Crystal Structure and Conformational Analysis of 7,13-Abietadien-18-oic Acid

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The crystal and molecular structures of title compound **1** have been determined by single-crystal X-ray diffraction analysis. Crystals are monoclinic, space group $P2_1$, with $a=14.058(2)$, $b=11.911(1)$, $c=11.753(2)$ Å, $\beta=111.73(1)°$, $Z=4$. The structure identification was refined by full-matrix least-squares calculations to a final R of 0.054 for 2899 independently observed reflections. The crystallographic asymmetric unit contains two independent molecules with similar geometries and planar conformations. In each molecule, cyclohexane ring A has a typical chair form. Cyclohexene rings B and C, containing of two conjugated double bonds, have half-chair conformations. The relative stereochemistry for both molecules is *trans* fusion for the A/B ring junction [14.9(2) and 14.6(3)°], *anti* between C9 hydrogen and C10 methyl (steroid numbering), and coplanar for the B/C ring junction [5.7(2) and 3.5(2)°]. The dihedral angles between the mean plane of ring A and the carboxyl group are nearly right angles [74.6(2) and 86.2(2)°]. Thermal motion analysis in LST rigid-body approximation and potential energy calculations suggest that the isopropyl groups are more freely in these regions. The isopropyl C atoms had large thermal motions. The hydrogen bonds of carboxyl groups are rigid between two independent molecules.

Matsubara et al. have analysed[1] in detail the rosinous components of *Pinus Elliottii* (Engelmann spruce), afforestation trees in the southern provinces of China, by gas chromatography and mass spectrometry (GC/MS), and compared the components with those of *Pinus Elliotti* Engelm of the southeastern part of North America and of Chinese gum resins (*Pinus massoniana* Lamb). Rosinous components of living pine trees are approximately 90% resin acids (four main acids and seven minor acids) and 10% nonacidic materials. The acids with tricycles and steroid-like molecules are classified into two groups according to the substituent groups at the C13 position: the abientic type, which has isopropyl or isopropylidene, and the primaric type, which has gem-configuration of methyl and vinyl groups. The melting point range of the abientic type is wide [150—213 °C]. Abientic acid (7,13-abietadien-18-oic acid), the title compound **1**, is the principal component in resin acids and is unstable to heat and cold. The relative stereochemistry of the ring conformations and ring junctions of tricycles is *trans* or *cis* for the A/B ring junction, *syn* or *anti* between C9-X and C10-Y, and *cis* for the B/C ring junction (Chart 1).[2—4] We used thermal motion analysis and potential energy calculations for the two side groups of both molecules for large thermal motions, to verify the relative stereochemistry of **1**.

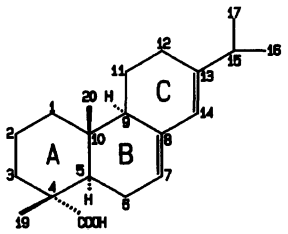


Chart 1.

Experimental

Crystals of **1** were recrystallized as colorless prisms from an aqueous ethanol solution by slow evaporation. Mp 159—168 °C, $[\alpha]_D^{25}-104.4°$ ($c=0.5$, EtOH). Data were collected at room temperature [22 °C]. The crystals are fragile at ordinary temperatures and oxidize easy with atmospheric oxygen.

Crystal Data. $C_{20}H_{30}O_2$, $M_r=302.46$, monoclinic, $a=14.058(2)$, $b=11.911(1)$, $c=11.753(2)$ Å, $\beta=111.73(1)°$, $V=1828.1(6)$ Å^3. Preliminary cell data were obtained from Weissenberg and precession photographs with Cu $K\alpha$ ($\lambda=1.5418$ Å) radiation, and accurate unit-cell dimensions were obtained by least-squares refinement of the setting angles of 23 reflections ($10.0\leq 2\theta\leq 46.5°$) measured on an automatic diffractometer. Space group $P2_1$, $Z=4$, $D_x=1.099$ g cm^{-3}, λ (Cu $K\alpha$)=1.5148 Å, μ (Cu $K\alpha$)=5.01 cm^{-1}, $F(0\,0\,0)=664$. Approximate crystal dimensions: 0.2×0.2×0.2 mm.

Data Collection and Processing. Three-dimensional intensity data were collected on a Rigaku AFC-5 diffractometer. Integrated intensities were measured for $2\theta<140°$ by the ω–2θ scan technique with graphite-monochromatized Cu $K\alpha$ radiation and a scintillation counter. Three standard reflections ($\bar{5}3\bar{1}$, $\bar{3}3\bar{2}$, $1\bar{2}3$) were monitored every 100 reflections and showed little variation. No decay corrections were done. Thus 3551 independent reflections ($-17\leq h\leq 15$; $-14\leq k\leq 0$; $0\leq l\leq 14$) were recorded, of which 2899 intensities with $I\geq\sigma(I)$ were observed. All intensities were corrected for Lorentz and polarization factors, and the normalized structure factors $|E_o(\boldsymbol{h})|$ and structure amplitudes $|F_o(\boldsymbol{h})|$ were derived. Absorption correction was not done because the specimen was small.

