



# Crystal structure of 3a,6,6,9a-tetra-methyl-dodecahydronaphtho[2,1-*b*]furan-2-ol

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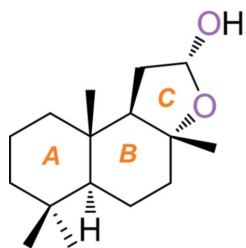
The title compound (common name: sclaral), C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>, is a sclareolide derivative, which was synthesized from sclareolide itself. In the molecule, the two six-membered rings, *A* and *B*, of the labdane skeleton adopt chair conformations and the five-membered O-containing heterocyclic ring *C* displays an envelope conformation, with the methine C atom of the fused C—C bond as the flap. In the crystal, molecules are linked by O—H...O hydrogen bonds, forming chains propagating along [100].

**Keywords:** crystal structure; sclareolide; sclaral; hydrogen bonding.

**CCDC reference:** 1421899

## 1. Related literature

For the chemistry and biological importance of sclareolides and the title compound, see: Dixon *et al.* (2012); Michaudel *et al.* (2015); Sun *et al.* (2013). For previously reported spectroscopic and analytical data for the title compound, see: Margaros *et al.* (2007). For related structures, see: Martínez-Carrera *et al.* (1978); Huang *et al.* (2008).



## 2. Experimental

### 2.1. Crystal data

C <sub>16</sub> H <sub>28</sub> O <sub>2</sub>	<i>V</i> = 1465.0 (3) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 252.38	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Mo <i>K</i> α radiation
<i>a</i> = 7.1675 (8) Å	<i>μ</i> = 0.07 mm <sup>-1</sup>
<i>b</i> = 11.2654 (13) Å	<i>T</i> = 296 K
<i>c</i> = 18.144 (2) Å	0.22 × 0.20 × 0.18 mm

### 2.2. Data collection

Bruker SMART CCD diffractometer	9607 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	2658 independent reflections
<i>T</i> <sub>min</sub> = 0.984, <i>T</i> <sub>max</sub> = 0.987	2299 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.030

### 2.3. Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.046	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.127	<i>Δρ</i> <sub>max</sub> = 0.40 e Å <sup>-3</sup>
<i>S</i> = 1.08	<i>Δρ</i> <sub>min</sub> = -0.20 e Å <sup>-3</sup>
2658 reflections	1 restraint
181 parameters	

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H1O...O1 <sup>i</sup>	0.93 (2)	1.90 (2)	2.773 (2)	155 (3)

Symmetry code: (i) *x* - ½, -*y* + ¾, -*z* + 1.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL*.

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5201).

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## supporting information

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## Crystal structure of 3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-*b*]furan-2-ol

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### S1. Comment

The title compound, sclaral, is an important reaction intermediate in the synthesis of some natural products. It is used as a precursor of borono-sclareolide which makes the direct coupling of a terpenoid "donor" with a non-terpenoid "acceptor" possible (Dixon et al., 2012). It is also used to produce analogs of hongoquercin A, an antibiotic of fungal origin (Michaudel et al., 2015; Sun et al., 2013). Moreover, sclaral is an intermediate in the production of important natural products, such as (+)-premnalane A (Margaros et al., 2007). The title compound has been synthesized and we report herein on its crystal structure,

The molecular structure of the title compound is shown in Fig. 1. The molecule possesses a highly rigid structure, composed of three main rings (A, B and C). The six-membered rings, A (C5/C6/C8—C11) and B (C1—C6), adopt chair conformations, while the five-membered O-containing heterocyclic ring C (C1/C2/C14/C15/O1) displays an envelope conformation, in which atom C1 is the flap.

