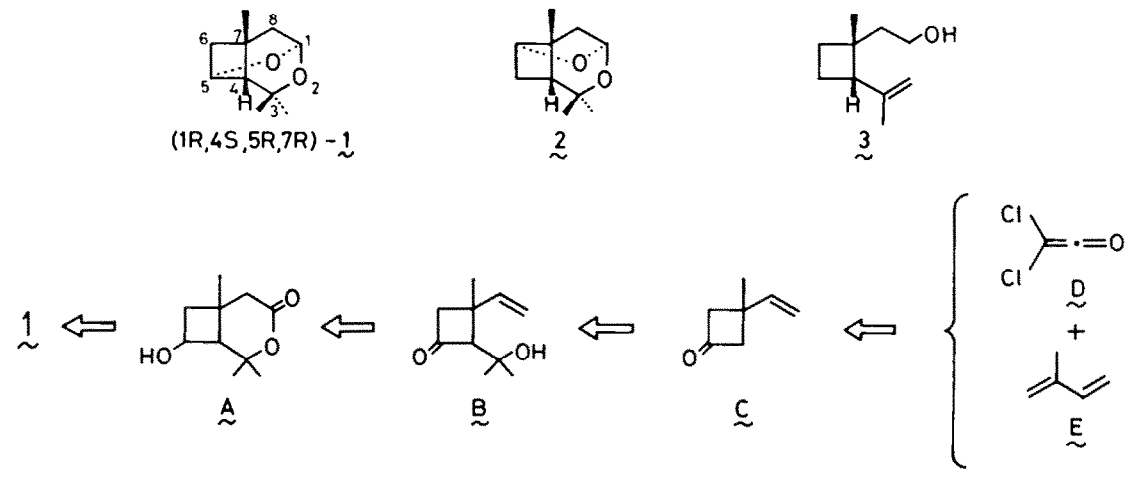

Fig. 1. Retrosynthetic analysis of lineatin.

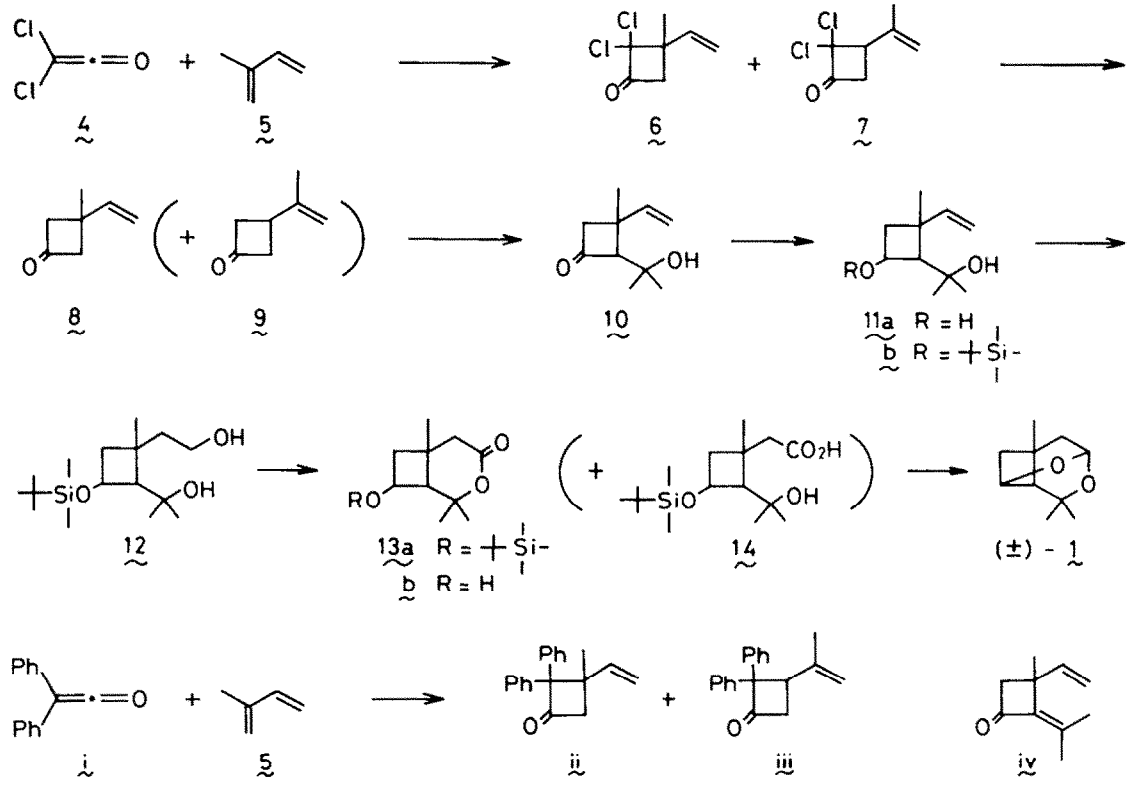

Fig. 2. Synthesis of racemic lineatin.

13a and **14**) seemed easier. Reduction of **10** with Li(sec-Bu)$_3$BH gave **11a** as a crude isomeric mixture. This particular reducing agent was chosen because we found previously that it preponderantly yields a more hindered cyclobutanol.[6] The newly generated OH group was protected by treating **11a** with t-BuMe$_2$SiCl and imidazole in DMF to give **11b** in 56% yield from **8**. Hydroboration–oxidation of **11b** proceeded smoothly to give **12** as a stereoisomeric mixture in 93% yield. This was oxidized with pyridinium dichromate (PDC)[13] in CH_2Cl_2 to afford a mixture of a lactone **13a** and an acid **14**. Separation of the mixture by silica gel chromatography was readily accomplished to give crystalline **13a** in 53% yield and crystalline **14** in 15% yield.† Removal of the silyl protective group of **13a** with (n-Bu)$_4$NF yielded the key hydroxy lactone **13b** as crystals in 76% yield. Reduction of **13b** with (iso-Bu)$_2$AlH (DIBALH) was followed by acidification with dil HCl to give (±)-lineatin **1** in 47% yield after distillation.‡ The over-all yield of (±)-lineatin **1** from Cl_3CCOCl by this nine-step synthesis was 3.8%.

†The reason was unclear for the modest isolated yield of **14** compared with that of **13a**. It might have been strongly adsorbed on the silica gel.

‡Due to the extreme volatility of **1**, concentration of its solution or its purification by distillation always caused a considerable loss of the material.

This was a remarkable improvement which enabled us to prepare gram-quantities of (±)-lineatin for field tests.