Structure Analysis and Refinement. The structure was solved by the application of direct methods. The program DIRECTER[5] yielded the positions for 34/44 non-hydrogen atoms. The other 10 atoms were obtained from the program SEARCHER.[5] The approximate coordinates were refined by full-matrix least-squares to minimized $\Sigma w[|F_o(\boldsymbol{h})|-|F_c(\boldsymbol{h})|]^2$ with $w=1.0$. No further appropriate weighting scheme could be found from an analysis of ΔF

Table 1. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a] with esds in Parentheses

(a) Molecule 1

Atom	x	y	z	U_{eq}/Å^2
C(1)	0.8769(4)	0.2815(0)	0.2712(5)	0.083(3)
C(2)	0.8629(4)	0.1716(6)	0.2030(7)	0.105(4)
C(3)	0.7703(4)	0.1091(6)	0.2116(5)	0.087(3)
C(4)	0.6705(3)	0.1765(6)	0.1549(3)	0.066(2)
C(5)	0.6860(3)	0.2946(5)	0.2134(3)	0.058(2)
C(6)	0.5929(4)	0.3697(6)	0.1614(5)	0.086(3)
C(7)	0.6081(3)	0.4826(6)	0.2177(5)	0.085(3)
C(8)	0.7010(3)	0.5233(6)	0.2876(4)	0.069(2)
C(9)	0.7957(3)	0.4546(5)	0.3142(4)	0.062(2)
C(10)	0.7847(3)	0.3615(5)	0.2211(3)	0.061(2)
C(11)	0.8873(4)	0.5296(6)	0.3431(6)	0.087(3)
C(12)	0.8967(4)	0.6129(6)	0.4415(5)	0.090(3)
C(13)	0.8020(4)	0.6788(6)	0.4155(5)	0.092(3)
C(14)	0.7141(4)	0.6330(6)	0.3456(5)	0.091(3)
C(15)	0.8165(6)	0.7902(7)	0.4830(8)	0.128(5)
C(16)	0.7407(20)	0.8315(18)	0.4939(32)	0.598(40)
C(17)	0.8700(10)	0.8695(8)	0.4211(12)	0.215(9)
C(18)	0.5942(3)	0.1127(6)	0.1929(4)	0.071(2)
C(19)	0.6347(5)	0.1737(7)	0.0149(4)	0.090(3)
C(20)	0.7791(6)	0.4095(7)	0.0992(5)	0.094(3)
O(21)	0.5923(3)	0.1247(6)	0.2969(3)	0.114(2)
O(22)	0.5378(3)	0.0426(6)	0.1195(3)	0.116(3)

(b) Molecule 2

Atom	x	y	z	U_{eq}/Å^2
C(1′)	0.2469(4)	−0.3742(6)	0.2604(4)	0.077(3)
C(2′)	0.3569(4)	−0.3850(7)	0.3529(6)	0.092(3)
C(3′)	0.4200(4)	−0.2900(6)	0.3367(5)	0.083(3)
C(4′)	0.3817(3)	−0.1746(6)	0.3595(3)	0.071(2)
C(5′)	0.2650(3)	−0.1640(6)	0.2770(4)	0.064(2)
C(6′)	0.2192(4)	−0.0536(6)	0.2988(6)	0.093(3)
C(7′)	0.1091(4)	−0.0430(6)	0.2183(6)	0.098(3)
C(8′)	0.0520(3)	−0.1296(6)	0.1597(4)	0.081(3)
C(9′)	0.0960(3)	−0.2462(6)	0.1631(4)	0.072(2)
C(10′)	0.1958(3)	−0.2646(6)	0.2769(3)	0.065(2)
C(11′)	0.0159(4)	−0.3354(7)	0.1392(6)	0.098(3)
C(12′)	−0.0780(4)	−0.3111(8)	0.0252(6)	0.107(4)
C(13′)	−0.1190(4)	−0.1959(7)	0.0238(5)	0.105(3)
C(14′)	−0.0564(4)	−0.1150(7)	0.0845(6)	0.106(4)
C(15′)	−0.2331(6)	−0.1764(10)	−0.0471(8)	0.159(6)
C(16′)	−0.2946(7)	−0.2229(14)	0.0282(14)	0.212(11)
C(17′)	−0.2681(11)	−0.2030(21)	−0.1675(12)	0.260(14)
C(18′)	0.4344(3)	−0.0854(6)	0.3102(4)	0.075(2)
C(19′)	0.4068(5)	−0.1525(8)	0.4964(4)	0.104(4)
C(20′)	0.1705(5)	−0.2706(8)	0.3935(5)	0.092(3)
O(21′)	0.4319(3)	−0.0924(6)	0.2038(3)	0.116(2)
O(22′)	0.4822(3)	−0.0075(5)	0.3798(3)	0.111(2)

a) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as: $U_{eq}=1/(6\pi^2)(\sum_i \sum_j \beta_{ij}\, a_i\, a_j.)$

values. Sixty hydrogen atoms were located on difference-Fourier synthesis. Inclusion of the hydrogen atoms in subsequent cycles of least-squares refinement reduced R to 0.054, wR=0.046, S=0.60(1) with 635 variables and (Δ/σ)=0.09 (av.), 0.66 (max. for x, y, z parameters), and 0.84 (max. for temperature factors) for the 2899 reflections with $I \geq \sigma(I)$. Max. and min. peak heights in the final difference Fourier map were 0.16 and −0.02 eÅ^{-3}. Atomic scattering factors used in all calculations were taken from Ref. 6. All computations were performed on an NEC PC-9801RA personal computer with a DS*SYSTEM.[5]

The two independent molecules are referred to here as molecules 1 and 2. The final atomic coordinates are given in Table 1.[7]

Results and Discussion

Bond distances, angles, and torsion angles are given in Tables 2 and 3. The bond distances of the two molecules are not unusual except for C(15)–C(16) and C(15′)–C(17′). All bond angles are in good agreement with each other and are normal values. The torsion angles of the molecular skeletons are almost the same except for the isopropyl and carboxyl groups. Figure 1 shows the atom-numbering scheme and the conformations of molecules 1 and 2. The packing of the two independent molecules in the unit cell along the c axis is illustrated in Fig. 2. The two molecules are related by hydrogen bonds approximately parallel to the ac plane.

The ring puckering parameters according to Cremer and Pople[8] and displacement asymmetric parameters defined by Nardelli[9] of the two molecules are shown in Table 4.

