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Methyl 12-bromo-13,14-dinitrodeisopropyldehydroabietate

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The title compound, $C_{18}H_{21}BrN_2O_6$, exhibits weak intermolecular C—H···Br and C—H···O hydrogen bonds, which stabilize the structure. The title compound represents a new derivative of dehydroabietic acid.

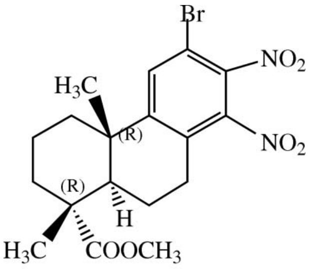
Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.004 Å
R factor = 0.030
wR factor = 0.064
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Pine resin is a very abundant renewable source mainly composed of diterpenic resin acids of the general formula $C_{19}H_{29}COOH$. This raw material has a wide range of industrial uses and is also a source of fine chemicals (Zinkel & Russell, 1989). Dehydroabietic acid can be easily obtained by catalytic dehydrogenation of abietic type resin acids. A considerable interest has been devoted to this easily available compound as a starting material, either as the free acid or ester, for the synthesis of other important natural or bioactive compounds mainly through transformations that involve the benzylic or aromatic positions of the molecule (Roy *et al.*, 2003).



(I)

The molecular structure of the title compound, (I), is shown in Fig. 1. As expected for diterpenic compounds (Silvestre *et al.*, 1998), rings *A* (atoms C9–C14) and *B* (C5–C10) show a

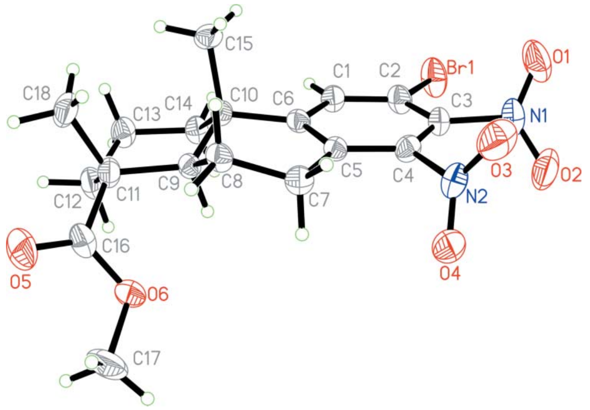


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atom-labelling scheme. H atoms are represented by small spheres of arbitrary radius.

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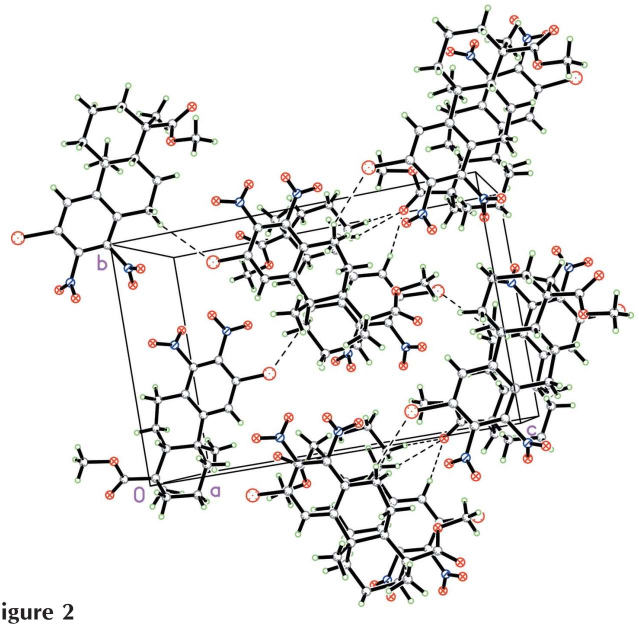

Figure 2
The packing of (I), viewed approximately along the *a* axis, with weak C—H···O and C—H···Br hydrogen bonds indicated by dashed lines.

trans ring junction, with two methyl groups in axial positions of the six-membered rings. The torsion angles show classical chair and half-chair conformations for rings *A* and *B*, respectively. The overall geometry of (I) is comparable to that found for both 12-acetyldehydroabietate (Silvestre *et al.*, 1998) and methyldehydroabietate (Hamodrakas *et al.*, 1978), apart from the substituted Br atom and the two adjacent nitro groups on the benzene ring. The ester group is planar. The average C—C bond length in the benzene ring is 1.391 Å and the bond angles in the benzene ring are normal, *viz*. close to 120°.

In the crystal packing of (I) (Fig. 2), there are weak intermolecular C—H···O and C—H···Br hydrogen bonds, which stabilize the structure.

