STUDIES IN SESQUITERPENES—XXV

A SYNTHESIS OF α -SELINENE

G. L. CHETTY, G. S. KRISHNA RAO, SUKH DEV and D. K. BANERJEE Organic Chemistry Department, Indian Institute of Science, Bangalore, India

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Abstract—The conversion of α -cyperone into α -selinene is described.

(+)- α -SELINENE (α -eudesmene), first obtained¹ by the dehydrohalogenation of selinene dihydrochloride and now known to occur in a number of essential oils,² possesses the structure³ and absolute stereochemistry⁴ depicted in I. Since α -cyperone (II)^{4.5} has been synthesized,⁶ its conversion into I amounts to a total synthesis of α -selinene and forms the subject of this paper (Fig. 1). Correlation of α -cyperone with some other sesquiterpenoids of the same group has been described.⁷



Lithium-liquid ammonia reduction of α -cyperone, using ammonium chloride as the proton donor gave the dihydro- α -cyperone (III)^{8,9} which should¹⁰⁻¹³ have the stereochemistry shown. This is supported by the ORD-measurements (Fig. 2), the sign and shape of the curve being in accord with that observed¹⁴ for the tetrahydrosantonin (IX) or lophanone (X). Reduction of III with tri-t-butoxyaluminium

- ¹ F. W. Semmler and F. Risse, Ber. Dtsch. Chem. Ges. 45, 3301 (1912); 46, 599 (1913).
- ³ For a list see: E. Gildmeister and Fr. Hoffmann, *Die Ätherischen Öle* (4th Edition revised by W. Triebs and D. Merkel) Vol. IIIa, p. 274. Akademie-Verlag, Berlin (1960).
- ⁸ L. Ruzicka and M. Stoll, *Helv. Chim. Acta* 5, 926 (1922); P. A. Plattner, A. Furst and J. Hellerbach, *Ibid.* 30, 2158 (1947).
- ⁴ D. H. R. Barton, Chem. & Ind. 664 (1953); W. Klyne, J. Chem. Soc. 3072 (1953); R. Riniker, J. Kalovda, D. Arigoni, A. Furst, O. Jeger, A. M. Gold and R. B. Woodward, J. Amer. Chem. Soc. 76, 313 (1956).
- ⁵ A. E. Bradfield, B. H. Hegde, B. S. Rao, J. L. Simonsen and A. E. Gillam, J. Chem. Soc. 667 (1936); A. E. Bradfield, R. R. Pritchard and J. L. Simonsen, J. Chem. Soc. 760 (1937).
- ⁶ R. Howe and F. J. McQuillin, J. Chem. Soc. 2423 (1955).
- ⁷ A. R. Pinder and R. A. Williams, J. Chem. Soc. 2773 (1963).
- ⁸ G. S. Krishna Rao, Ph. D thesis, p. 87. Bombay University (1955).
- * R. Howe and F. J. McQuillin, J. Chem. Soc. 2670 (1956).
- ¹⁰ D. H. R. Barton and C. H. Robinson, J. Chem. Soc. 3045 (1954).
- ¹¹ H. E. Zimmerman, J. Amer. Chem. Soc. 78, 1168 (1956).
- ¹⁸ A. J. Birch, H. Smith and R. E. Thronton, J. Chem. Soc. 1339 (1957).
- ¹⁸ G. Stork and S. D. Darling, J. Amer. Chem. Soc. 82, 1512 (1960); 86, 1761 (1964).
- ¹⁴ C. Djerassi, Optical Rotatory Dispersion pp. 80, 148. McGraw-Hill, New York (1960).



hydride¹⁵ yielded a solid alcohol quantitatively, which on mechanistic considerations¹⁶ must be assigned the stereochemistry depicted in IV. The β -equatorial conformation of the hydroxyl is supported by the molecular rotational data (Table 1). The proton attached to the carbon carrying the hydroxyl must have an axial conformation as seen from the multiplicity of its signal (1H multiplet located between 167 and 195 c/s and centred at 180 c/s; the signal, as expected, shifted downfield by 77 c/s in the acetate) in the PMR spectrum, the large coupling being consistent¹⁷ only with *trans*-diaxial coupling.