Synthesis of both the enantiomers of lineatin

In order to synthesize both the enantiomers of lineatin, we turned our attention to the optical resolution of the racemic hydroxy lactone **13b** as shown in Fig. 3. For this purpose we employed a resolving agent recently described by Martel *et al.*, (1*R*, 4*R*, 5*S*) - (+) - 4 - hydroxy - 6,6 - dimethyl - 3 - oxabicyclo[3.1.0]hexan - 2 - one v.[14] This is readily obtainable from commercially available (1*R*, 3*R*)-(+)-chrysanthemic acid vi, the acid component of pyrethroid insecticides.[14c,15] Remarkable success was reported in resolving various alcohols including allethrolone[14] and 4-hydroxy-3-cyclopenten-1-one[16] by using this resolving agent. The racemic hydroxy lactone **13b** was treated with v in the presence of TsOH to give a mixture of diastereomeric ethers **15** and **16**. This was separated by medium pressure liquid chromatography to give a less polar crystalline ether **15** followed by a more polar crystalline ether **16**, both in 87.6% yield.

The structure of the less polar diastereomer was determined as **15** by its single-crystal X-ray analysis (see Experimental). The structure was solved by MULTAN 78[17] with final agreement values of $R = 0.035$ and $R_w = 0.045$. The ORTEP computer drawing of **15** is shown in Fig. 4. The absolute configuration shown in Fig. 4 is based on the known absolute configuration of the resolving agent v.

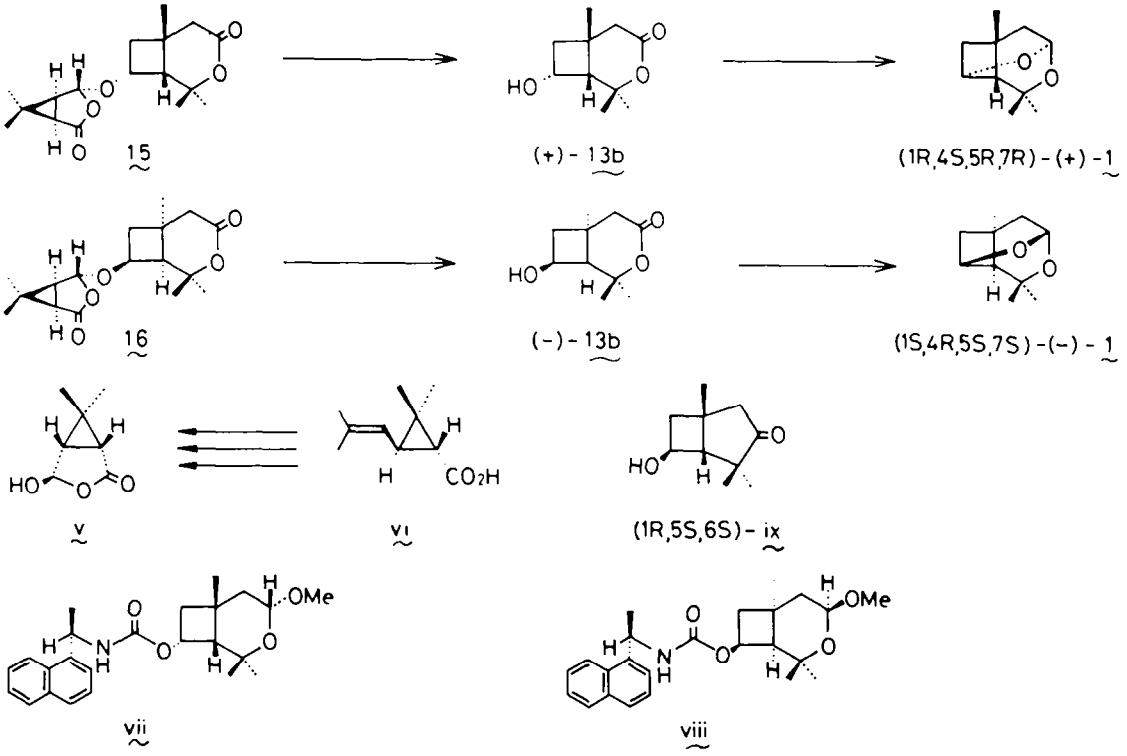

Fig. 3. Synthesis of lineatin enantiomers.

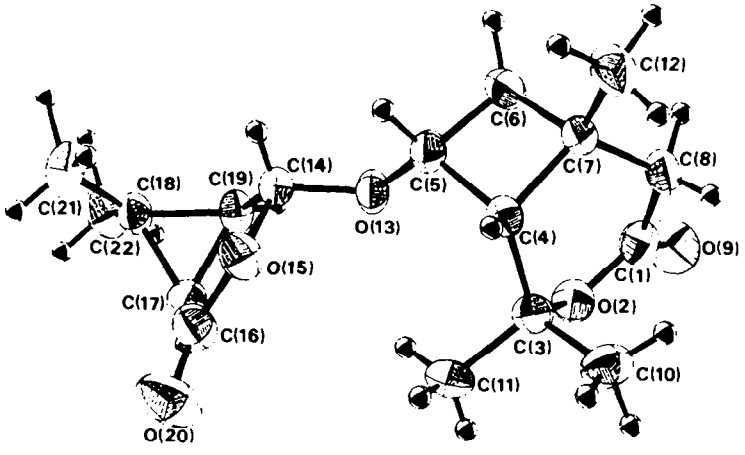

Fig. 4. Computer-generated perspective drawing of the X-ray model of **15**.

Conversion of **15** to (1*R*, 4*S*, 5*R*, 7*R*)-lineatin **1** was straightforward. Upon treatment with HCl–MeOH, the ether **15** gave (+)-hydroxy lactone **13b** as crystals in 86% yield. Reduction of (+)-**13b** with DIBALH was followed by acid treatment to give (+)-lineatin **1** (873.8 mg), $[\alpha]_D^{21.5}$ + 85.8° (($CHCl_3$), in 56% yield after distillation. The absolute configuration of (+)-lineatin was thus established as (1*R*, 4*S*, 5*R*, 7*R*) on the basis of the above-mentioned X-ray analysis of **15**. This is in accord with the suggestion made by Slessor *et al.*[7] basing mainly on the chromatographic properties and ^{1}H-NMR data of **vii** and **viii**, which were their intermediates served for the optical resolution.[7] Our earlier suggestion that (+)-lineatin might be the (1*S*, 4*R*, 5*S*, 7*S*)-isomer was based mainly on the interpretation of the CD data of both the enantiomers of **ix**. The enantiomer which exhibited a negative Cotton effect was assumed to be (1*R*, 5*S*, 6*S*)-**ix**. This was in error. In retrospect, the octant rule should not have been applied to interprete the CD of such a strained cyclopentanone like **ix** with a fused cyclobutane ring. Whenever possible an X-ray analysis should be attempted in the case like this where ambiguity cannot be excluded by other methods such as CD.

