

Maleopimaric anhydride ethyl ester

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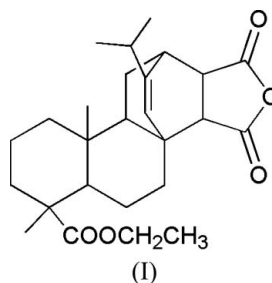
Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
 R factor = 0.070
 wR factor = 0.156
Data-to-parameter ratio = 8.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{26}\text{H}_{36}\text{O}_5$, is a derivative of abietic acid formed by an *endo*-Diels–Alder reaction between maleic anhydride and the diene levopimaric acid ethyl ester. The two fused and unbridged cyclohexane rings have chair conformations and the anhydride ring is planar.

Comment

Rosin, a versatile natural resin, possesses a rare combination of many desirable properties and has consequently found innumerable industrial uses in a modified form or in conjunction with other natural or synthetic resins (McCoy, 2000). Abietic acid is the major component of colophony (rosin) and is used as a chiral starting material and a useful synthetic intermediate (Arno *et al.*, 2000). Numerous commonly used products can be made from abietic acid, such as paper sizing, printing inks, adhesives, glues, technical resins, synthetic rubber, cosmetics and dental materials (Burge, 1981; Downs *et al.*, 1999).



The title compound, (I), whose structure is reported here, is a Diels–Alder adduct of ethyl abietate and maleic anhydride; during the reaction, ethyl abietate is isomerized to levopimaric

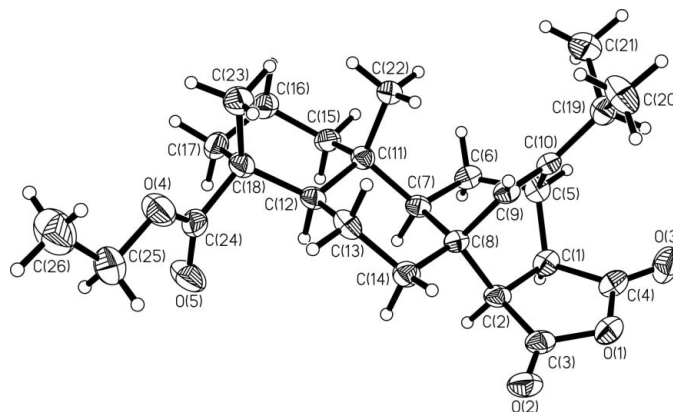


Figure 1
Molecular structure of (I), showing the atom-labeling scheme and 30% probability displacement ellipsoids.

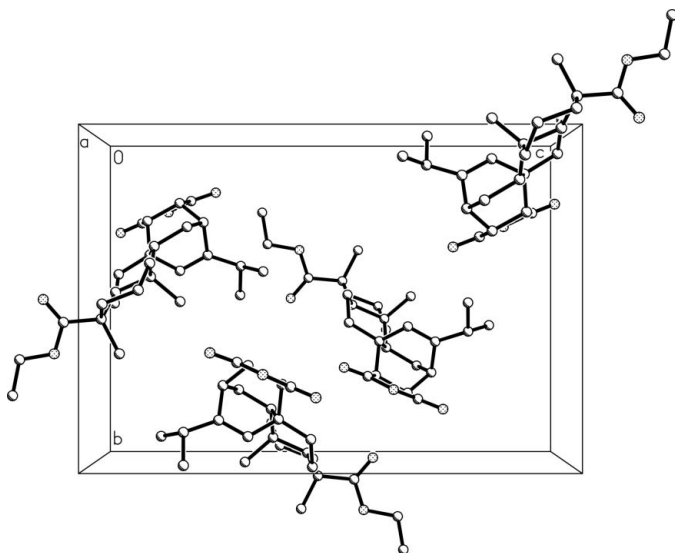


Figure 2
Packing diagram for (I), viewed along the *b* axis. H atoms have been omitted.

acid ethyl ester. The two fused and unbridged cyclohexane rings have chair conformations and the anhydride ring is planar. The configuration about the C9=C10 bond is *Z* (Fig. 1, Table 1). This maleated rosin has commercial applications in the manufacture of paper sizing, varnishes and surface coatings.

Experimental

Ethyl abietate was obtained as a pale-yellow oil following the procedure of Abad *et al.* (1985). A solution of maleic anhydride (9.8 g), ethyl abietate (16.5 g) and 4 drops of phosphoric acid in toluene (70 ml) was stirred and heated at 388 K for 6 h (Lee *et al.*, 2001). The solution was cooled, diluted with CHCl₃ (50 ml), washed with water (60 ml), dried (MgSO₄), and concentrated to dryness. Recrystallization from ethyl acetate afforded the adduct, (I) (13.5 g, 70%), as colourless crystals.

Crystal data

C₂₆H₃₆O₅
M_r = 428.55
 Orthorhombic, *P*2₁2₁2₁
a = 9.2973 (6) Å
b = 13.2060 (9) Å
c = 19.0372 (13) Å
V = 2337.4 (3) Å³
Z = 4
D_x = 1.218 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 3834 reflections
 θ = 2.4–27.6°
 μ = 0.08 mm⁻¹
T = 293 (2) K
 Block, colourless
 0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.767, *T_{max}* = 0.984
 9763 measured reflections

2354 independent reflections
 2292 reflections with *I* > 2σ(*I*)
R_{int} = 0.030
 θ_{\max} = 25.0°
h = -10 → 11
k = -15 → 6
l = -22 → 21

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.070
wR (*F*²) = 0.156
S = 1.28
 2354 reflections
 280 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 1.3297P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C2–C8	1.568 (6)	C8–C9	1.492 (6)
C7–C11	1.555 (6)	C11–C12	1.554 (6)
C7–C8	1.577 (6)	C12–C18	1.557 (7)
O2–C3–C2	130.6 (5)	C15–C11–C22	108.5 (4)
O3–C4–C1	129.3 (5)	C22–C11–C12	113.9 (4)
C9–C10–C19	128.2 (4)		
C5–C1–C2–C3	-127.3 (4)	C1–C5–C10–C9	-57.6 (5)
C6–C7–C8–C14	179.1 (4)	C23–C18–C24–O5	180.0 (6)
C14–C8–C9–C10	-179.7 (4)	C23–C18–C24–O4	-0.9 (7)
C6–C5–C10–C9	58.0 (5)		

In the absence of significant anomalous dispersion effects, Friedel pairs were averaged. H atoms were placed in idealized positions and allowed to ride on the respective parent atoms with C–H 0.93–0.97 Å, and *U*_{iso}(H) = 1.2–1.5*U*_{eq}(parent atom).

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick, 1999); software used to prepare material for publication: SHELXL97.

This work was financially supported by the National 973 Programme of China (contract No. 2003CB114400).

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