The dihydrocyperol (IV) may be obtained in a single step by the lithium-liquid ammonia-ethanol reduction or, better still, by the sodium-n-propanol reduction of

- ¹⁵ H. C. Brown and R. F. McFarlin, J. Amer. Chem. Soc. 78, 252 (1956); O. H. Wheeler and J. L. Mateos, Canad. J. Chem. 36, 1431 (1958).
- ¹⁶ W. G. Dauben, G. J. Fonken and D. S. Noyce, J. Amer. Chem. Soc. 78, 2579 (1956); W. G. Dauben, E. J. Blanz, J. Jin and R. A. Micheli, *Ibid.* 78, 3752 (1956).
- ¹⁷ L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry pp. 83-87. Pergamon Press, London (1959).



FIG. 2. ORD curve of dihydro cyperone (III).

Parent alcohol.		Δ_1	Δ,		
		(ROAc)-(ROH)	$(\mathbf{R} = \mathbf{O})$ -(\mathbf{ROH})		
Lophanol (XI)	8	+78	-9		
Citrostanol (XI	I) ¹⁸	+64	-39		
Dihydrocyperol (IV)		+46	-21		
		но			
x	2	C	ΣΣ R • C _B H _{i7}		
			$XII R = C_{10}H_{21}$		

TABLE 1. MOLECULAR ROTATIONAL DIFFERENCES

¹⁸ C. Djerassi, G. W. Krakower, A. J. Lemin, L. H. Lin, J. S. Mills and R. Villotti, *J. Amer. Chem. Soc.* 80, 6286 (1958); Y. Mazur, A. Wiezman and F. Sondheimer, *Ibid.* 80, 6293 (1958).

 α -cyperone. As expected,¹⁹ alcohol IV being thermodynamically favoured, predominates in these reactions.

Once the stereochemistry of dihydrocyperol was established (IV), a suitable elimination reaction which would selectively furnish α -selinene (I) was required. Since in IV the C₃—OH and the C₄—H have a *cis*-relationship, a *cis*-elimination reaction was evident.²⁰ Menthol in which the hydroxyl has the same conformation and environment as the OH in IV, is known²¹ to furnish a preponderance of Δ^3 -*p*-menthene in the pyrolysis of several of its esters, the best yield (90%) being obtained from the borate ester.²² The *m*-borate ester (V) of IV on pyrolysis gave an olefin mixture in high yield. The IR spectrum of the crude product shows the required compound as the major component. Both GLC and AgNO₃-SiO₂ gel TLC²³ show the presence of at least five components of which three are minor. The major components were readily separated by preparative GLC or chromatography over silica-gel-silver nitrate²⁴ and

	α-Selinene (I)		VII	VIII	
	Synthetic	Natural ²⁷	VII	vii viii	
GLC purity	>99%		>99%	>99%	
b.p./mm n/t	126–127°/10 mm 1·5022/30°	100-102°/2·2-2·3 mm 1·5030-1·5040/20°	124-125°/10 mm 1·4984/30°	124–125°/10 mm 1·4972/30°	
[a] ^{CHOI}	+15.7°	+18°†	46 -6°	-147-1°	
R ₈ 33	1.754		1.397	2.055	
IR spectrum*	796, 808 cm ⁻¹		687, 727 cm ⁻¹	800 cm ⁻¹	

TABLE	2. 3	PROPERTIES	OF	α -SELINENE	AND	ITS	ISOMERS
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* Bands which can distinguish the isomers in a mixture.

 $\dagger \alpha_{\rm D}$.

on the basis of evidence discussed below were recognized as I and VII.

The major component (60%) was recognized as the desired α -selinene (I) both from its physical properties (Table 2) and the IR spectrum which is identical with that reported by Pliva *et al*.²⁵ The PMR spectrum is in accord with the structure I; the fact that the C₄-methyl signal is not sharp must be ascribed to allylic and 'homoallylic' coupling.²⁶

The second major component (25%) shows in the IR and PMR spectra bands assignable to $>C=CH_2$ (IR: 882, 1650, 1780 and 3080 cm⁻¹; PMR: 2H signal at 279 c/s), *cis* -CH=CH- (IR: 687 cm⁻¹; PMR: 2H signal at 327 c/s), CH₃--CH- (PMR: 3H doublet centred at 58 c/s, J = 6.5 c/s) and a vinylic methyl

¹⁹ D. H. R. Barton, J. Chem. Soc. 1027 (1953).