The more polar diastereomeric ether **16** gave (−)-hydroxy lactone **13b** in 76% yield, which gave (1*S*, 4*R*, 5*S*, 7*S*)-(−)-lineatin (834.2 mg), $[\alpha]_D^{22}$ − 87.7° ($CHCl_3$), 58% yield after distillation. The spectral data of our (±)-, (+)- and (−)-lineatin were identical with those reported earlier.[3,6]

Determination of the optical purity of lineatin enantiomers

As described above, our lineatin enantiomers (+)-**1** and (−)-**1** were prepared from highly crystalline diastereomeric ethers **15** and **16**, respectively. The optical purity of our products therefore seemed very high. None the less, a direct measurement of their optical purity seemed preferable so that we can eliminate even a trace of doubt on the high purity of our samples. Lineatin **1** contains no reactive functional group in the molecule. Its derivatization is therefore impossible. Only two methods are thus available for the determination of its optical purity: (i) NMR measurement in the presence of a chiral shift reagent and (ii) GLC separation on a chiral stationary phase.[18]

A ^{1}H-NMR study at 400 MHz of our synthetic (±)-, (+) and (−)-lineatin **1** was carried out as follows. In the absence of a chiral shift reagent three CH_3 signals due to (±)-lineatin show no splitting and a doublet due to C-1 proton as well as a triplet due to C-5 proton are observable (Fig. 5a). When a chiral shift reagent tris[3-heptafluorobutanoyl - *d* - camphorato] europium (III) [Eu(hfc)$_3$] was added to (±)-lineatin, the CH_3 singlets splitted to give three pairs of two singlets and the signals due to C-1 and C-5 protons were observed as completely separated pairs of signals (Fig. 5b). In Fig. 5(c and d), ^{1}H-NMR spectra of (+)- and (−)-lineatin in the presence of Eu(hfc)$_3$ are shown, in which no splitting of the signals is detectable confirming the almost 100% optical purity of our lineatin enantiomers. We also attempted to check the optical purity of (+)- and (−)-lineatin by ^{13}C-NMR spectroscopy at 25 MHz. The splitting of the signals due to (±)-lineatin after the addition of Eu(hfc)$_3$, however, was not remarkable enough to allow quantitative determination of the optical purity. The ^{13}C-NMR spectra are listed in Ref. 18.

Quite recently it became possible to separate enantiomers using GLC by taking advantage of chiral recognition exhibited by chiral stationary phases. Schurig's complexation GLC is one of the most successful methods in this area.[18,19] "Complexation GLC" is a technique that utilizes the rapid and the reversible coordination equilibrium between a substrate and the solution of a metal coordination compound in a non-volatile liquid. Resolution of (±)-lineatin on bis[3-heptafluorobutanoyl-*d*-camphorato] copper (II) was achieved by using this method.[20] As shown in Fig. 6 kindly supplied by Prof. V-Schurig, our (+)-lineatin was >99 (±0.5)% optically pure and the (−)-isomer was of 98.4 (±0.5)% optical purity. By this GLC method using our sample as a standard, Klimetzek *et al.* proved that all three *Trypodendron* spp. (*T. lineatum*, *T. domesticum* and *T. signatum*) enantioselectively produce (+)-lineatin **1** with an optical purity of 99 ± 0.5%.[21]

In conclusion we developed a new and efficient route to both racemic and optically active lineatin and established unambiguously the (1*R*, 4*S*, 5*R*, 7*R*)-stereochemistry of (+)-lineatin. By the present synthetic procedure, gram-quantities of (±)-lineatin was suppplied for practical field tests.

EXPERIMENTAL

All b.ps and m.ps were uncorrected. IR spectra were determined as films for liquids and as Nujol mulls for solids on a Jasco A-102 spectrometer. NMR spectra were recorded at 60 MHz with TMS as an internal standard unless otherwise stated. Optical rotations were measured on a Jasco DIP-140 polarimeter. HPLC analyses were performed on a Shimadzu LC-2 chromatograph. GLC analyes were performed on a Jeol JGC-20K or Yanaco GCG-550F gas chromatographs.

A mixture of 2,2-dichloro-3-methyl-3-vinyl-1-cyclobutanone **6** *and 2,2-dichloro-3-isopropenyl-1-cyclobutanone* **7**. A mixture of Cl_3CCOCl (209 g) and $POCl_3$ (159 g) was added dropwise during 2.5 hr to a stirred and ice-cooled mixture of **5** (68 g) and Zn–Cu couple (74 g)[10] in dry ether (1 l) at 10 ~ 25° under N_2. After the addition, the mixture was stirred for 1 hr at 20° and for another hr under reflux. After cooling, it was filtered through Celite. The filtrate was poured into ice-water (300 ml) and extracted with ether. The ether soln was washed with $NaHCO_3$ soln and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 155 g (86.5%) of a mixture of **6** and **7** as a crude unstable oil, ν_{max} 1815 (vs), 1645 (m), 990 (s), 930 (m), 765 (s) cm^{-1}; δ ($CDCl_3$) 1.46 (2.3H, s, CH_3 of **6**), 1.90 (0.7 H, s, CH_3 of **7**), 2.88 (1H, d, J = 16 Hz), 3.48 (1H, d, J = 16Hz), ~3.1–~3.6 (~0.25H, m), 4.7 ~ 5.4 (2H, m), 5.86 ~ 6.32 (0.75H, dd, J_1 = 14, J_2 = 10 Hz; GLC (column, 5% OV-17, 2m × 4mm at 80°; carrier gas, N_2, 50ml/min): R_t 5.38 min (71.94%), 7.10 min (21.76%). This was directly used for the next step.

3 - Methyl - 3 - vinyl - 1 - cyclobutanone **8** *and 3 - isopropenyl - 1 - cyclobutanone* **9**. The above crude mixture of **6** and **7** (155 g) was added dropwise to a stirred and ice-cooled suspension of Zn dust (283 g) in AcOH (1 l) at 20 ~ 25°. The mixture was stirred for 24 hr at room temp and then for 2 hr at 70°. After cooling, the mixture was diluted with ether (1 l) and filtered through Celite. The solid was washed with ether. The combined filtrate and washings were mixed with water (500 ml) and carefully neutralized by the addition of solid $NaHCO_3$. The precipitated NaOAc was filtered off and the filtrate was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* at < 10°. The residual crude oil was distilled to give 68.9 g of an oil, b.p. 90 ~ 115°/90 ~ 110 mmHg. This was submitted to the spinning-band distillation. The desired ketone **8** (44.1 g, 38.9% from Cl_3CCOCl) boiled at 86°/110 mmHg, n_D^{21} 1.4487; ν_{max} 1790 (s), 1645 (m), 915 (m) cm^{-1}; δ ($CDCl_3$) 1.40 (3H, s), 1.5 ~ 3.3 (4H, m), 4.8 ~ 5.2 (2H, m), 5.8 ~ 6.4 (1H, dd, J_1 = 14, J_2 = 10 Hz); GLC (column, 5% PEG-20M, 2m × 4mm at 80°; carrier gas, N_2, 50 ml/min): R_t 2.12 min (single peak). (Found: C, 75.99; H, 9.09. Calc for $C_7H_{10}O$: C, 76.32; H, 9.15%. The isomer **9** (17.9 g, 15.3% from Cl_3CCOCl)