Thermal motion analysis of the anisotropic displacement parameters (ADPs) was carried out in LST rigid-body approximation as described by Schomaker and Trueblood[10] and Trueblood[11] with consideration of the

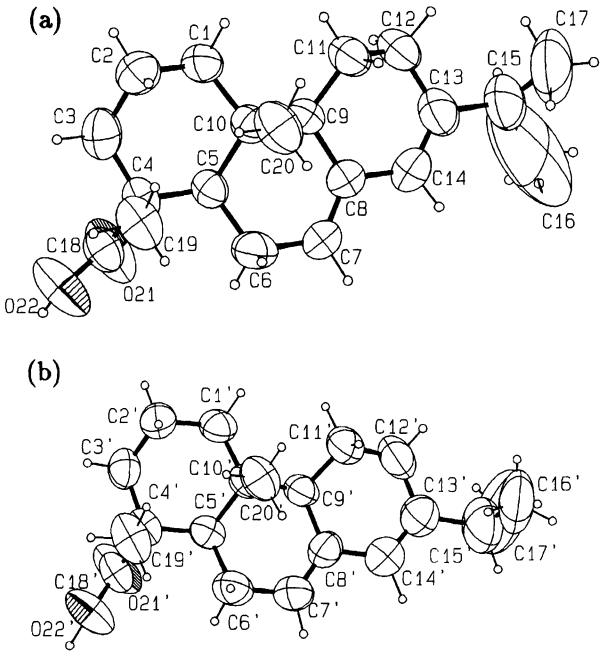


Fig. 1. ORTEP drawing[21] with atoms numbered as we look down the c axis. (a) Molecule 1; (b) molecule 2. Octant-shaded ellipsoids are oxygen atoms.

Table 2. Bond Distances (l), Angles (θ), and Torsion Angles (τ) for Molecule 1 with esds in Parentheses

(a) Bond distances/Å

	l/Å		l/Å		l/Å
C(1)–C(2)	1.509(8)	C(7)–C(8)	1.350(6)	C(13)–C(15)	1.521(11)
C(2)–C(3)	1.533(10)	C(8)–C(9)	1.493(7)	C(15)–C(16)	1.223(33)
C(3)–C(4)	1.538(7)	C(9)–C(10)	1.524(8)	C(15)–C(17)	1.546(18)
C(4)–C(5)	1.545(9)	C(9)–C(11)	1.500(8)	C(4)–C(18)	1.511(8)
C(5)–C(10)	1.573(7)	C(11)–C(12)	1.491(10)	C(4)–C(19)	1.532(6)
C(10)–C(1)	1.540(6)	C(12)–C(13)	1.477(8)	C(18)–O(21)	1.240(6)
C(5)–C(6)	1.515(7)	C(13)–C(14)	1.322(8)	C(18)–O(22)	1.250(7)
C(6)–C(7)	1.479(10)	C(14)–C(8)	1.454(9)	C(10)–C(20)	1.518(8)

(b) Bond angles/deg

	θ/°		θ/°
C(10)–C(1)–C(2)	114.1(4)	C(14)–C(8)–C(7)	122.3(5)
C(1)–C(2)–C(3)	109.5(6)	C(12)–C(13)–C(15)	114.8(5)
C(2)–C(3)–C(4)	112.3(5)	C(14)–C(13)–C(15)	126.7(6)
C(3)–C(4)–C(5)	109.1(3)	C(13)–C(15)–C(16)	116.9(30)
C(4)–C(5)–C(10)	117.6(4)	C(13)–C(15)–C(17)	106.4(10)
C(4)–C(5)–C(6)	113.6(3)	C(16)–C(15)–C(17)	113.5(42)
C(5)–C(10)–C(1)	107.9(4)	C(3)–C(4)–C(18)	104.1(5)
C(10)–C(5)–C(6)	109.6(5)	C(3)–C(4)–C(19)	109.7(5)
C(5)–C(6)–C(7)	113.3(4)	C(5)–C(4)–C(18)	109.0(4)
C(6)–C(7)–C(8)	123.1(5)	C(5)–C(4)–C(19)	115.7(5)
C(7)–C(8)–C(9)	121.2(5)	C(18)–C(4)–C(19)	108.7(4)
C(8)–C(9)–C(10)	113.7(3)	C(4)–C(18)–O(21)	120.7(5)
C(9)–C(10)–C(5)	105.3(3)	C(4)–C(18)–O(22)	118.0(4)
C(8)–C(9)–C(11)	110.2(5)	O(21)–C(18)–O(22)	121.2(6)
C(9)–C(11)–C(12)	113.2(5)	C(1)–C(10)–C(9)	109.2(3)
C(11)–C(12)–C(13)	112.3(4)	C(1)–C(10)–C(20)	109.6(5)
C(12)–C(13)–C(14)	118.2(6)	C(5)–C(10)–C(20)	113.6(4)
C(13)–C(14)–C(8)	126.1(5)	C(9)–C(10)–C(20)	111.1(5)
C(14)–C(8)–C(9)	116.5(4)	C(10)–C(9)–C(11)	116.5(5)

