

Table 2. Hydrogen-bonding and close-contact geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O3—H33...O2'	0.82	1.842	2.649 (14)	168
O3'—H33'...O2''	0.82	1.858	2.666 (17)	168
C2—H2B...O2''	0.97	2.69	3.393 (9)	130
C7—H7A...O1'''	0.93	2.59	3.388 (3)	144

Symmetry codes: (i)  $-x, 1-y, -z$ ; (ii)  $x, 1+y, z$ ; (iii)  $x-1, y-1, z$ .

All non-carboxyl H atoms were found in electron-density difference maps but replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms, with their displacement parameters free to refine. Residual electron density near both the carboxyl O atoms, and averaging of carboxyl bond lengths and angles, was indicative of carboxyl disorder. The disordered carboxyl group was modeled as two rotational conformers, with carboxyl O-atom occupancies initially set to 50%. Each carboxyl group was restrained to be planar during the early cycles of refinement, but this restraint was removed once the refinement had converged. Carboxyl H atoms (with occupancies of 50% each) were added in calculated positions to the carboxyl O atom of each conformer having the longest C—O bond; their displacement parameters were fixed at 0.08 Å<sup>2</sup>. The site occupancies of the two carboxyl O atoms and the H atom for both conformers were then allowed to refine with total occupancy constrained to be unity. The disordered C=O and C=O' bond lengths were restrained to be equal to each other within 0.005 Å; the same restraint was imposed on the disordered C—O and C—O' bond lengths. The major carboxyl conformer refined to a site occupancy of 54 (2)%, and the minor component was 46 (2)%.

Data collection: XSCANS (Siemens, 1996). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1994). Program(s) used to refine structure: SHELXTL/PC. Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXTL/PC.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1433). Services for accessing these data are described at the back of the journal.

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## β-Dihydroentandrophragmin—Ethyl Acetate (1/0.355)

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### Abstract

Although the title compound, C<sub>43</sub>H<sub>58</sub>O<sub>17</sub>·0.355C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, from *Entandrophragma cylindricum*, exhibits significant disorder in its ester side chains, it was possible to determine the absolute configurations of the (2*S*)-2-methylbutanoate and (2*S*)-2-hydroxy-2-methylbutanoate side-chain groups by comparison with the stereochemistry of the core secotetranortriterpenoid skeleton.

### Comment

The commercially important mahogany timber trees of the genus *Entandrophragma* produce a small number of highly functionalized structurally complex secotetranortriterpenes, such as utilin, (I), and entandrophragmin, (II), which are characterized by the presence of an orthoester function (Arene *et al.*, 1966; Taylor & Wragg, 1967; Harrison *et al.*, 1970; Taylor, 1974; Halsall *et al.*, 1977). Interest in natural products containing this relatively rare structural unit is stimulated by the toxic and antileukaemic activities of other orthoester-containing natural products, such as the daphnetoxin-type Thymelaeaceae diterpenoids (Evans & Taylor, 1983; Baxter & Ziegler, 1994). β-Dihydroentandrophragmin, (III), was isolated previously by Halsall *et al.* (1977) and its structure deduced by comparison of its <sup>13</sup>C and <sup>1</sup>H NMR spectra with those of entandrophragmin, the structure and stereochemistry of which were in turn based on the crystal structure of utilin (Harrison *et al.*, 1970). However, the absolute stereochemistry of the 2-methylbutanoate and 2-hydroxy-2-methylbutanoate side chains



tioned between 50% aqueous EtOH (250 ml) and diethyl ether (500 ml) and the residue from the ether extract subjected to column chromatography on silica using hexane and EtOAc–hexane mixtures as eluants. Fractions containing (III) were concentrated *in vacuo* and the compound was crystallized from EtOAc–hexane as its EtOAc solvate: m.p. 521–523 K; [ $\alpha$ ]<sub>D</sub> –11° (c 1.09, CHCl<sub>3</sub>); MS *m/z*: 847.3762 [(*M* + 1)<sup>+</sup>, C<sub>43</sub>H<sub>59</sub>O<sub>17</sub> requires 847.3740]. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data were in accord with those previously reported (Halsall *et al.*, 1977). Mass spectra were obtained using a Kratos MS50TS spectrometer in the +FAB mode with a glycerol matrix. NMR spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> on a Bruker AC360 spectrometer.

#### Crystal data

C<sub>43</sub>H<sub>58</sub>O<sub>17</sub>·0.355C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 878.17  
 Trigonal  
*P*3<sub>1</sub>2<sub>1</sub>  
*a* = 11.0341 (8) Å  
*c* = 62.874 (9) Å  
*V* = 6629.4 (12) Å<sup>3</sup>  
*Z* = 6  
*D<sub>x</sub>* = 1.320 Mg m<sup>–3</sup>  
*D<sub>m</sub>* not measured

Cu K $\alpha$  radiation  
 $\lambda$  = 1.54184 Å  
 Cell parameters from 59 reflections  
 $\theta$  = 20–22°  
 $\mu$  = 0.852 mm<sup>–1</sup>  
*T* = 150 (2) K  
 Tablet  
 0.40 × 0.40 × 0.10 mm  
 Colourless

#### Data collection

Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)  
 $\omega$  scans with learnt-profile method (Clegg, 1981)  
 Absorption correction: by integration (see below)  
*T*<sub>min</sub> = 0.727, *T*<sub>max</sub> = 0.920  
 5589 measured reflections

4548 independent reflections  
 3746 reflections with *I* > 2 $\sigma$ (*I*)  
*R*<sub>int</sub> = 0.066  
 $\theta$ <sub>max</sub> = 60.09°  
*h* = –9 → 10  
*k* = –11 → 11  
*l* = –33 → 70  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: <3%

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.075  
*wR*(*F*<sup>2</sup>) = 0.210  
*S* = 1.043  
 4548 reflections  
 638 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.1102P)^2 + 12.5558P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.059$

$\Delta\rho_{\max} = 0.53 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.50 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELX97*  
 Extinction coefficient: 0.00076 (12)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.9 (5)

The approximate crystal shape was refined using *X-SHAPE* (Stoe & Cie, 1997) and symmetry-related data to give a shape bounded by eight crystal faces. This crystal shape was then used to calculate absorption corrections using *SHELXTL* (Sheldrick, 1994). Data could not be collected beyond  $\theta_{\max} = 60^\circ$  because of the presence of the low-temperature device. Accordingly, the ratio of reflections to parameters is lower than would have been desired.

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *SHELXTL* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1227). Services for accessing these data are described at the back of the journal.

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### ortho-(1-Naphthoyl)benzoic Acid

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#### Abstract

The title acid, C<sub>18</sub>H<sub>12</sub>O<sub>3</sub>, crystallized in the centrosymmetric space group *C2/c* and exhibits carboxyl group hydrogen bonding of the cyclic dimer type about a center of symmetry. The O<sub>donor</sub>–O<sub>acceptor</sub> distance in the hydrogen bond is 2.692 (2) Å. In addition, seven C–H groups and the three O atoms in the molecule are involved in significantly attractive C–H···O interactions