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rac-2-{3-[1-(Acetyloxy)ethyl]-2,2-dimethylcyclobutyl}acetic acid

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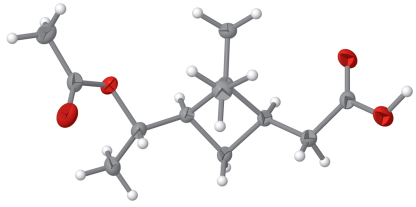
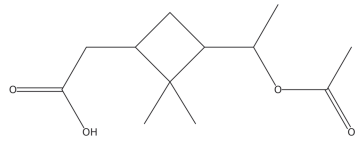
The title compound, $C_{12}H_{20}O_4$, was prepared from α-pinene in three steps. The ester and acid moieties are *cis* on the slightly folded cyclobutane ring. In the crystal, carboxylic acid bound dimers form layers parallel to $(\bar{2}02)$.

3D view



Chemical scheme



Structure description

As part of a project on strained carbocycles (Detert & Schollmeyer, 2017; Herges *et al.*, 2005), the title compound, $C_{12}H_{20}O_4$ (Fig. 1), was prepared from racemic α-pinene by permanganate oxidation, borohydride reduction of the pinonic acid to pinolic acid and acetylation. The compound crystallizes in the monoclinic space group *C*2/*c* with the asymmetric unit containing eight molecules. Two enantiomeric molecules are connected *via* two hydrogen bridges of the carboxylic acids, forming centrosymmetric dimers. The distance between the oxygen atoms forming the hydrogen bond is 2.6547 (13) Å. These dimers are arranged in layers parallel to the $(\bar{2}02)$ plane (Table 1, Fig. 2). The central cyclobutane ring is folded in a butterfly-like manner: the planes defined by C1,C2,C4 and by C2, C3, C4 subtend an angle of 24.61 (12)°, which is due to the bulky methyl groups at C2. However, it is significantly smaller than the ideal angle of 35° (Bucourt, 1974). The acetic acid substituent on C1 and the acetoxyethyl on C3 are *cis* and on the open side of the folded cyclobutane. The geminal methyl groups on C2 open an angle of 110.39 (10)° and provoke an elongation of the cyclobutane bond lengths *e.g.* C1—C2 = 1.5697 (15) Å *versus* C1—C4 = 1.5467 (15) Å. A deviation of only 0.0193 (10) Å for O8 destroys the otherwise perfect planarity of the acetic acid unit O7,O8,C5,C6.

Synthesis and crystallization

The title compound was prepared from α-pinene by phase-transfer-catalyzed oxidation with permanganate according to Hünig *et al.* (1979) (43% yield) followed by reduction with sodium borohydride according to Fernández *et al.* (2001) (94% yield). The resulting

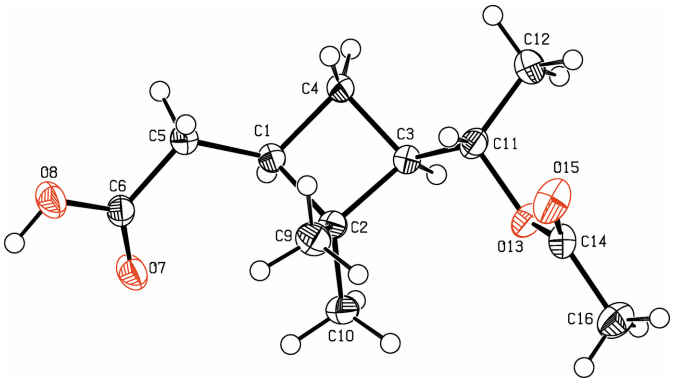


Figure 1
View of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

diastereomeric mixture of pinolic acids (2.00 g) was dissolved in benzene (5 ml), acetic acid (2.58 g) and toluenesulfonic acid (0.47 g) were added. The mixture was refluxed for 3.5 h and water was separated using a Dean–Stark trap. The mixture was washed with water, the aqueous phase extracted with toluene and the combined organic layers were dried and the solvents removed *in vacuo*. The residue thus obtained was dissolved in heptane (5 ml), treated with active charcoal and filtered. Upon cooling, the mixture separated into two phases, the lower layer was dissolved in heptane (15 ml) and upon cooling for 3 days. The precipitated solid was recrystallized from heptane to yield 0.22 g (9%) of colorless crystals with m.p. = 360–362 K. Hergueta *et al.* (2003) report a melting point of the enantiopure compound of 258-258 K. Their NMR data correspond well with the results from the racemate, except a general deep-field shift of all H-NMR signals and a high-field shift of *ca* 0.25 p.p.m. in C-NMR. The numbering of H- and C-signals follows IUPAC nomenclature. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.77 (*dq*, *J* = 10.2, 6.2 Hz, 1H, 1″-H), 2.41–2.15 (*m*, 3H, 2-H, 1′-H), 2.14–1.93 (*m*, 2H, 3′-H, 4′-H), 2.00 (*s*, 3H, 4″-H), 1.30–1.16 (*m*, 1H, 4′-H), 1.08 (*s*, 3H, 5″-H), 1.06 (*d*, *J* = 6.2 Hz, 3H, 2″-H), 0.88 (*s*, 3H, 6″-H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 179.3 (C-1), 170.7 (C-3″), 71.9 (C-1″), 47.1 (C-3′), 40.0 (C-2′), 37.9 (C-1′), 35.0 (C-2), 30.5 (C-5″), 26.5 (C-4′), 21.6 (C-4″), 17.7 (C-2″), 16.9 (C-6″).

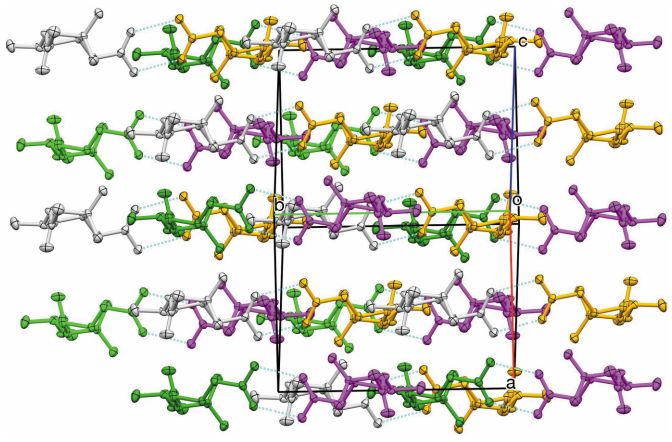


Figure 2
Part of the packing diagram. Hydrogen bonds are drawn with dashed lines. View along the [101] direction. The color of the molecules corresponds to the generating symmetry operator.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8*O*···O7^{i}	0.90 (2)	1.75 (2)	2.6547 (13)	178 (2)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{20}O_4$
M_r	228.28
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	120
a, *b*, *c* (Å)	9.8411 (4), 12.3319 (5), 21.0912 (10)
β (°)	94.254 (4)
V (Å^3)	2552.56 (19)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.55 × 0.29 × 0.25
Data collection	
Diffractometer	Stoe *IPDS* 2T
Absorption correction	Integration [*X-RED32* (Stoe & Cie, 2020), absorption correction by Gaussian integration (Coppens, 1970)]
T_{min}, T_{max}	0.966, 0.982
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6713, 3019, 2607
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.040, 0.110, 1.03
No. of reflections	3019
No. of parameters	215
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.17

Computer programs: *X-AREA WinXpose*, *Recipe* and *Integrate* (Stoe & Cie, 2020), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2020).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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