(c) Torsion angles/deg

	τ/°		τ/°
C(2)–C(1)–C(10)–C(20)	−72.2(6)	C(10)–C(5)–C(6)–C(7)	−46.2(6)
C(2)–C(1)–C(10)–C(5)	51.9(6)	C(5)–C(6)–C(7)–C(8)	13.8(8)
C(2)–C(1)–C(10)–C(9)	165.9(5)	C(6)–C(7)–C(8)–C(9)	−.9(9)
C(10)–C(1)–C(2)–C(3)	−60.4(6)	C(6)–C(7)–C(8)–C(14)	−177.8(6)
C(1)–C(2)–C(3)–C(4)	60.5(7)	C(7)–C(8)–C(14)–C(13)	179.8(6)
C(2)–C(3)–C(4)–C(5)	−53.6(6)	C(7)–C(8)–C(9)–C(10)	22.4(7)
C(2)–C(3)–C(4)–C(18)	−169.7(5)	C(7)–C(8)–C(9)–C(11)	155.3(5)
C(2)–C(3)–C(4)–C(19)	74.1(6)	C(14)–C(8)–C(9)–C(11)	−27.6(7)
C(3)–C(4)–C(18)–O(21)	80.2(6)	C(14)–C(8)–C(9)–C(10)	−160.5(5)
C(3)–C(4)–C(18)–O(22)	−95.4(6)	C(8)–C(9)–C(10)–C(5)	−52.4(5)
C(3)–C(4)–C(5)–C(6)	178.4(5)	C(8)–C(9)–C(10)–C(1)	−168.1(4)
C(3)–C(4)–C(5)–C(10)	48.4(6)	C(8)–C(9)–C(11)–C(12)	52.8(7)
C(5)–C(4)–C(18)–O(21)	−36.0(7)	C(8)–C(9)–C(10)–C(20)	71.0(6)
C(5)–C(4)–C(18)–O(22)	148.4(5)	C(11)–C(9)–C(10)–C(5)	177.8(4)
C(18)–C(4)–C(5)–C(10)	161.5(4)	C(11)–C(9)–C(10)–C(1)	62.1(6)
C(18)–C(4)–C(5)–C(6)	−68.6(5)	C(10)–C(9)–C(11)–C(12)	−175.7(5)
C(19)–C(4)–C(5)–C(10)	−75.8(6)	C(11)–C(9)–C(10)–C(20)	−58.9(6)
C(19)–C(4)–C(5)–C(6)	54.1(6)	C(9)–C(11)–C(12)–C(13)	−52.9(7)
C(19)–C(4)–C(18)–O(22)	21.5(7)	C(11)–C(12)–C(13)–C(14)	26.6(8)
C(19)–C(4)–C(18)–O(21)	−162.9(5)	C(11)–C(12)–C(13)–C(15)	−158.5(6)
C(4)–C(5)–C(10)–C(1)	−46.9(5)	C(12)–C(13)–C(15)–C(16)	−159(2)
C(6)–C(5)–C(10)–C(1)	−178.6(4)	C(12)–C(13)–C(15)–C(17)	72.9(9)
C(4)–C(5)–C(10)–C(20)	74.9(6)	C(15)–C(13)–C(14)–C(8)	−176.1(6)
C(4)–C(5)–C(10)–C(9)	−163.4(4)	C(14)–C(13)–C(15)–C(17)	−112.7(9)
C(4)–C(5)–C(6)–C(7)	−180.0(5)	C(12)–C(13)–C(14)–C(8)	−1.8(10)
C(6)–C(5)–C(10)–C(20)	−56.9(6)	C(13)–C(14)–C(8)–C(9)	2.7(9)
C(6)–C(5)–C(10)–C(9)	64.9(5)	C(14)–C(13)–C(15)–C(16)	15(2)

Table 3. Bond Distances (l), Angles (θ), and Torsion Angels (τ) for Molecule 2 with esds in Parentheses

(a) Bond distances/Å

	l/Å		l/Å		l/Å
C(1′)–C(2′)	1.531(6)	C(7′)–C(8′)	1.332(9)	C(13′)–C(15′)	1.527(9)
C(2′)–C(3′)	1.492(10)	C(8′)–C(9′)	1.515(9)	C(15′)–C(16′)	1.550(19)
C(3′)–C(4′)	1.536(10)	C(9′)–C(10′)	1.554(5)	C(15′)–C(17′)	1.352(17)
C(4′)–C(5′)	1.572(6)	C(9′)–C(11′)	1.498(9)	C(4′)–C(18′)	1.527(9)
C(5′)–C(10′)	1.542(8)	C(11′)–C(12′)	1.520(7)	C(4′)–C(19′)	1.537(7)
C(10′)–C(1′)	1.536(9)	C(12′)–C(13′)	1.485(12)	C(18′)–O(21′)	1.241(6)
C(5′)–C(6′)	1.527(10)	C(13′)–C(14′)	1.322(10)	C(18′)–O(22′)	1.254(8)
C(6′)–C(7′)	1.492(7)	C(14′)–C(8′)	1.461(7)	C(10′)–C(20′)	1.540(8)

(b) Bond angles/deg

	θ/°		θ/°
C(10′)–C(1′)–C(2′)	112.2(4)	C(14′)–C(8′)–C(7′)	120.9(6)
C(1′)–C(2′)–C(3′)	109.7(5)	C(12′)–C(13′)–C(15′)	118.2(8)
C(2′)–C(3′)–C(4′)	113.2(5)	C(14′)–C(13′)–C(15′)	122.6(9)
C(3′)–C(4′)–C(5′)	108.5(4)	C(13′)–C(15′)–C(16′)	109.2(9)
C(4′)–C(5′)–C(10′)	116.9(4)	C(13′)–C(15′)–C(17′)	115.9(12)
C(4′)–C(5′)–C(6′)	112.0(4)	C(16′)–C(15′)–C(17′)	116.7(16)
C(5′)–C(10′)–C(1′)	109.7(4)	C(3′)–C(4′)–C(18′)	107.9(4)
C(10′)–C(5′)–C(6′)	111.4(4)	C(3′)–C(4′)–C(19′)	112.1(5)
C(5′)–C(6′)–C(7′)	111.7(5)	C(5′)–C(4′)–C(18′)	104.7(4)
C(6′)–C(7′)–C(8′)	123.2(6)	C(5′)–C(4′)–C(19′)	114.4(4)
C(7′)–C(8′)–C(9′)	122.3(4)	C(18′)–C(4′)–C(19′)	108.8(5)
C(8′)–C(9′)–C(10′)	112.5(4)	C(4′)–C(18′)–O(21′)	119.9(5)
C(9′)–C(10′)–C(5′)	105.0(4)	C(4′)–C(18′)–O(22′)	119.0(4)
C(8′)–C(9′)–C(11′)	112.0(4)	C(21′)–C(18′)–O(22′)	121.0(6)
C(9′)–C(11′)–C(12′)	112.2(6)	C(1′)–C(10′)–C(9′)	109.1(4)
C(11′)–C(12′)–C(13′)	113.1(6)	C(1′)–C(10′)–C(20′)	110.2(5)
C(12′)–C(13′)–C(14′)	119.2(5)	C(5′)–C(10′)–C(20′)	112.8(4)
C(13′)–C(14′)–C(8′)	125.2(7)	C(9′)–C(10′)–C(20′)	109.8(4)
C(14′)–C(8′)–C(9′)	116.7(5)	C(10′)–C(9′)–C(11′)	116.0(5)