- ²¹ C. H. DePuy and R. W. King, Chem. Revs. 60, 438 (1960).
- ²³ G. L. O'Connor and H. R. Nace, J. Amer. Chem. Soc. 77, 1578 (1955). DePuy and King (Ref. 21, p. 453) state that since borate esters are linear, they must be unfavourable for a cyclic transition state, and hence pyrolysis of borate esters may not, in fact, be a multicentre-type elimination.
- ¹³ A. S. Gupta and Sukh Dev, J. Chromatog. 12, 189 (1963).
- ⁸⁴ N. P. Damodaran and Sukh Dev, Tetrahedron Letters 1941 (1963).
- ²⁵ J. Pliva, M. Horak, V. Herout and F. Sorm, Terpenspektren p. 81. Akademie-Verlag, Berlin (1960).
- ⁴⁴ S. Sternhell, Rev. Pure and Appl. Chem. 14, 15 (1964).
- ¹⁷ Y. R. Naves, Bull. Soc. Chim. Fr. 292 (1956).

²⁰ The alternative, S_N2 substitution followed by *trans*-diaxial elimination, gave in a number of experiments (PCl₅; quinoline or pyridine) only poor yields of products, which were mixtures.

(PMR: signal centred at 103 c/s, J = 1.5 c/s). These data are in accord with the expected structure VII.

Among the minor products of the pyrolytic reaction, one ($\sim 8\%$) was obtained pure by chromatography over AgNO₃-SiO₂ gel. The following structural features were clear from its spectra: one isopropyl group (PMR: 6H doublet centred at 62 c/s, J = 6.5 c/s), one vinylic methyl (PMR: 99 c/s signal) and two vinylic protons (2H signal centred at 319 c/s.) In the UV it did not show any maximum between 215-300 m μ . These results indicate two possible structures (VIII) for this compound, but the one with Δ^7 was preferred as the PMR spectrum does not exhibit any signal at ~ 150 c/s expected²⁸ for the C₅ proton in the alternate structure.

In another set of experiments pyrolysis of the ethyl carbonate (VI) was investigated. In this case the product was shown by GLC (both analytical and preparative) to consist almost entirely of I (35%) and VII (65%); however, TLC (AgNO₃-SiO₂ gel) shows that traces of minor components encountered in the borate pyrolysis product were also present.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Pet. ether refers to the fraction b.p. $40-60^{\circ}$. All solvent extracts were dried over Na₃SO₄. Optical rotations were measured in CHCl₃.

IR spectra were taken on a Perkin-Elmer infracord model 137E. All PMR spectra were taken in $\sim 10\%$ CCl₄ solution on a Varian Associates A-60 spectrometer, with tetramethylsilane as the internal standard; the signals are recorded in c/s from tetramethylsilane as zero.

Gas-liquid chromatography. All analytical runs were made on 5' columns (internal diameter $\frac{1}{2}$ ") packed with either 20% polyester (diethylene glycol succinate) or 20% silicone (SE 30) on 60-80 mesh Chromosorb W, using H_a as the carrier gas (30-70 ml/min) on "Aerograph" model A-350-B. Preparative GLC were run on Perkin-Elmer Vapour Fractometer model 154-D.

a-Cyperone (II)

The essential oil³⁰ (375 g) from the rhizomes of *Cyperus rotundus* was carefully fractionated on a packed column³⁰ and the fraction b.p. $148-157^{\circ}/6$ mm (106 g) collected separately. This cut on refractionation furnished a fraction b.p. $132-133^{\circ}/2$ mm (68 g, n_D^{36} 1.5223) which was rich in α -cyperone; 10 g of this material yielded by the pyridine method 6 g of pure *semicarbazone* (alc), m.p. 214-216°. By strict adherence to the following procedure pure α -cyperone could be regenerated without isomerization to β -cyperone.

Well-powdered α -cyperone semicarbazone (4.6 g), oxalic acid (9.2 g), water (75 ml) and n-heptane (200 ml) were heated (oil bath at ~115°) and mechanically stirred till all solids disappeared (2 hr). After cooling, the heptane layer was separated and the aqueous portion extracted with ether (25 ml × 3). The combined extracts were washed with 5% NaHCO₅ aq (25 ml × 3), brine and dried. Removal of solvent and distillation yielded pure α -cyperone (3.5 g, 96%): b.p. 119-120°/0.6 mm, n_{25}^{56} 1.5280, $[\alpha]_{27}^{57}$ +71.3° (c, 1%); $\lambda_{max}^{56,01}$ 248.5 m μ (ϵ , 15,240), ϵ_{300} 36. IR spectrum (liq.): C=O 1680; C=C 3100, 1620, 896 cm⁻¹.