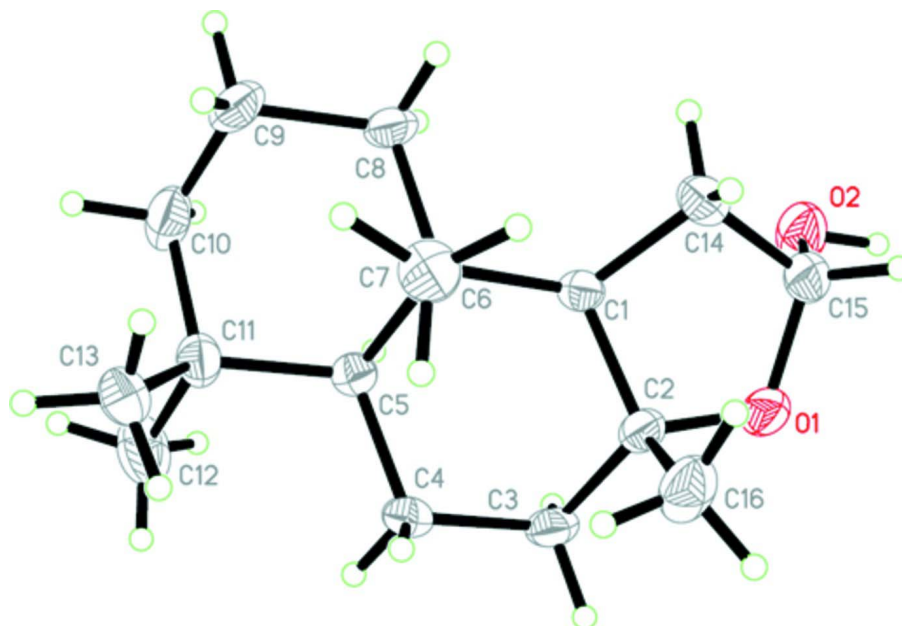
In the crystal, molecules are linked via O—H...O hydrogen bonds forming chains propagating along the *a* axis direction (Table 1 and Fig. 2).

### S2. Synthesis and crystallization

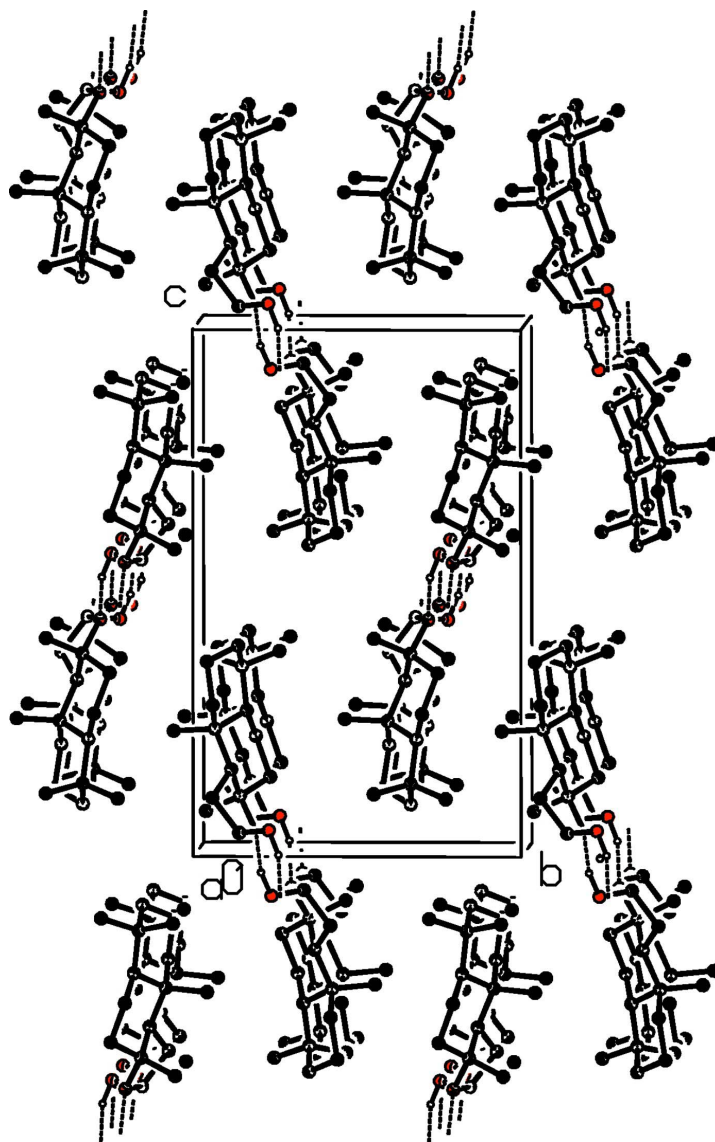
A solution of (+)-sclareolide (10.0 g, 40.0 mmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (100ml) was cooled to 195 K and DIBAL-H (1.5M in toluene, 32ml, 48.0 mmol, 1.2 eq) was added drop wise over 20 min, and stirring was continued for an additional 60 min. Water was then slowly added until the bubbles vanished then the temperature of the mixture was allowed to rise to rt. The mixture was stirred at rt for 30min, and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 ml). The combined organic extracts were washed with saturated aqueous NaHCO<sub>3</sub> solution (3 × 50 ml) and washed with brine (3 × 50 ml), dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure, affording the title compound, sclaral (yield: 9.37 g, 93 %, 3.7:1 lactol:aldehyde) as a white solid. Spectroscopic and analytical data matches reported previously (Margaros *et al.*, 2007). The white solid was recrystallized from EtOH to afford colourless crystals.