c) Torsion angles/deg

	τ/°		τ/°
C(2′)–C(1′)–C(10′)–C(20′)	−72.5(6)	C(10′)–C(5′)–C(6′)–C(7′)	−48.3(6)
C(2′)–C(1′)–C(10′)–C(5′)	52.3(6)	C(5′)–C(6′)–C(7′)–C(8′)	16.3(8)
C(2′)–C(1′)–C(10′)–C(9′)	166.8(5)	C(6′)–C(7′)–C(8′)–C(9′)	−4.1(9)
C(10′)–C(1′)–C(2′)–C(3′)	−60.6(6)	C(6′)–C(7′)–C(8′)–C(14′)	178.4(6)
C(1′)–C(2′)–C(3′)–C(4′)	61.6(7)	C(7′)–C(8′)–C(14′)–C(13′)	−179.5(6)
C(2′)–C(3′)–C(4′)–C(5′)	−53.4(6)	C(7′)–C(8′)–C(9′)–C(10′)	23.0(7)
C(2′)–C(3′)–C(4′)–C(18′)	−166.2(5)	C(7′)–C(8′)–C(9′)–C(11′)	155.7(5)
C(2′)–C(3′)–C(4′)–C(19′)	74.0(6)	C(14′)–C(8′)–C(9′)–C(11′)	−26.6(7)
C(3′)–C(4′)–C(18′)–O(21′)	52.0(6)	C(14′)–C(8′)–C(9′)–C(10′)	−159.3(5)
C(3′)–C(4′)–C(18′)–O(22′)	−126.0(6)	C(8′)–C(9′)–C(10′)–C(5′)	−51.1(5)
C(3′)–C(4′)–C(5′)–C(6′)	177.1(5)	C(8′)–C(9′)–C(10′)–C(1′)	−168.6(4)
C(3′)–C(4′)–C(5′)–C(10′)	46.9(6)	C(8′)–C(9′)–C(11′)–C(12′)	50.0(7)
C(5′)–C(4′)–C(18′)–O(21′)	−63.4(7)	C(8′)–C(9′)–C(10′)–C(20′)	70.5(6)
C(5′)–C(4′)–C(18′)–O(22′)	118.6(5)	C(11′)–C(9′)–C(10′)–C(5′)	178.2(4)
C(18′)–C(4′)–C(5′)–C(10′)	161.8(4)	C(11′)–C(9′)–C(10′)–C(1′)	60.7(6)
C(18′)–C(4′)–C(5′)–C(6′)	−67.9(5)	C(10′)–C(9′)–C(11′)–C(12′)	−179.1(5)
C(19′)–C(4′)–C(5′)–C(10′)	−79.1(6)	C(11′)–C(9′)–C(10′)–C(20′)	−60.2(6)
C(19′)–C(4′)–C(5′)–C(6′)	51.1(6)	C(9′)–C(11′)–C(12′)–C(13′)	−50.7(7)
C(19′)–C(4′)–C(18′)–O(22′)	−4.1(7)	C(11′)–C(12′)–C(13′)–C(14′)	26.9(8)
C(19′)–C(4′)–C(18′)–O(21′)	173.8(5)	C(11′)–C(12′)–C(13′)–C(15′)	−152.4(6)
C(4′)–C(5′)–C(10′)–C(1′)	−47.0(5)	C(12′)–C(13′)–C(15′)–C(16′)	76(1)
C(6′)–C(5′)–C(10′)–C(1′)	−177.5(4)	C(12′)–C(13′)–C(15′)–C(17′)	−58(1)
C(4′)–C(5′)–C(10′)–C(20′)	76.3(6)	C(15′)–C(13′)–C(14′)–C(8′)	176.3(6)
C(4′)–C(5′)–C(10′)–C(9′)	−164.1(4)	C(14′)–C(13′)–C(15′)–C(17′)	123(1)
C(4′)–C(5′)–C(6′)–C(7′)	178.7(5)	C(12′)–C(13′)–C(14′)–C(8′)	−3(1)
C(6′)–C(5′)–C(10′)–C(20′)	−54.2(6)	C(13′)–C(14′)–C(8′)–C(9′)	2.8(9)
C(6′)–C(5′)–C(10′)–C(9′)	65.4(5)	C(14′)–C(13′)–C(15′)–C(16′)	−103(1)