Dihydro- α -cyperone (III)

(i) Lithium-liquid ammonia reduction of α -cyperone. Pure α -cyperone (1.0 g) in dry ether (40 ml) was introduced into a stirred solution of Li (0.2 g) in liq. NH₄ (300 ml) under anhydrous conditions. Stirring was continued for $\frac{1}{2}$ hr, after which, solid NH₄Cl (4.0 g) was added and the NH₄ allowed to evaporate. The product was diluted with water (150 ml) and then extracted with ether (20 ml \times 4). The extracts were washed with brine (10 ml \times 3), dried and the solvent removed using a column. The residue on distillation gave dihydro- α -cyperone (0.93 g, 92%) as a colourless liquid, b.p. 105–107°/ 0.3 mm.

¹⁸ Ref. 17, pp. 50-65.

²⁹ Supplied by S. H. Kelkar and Co., Bombay.

³⁰ Manufactured by Emil Greiner Co., New York.

The above product (0.93 g) was converted into its *semicarbazone* (pyridine method), which recrystallized from EtOH in white needles, m.p. 185–186°, yield 0.8 g (68%). (Found: N, 15·32. C₁₈H₃₇ON₈ requires: N, 15·16%.) Pure dihydro- α -cyperone was regenerated (procedure described for α -cyperone), b.p. 116–117°/0.6 mm, n_{35}^{35} 1·4960, $[\alpha]_{25}^{35}$ –15·1° (c, 1·8%). IR spectrum (liq.): C=O 1701; C=C 3077, 1639, 887 cm⁻¹. (Found: C, 81·77; H, 10·89. C₁₈H₃₄O requires: C, 81·82; H, 10·91%.)

The 2,4-dinitrophenylhydrazone (HCl method) on crystallization from glacial AcOH was obtained in glistening yellow flakes, m.p. 169–170°. (Found: N, 13.81. $C_{21}H_{88}O_4N_4$ requires N: 14.00%.)

(ii) Pyridine-CrO₃ oxidation of dihydro- α -cyperol (IV). To a solution of CrO₃ (3.0 g) in dry pyridine (30 ml), maintained at 0°, a pyridine solution of dihydro- α -cyperol (2.0 g, vide infra; in 20 ml pyridine) was added and the mixture left aside at room temp (25-30°) for 18 hr. The dihydro- α -cyperone (1.6 g) was obtained as a colourless liquid, b.p. 140-141°/3 mm. The product readily yielded a semicarbazone, m.p. 186-187°, which was undepressed on admixture with a sample of semicarbazone obtained under (i). Both samples of III had identical IR spectra.

Dihydro-a-Cyperol (IV)

(i) Lithium aluminium tri-t-butoxy hydride reduction of dihydro- α -cyperone (III). Anhydrous t-butanol (0.5 ml) was slowly added to a solution of LAH (100 mg, 0.0025 moles) in dry tetrahydro-furan (10 ml) kept at 0°. Dihydro- α -cyperone (0.11 g, 0.0005 moles) in tetrahydrofuran (5 ml) was added with shaking and the mixture allowed to stand at 0° for $\frac{1}{2}$ hr and then at room temp for 18 hr. The reaction mixture was poured into ice-cold 1N HCl (25 ml) and extracted with pet. ether (10 ml × 4). The extracts were washed with NaHCO₂ aq (5 ml × 3), brine, dried and the solvent flashed off. The waxy solid (106 mg) was purified by sublimation (\sim 65°/0.3 mm) to furnish IV as white needles, m.p. 74°, [α]³⁶₂ - 5·1° (c, 5%), yield 0·1 g, 90%. IR spectrum (Nujol): OH 3300, 1030; C=C 3100, 1650, 890 cm⁻¹. (Found: C, 81.09; H, 11.69. C₁₅H₁₈₀O requires: C, 81.08; H, 11.71%.)