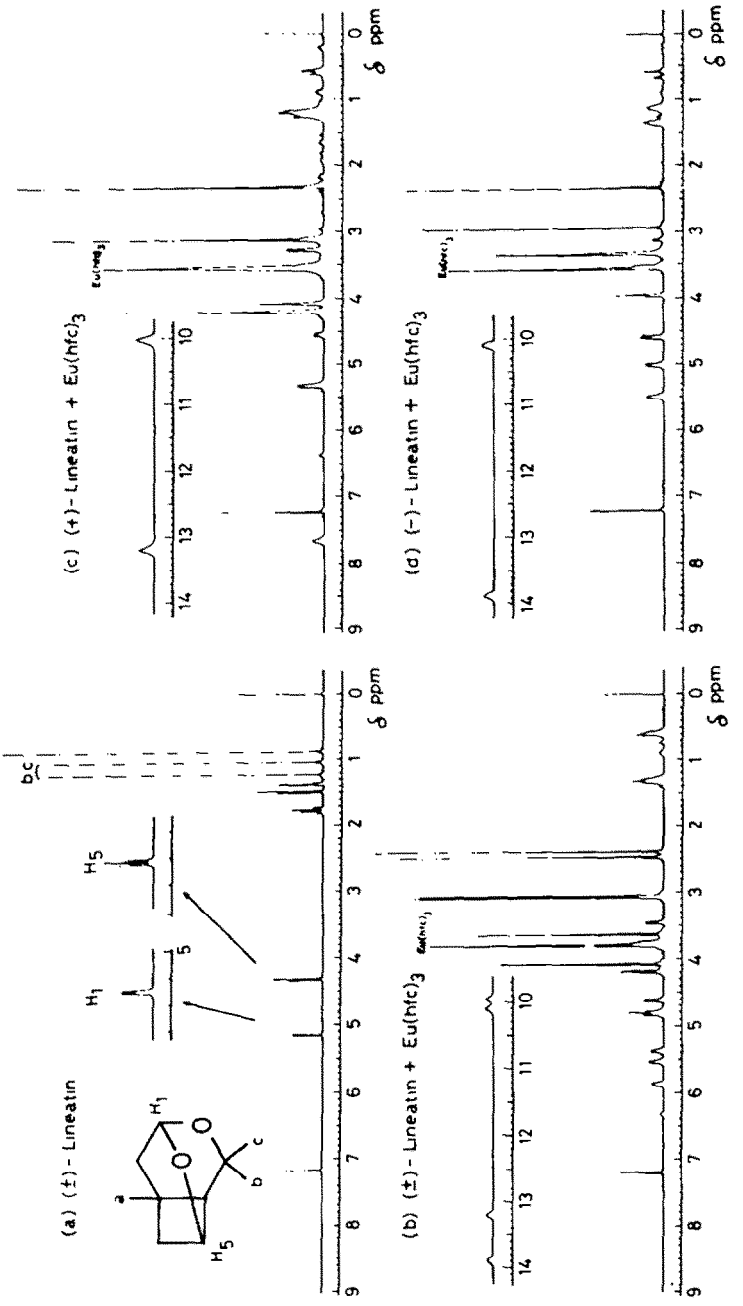

Fig. 5. ^{1}H-NMR spectra of lineatin (37.8 mg) without or with Eu(hfc)$_3$ (120 mg) in benzene-d_6 (0.4 ml) at 400 MHz. (a) Racemate without Eu(hfc)$_3$, (b) Racemate with Eu(hfc)$_3$, (c) (+)-Enantiomer with Eu(hfc)$_3$, (d) (−)-Enantiomer with Eu(hfc)$_3$.

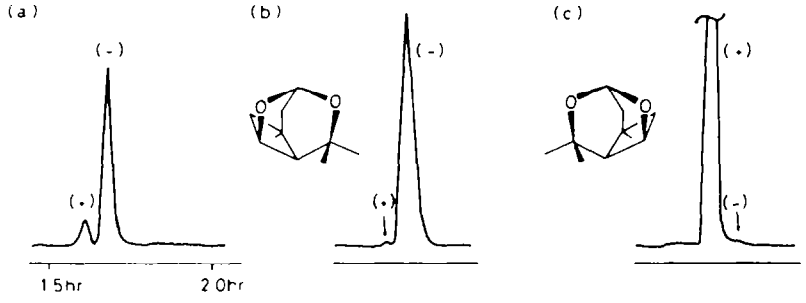

Fig. 6. Determination of optical purity of lineatin enantiomers by complexation GLC. (a) (−)-Lineatin was co-injected with (±)-lineatin on 18 m × 0.3mm soft glass capillary column coated with a soln of 0.027M bis [3-heptafluorobutanoyl-*d*-camphorato] copper (II) in OV 101; oven temp: 35°, 0.35 bar N_2, split: 1/50. (b) (−)-Lineatin was injected on the same column under the same condition. Optical purity: 98.4 (±0.5)%. (c) (±)-Lineatin was injected on 62m × 0.3mm Pyrex glass capillary column coated with a soln of 0.05M bis[3-heptafluorobutanoyl-*d*-camphorato]copper (II) in OV 101; oven temp 45°, 0.4 bar N_2, split: 1/50. Optical purity 99 (±0.5)%.

boiled at 99°/110 mmHg, n_D^{21} 1.4532; ν_{max} 1780 (s), 1640 (m), 1375 (s), 1105 (s), 885 (s) cm^{-1}; δ ($CDCl_3$) 1.77 (3H, s), 2.65 ~ 2.85 (1H, m), 3.00 (4H, s), 4.77 (2H, br. s); GLC (column, 5% PEG-20M, 2m × 4mm at 80°; carrier gas, N_2, 50 ml/min): R_t 4.58 min (single peak).

2 - (1 - *Hydroxy* - 1 - *methylethyl*) - 3 - *methyl* - 3 - *vinyl* - 1 - *cyclobutanone* **10**. A soln of LiN(i-Pr)$_2$ in THF was prepared by the dropwise addition of a soln of n-BuLi in n-hexane (1.37M, 803 ml) to a stirred and cooled soln of (i-Pr)$_2$NH (168 ml) in dry THF (400 ml) at −74° under Ar. To this was added **8** (110 g) dropwise with stirring and cooling at −74°. The mixture was stirred for 1 hr at −74°. Dry acetone (148 ml) was added dropwise to the stirred mixture at −74 ~ −60°. The mixture was left to stand at −74° for 14 hr. It was then poured into ice-cooled sat NH_4Cl soln (1 l) and extracted with ether. The ether soln was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 180 g of crude **10**. An analytical sample was obtained by chromatography over silica gel. Its properties are: $n_D^{21.5}$ 1.4723; ν_{max} 3500 (m), 1775 (s), 1640 (m), 910 (m) cm^{-1}; δ ($CDCl_3$) 0.90 ~ 1.65 (9H, m), 2.7 ~ 2.95 (3H, m), 3.05 ~ 3.25 (1H, m), 4.85 ~ 5.30 (2H, m), 5.85 ~ 6.60 (1H, m); GLC (5% PEG-20M, 2m × 4mm at 130°; carrier gas, N_2 50 ml/min): R_t 6.97 min (46.8%), 7.85 min (53.2%); MS: *m/z* 150 (M^+-H_2O). (Found: C, 70.87; H, 9.59. Calc for $C_{10}H_{16}O_2$: C, 71.38; H, 9.60%).