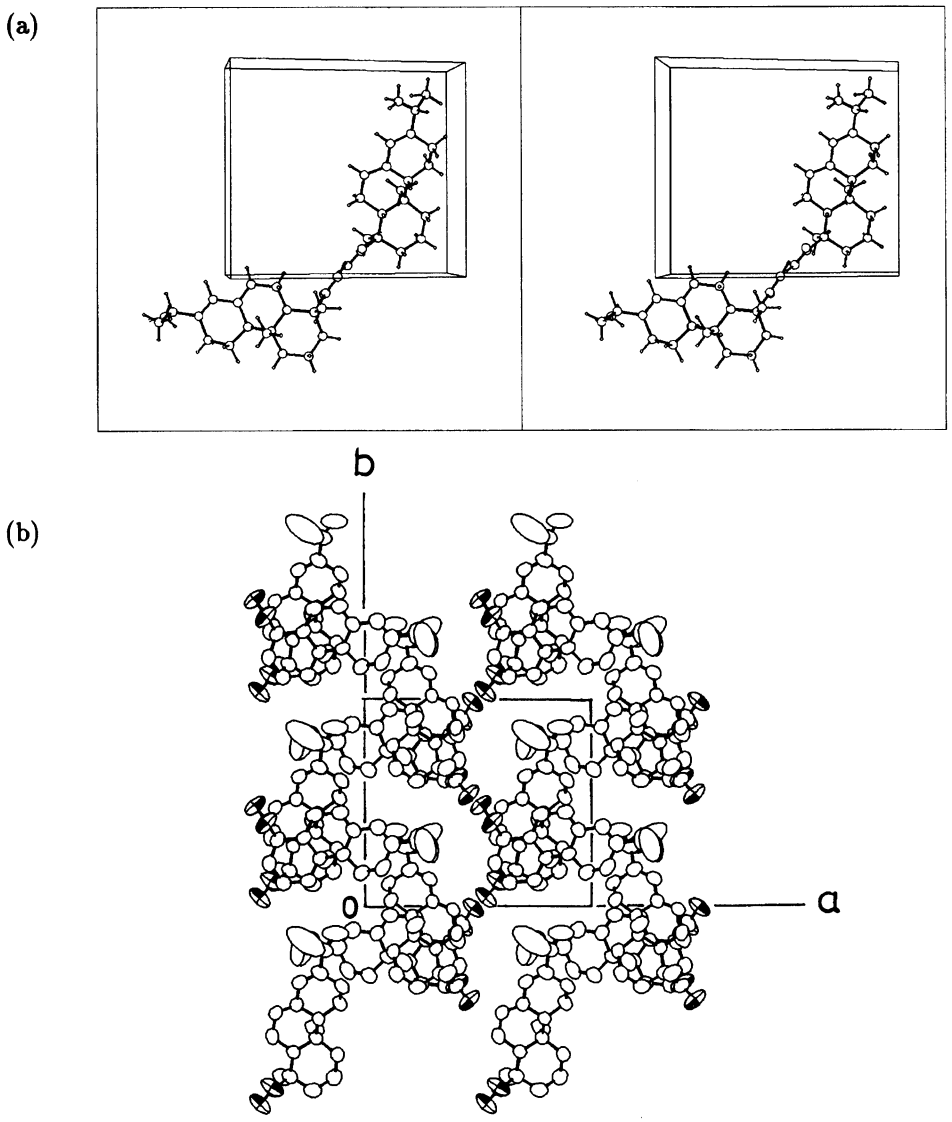


Fig. 2. Molecular packing as we look down the *c* axis. (a) Stereoscopic view of two crystallographically independent molecules in an asymmetric unit; (b) view of unit cell, with H atoms omitted for clarity. The origin is at the lower-left corner, the *a* axis is vertical, and the *c* axis is horizontal.

correlation of internal and overall motions according to the method of Dunitz and White[12] with the program THMA14.[13] The ADPs are shown in Table 5.

Conformation of the Cyclohexane. In Table 4, the ring puckering parameters of ring A indicate a chair conformation distorted slightly from the ideal chair form of cyclohexane with $|q_3| \gg q_2$ and $Q_T < 0.63$ Å. Ring A adopts C(2), C(2′) [both 0.70(1) Å] above and C(5) 0.57(1), C(5′) 0.56(1) Å below the mean plane of 1, 3, 4, and 10 carbons of both molecules.

Conformation of the Cyclohexenes. The Q_T and displacement asymmetric parameters of rings B and C in Table 4 indicate that these rings have half-chair conformations in both molecules. In both, the mean planes of the skeleton defined by the seven atoms of rings B and C [6, 7, 8, 9, 12, 13, and 14 carbons] are almost coplanar, and the maximum deviations of these atoms are 0.020(7) and 0.025(5) Å. The dihedral angles between these skeletons and ring A are 19.6(2) and 18.1(2)°. The relative stereochemistry is *trans* fusion for the A/B ring junction and *anti* between the C9 hydrogen and the C10 methyl.

Analysis of Side Groups. As can be seen from the ellipsoid in Fig. 1, atomic displacements are pronounced for both molecules and the internal motions or static displacements have some relevance particularly for the isopropyl and carboxyl groups.

Large thermal motions of the terminal atoms of two independent molecules contained in an asymmetric unit are often observed in steroid structures.[14,15] For observation of such a phenomenon, if present, thermal motion analysis of the ADPs was carried out. In Table 5, results of the rigid-body test done by Hirshfeld's method[16] indicate that the ADPs are of poor qual-

Table 4. Ring Puckering Parameters (Q_T, q_2, q_3, ϕ_2, θ_2) and Displacement Asymmetric Parameters (DAP: D_s, D_2) of Rings A, B, and C