### S3. Refinement

The CH H atoms (H1, H5 and H15) and the hydroxyl H atom (H1O) were located in a difference Fourier map. The CH H atoms were freely refined while the OH H atom was refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The remaining C-bound H atoms were placed in calculated positions and refined as riding: C—H = 0.96–0.97 Å with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{C})$  for other H atoms.

**Figure 1**

A view of the molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**

View along the *a* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1), and C-bound H atoms have been omitted for clarity.

### 3a,6,6,9a-Tetramethyldodecahydronaphtho[2,1-*b*]furan-2-ol

#### Crystal data

$C_{16}H_{28}O_2$

$M_r = 252.38$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.1675$  (8) Å

$b = 11.2654$  (13) Å

$c = 18.144$  (2) Å

$V = 1465.0$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 560$

$D_x = 1.144$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2540 reflections

$\theta = 3.1$ – $21.6^\circ$

$\mu = 0.07$  mm<sup>-1</sup>

$T = 296$  K

Block, colourless

$0.22 \times 0.20 \times 0.18$  mm

*Data collection*

Bruker SMART CCD  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
phi and  $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Bruker, 2002)  
 $T_{\min} = 0.984$ ,  $T_{\max} = 0.987$

9607 measured reflections  
2658 independent reflections  
2299 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$   
 $\theta_{\text{max}} = 25.3^\circ$ ,  $\theta_{\text{min}} = 2.1^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -13 \rightarrow 13$   
 $l = -21 \rightarrow 16$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.127$   
 $S = 1.08$   
2658 reflections  
181 parameters  
1 restraint  
Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map  
Hydrogen site location: inferred from  
neighbouring sites  
H atoms treated by a mixture of independent  
and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.258P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0482 (3)	0.86847 (19)	0.67801 (12)	0.0348 (5)
C2	0.2058 (3)	0.8474 (2)	0.62309 (12)	0.0392 (5)
C3	0.3421 (3)	0.7594 (2)	0.65591 (13)	0.0469 (6)
H3A	0.4488	0.7504	0.6235	0.056*
H3B	0.2825	0.6826	0.6612	0.056*
C4	0.4067 (3)	0.8050 (2)	0.73202 (13)	0.0443 (5)
H4A	0.4901	0.7471	0.7539	0.053*
H4B	0.4759	0.8783	0.7255	0.053*
C5	0.2429 (3)	0.82737 (18)	0.78462 (12)	0.0342 (5)
C6	0.1029 (3)	0.91962 (17)	0.75332 (11)	0.0339 (5)
C7	0.1778 (4)	1.04780 (19)	0.74731 (14)	0.0515 (6)
H7A	0.1100	1.0896	0.7098	0.077*
H7B	0.3078	1.0459	0.7347	0.077*
H7C	0.1620	1.0875	0.7937	0.077*
C8	-0.0711 (3)	0.9208 (3)	0.80299 (14)	0.0519 (6)