2 - *Isopropylidene* - 3 - *methyl* - 3 - *vinyl* - 1 - *cyclobutanone* **iv**. A soln of LiN(i-Pr)$_2$ in THF was prepared from n-BuLi in n-hexane (1.44M, 6.88 ml, (i-Pr)$_2$NH (1.34 ml) and THF (5 ml) at −78° under Ar. To this was added **8** (1.0 g) followed by acetone (1.4 ml) at −78°. The reaction temp was raised to 0° during 3 hr. The mixture was stirred for 2 days at room temp. It was then poured into brine and extracted with $CHCl_3$. The $CHCl_3$ soln was dried (Na_2SO_4) and concentrated *in vacuo* to give 1.65 g of a crude oil. This was chromatographed over silica gel to give 1.06 g (77.5%) of **iv**, ν_{max} 1745 (s), 1720 (m), 1670 (s), 1180 (m), 1075 (m), 1035 (m), 910 (m) cm^{-1}; δ ($CDCl_3$) 1.48 (3H, s), 1.69 (3H, s), 2.07 (3H, s), 2.70 (2H, s), 4.8 ~ 5.3 (2H, m), 5.8 ~ 6.3 (1H, dd, J_1 = 14, J_2 = 10Hz); GLC (column, 5% PEG-20M, 2m × 4mm at 130°; carrier gas, N_2, 50 ml/min): R_t 2.07 min.

2 - (1 - *Hydroxy* - 1 - *methylethyl*) - 3 - *methyl* - 3 - *vinyl* - 1 - *cyclobutanol* **11a**. A soln of **10** (180 g) in THF (100 ml) was added dropwise during 1 hr to a stirred and cooled soln of Li(sec-Bu)$_3$BH (L-selectride, 1M in THF, 1.5 l) at −70° under Ar. The reaction temp was raised during 2 hr to room temp. The stirring was continued for 14 hr at room temp. A soln of NaOAc (1 M in H_2O, 140 ml) was gradually added to the stirred soln. 30% H_2O_2 (700 ml) was then gradually added with stirring and ice-cooling at < 30°. The stirring was continued for an additional hr at room temp. The mixture was concentrated *in vacuo* to remove THF. The residue was extracted with ether. The ether soln was washed with brine, dried (Na_2SO_4) and concentrated *in vacuo* to give **11a** (176 g) as a crude oil. A portion of it was purified by silica gel chromatography to give an analytical sample, $n_D^{21.5}$ 1.4714; ν_{max} 3330 (s), 1635 (m), 1165 (s), 905 (m)cm^{-1}; δ ($CDCl_3$) 1.1 ~ 1.6 (9H, m), 1.95 ~ 2.4 (3H, m), 4.4 ~ 5.15 (4H, m), 5.65 ~ 6.85 (1H, m); MS: *m/z* 152 (M^+-H_2O). (Found: C, 69.59; H, 10.40. Calc for $C_{10}H_{18}O_2$: C, 70.53; H, 10.68%.)

1 - (*t* - *Butyldimethylsilyloxy*) - 2 - (1 - *hydroxy* - 1 - *methylethyl*) - 3 - *methyl* - 3 - *vinylcyclobutane* **11b**. A soln of **11a** (176 g) in dry DMF (100 ml) was added dropwise to a stirred soln of t-$BuMe_2SiCl$ (200 g) and imidazole (102 g) in dry DMF (500 ml) at room temp. The stirring was continued for 2 days at room temp. The mixture was diluted with water (3 l) and extracted with ether. The ether soln was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 322 g of a crude oil. This was distilled to give 180 g (55.8% from **8**) of **11b**, b.p. 99 ~ 102°/0.07 ~ 0.25 mmHg. A portion of it was further purified by silica gel chromatography to give an analytical sample, n_D^{21} 1.4557; ν_{max} 3530 (s), 1640 (m), 1255 (s), 1160 (s), 995 (s), 930 (s), 830 (s), 775 (s) cm^{-1}; δ ($CDCl_3$) 0.10 (6H, s), 0.90 (9H, s), 1.05 ~ 1.25 (9H, m), 1.9 ~ 2.4 (3H, m), 4.1 ~ 5.0 (4H, m), 5.65 ~ 6.83 (1H, m); GLC (column, 5% SE-30, 2m × 4mm at 100° + 5°/min; Carrier gas, N_2, 1 ~ 1.4 kg/cm^2): R_t 9.96 min (no separation of the stereoisomers). (Found: C, 66.59; H, 11.51. Calc for $C_{16}H_{32}O_2Si$: C, 67.53; H, 11.36%.)

1 - (*t* - *Butyldimethylsilyloxy*) - 2 - (1 - *hydroxy* - 1 - *methylethyl*) - 3 - (2 - *hydroxyethyl*) - 3 - *methylcyclobutane* **12**. A soln of B_2H_6 in THF (1M, 1.1 l) was added dropwise to a stirred and ice-cooled soln of **11b** (88.7 g) in dry THF (200 ml) at 20 ~ 30° under N_2. After stirring for 3 hr at room temp, the mixture was ice-cooled. To the stirred soln was added THF-water (2:1, 300 ml). The stirring was continued for 1 hr. To the stirred and ice-cooled soln were gradually added 3N-NaOH soln (600 ml) and 35% H_2O_2 (200 ml). After the addition, the mixture was stirred for 1 hr at room temp. The THF soln was separated and the aq layer was extracted with $CHCl_3$. The combined THF-$CHCl_3$ soln was concentrated *in vacuo*. The residue was dissolved in $CHCl_3$. The $CHCl_3$ soln was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to give 113 g of a crude oil. This was chromatographed over silica gel (Merck, 70 ~ 230 mesh, 1 kg). Elution with n-hexane-acetone (10:1) yielded 76.1 g (93.2%) of **12**, $n_D^{21.5}$ 1.4623; ν_{max} 3520 (s), 3440 (s), 1255 (s), 1160 (s), 995 (s), 930 (s), 830 (s), 775 (s), cm^{-1}; δ 0.10 (6H, s), 0.90 (9H, s), 1.15 (3H, s), 1.20 (6H, s), 1.55 ~ 2.45 (5H, m), 3.35 ~ 3.85 (2H, m), 4.25 ~ 4.70 (1H, m); GLC (column, 5% SE-30, 2m × 4mm at 140°; carrier gas, N_2, 2kg/cm^2): R_t 13.46 min (52.1%), 13.98 min (47.9%). (Found: C, 63.16; H, 11.49. Calc for $C_{16}H_{34}O_3Si$: C, 63.51; H, 11.35%.)