Ring	Parameter	Molecule 1	Molecule 2
A	Q_T/Å	0.555(6)	0.554(5)
	q_2/Å	0.085(6)	0.091(5)
	q_3/Å	0.548(5)	0.547(5)
	ϕ_2/deg	68.5(33)	62.3(27)
	θ_2/deg	8.8(5)	9.4(5)
	D_s	C(2)=0.009(2)	C(2′)=0.003(2)
	D_2	C(3)–C(2)=0.019(2)	C(3′)–C(2′)=0.025(2)
B	Q_T/Å	0.545(4)	0.536(4)
	q_2/Å	0.415(4)	0.393(5)
	q_3/Å	0.353(5)	0.364(5)
	ϕ_2/deg	−37.9(7)	−36.8(8)
	θ_2/deg	49.7(6)	47.6(6)
	D_s	C(7)=0.108(3)	C(7′)=0.109(2)
	D_2	C(5)–C(10)=0.032(2)	C(5′)–C(10′)=0.025(2)
C	Q_T/Å	0.440(6)	0.426(5)
	q_2/Å	0.344(5)	0.330(6)
	q_3/Å	0.275(6)	0.269(6)
	ϕ_2/deg	118.1(9)	119.9(10)
	θ_2/deg	51.3(8)	50.8(8)
	D_s	C(11)=0.006(3)	C(11′)=0.092(2)
	D_2	C(11)–C(9)=0.095(2)	C(8′)–C(14′)=0.095(2)

ity; differences in the mean-square displacement amplitudes (ΔMSDAs) along the bonded direction [esd for ΔMSDAs is 0.0318 Å^2] are larger than $\bar{\sigma}$(ADP) [the mean σ(ADP) is 0.0083 Å^2]. The analysis is complicated by the large agreement indices R_{wU} and strong correlation at room temperature. The largest principal axis of the L tensor, L_1, corresponds to librational motion about the bonded direction. The large values of the T tensor corresponding to translations of the origin measured from the molecular center of mass correlate strongly with the rotation to keep the atomic displacements and these are distributed evenly over all of the important degrees of freedom. That the mean-square libration amplitudes $<\phi^2>$ are large means that thermal motions vary freely. Corrections of bond lengths with rigid-body motion and internal motions shown in Table 6 were derived from the calculated translations. The lower and upper bounds involving hydrogen atoms were followed by Busing and Levy.[17] Uncorrected bond lengths of the isopropyl groups and the carboxyl groups (attached rigid groups, ARGs) tend to become shorter compared with normal values, but the bond lengths of ARGs corrected by thermal motion corrections have the expected values except for the isopropyl groups. In the isopropyl groups, the displacements are localized in translation along the C(15)–C(16), C(15)–C(17), C(15′)–C(16′), and C(15′)–C(17′) axes. For the carboxyl groups, the compound is not rigid except for hydrogen bonds with adjacent molecules.

With the two independent molecules, potential energy calculations were carried out with the program ROTENER,[18] which makes use of a function of the type $E_{ij}=-A_{ij}r_{ij}^{-6}+B_{ij}\exp(-C_{ij}r_{ij})$. Figure 3 shows the potential energy profiles with the van der Waals energy for the rotation of the two side groups. Atomic charges are calculated by the method of Gasteiger and Marsili.[19] We assume that there is no geometrical change during rotation of the fragment, and the Coulombic energy is neglected. Rotations of the isopropyl groups of Fig. 3a are different in symmetry and in energy; the C(13′)–C(15′) group has approximate twofold symmetry and maxima of more than 40 kJ mol^{-1} [−85.0, ΔE=43 and 80.0°, ΔE=54 kJ mol^{-1}], but C(13)–C(15) has no twofold pattern and maxima energies are 51 [−80.0°] and 9.6 kJ mol^{-1} [140.0°]. The maxima of the C(13)–C(15) and C(13′)–C(15′) groups are doubtless too high, since no readjustment of atomic positions was allowed. But the C(13)–C(15) group permits counterclockwise rotation. The peaks in the curves are due to repulsive interactions between the isopropyl groups and ring C. The potential energy barriers of the carboxyl groups of Fig. 3b are essentially due to the steric hindrance caused by the hydrogen bond of the other asymmetric molecule bound to O(22)···O(21′) and O(22′)···O(21). These plots indicate that the crystalline conformation is not exactly coincident with the potential energy minimum, being shifted [30°, ΔE=−8.9 kJ mol^{-1} for the C(13)–C(15) group] and by hydrogen bonds [O(22)···O(21′) and O(22′)···O(21)]. This situation may be a consequence of packing effects.

The poor quality of the ADPs limits the precision of the barrier heights calculated from them. The ADP

Table 5. Analysis of the Anisotropic Displacement Parameters (ADPs) in Terms of LST Rigid-Body Motion and Internal Motions

(a) The mean square displacement amplitude (ΔMSDAs)
$\overline{\Delta}$: average differences of ΔMSDAs (Å^2) along the interatomic directions,
=0.0222 (for all pairs of atoms),
=0.0141 (for bonded atoms).
These values should be compared with mean esd for U_{obs} [$\bar{\sigma}(U_{obs})$] of 0.0083, which implies an esd for ΔMSDAs of about 0.0318.

(b) Agreement index R_{wU}[a)] and goodness of fit[b)]

		Rigid-body motion	Internal motions
R_{wU}	All	0.304	0.222
	Diagonal	0.238	0.176
Goodness of fit		6.57	4.71

a) $R_{wU}=[\Sigma w(\Delta U)^2/\Sigma w(U_{obs})^2]^{1/2}$, where $\Delta U=U_{ij}(obs)-U_{ij}(calc)$, w=reciprocal of $\sigma(U_{ij}(obs))^2$.
b) Goodness of fit $=[\Sigma w(\Delta U)^2/(No-Np)]^{1/2}$, where No= number of independent observations, =264, Np=number of parameters, =20.

