Table 2. Hydrogen-bonding and close-contact geometry  $(\overset{\circ}{A} \circ)$ 

(21, )					
D—H···A	D—H	$H \cdot \cdot \cdot A$	$D \cdot \cdot \cdot A$	$D - H \cdot \cdot \cdot A$	
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′ <sup>µ</sup>	0.97	2.69	3.393 (9)	130	
C7—H7A· · ·O1 <sup>™</sup>	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  $0.08\text{\AA}^2$ . 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.

#### References

- Berkovitch-Yellin, Z. & Leiserowitz, L. (1982). J. Am. Chem. Soc. 104, 4052–4064.
- Borthwick, P. W. (1980). Acta Cryst. B36, 628-632.
- Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1996). Acta Cryst. C52, 684-687.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Jönsson, P.-G. (1972). Acta Chem. Scand. 26, 1599-1619.
- Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1997). Acta Cryst. C53, 1838-1842.
- Lalancette, R. A., Thompson, H. W. & Brunskill, A. P. J. (1998). Acta Cryst. C54, 421-424.
- Leiserowitz, L. (1976). Acta Cryst. B32, 775-802.
- Lloyd, H. A. & Horning, E. C. (1954). J. Am. Chem. Soc. 76, 3651-3653.
- Meier, B. H., Graf, F. & Ernst, R. R. (1982). J. Chem. Phys. 76, 767-779.
- Nagaoka, S., Terao, T., Imashiro, F., Hirota, N. & Hayashi, S. (1983). J. Chem. Phys. **79**, 4694–4703.

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- Sheldrick, G. M. (1994). SHELXTL/PC Users Manual. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). XSCANS Users Manual. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). Acta Cryst. C48, 66–70.
- Wilson, C. C., Shankland, N. & Florence, A. J. (1996). J. Chem. Soc. Faraday Trans. 92, 5051–5057.

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

ROBERT L. BAXTER, FOKKE J. J. DIJKSMA, ROBERT O. GOULD AND SIMON PARSONS

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland. E-mail: r.o.gould@ed.ac.uk

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### Abstract

Although the title compound,  $C_{43}H_{58}O_{17}.0.355C_4H_8O_2$ , from *Entandrophragma cylindricum*, exhibits significant disorder in its ester side chains, it was possible to determine the absolute configurations of the (2S)-2-methylbutanoate and (2S)-2-hydroxy-2-methylbutanoate sidechain 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 orthoestercontaining natural products, such as the daphnetoxintype Thymelaeceae diterpenoids (Evans & Taylor, 1983; Baxter & Ziegler, 1994).  $\beta$ -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 remained undetermined. In the course of our studies on the characterization of biologically active plant products, we have isolated (III) from the heartwood of *E. cylindricum* and describe here its crystal structure and stereochemistry.



 $\beta$ -Dihydroentandrophragmin, (III), was crystallized as its ethyl acetate solvate (C<sub>43</sub>H<sub>58</sub>O<sub>17</sub>.0.355EtOAc) as colourless plates from EtOAc-hexane. Its identity was confirmed by mass spectroscopy and <sup>13</sup>C NMR spectra, which were in accord with previously reported data (Halsall et al., 1977). The crystallographic identification was based on refinement of the core structure of the known stereochemistry at the secotetranortriterpenoid skeleton, which gave typical bond lengths and angles. The core structure and stereochemistry of  $\beta$ -dihydroentandrophragmin, (III), found here are in total agreement with the structure of the secotetranortriterpenoid core described by Harrison et al. (1970). However, the substituent ester functions, namely 2-hydroxy-2-methylbutanoate  $(R_1)$ , 2-methylbutanoate  $(R_2)$ , the isobutyrate group  $(R_3)$ , and the methyl acetyl group at C5, all suffered twofold disorder. The isobutyrate group  $(R_3)$ shows a 0.45 (15)/0.55 (15) disorder ratio. The ethyl acetate solvent is disordered about a twofold axis and is also found to have short contacts with  $R_2$  and  $R_1$ . This, combined with the short contact between  $R_1$  and the methyl acetyl side chain at C5, rules out the possibility of the simultaneous occupation of these sites. Because of this inter-relationship among  $R_1$ ,  $R_2$ , the methyl acetyl group and the ethyl acetate, the site occupancies for their two parts were refined jointly to 0.711(9)/0.289(9). Stable refinement was achieved by restraining the bonds and the 1–3 distances in the disordered regions to have typical values with an s.u. of 0.01 Å. The entire structure was restrained such that bonded atoms have equal  $U^{ij}$  with an s.u. of 0.05 Å<sup>2</sup> and those components in the direction of the bond have equal  $U^{ij}$  with an s.u. of 0.01 Å<sup>2</sup>. The total number of restraints applied is 828.