7 - (*t* - *Butyldimethylsilyloxy*) - 1,5,5 - *trimethyl* - 4 - *oxabicyclo*[4.2.0]*octan* - 3 - *one* **13a** *and* [3 - (*t*-*butyldimethylsilyloxy*) - 2 - (1 - *hydroxy* - 1 - *methylethyl*) - 1 - *methylcyclobutyl*]*acetic acid* **14**. PDC (242 g) was suspended in dry CH_2Cl_2 (1 l) by stirring for 20 min at room temp. A soln of **12** (74.5 g) in CH_2Cl_2 (100 ml) was added dropwise to the stirred suspension of PDC at 20 ~ 25° with occasional cooling. The stirring was continued for 24 hr at 30°. Then

the mixture was diluted with ether (2 l), stirred for 10 min and filtered through Celite. The solid was washed with ether. The combined filtrate and washings were filtered through a short column of Florisil (100 ~ 200 mesh, *ca* 250 g) and concentrated *in vacuo* to give 69.5 g of a crude mixture of **13a** and **14** as an oil. This was chromatographed over silica gel (Merck, 70 ~ 230 mesh, 800 g). Elution with n-hexane–acetone (20:1) yielded 39.8 g (53%) of **13a** as prisms from pet. ether, m.p. 60.5 ~ 61.0°; ν_{max} (Nujol) 1725 (s), 1250 (s), 1155 (s), 1105 (s), 995 (s), 835 (s), 775 (s) cm^{-1}; δ (100 MHz, $CDCl_3$) 0.03 (6H, s), 0.92 (9H, s), 1.30 (3H, s), 1.36 (3H, s), 1.56 (3H, s), 1.66 ~ 2.40 (3H, m), 2.53 (2H, d, J = 2 Hz), 4.6 ~ 4.8 (1H, m). (Found: C, 64.34; H, 9.93. Calc for $C_{16}H_{30}O_3Si$: C, 64.37; H, 10.15%). Further elution with ether gave 11.7 g (14.7%) of **14** as needles from n-hexane, m.p. 94.5 ~ 96°; ν_{max} (Nujol) 3370 (m), 3090 (m), ~ 2700 (w), 1730 (s), 835 (s) cm^{-1}; δ ($CDCl_3$) 0.08 (6H, s), 0.92 (9H, s), 1.18 (3H, s), 1.24 (3H, s), 1.60 (3H, s), 1.78 ~ 2.35 (3H, m), 2.43 (2H, s), 4.55 ~ 4.83 (1H, m). (Found: C, 60.52; H, 10.07. Calc for $C_{16}H_{32}O_4Si$: C, 60.70; H, 10.21%.)

(±) - 7 - *Hydroxy* - 1,5,5 - *trimethyl* - 4 - *oxabicyclo*[4.2.0]*octan* - 3 - *one* **13b**. A soln of $(n\text{-}Bu)_4NF$ in THF (1M, 107 ml) was added dropwise during 20 min to a stirred and ice-cooled soln of **13a** (26.7 g) in dry THF (98 ml) at 2 ~ 5°. The stirring was continued for 3 hr at 3 ~ 5°. The mixture was then poured into ice-cooled NH_4Cl soln (100 ml) and extracted with $CHCl_3$. The $CHCl_3$ soln was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel (Merck, 70 ~ 230 mesh, 250 g). Elution with ether yielded 12.5 g (75.9%) of **13b** as prisms from ether, m.p. 64 ~ 65°; ν_{max} (Nujol) 3430 (s), 1695 (vs), 1325 (s), 1205 (m), 1150 (s), 1095 (m), 985 (s), 950 (m) cm^{-1}, δ (100MHz, $CDCl_3$) 1.28 (3H, s), 1.38 (3H, s), 1.64 (3H, s), 1.7 ~ 2.4 (3H, m), 2.50 (2H, d, J = 1.5 Hz), 4.5 ~ 4.9 (1H, m); GLC (5% PEG-20M, 2m × 4mm at 190°; carrier gas, N_2, 50 ml/min): R_t 14.87 min (single peak). (Found: C, 65.18; H, 8.64. Calc for $C_{10}H_{16}O_3$: C, 65.18; H, 8.77%.)

(±) - 3,3,7 - *Trimethyl* - 2,9 - *dioxatricyclo*[3.3.1.$0^{4,7}$]*nonane* (*lineatin*) **1**. A soln of DIBALH (25 w/v% in n-hexane, 84.2 ml) was added dropwise to a stirred and cooled soln of (±)-**13b** (12.0 g) in dry ether (94 ml) at −74° under Ar. The reaction temp was raised to −50° during 1 hr. 1N-HCl soln (196 ml) was added with stirring and cooling. The temp was raised to room temp during 1 hr. 6N-HCl soln (24 ml) was added and the mixture was stirred for 1 hr. It was then extracted with n-pentane (100 ml × 4). The extract was washed with sat $NaHCO_3$ soln and brine, dried ($MgSO_4$) and concentrated under atm press. The residue was distilled to give 4.17 g (37.7%) of (±)-**1**, b.p. 110°/53 mmHg; ν_{max} 2970 (s), 2930 (s), 2870 (s), 1470 (m), 1450 (m), 1380 (s), 1360 (s), 1340 (s), 1315 (s), 1240 (m), 1220 (s), 1185 (s), 1170 (s), 1125 (vs), 1100 (s), 1075 (s), 1015 (s), 1000 (s), 965 (vs), 900 (vs), 865 (m), 830 (s), 810 (m), 790 (s), 730 (m), 695 (w) cm^{-1}; δ ($CDCl_3$) 1.15 (6H, s), 1.23 (3H, s), 1.50 ~ 2.15 (5H, m), 4.4 ~ 4.6 (1H, m), 5.0 ~ 5.15 (1H, m); MS: *m/z* 168 (M^+), 169 ($M^+ + 1$). These spectral data were identical with those reported in our previous synthesis.[3,6] GLC (column, 5% SE-30, 2m × 4mm at 100°; carrier gas, N_2, 1 kg/cm^2): R_t 3.60 min (single peak). In one occasion, starting from 611 mg of (±)-**13b**, 263 mg (46.6%) of (±)-**1**, b.p. 110°/53 mmHg, was obtained.