H8A	-0.1541	0.9836	0.7869	0.062*
H8B	-0.1368	0.8460	0.7976	0.062*
C9	-0.0233 (4)	0.9397 (3)	0.88443 (15)	0.0655 (8)
H9A	0.0283	1.0186	0.8910	0.079*
H9B	-0.1363	0.9343	0.9136	0.079*
C10	0.1147 (4)	0.8493 (3)	0.91114 (14)	0.0620 (8)
H10A	0.0560	0.7717	0.9097	0.074*
H10B	0.1444	0.8665	0.9622	0.074*
C11	0.2970 (3)	0.8434 (2)	0.86729 (13)	0.0462 (6)
C12	0.4061 (5)	0.7330 (3)	0.89311 (17)	0.0775 (9)
H12A	0.5323	0.7377	0.8756	0.116*
H12B	0.3480	0.6628	0.8738	0.116*
H12C	0.4059	0.7298	0.9460	0.116*
C13	0.4176 (4)	0.9519 (3)	0.88354 (15)	0.0579 (7)
H13A	0.5198	0.9547	0.8494	0.087*
H13B	0.4652	0.9468	0.9329	0.087*
H13C	0.3438	1.0226	0.8786	0.087*
C14	-0.1012 (4)	0.9213 (2)	0.62815 (14)	0.0520 (6)
H14A	-0.0739	1.0033	0.6157	0.062*
H14B	-0.2240	0.9166	0.6504	0.062*
C15	-0.0850 (3)	0.8402 (2)	0.56099 (14)	0.0495 (6)
H15	-0.112 (4)	0.884 (2)	0.5155 (15)	0.059*
C16	0.3106 (4)	0.9544 (3)	0.59153 (15)	0.0622 (7)
H16A	0.3743	0.9313	0.5472	0.093*
H16B	0.3997	0.9823	0.6270	0.093*
H16C	0.2234	1.0166	0.5805	0.093*
H1	0.007 (3)	0.7879 (18)	0.6884 (10)	0.024 (5)*
H5	0.168 (3)	0.751 (2)	0.7848 (12)	0.040 (6)*
O1	0.1024 (2)	0.79612 (16)	0.56104 (8)	0.0520 (5)
O2	-0.2051 (3)	0.7454 (2)	0.56902 (11)	0.0678 (6)
H1O	-0.242 (4)	0.715 (3)	0.5234 (11)	0.081*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0291 (10)	0.0358 (11)	0.0396 (11)	0.0007 (9)	0.0009 (9)	-0.0037 (9)
C2	0.0342 (10)	0.0491 (12)	0.0342 (11)	-0.0040 (10)	0.0055 (10)	-0.0055 (10)
C3	0.0352 (11)	0.0571 (14)	0.0485 (14)	0.0072 (11)	0.0082 (11)	-0.0129 (11)
C4	0.0313 (10)	0.0529 (13)	0.0485 (14)	0.0097 (10)	0.0001 (10)	-0.0055 (10)
C5	0.0331 (10)	0.0328 (10)	0.0368 (11)	-0.0020 (9)	0.0018 (9)	-0.0018 (9)
C6	0.0270 (9)	0.0355 (10)	0.0393 (11)	0.0012 (9)	0.0011 (9)	-0.0073 (9)
C7	0.0607 (15)	0.0336 (12)	0.0601 (15)	0.0041 (11)	-0.0055 (13)	-0.0088 (11)
C8	0.0304 (11)	0.0749 (16)	0.0503 (14)	0.0045 (11)	0.0059 (11)	-0.0221 (13)
C9	0.0430 (13)	0.104 (2)	0.0498 (15)	-0.0091 (15)	0.0137 (12)	-0.0322 (16)
C10	0.0613 (16)	0.090 (2)	0.0352 (13)	-0.0243 (16)	0.0041 (13)	-0.0063 (13)
C11	0.0474 (13)	0.0528 (13)	0.0385 (12)	-0.0035 (11)	-0.0058 (11)	-0.0025 (10)
C12	0.092 (2)	0.078 (2)	0.0620 (18)	0.0127 (19)	-0.0247 (18)	0.0158 (15)
C13	0.0434 (13)	0.0751 (17)	0.0551 (15)	-0.0065 (13)	-0.0103 (13)	-0.0149 (14)

