(Fig. 1a) case a reduction of 3·9° (average) is found whereas for the bidentate mode (Fig. 1b) a considerable change of 13·1° (average) is involved. These changes reflect the relative lack of strain in the five-membered ring compared with the considerable strain involved in the four-membered ring.

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Structure and Absolute Configuration of (−)-Sclareol-8-acetate†

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Abstract. Natural (−)-sclareol, of which the principal source is clary sage (*Salvia sclarea* L.), was recently used for a new synthesis of Ambrox®, one of the most important ambergris fragrance chemicals [Decorzant, Vial, Näf & Whitesides (1987). *Tetrahedron*, 43, 1871–1879]. (−)-Sclareol-8-acetate: $C_{22}H_{38}O_3$, m.p. 395–396 K, $[\alpha]_D^{20°C} = -35\cdot8°$ ($c = 1\cdot2\%$ in $CHCl_3$), $M_r = 350\cdot5$, orthorhombic, $P2_12_12_1$, $a = 6\cdot5001$ (7), $b = 16\cdot287$ (5), $c = 19\cdot497$ (6) Å, $V = 2064\cdot1$ (9) Å³, $Z = 4$, $F(000) = 776$, $D_x = 1\cdot128$ Mg m⁻³, λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 0\cdot068$ mm⁻¹, $T = 180$ K, $R = 0\cdot066$ for 1299 observed reflections [$|F_o| \geq 3\sigma(F_o)$ and $|F_o| \geq 9\cdot0$]. The (13R) configuration has been confirmed in spite of the presence of 9% of 13-*epi*-sclareol-8-acetate in the crystal. The hydroxyl group attached to C(13) is involved in an intermolecular hydrogen bond with the carbonyl of the acetate. The six-membered rings are *trans*-fused and both are in the chair conformation.

Introduction. Sclareol is a diterpene widely distributed in nature. It is a major component in the oil of clary sage (*Salvia sclarea* L.) and is present in several species of tobacco. It has been used to prepare a series of ambra odorants (Ohloff, 1982), Ambrox®(III) (Decorzant, Vial, Näf & Whitesides, 1987), drim-9(11)-8-ol (Leite, Sarragiotto, Imamura & Marsaioli, 1986), olean-11,12;13,18-diene, a pentacyclic triterpene derived from β-amyrin (Corey, Hess & Proskow, 1963), a vitamin K analog (Orgiyan & Lazurevskii, 1965), and other diterpenes such as manool (Büchi & Biemann, 1957; Ohloff 1958) and labdanolic acid (Bory & Lederer, 1957). Sclareol shows some interesting biological activity. It inhibited wheat coleoptiles

† {1R-[1α(R*),2β,4aβ,4aα]}-2-(Acetyloxy)-α-ethenyldecahydro-α,2,5,5,8a-pentamethyl-1-naphthalenepropanol; (13R)-8α-acetoxy-labd-14-en-13-ol.

growth (Severson, Cutler, Cole, Jackson, Sisson, Johnson, Herzog & Stephenson, 1985; Cutler, Reid & Deletang, 1977), reduced infection with rust in French beans, broad beans and wheat (Bailey, Carter, Burden & Wain, 1974), and markedly inhibited the radial extension of fungal colonies grown in agar (Bailey, Vincent & Burden, 1974).

Although the stereochemistry of the substituted decaline skeleton is well known (Klyne & Buckingham, 1978; Barltrop & Bigley, 1959), the configuration at the C(13) atom has been subject to much debate. Büchi & Biemann (1957) adopt the (13S) configuration whereas (13R) was selected by Barltrop & Bigley (1959) and Bigley, Rogers & Barltrop (1960). Subsequently, these workers opted (Bigley, Rogers & Barltrop, 1962) for the (13S) configuration. However, Soucek & Vlad (1962) found by chemical degradation that sclareol has the (13R) configuration and the latter chirality was commonly adopted. In order to establish the chirality of C(13), the crystal structure of (−)-sclareol-8-acetate (I) [adequate crystals of the natural (−)-sclareol (II) were not available] was determined.

(I)   (II)

(III)   (IV)
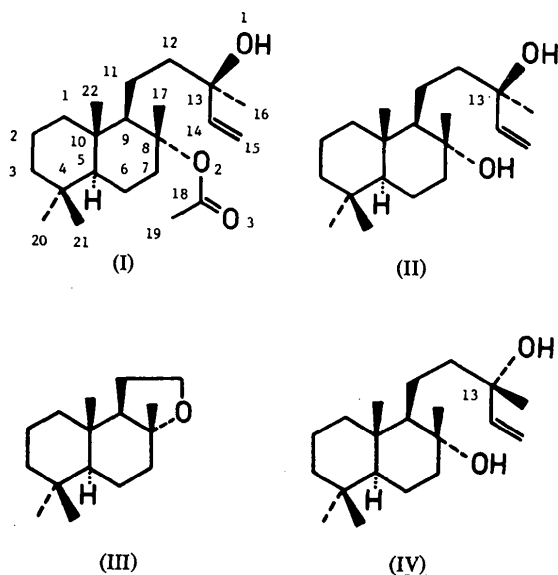
Experimental. Single crystals of (I) were grown from hexane solution at 243 K. Colourless crystal of average dimensions $0.25 \times 0.35 \times 0.40$ mm; Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$, cell dimensions from 21 reflections ($2\theta = 18–25°$), data collection: (sinθ)/$\lambda \leq 0.550$ Å^{-1}, $h\,0\rightarrow7$, $k\,0\rightarrow20$, $l\,0\rightarrow21$; $\omega/2\theta$ scans, ω-scan angle $1.2°$, two standard reflections varied by a maximum of $2.8\sigma(I)$; 1712 measured unique reflections; 1299 observed with $|F| \geq 3\sigma(F)$ and $|F| \geq 9$; Lorentz–polarization; no absorption correction; systematic absences $h00$:

$h = 2n+1$, $0k0$: $k = 2n+1$, $00l$: $l = 2n+1$; structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Two block-matrix least-squares refinements using $|F|$ values. 227 parameters refined; no secondary-extinction correction. All coordinates of H atoms were calculated except for the hydroxyl group where the H atom was located from a difference electron density map but not refined. $R = 6.6\%$; $w = 1$; $S = 4.25$; max. and ave. ratio of $|$shift$|$ to e.s.d.: 0.009 and 0.064 respectively; max. and min. heights in the final difference electron density map of 0.42 and -0.28 e Å^{-3}. All calculations performed with a local version of *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEPII* (Johnson, 1976). It should be noted that the sclareol from clary sage is a mixture (9:1) of sclareol (II) and 13-*epi*-sclareol (IV). All attempts to separate the two diastereoisomers, fractional crystalization, chromatography over SiO$_2$, Al$_2$O$_3$, Lobar column and HPLC did not lead to any enrichment of one or other of the diastereoisomers of sclareol, sclareol-8-acetate or -8,13-diacetate, to more than a 91:9 ratio.

Discussion. Final positional parameters and, for non-hydrogen atoms, equivalent isotropic temperature factors are given in Table 1.* Bond distances and relevant torsion angles are to be found in Table 2. The absolute configuration of the molecule is shown in Fig. 1. The crystals studied contain a mixture (91:9) of sclareol-8-acetate (I) and 13-*epi*-sclareol-8-acetate. In a difference electron density map, only one site was observed for each substituent attached to C(13). These positions have been assigned to C(16) and O(1) and refined with anisotropic displacement parameters. The main interest of this study being precisely the un-ambiguous distinction between these two substituents, several arguments can be invoked to confirm that (13R) is the correct configuration: (i) The bond lengths C(13)–C(16) [1.543 (11)] and C(13)–O(1) [1.428 (9) Å] are in good agreement with the standard values observed for C–C$_{(methyl)}$ and C–O$_{(hydroxyl)}$ distances respectively. (ii) The hydroxyl group is involved in an intermolecular hydrogen bond with the carbonyl oxygen of the acetate fragment [O(1)···O(3)($1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) = 2.870 (7) Å]. Moreover, the H atom of the hydroxyl group has been well observed on a difference electron density map and the resulting geometry can be considered as satisfactory [distance O(1)–H(O1) = 0.93 Å, angle C(13)–O(1)–H(O1) =

Table 1. *Fractional coordinates and, for non-hydrogen atoms, equivalent isotropic temperature factors,* U_{eq} *($\text{Å}^2 \times 10^3$), with e.s.d.'s in parentheses*

U_{eq} is the average of eigenvalues of U.

	x	y	z	U_{eq}
O(1)	0·4660 (9)	−0·1869 (3)	0·1881 (3)	34·6 (19)
O(2)	0·5167 (8)	0·0669 (3)	0·15866 (23)	25·5 (16)
O(3)	0·6184 (10)	0·1728 (3)	0·2255 (3)	38·4 (19)
C(1)	0·6043 (13)	−0·0416 (4)	−0·0680 (4)	26·2 (24)
C(2)	0·6745 (14)	−0·0319 (5)	−0·1429 (4)	35 (3)
C(3)	0·6479 (15)	0·0569 (5)	−0·1666 (4)	38 (3)
C(4)	0·7592 (13)	0·1206 (5)	−0·1216 (4)	33 (3)
C(5)	0·6958 (12)	0·1060 (4)	−0·0449 (4)	25·7 (24)
C(6)	0·7818 (13)	0·1675 (4)	0·0060 (4)	30 (3)
C(7)	0·6679 (13)	0·1622 (4)	0·0751 (4)	29 (3)
C(8)	0·6804 (12)	0·0766 (4)	0·1057 (3)	24·1 (24)
C(9)	0·6061 (11)	0·0109 (4)	0·0535 (3)	20·9 (23)
C(10)	0·7184 (12)	0·0171 (4)	−0·0178 (3)	20·8 (24)
C(11)	0·5980 (12)	−0·0759 (4)	0·0839 (4)	26·2 (24)
C(12)	0·3762 (12)	−0·1067 (4)	0·0898 (4)	29·2 (25)
C(13)	0·3488 (13)	−0·1922 (5)	0·1226 (4)	30 (3)
C(14)	0·1250 (15)	−0·2102 (6)	0·1267 (5)	45 (3)
C(15)	0·0167 (18)	−0·2102 (6)	0·1792 (6)	83 (5)
C(16)	0·4543 (15)	−0·2602 (5)	0·0802 (4)	41 (3)
C(17)	0·8893 (13)	0·0598 (5)	0·1396 (4)	30·0 (24)
C(18)	0·5008 (14)	0·1166 (5)	0·2138 (4)	35 (3)
C(19)	0·3227 (14)	0·0920 (6)	0·2572 (4)	40 (3)
C(20)	0·6808 (14)	0·2060 (5)	−0·1444 (4)	40 (3)
C(21)	0·9948 (14)	0·1162 (5)	−0·1344 (4)	42 (3)
C(22)	0·9456 (11)	−0·0138 (4)	−0·0122 (4)	27·4 (25)
H(O1)	0·4428	−0·2374	0·2107	51