Optical resolution of (±)-**13b**. A soln of (±)-**13b** (1.5 g), v (1.16 g) and *p*-TsOH (12 mg) in C_6H_6 (50 ml) was stirred and heated under reflux for 30 min wth continuous removal of water by a Dean–Stark water separator. The soln was concentrated *in vacuo*. The residual oil (2.82 g) was separated by medium pressure liquid chromatography employing a Merck Lobar column Grosse C. Elution with CH_2Cl_2–acetone (50:1) yielded 701 mg of **15** (R_f value upon silica gel TLC: 0.44; $CHCl_3$–acetone = 20:1), 679 mg of **16** (R_f value upon silica gel TLC:0.32; $CHCl_3$–acetone = 20:1) and 892 mg of a mixture of **15** and **16**. The mixture was rechromatographed over a Merck Lobar column Grosse B in the same manner to give 322 mg of **15**, 408 mg of **16** and 98.6 mg of a mixture of **15** and **16**. This mixture was again rechromatographed on a Merck Lobar column Grosse B in the same manner to give 76.5 mg of **15** and 12.6 mg of **16**. The combined yield of (1*S*, 6*S*, 7*R*) - 7 - [(1*R*, 4*R*, 5*S*) - 6,6 - *dimethyl* - 2 - *oxo* - 3 - *oxabicyclo*[3.1.0]*hexyloxy*] - 1,5,5 - *trimethyl* - 4 - *oxabicyclo*[4.2.0]*octan* - 3 - *one* **15** was 1.10 g (87.6%). Recrystallization from EtOH gave prisms, m.p. 143 ~ 144°; $[\alpha]_D^{23}$ − 108.0° (c = 1.06, EtOH); ν_{max} (Nujol) 1770 (s), 1730 (vs), 1155 (vs), 1115 (vs), 1100 (s), 990 (s) 945 (vs) cm^{-1}; ^{1}H-NMR δ (200 MHz, $CDCl_3$) 1.16 (6H, s), 1.34 (3H, s), 1.37 (3H, s), 1.51 (3H, s), 1.16 ~ 2.67 (7H), 4.66 (1H, dt, J_1 = 6, J_2 = 2 Hz), 5.03 (1H, d, J = 0.2 Hz); ^{13}C-NMR δ (50 MHz, $CDCl_3$) 15.09, 24.67, 25.20, 27.00, 28.15, 29.65, 29.84, 34.22, 35.25, 39.02, 41.63, 49.27, 68.72, 81.93, 97.56, 172.17, 173.46; HPLC (column, Partisil 5, 25 cm × 4.6 mm; $CHCl_3$–THF–MeOH = 1000:50:1, 1.5 ml/min; RI detector): R_t 13.4 min. (Found: C, 66.24; H, 7.87. Calc for $C_{17}H_{24}O_5$: C, 66.20; H, 7.86%). The combined yield of (1*R*, 6*R*, 7*S*) - 7 - [(1*R*, 4*R*, 5*S*) - 6,6 - *dimethyl* - 2 - *oxo* - 3 - *oxabicyclo*[3.1.0]*hexyloxy* - 1,5,5 - *trimethyl* - 4 - *oxabicyclo*[4.2.0]octan-3-one **16** was 1.10 g (87.6%). Recrystallization from EtOH gave rods, m.p. 124 ~ 125°; $[\alpha]_D^{23}$ −65.1° (c = 1.02, EtOH); ν_{max} (Nujol) 1765 (vs), 1725 (s) 1155 (s), 1115 (s), 985 (s), 940 (vs) cm^{-1}. ^{1}H-NMR δ (200 MHz $CDCl_3$) 1.15 (6H, s), 1.29 (3H, s), 1.36 (3H, s), 1.53 (3H, s), 1.19 ~ 2.68 (7H), 4.48 (1H, dt, J_1 = 6, J_2 = 2 Hz), 5.09 (1H, d, J = 0.2 Hz); ^{13}C-NMR δ (50MHz, $CDCl_3$) 15.06, 24.43, 25.25, 26.75, 28.67, 29.70, 30.08, 33.58, 35.15, 41.30, 42.47, 50.70, 72.37, 81.29, 102.15, 171.75, 172.42; HPLC (Column, Partisil 5, 25 cm × 4.6 mm; $CHCl_3$–THF–MeOH = 1000:50:1, 1.5 ml/min; RI detector): R_t 18.4 min. (Found: C, 66.31; H, 7.96. Calc for $C_{17}H_{24}O_5$: C, 66.20; H, 7.86%.)

(1*S*, 6*S*, 7*R*) - (+) - 7 - *Hydroxy* - 1,5,5 - *trimethyl* - 4 - *oxabicyclo*[4.2.0]*octan* - 3 - *one* **13b**. A small drop of conc HCl was added to a stirred soln of **15** (4.27 g) in MeOH (15 ml) at room temp. The stirring was continued for 2 hr at room temp. The mixture was neutralized with sat $NaHCO_3$ soln (1 ml) and concentrated *in vacuo*. The residue was dissolved in $CHCl_3$. The $CHCl_3$ soln was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed over silica gel to give 2.20 g (86.3%) of (1*S*, 6*S*, 7*R*)-**13b** as needles from ether, m.p. 90 ~ 91°; $[\alpha]_D^{21.7}$ + 48.2° (c = 1.00, CCl_4); CD (c = 0.112, MeOH: $[\theta]_{318}^{25}$ + 6004; ν_{max} (Nujol) 3420 (s), 1690 (vs), 1360 (s), 1305 (s), 1270 (s), 1145 (s), 1130 (vs), 990 (s) cm^{-1} (The IR spectrum was different from that of (±)-**13b**. The racemate is therefore not a racemic mixture but a racemic compound.) The NMR spectrum was identical with that of (±)-**13b**. (Found: C, 65.08; H, 8.77. Calc for $C_{10}H_{16}O_3$: C, 65.18; H, 8.77%.)

(1*R*, 6*R*, 7*S*) - (−) - 7 - *Hydroxy* - 1,5,5 - *trimethyl* - 4 - *oxabicyclo*[4.2.0]*octan* - 3 - *one* **13b**. In the same manner as above 4.20 g of **16** gave 1.90 g (75.7%) of (1*R*, 6*R*, 7*S*)-**13b** as needles, m.p. 90 ~ 91°, $[\alpha]_D^{21.6}$ − 47.2° (c = 1.00, CCl_4); CD(c = 0.106, MeOH): $[\theta]_{318}^{25}$ − 5649. (Found: C, 65.24; H, 8.80. Calc for $C_{10}H_{16}O_3$: C, 65.18; H, 8.77%.) The IR and NMR spectra were identical with those of (+)-**13b**.