C14	0.0439 (13)	0.0601 (15)	0.0520 (14)	0.0096 (12)	-0.0092 (12)	-0.0063 (12)
C15	0.0407 (12)	0.0673 (15)	0.0404 (13)	-0.0035 (12)	-0.0050 (11)	-0.0024 (12)
C16	0.0648 (16)	0.0754 (18)	0.0463 (14)	-0.0191 (15)	0.0090 (14)	0.0086 (13)
O1	0.0417 (8)	0.0749 (11)	0.0393 (9)	-0.0020 (9)	0.0020 (8)	-0.0166 (8)
O2	0.0591 (11)	0.0950 (15)	0.0494 (11)	-0.0205 (11)	-0.0057 (10)	-0.0045 (10)

*Geometric parameters (Å, °)*

C1—C14	1.523 (3)	C6—C8	1.539 (3)
C1—C2	1.525 (3)	C6—C7	1.544 (3)
C1—C6	1.534 (3)	C8—C9	1.532 (4)
C2—O1	1.466 (3)	C9—C10	1.500 (4)
C2—C3	1.513 (3)	C10—C11	1.531 (3)
C2—C16	1.531 (3)	C11—C13	1.526 (3)
C3—C4	1.544 (3)	C11—C12	1.542 (4)
C4—C5	1.534 (3)	C14—C15	1.527 (3)
C5—C6	1.552 (3)	C15—O2	1.380 (3)
C5—C11	1.560 (3)	C15—O1	1.432 (3)
C14—C1—C2	101.16 (18)	C1—C6—C5	103.87 (16)
C14—C1—C6	124.19 (19)	C8—C6—C5	108.38 (18)
C2—C1—C6	116.81 (16)	C7—C6—C5	115.30 (17)
O1—C2—C3	111.75 (18)	C9—C8—C6	112.63 (18)
O1—C2—C1	100.87 (15)	C10—C9—C8	111.4 (2)
C3—C2—C1	108.84 (18)	C9—C10—C11	115.1 (2)
O1—C2—C16	105.71 (18)	C13—C11—C10	110.4 (2)
C3—C2—C16	110.26 (19)	C13—C11—C12	107.4 (2)
C1—C2—C16	119.00 (19)	C10—C11—C12	108.0 (2)
C2—C3—C4	109.12 (18)	C13—C11—C5	114.8 (2)
C5—C4—C3	112.42 (17)	C10—C11—C5	107.00 (18)
C4—C5—C6	112.15 (17)	C12—C11—C5	109.0 (2)
C4—C5—C11	115.27 (17)	C1—C14—C15	100.75 (19)
C6—C5—C11	115.79 (17)	O2—C15—O1	108.5 (2)
C1—C6—C8	108.51 (17)	O2—C15—C14	109.4 (2)
C1—C6—C7	112.17 (19)	O1—C15—C14	106.16 (19)
C8—C6—C7	108.36 (19)	C15—O1—C2	109.75 (17)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H1O...O1 <sup>i</sup>	0.93 (2)	1.90 (2)	2.773 (2)	155 (3)

Symmetry code: (i)  $x-1/2, -y+3/2, -z+1$ .