Table 2. *Interatomic distances (Å) and selected torsion angles (°) with e.s.d.'s in parentheses*

O(1)—C(13)	1·428 (9)	C(6)—C(7)	1·541 (11)
O(2)—C(8)	1·491 (9)	C(7)—C(8)	1·518 (10)
O(2)—C(18)	1·350 (9)	C(8)—C(9)	1·554 (10)
O(3)—C(18)	1·214 (10)	C(8)—C(17)	1·535 (11)
C(1)—C(2)	1·537 (11)	C(9)—C(10)	1·574 (10)
C(1)—C(10)	1·556 (10)	C(9)—C(11)	1·534 (10)
C(2)—C(3)	1·528 (11)	C(10)—C(22)	1·565 (11)
C(3)—C(4)	1·540 (11)	C(11)—C(12)	1·531 (11)
C(4)—C(5)	1·570 (11)	C(12)—C(13)	1·542 (11)
C(4)—C(20)	1·548 (11)	C(13)—C(14)	1·486 (13)
C(4)—C(21)	1·553 (13)	C(13)—C(16)	1·543 (11)
C(5)—C(6)	1·517 (11)	C(14)—C(15)	1·243 (15)
C(5)—C(10)	1·548 (10)	C(18)—C(19)	1·488 (12)

C(18)—O(2)—C(8)—C(9)	−174·0 (6)	C(5)—C(6)—C(7)—C(8)	57·8 (9)
C(8)—O(2)—C(18)—C(19)	179·8 (5)	C(6)—C(7)—C(8)—C(9)	−53·4 (9)
C(10)—C(1)—C(2)—C(3)	−56·5 (9)	C(7)—C(8)—C(9)—C(10)	52·7 (8)
C(2)—C(1)—C(10)—C(5)	53·8 (8)	C(8)—C(9)—C(10)—C(5)	−53·8 (8)
C(1)—C(2)—C(3)—C(4)	56·0 (10)	C(8)—C(9)—C(11)—C(12)	112·4 (7)
C(2)—C(3)—C(4)—C(5)	−51·9 (9)	C(9)—C(11)—C(12)—C(13)	−177·6 (6)
C(3)—C(4)—C(5)—C(10)	51·3 (9)	C(11)—C(12)—C(13)—C(14)	177·6 (7)
C(10)—C(5)—C(6)—C(7)	−60·0 (8)	O(1)—C(13)—C(14)—C(15)	9·8 (14)
C(4)—C(5)—C(10)—C(1)	−52·3 (9)	C(12)—C(13)—C(14)—C(15)	−106·8 (12)
C(6)—C(5)—C(10)—C(9)	57·2 (8)		

111°]; (iii) After interchange of the C(16) and O(1) positions, the structure refinement leads to a negative value of the determinant of the tensor associated with C(16) and thus confirms an electron deficiency at this position. In conclusion, the chirality of the substituted decaline being known (Klyne & Buckingham, 1978; Barltrop & Bigley, 1959) and the relative (13R) configuration being confirmed in this work, the absolute configurations of compounds (I) and (II) are well established.
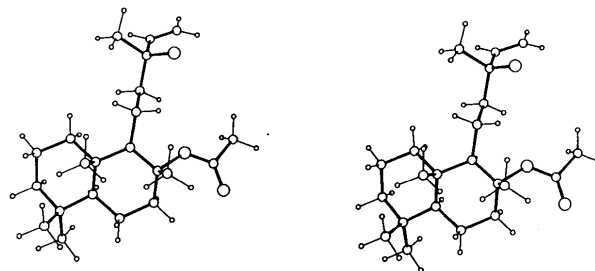

Fig. 1. Stereopair showing the configuration of the molecule.

The vinylic fragment [and particularly the C(15) atom] is affected by large atomic displacements and this explains the relatively short observed distance between the C(14) and C(15) atoms [1·243 (15) Å]. The six-membered rings of the decaline are *trans*-fused and both are in a chair conformation.

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