(1*R*, 4*S*, 5*R*, 7*R*) - (+) - 3,3,7 - *Trimethyl* - 2,9 - *dioxatricyclo*[3.3.1.$0^{4,7}$] *nonane* (*lineatin*) **1**. In the same manner as described for the preparation of (±)-**1**, 1.70 g of (+)-**13b** yielded 874 mg (56.3%) of (+)-**1**, b.p. 110°/53 mmHg; $n_D^{21.7}$ 1.4586; $[\alpha]_D^{21.5}$ + 85.8° (c = 1.1, $CHCl_3$); $[\alpha]_D^{21.5}$ + 85.8° (c = 1.0, n-pentane) (lit.[7] $[\alpha]_D^{24}$ + 66.3 ± 3.5° (*c* = 3.1,$CHCl_3$); Prof. Slessor's lineatin enantiomers were not optically pure as revealed by Prof. Schurig's complexation GLC analysis according to Prof. Schurig's personal communication to K. M.); We previously reported the $[\alpha]_D$ value of (+)-**1** to be $[\alpha]_D^{22}$ − 36° (c = 0.2, n-pentane).[6] This erroneous result was due to the scarcity of the material. Prof. Schurig's GLC analysis showed our previous (+)-**1** to be of 82% e.e.); ^{13}C-NMR δ (25 MHz, $CDCl_3$) 26.27, 27.83, 28.99, 37.80, 42.16, 43.47, 48.15, 71.40, 72.37, 92.72, 128.30; MS: *m/z* 168.1098 ($M^+ = C_{10}H_{16}O_2$). The spectral data were same as those of (±)-**1**.

(1*S*, 4*R*, 5*S*, 7*S*) - (−) - 3,3,7-*Trimethyl* - 2,9 - *dioxatricyclo*[3.3.1.$0^{4,7}$]*nonane* (*lineatin*) **1**. Similarly as above (−) -**13b** (1.57 g) gave (−)-**1** (834 mg, 58.1%), b.p. 110°/53 mm; $n_D^{21.7}$ 1.4588; $[\alpha]_D^{21.7}$ − 87.7° (*c* = 1.2, $CHCl_3$); $[\alpha]_D^{21.7}$ − 87.6° (*c* = 1.1, n-pentane) (lit.[7] $[\alpha]_D^{23}$ − 71.6° ± 2.0° (c = 3.6, $CHCl_3$); lit.[6] $[\alpha]_D^{22}$ − 40° (*c* = 0.05, n-pentane). This sample was of 74% e.e. as shown by Prof. Schurig's GLC analysis); MS: *m/z* 168.1162 ($M^+ = C_{10}H_{16}O_2$). The spectral properties of (−)-**1** were identical with those described for (±)-**1**. For the determination of the optical purity of (+)- and (−)-**1**, see the text.

Table 1. Final positional and equivalent isotropic thermal parameters for the non-hydrogen atoms

Atom	x	y	z	Beq, Å^2
C(1)	-0.0048(2)	0.6065(0)	0.8152(3)	3.33(4)
O(2)	0.0734(1)	0.7104(2)	0.8485(2)	3.17(3)
C(3)	0.1776(2)	0.6470(3)	0.8892(3)	2.80(4)
C(4)	0.2098(1)	0.5189(3)	0.7559(3)	2.51(3)
C(5)	0.2261(2)	0.5614(3)	0.5617(3)	3.02(4)
C(6)	0.1253(2)	0.4752(3)	0.5149(3)	4.02(5)
C(7)	0.1214(2)	0.3990(3)	0.6979(3)	2.68(4)
C(8)	0.0189(2)	0.4288(3)	0.7869(3)	3.15(4)
O(9)	-0.0906(1)	0.6636(3)	0.8081(3)	5.31(4)
C(10)	0.1767(2)	0.5685(4)	1.0694(3)	4.08(5)
C(11)	0.2437(2)	0.8018(3)	0.8928(3)	4.14(5)
C(12)	0.1498(2)	0.2162(3)	0.7095(4)	4.32(5)
O(13)	0.2310(1)	0.7294(2)	0.5080(2)	3.06(3)
C(14)	0.3219(1)	0.7765(3)	0.4282(3)	2.66(4)
O(15)	0.4050(1)	0.7931(2)	0.5535(2)	3.28(3)
C(16)	0.4309(2)	0.9552(3)	0.5781(3)	3.46(4)
C(17)	0.3768(2)	1.0597(3)	0.4516(3)	2.97(4)
C(18)	0.3949(2)	1.0232(3)	0.2595(3)	2.91(4)
C(19)	0.3063(1)	0.9447(3)	0.3499(3)	2.80(4)
O(20)	0.4899(2)	0.9938(3)	0.6922(2)	5.73(4)
C(21)	0.4873(2)	0.9276(4)	0.2049(3)	4.29(5)
C(22)	0.3666(2)	1.1635(4)	0.1421(3)	4.45(5)

X-Ray analysis of **15**. Crystals suitable for X-ray analysis were obtained by recrystallization of **15** from EtOH. The crystal chosen was mounted in a general orientation and had dimensions of ca. 0.30 × 0.30 × 0.40 mm. Unit-cell parameters were refined by least-squares on 2θ values for 25 reflections measured on a diffractometer with Mo Kα radiation (λ = 0.71073 Å). Crystal data are: $C_{17}H_{24}O_5$, monoclinic, space group $P2_1$, a = 12.981 (2), b = 8.104 (2), c = 7.742 (1) Å, β = 91.00(1)°, V = 814.3(4) Å^3, Z = 2, Dx = 1.258 gcm^{-1}, μ(MoKα) = 0.86 cm^{-1}. Intensities were measured with graphite monochromatized Mo Kα radiation on an Enraf-Nonius CAD 4 diffractometer. An ω-2θ scan at 1.68–6.71°min^{-1} over a range of (1.0 + 0.35 tan θ) degrees in ω was employed. Data were measured to 2θ = 55°. The intensities of 3 check reflections, measured every 3600s throughout the data collection, remained constant to within 3%. A total of 1682 independent reflections, ($I > 3\sigma(I)$), were used for the structure determination. Corrections for the Lorentz and polarization factors were made, but no correction for absorption was applied. All non-H atoms were located by direct method with use of MULTAN 78[17]. After refinement of their positions and anisotropic thermal parameters, all H positions were located from a difference Fourier map. Full matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for non-hydrogen atoms, and isotropic thermal parameters for H atoms led to final agreement values of R = 0.035 and Rw = 0.045. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$, where $w = (\sigma^2(Fo) + (0.03Fo)^2)^{-1}$ $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $Rw = [\Sigma w(|Fo| - |Fc|)^2/w|Fo|^2]^{1/2}$. Final positional and equivalent isotropical thermal parameters for the non-H atoms are given in Table 1. All calculations were carried out on PDP 11/34 computer by using Enraf-Nonius SDP (Structure Determination Package) programs.

Supplementary material available. Crystallographic data including positional and thermal parameters as well as bond distance and angle calculation have been deposited with the Cambridge Crystallographic Data Centre (CCDC) in England.

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