The 3,5-dinitrobenzoate, crystallized as white silky needles (EtOH), m.p. 156-157°, $[\alpha]_{\rm D}$ + 37.36° (c, 2.6%). (Found: N, 6.86. C₂₃H₂₈O₆N₂ requires: N, 6.73%.)

The acetate was prepared by the acetyl chloride-pyridine method: b.p. $128-129^{\circ}/1.2 \text{ mm}$, $[\alpha]_{10}^{20}$ + 13.3° (c, 1.5%). IR spectrum (liq.): OAc 1748, 1245, 1030; C=C 1648, 890 cm⁻¹. (Found: C, 77.09; H, 10.68. C₁₇H₁₈O₂ requires: C, 77.21; H, 10.67%.)

(ii) Sodium-n-propanol reduction of α -cyperone (II). To a solution of α -cyperone (10.9 g, 0.05 mole) in n-propanol (300 ml), Na (11.5 g; 0.5 g atoms) was added rapidly, the immediate vigorous reaction being maintained by heating on a steam-bath till all the Na disappeared (~2 hr). The reaction mixture was cooled, diluted with water (1.3 l.) and extracted with benzene-ether (1:1; 100 ml × 4) and yielded a product (9.8 g), b.p. 126-128°/0.9 mm. GLC (polyester column, 200°) revealed the presence of one major (88%) and two minor components. The product (9.5 g) dissolved in benzene (25 ml) was treated with a solution of 3,5-dinitrobenzoyl chloride (19.7 g) in benzene (80 ml) and pyridine (6 ml) at 55° for 4 hr. The reaction mixture yielded the crude 3,5-dinitrobenzoate which was crystallized from EtOH to furnish silky needles (11.2 g), m.p. 156-157°, mixed m.p. with the sample from (i) was undepressed.

The pure 3,5-dinitrobenzoate (11 g) in EtOH (55 ml) was treated with NaOH (4·4 g in 11 ml water and 55 ml EtOH) at room temp (\sim 25°) and left overnight (15 hr). The Na salt of 3,5-dinitrobenzoic acid, which had crystallized out, was filtered off from the rose-coloured reaction mixture and washed with EtOH (5 ml × 4). The combined filtrate and washings were freed of solvent, the residue diluted with water (450 ml) and extracted with pet. ether (150 ml × 5). The extract yielded IV, b.p. 125°/0·8 mm, m.p. 71-72°, which on sublimation gave long white needles (5·5 g), m.p. 74°.

(iii) Lithium-liquid ammonia-ethanol reduction of α -cyperone (11). To α -cyperone (2 g) in dry ether (30 ml), dioxan (40 ml) and liq. NH₈ (500 ml), Li (0.51 g) was added with stirring. After the addition, the Li solution was stirred for 15 min and then EtOH (4.5 ml) was added. The product (IV) was obtained as a viscous liquid b.p. 129-131°/1.2 mm, yield 1.62 g. This was purified through its 3,5-dinitrobenzoate to give pure IV in 50% overall yield.

Pyrolysis of dihydro- α -cyperyl m-borate (V)

A mixture of dihydro- α -cyperol (2.22 g, 0.01 mole), boric acid (0.62 g, 0.01 mole) and dry toluene (10 ml) was gently refluxed in a flask attached to a modified^{a1} Dean-Stark apparatus, till no more

³¹ Sukh Dev, J. Indian Chem. Soc. 30, 443 (1953).

water separated. The solvent was distilled off from the reaction mixture, under suction (40 mm), from a bath, the temp of which was gradually raised from 100° to 170°. The resulting *m*-borate was pyrolysed by cautiously heating with a free flame, under red. press. (200 mm). The crude pyrolysate (1.85 g) was filtered through a bed of activated silica gel (25×2.0 cm) and the column washed with pet. ether (200 ml). The eluted material on distillation gave a colourless mobile liquid (1.77 g, 87%), b.p. 129–130°/12 mm. GLC (silicone column, 160°) of this material showed 4 peaks with areas in the ratio: 1:5:12:2, starting with the peak of least retention time. Retention times in terms of the first peak were 1, 1.15, 1.375 and 1.575 respectively. TLC (AgNO₃-silica gel¹⁸³) of the material showed 5 spots with R_8 values: 2.055, 1.863, 1.754, 1.397 and 0.904 (solvent system: benzene).