Experimental

Methyl 12-bromodehydroabietate (9.0 mmol) was added with vigorous stirring, over a period of 30 min, to a previously prepared mixture of fuming nitric acid (100%, 19 ml) and concentrated sulfuric acid (95–97%, 1.5 ml) maintained in an ice–water bath (273–278 K). The resulting mixture was poured into ice–water and filtered through a Buchner funnel to obtain a pale-yellow solid. Upon recrystallization from methanol, white crystals of (I) were obtained (yield 50%, m.p. 446–447 K). Single crystals were grown from absolute methanol.

Crystal data

$C_{18}H_{21}BrN_2O_6$
$M_r = 441.28$
Orthorhombic, $P2_12_12_1$
$a = 10.215$ (5) Å
$b = 11.003$ (5) Å
$c = 16.761$ (7) Å
$V = 1883.9$ (14) Å^3
$Z = 4$
$D_x = 1.556$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 8056 reflections
$\theta = 3.1$–25.3°
$\mu = 2.22$ mm^{-1}
$T = 193$ (2) K
Block, colourless
0.35 × 0.21 × 0.19 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min} = 0.495$, $T_{\max} = 0.658$
18829 measured reflections

3438 independent reflections
3178 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 25.3°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -18 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.064$
$S = 1.08$
3438 reflections
248 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 0.2102P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}
Absolute structure: (Flack, 1983), 1458 Friedel pairs
Flack parameter: −0.004 (8)

Table 1
Selected geometric parameters (Å, °).

Br1—C2	1.885 (2)	C1—C2	1.383 (4)
O1—N1	1.225 (3)	C1—C6	1.402 (4)
O2—N1	1.213 (3)	C2—C3	1.383 (4)
O3—N2	1.210 (3)	C3—C4	1.380 (4)
O4—N2	1.215 (3)	C4—C5	1.394 (4)
O5—C16	1.203 (3)	C5—C6	1.402 (3)
O6—C16	1.333 (3)	C5—C7	1.523 (3)
O6—C17	1.452 (3)	C10—C14	1.542 (4)
N1—C3	1.469 (3)	C10—C15	1.549 (4)
N2—C4	1.483 (3)	C11—C16	1.529 (4)
C16—O6—C17	115.7 (2)	C1—C2—Br1	118.6 (2)
O2—N1—O1	126.0 (3)	C3—C2—Br1	122.0 (2)
O2—N1—C3	117.7 (2)	C4—C3—N1	119.9 (2)
O1—N1—C3	116.3 (3)	C2—C3—N1	121.2 (2)
O3—N2—O4	125.1 (2)	C3—C4—N2	118.4 (2)
O3—N2—C4	117.6 (2)	C5—C4—N2	118.5 (2)
O4—N2—C4	117.2 (2)	O5—C16—O6	122.0 (3)
C2—C1—C6	121.8 (2)	O5—C16—C11	124.4 (3)
C4—C5—C6—C10	−175.2 (2)	C5—C6—C10—C9	−23.4 (3)
C7—C5—C6—C10	4.4 (4)	C11—C9—C10—C6	−173.4 (2)
C2—C1—C6—C10	175.2 (2)	C8—C9—C10—C14	174.9 (2)
C4—C5—C7—C8	163.9 (2)	C11—C9—C10—C14	−53.5 (3)
C6—C5—C7—C8	−15.7 (3)	C16—C11—C12—C13	−169.7 (2)
C5—C7—C8—C9	46.1 (3)	C11—C12—C13—C14	56.2 (3)
C7—C8—C9—C11	158.3 (2)	C12—C13—C14—C10	−57.6 (3)
C5—C6—C10—C14	−141.1 (2)	C6—C10—C14—C13	171.8 (2)
C5—C6—C10—C15	100.3 (3)	C15—C10—C14—C13	−72.8 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*B*···Br1$^{\rm i}$	0.99	3.03	3.832 (3)	139
C14—H14*A*···O5$^{\rm ii}$	0.98	2.67	3.589 (4)	154
C15—H15*A*···O5$^{\rm ii}$	0.98	2.59	3.430 (4)	144
C1—H1*A*···O5$^{\rm ii}$	0.95	2.63	3.433 (4)	142

Symmetry codes: (i) $-x+\frac{3}{2}, -y+1, z-\frac{1}{2}$; (ii) $-x+\frac{3}{2}, -y+2, z+\frac{1}{2}$.

H atoms were positioned geometrically and included in the refinement in the riding-model approximation, with C—H = 0.95, 0.98, 0.99 and 1.00 Å for aromatic, methyl, CH_2 and CH groups, respectively, and with $U_{iso}(H) = 1.5U_{eq}$(methyl C) and $1.2U_{eq}(C)$ for all others.

Data collection: *CRYSTALCLEAR* (Rigaku, 1999); cell refinement: *CRYSTALCLEAR*; data reduction: *CrystalStructure* (Rigaku/MSC, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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