Despite the disorder present in (III) and the indeterminate Flack (1983) parameter, the known core stereochemistry has made it possible to define the absolute configurations of both chiral centres of the ester side chains (C34 and C43). The absolute configuration at both of these in (III) is S. The most likely origin of the 2-hydroxy-2-methylbutanoate side chain of (III) is through biological hydride reduction of the *threo*-2,3-epoxy-2-methylbutanoate (Halsall *et al.*, 1977) side chain of (II), which now suggests that this ester must have  $2S_3R$  stereochemistry. Chemical interconversions of compounds (I), (II) and (III) have shown that (III) shares a common nucleus with entandrophragmin and utilin.

The packing arrangement of  $\beta$ -dihydroentandrophragmin shows two significant hydrogen bonds: an intramolecular O1...O8 contact of 2.624 (10) Å and an intermolecular O2...O1(y, x, -z) one of 2.759 (10) Å, which arranges the molecules in pairs each donating and accepting a proton.



Fig. 1. A view of (III).0.0355EtOAc with H atoms omitted. Only the major components of the disordered regions are shown.

### Experimental

For the isolation of (III), coarsely ground heartwood (1 kg) of *Entandrophragma cylindricum* was continuously extracted with light petroleum (333–353 K) at reflux in a Soxhlet apparatus for 12 h. After evaporation, the residue was parti-

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;  $[\alpha]_D -11^\circ$  (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

Cu $K\alpha$ radiation
Cell parameters from 59
reflections $\theta = 20-22^{\circ}$
$\mu = 0.852 \text{ mm}^{-1}$
Tablet $T = 150(2) \text{ K}$
$0.40 \times 0.40 \times 0.10$ mm Colourless

4548 independent reflections

3746 reflections with

3 standard reflections

frequency: 120 min

intensity decay: <3%

 $I > 2\sigma(I)$ 

 $R_{\rm int} = 0.066$ 

 $\theta_{\rm max} = 60.09^{\circ}$ 

 $h = -9 \rightarrow 10$ 

 $k = -11 \rightarrow 11$ 

 $l = -33 \rightarrow 70$ 

#### 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)  $T_{min} = 0.727, T_{max} = 0.920$ 5589 measured reflections

#### Refinement

Refinement on  $F^2$  $\Delta \rho_{\rm max} = 0.53 \ {\rm e} \ {\rm \AA}^{-3}$  $R[F^2 > 2\sigma(F^2)] = 0.075$  $\Delta \rho_{\rm min} = -0.50 \ {\rm e} \ {\rm \AA}^{-3}$  $wR(F^2) = 0.210$ Extinction correction: S = 1.043SHELX97 4548 reflections Extinction coefficient: 638 parameters 0.00076 (12) H atoms: see below Scattering factors from  $w = 1/[\sigma^2(F_o^2) + (0.1102P)^2]$ International Tables for + 12.5558P] Crystallography (Vol. C) where  $P = (F_o^2 + 2F_c^2)/3$ Absolute structure: Flack  $(\Delta/\sigma)_{\rm max} = 0.059$ (1983) Flack parameter = 0.9(5)

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.

#### References

- Arene, E. O., Bevan, C. W. L., Taylor, D. A. H. & Wragg, K. (1966). J. Chem. Soc. Chem. Commun. pp. 627–628.
- Baxter, R. L. & Ziegler, M. F. (1994). Bioorg. Biomed. Lett. 4, 2649– 2652.
- Clegg, W. (1981). Acta Cryst. A37, 22-28.
- Cosier, J. & Glazer, A. M. (1986). J. Appl. Cryst. 19, 105–107.Evans, F. J. & Taylor, S. E. (1983). Fortsch. Chem. Org. Naturst. 44, 73–87.
- Flack, H. D. (1983). Acta Cryst. A39, 876-881.
- Halsall, T. G., Wragg, K., Connolly, J. D., McLellan, M. A., Bredell, L. D. & Taylor, D. A. H. (1977). J. Chem. Res. (M), pp. 1727–1733.
- Harrison, H. R., Hodder, O. J. R., Bevan, C. W. L., Taylor, D. A. H. & Halsall, T. G. (1970). J. Chem. Soc. Chem. Commun. pp. 1388-1389.
- Sheldrick, G. M. (1994). SHELXTL. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). SHELX97. Program for the Solution and Refinement of Crystal Structures. University of Göttingen, Germany.
- Stoe & Cie (1990a). DIF4. Diffractometer Control Program. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1990b). REDU4. Data Reduction Program. Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1997). X-SHAPE. Stoe & Cie, Darmstadt, Germany.
- Taylor, D. A. H. (1974). J. Chem. Soc. Perkin Trans. pp. 437-441.
- Taylor, D. A. H. & Wragg, K. (1967). J. Chem. Soc. Chem. Commun. pp. 81–83.

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# ortho-(1-Naphthoyl)benzoic Acid

ROGER E. GERKIN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry. ohio-state.edu

The title acid, C<sub>18</sub>H<sub>12</sub>O<sub>3</sub>, crystallized in the centrosym-

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#### Abstract

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.

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# metric space group C2/c and exhibits carboxyl group hydrogen bonding of the cyclic dimer type about a center of symmetry. The O<sub>dongr</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