The separation of major components from the above mixture was effected by two methods.

(i) Preparative GLC. A total of 1 g of the above product was injected in 4 lots on a preparative GLC column (9' × 1", 25% diethylene glycol polysuccinate on 60-80 mesh Chromosorb W, 150°, N₂, 10 lbs/in³). Fractions corresponding to the top portion of peaks 2 and 3 were collected separately in specially-designed receivers, maintained at -10° . These fractions on distillation gave Δ^3 -selinene (VII, 0.12 g) and α -selinene (I, 0.3 g) respectively. The products showed single peaks in GLC and single spots in TLC; their physical constants are shown in Table 2. (Found for VII: C, 87.92; H, 11.77. Found for I: C, 88.01; H, 11.72. C₁₈H₂₄ requires: C, 88.16; H, 11.84%.)

(ii) Chromatography over AgNO₃-silica gel.²⁴ The unsaturated hydrocarbon mixture (1.75 g) in pet. ether (2 ml) was chromatographed on 15% AgNO₃-silica gel²³ (60 g, 20 \times 2.5 cm) and eluted with different solvents, following the course of separation by TLC (solvent system: benzene):

Frac. 1:	pet. ether	3 imes 20 ml	_
Frac. 2:	pet. ether-	2 imes 20 ml	0·43 g of VIII
	25% C ₆ H ₆		
Frac. 3:	pet. ether-	1×20 ml	0.25 g of VIII, I and
	25% C6H6		compd. of R_s 1.863.
Frac. 4:	pet. ether-	6×20 ml	0·55 g of I
	25% C6H6		
Frac. 5:	pet. ether-	6 imes 20 ml	
	25% C ₆ H ₆		0·14 g of I and VII
Frac. 6:	Benzene	4 imes 20 ml	
Frac. 7:	Benzene	4×20 ml	0·17 g of VII
Frac. 8:	Benzene	3×20 ml	0.02 g mostly VII.

Fractions 4 and 7 were distilled to give pure α -selinene and Δ^3 -selinene respectively. Fraction 2 which amounted to almost 25% of the starting material, was an artefact, produced during chromatography, as a comparison of its IR spectrum with that of the total olefin mixture did not reveal its presence in amounts greater than 10%. However, TLC clearly shows its presence ($R_s 2.055$) in the original mixture; in GLC its retention time is the same as Δ^3 -selinene on a polyester or silicone column. Distillation of fraction 2 gave pure VIII. (Found: C, 87.62; H, 11.78. C₁₅H₂₄ requires: C, 88.16; H, 11.84%.)

Pyrolysis of dihydro-a-cyperyl ethyl carbonate

Dihydro- α -cyperyl ethyl carbonate (VI). To a solution of dihydro- α -cyperol (1.05 g) in dry pyridine (25 ml), freshly distilled ethyl chloroformate (10 ml) was introduced dropwise at 0°. After allowing the reaction mixture to stand at room temp (20–27°) for 20 hr, it was poured into ice-cold aqueous AcOH (200 ml, 1:1) and the product extracted with ether (30 ml × 4) and the extracts worked up to give VI as a colourless liquid (1.35 g, 97%), b.p. 130–131°/0.5 mm, n_D^{30} 1.4821. IR spectrum (liq.): RCO-O 1733, 1263 and 1004; C=C 1639, 888 cm⁻¹. (Found: C, 73.25; H, 10.00. C₁₈H₃₀O₂ requires: C, 73.43; H, 10.27%.)

Pyrolysis. The above ester (1 g) was introduced dropwise in a column (35×1.4 cm), packed with pyrex glass pieces and heated in a vertical furnace³³ maintained at 400 $\pm 5^{\circ}$; the pyrolysis was

³³ Sukh Dev, J. Indian Chem. Soc. 30, 729 (1953).

carried out under a red. press. (200 mm) of N₁ during 1 hr. The pyrolysate (0.9 g) was filtered through a column of activated silica gel (15×1.5 cm) which was washed with pet. ether (200 ml). This eluate after solvent removal and distillation yielded 0.22 g of olefin mixture, b.p. 124–126°/10 mm. Further elution with ether (300 ml) gave 0.6 g of the starting ester.

The olefin mixture was separated by preparative GLC as described earlier, and the components identified as Δ^3 -selinene and α -selinene.

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