(c) L tensor (root-mean square of the librational tensor eigenvalues) and T tensor(root-mean square of the translational tensor eigenvalues)

		Rigid-body motion	Internal motions
L tensor/deg^2	L_1	4.68	4.47
	L_2	1.38	1.31
	L_3	1.21	0.79
T tensor/Å^2	T_1	0.316	0.268
	T_2	0.260	0.257
	T_3	0.235	0.240

(d) Mean-square libration amplitudes $<\phi^2>$ correlated to overall and internal motions with esds

Libration		$<\phi^2>$
Group	Along	(deg^2)
C(16), C(17)	C(13)–C(15)	128(94)
O(21), O(22)	C(4)–C(18)	332(33)
C(16′), C(17′)	C(13′)–C(15′)	366(87)
O(21′), O(22′)	C(4′)–C(18′)	328(32)

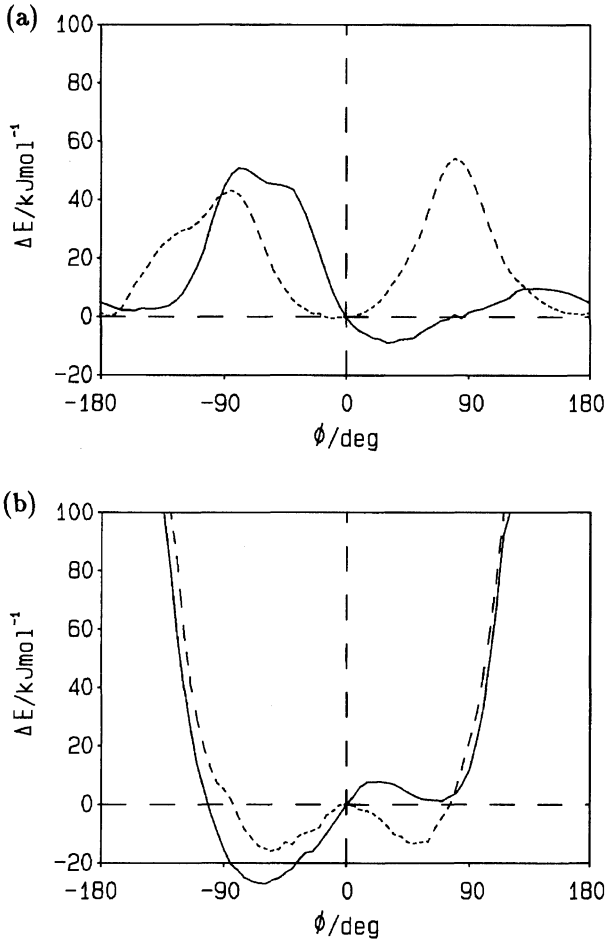
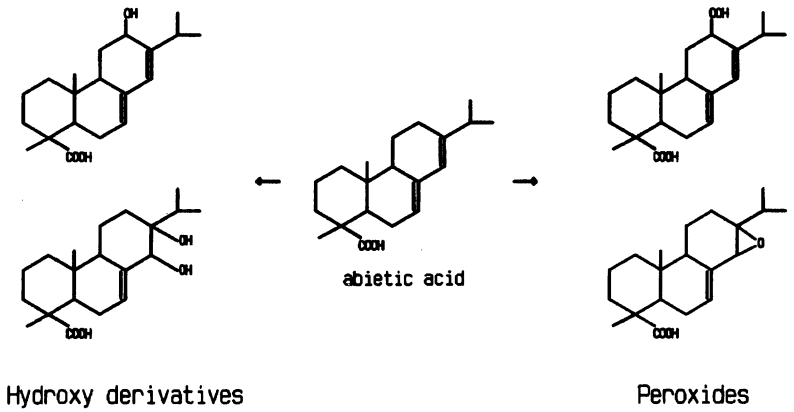


Fig. 3. Difference potential energies (ΔE) for rotation of side groups. (a) Rotation about C(13)–C(15) (solid lines) and C(13′)–C(15′) (dashed lines); (b) rotation about C(4)–C(18) (solid lines) and C(4′)–C(18′) (dashed lines). The positive values of the rotation angle ϕ correspond to counterclockwise rotation. The ϕ=0° value is for the conformation found in the crystal and the energy values are relative to the energy corresponding that conformation.

analysis and the potential energy calculations suggest that the isopropyl groups are free in these region and that the carboxyl groups are rigid because of hydrogen bonds. The translation displacements along the C(15)–C(16), C(15′)–C(16′), and C(15′)–C(17′) axes are local. In the difference map, there are no significant peaks of disorder in the regions of the isopropyl groups.

Air Oxidation. A single crystal of **1** on exposure to air for more than 6 months in the refrigerator became a turbid yellow. During the air oxidation of **1**, some intermediates probably formed on the exposed surface. A small amount of isopimaric acid of the pimaric type and of oxidation products was observed by GC/MS. The short distances and the large thermal motions of the isopropyl groups suggest that a conjugated double bond system is present through a free-radical chain mechanism, probably producing the hydroxyl groups and the peroxides (Scheme 1).

Cyrstal Packing. Two independent molecules of the asymmetric unit are connected by two strong O–H···O hydrogen bonds. The values for the C–O and C=O bond distances of the carboxyl group in each molecule are normal and equivalent within esd. Four weak C–H···O intramolecular contacts such as those reported by Taylor and Kennard[20)] are observed. These findings suggest that the carboxyl groups stabilize the asymmetric molecules, helped with intramolecular contacts. Table 7 describes the geometrical features of hydrogen bonds and C–H···O contacts. No other short contacts were observed in the crystal packing.



Scheme 1. Air oxidation of abientic acid.

Table 6. Experimental and Corrected Bond Distances (Å) of Side Groups

Atom	Uncorrected[a]	Corrected most[b]	Corrected ARGs[c]	Lower bounds[d]	Upper bounds[d]
C(13)–C(15)	1.521(11)	1.524	1.524	1.524	1.863
C(15)–C(16)	1.223(33)	1.226	1.245	1.438	2.500
C(15)–C(17)	1.546(18)	1.548	1.576	1.549	1.926
C(4)–C(18)	1.511(8)	1.512	1.512	1.511	1.699
C(18)–O(21)	1.240(6)	1.245	1.291	1.249	1.587
C(18)–O(22)	1.250(7)	1.252	1.301	1.258	1.600
C(13′)–C(15′)	1.527(9)	1.531	1.531	1.534	1.925
C(15′)–C(16′)	1.559(19)	1.553	1.630	1.553	2.012
C(15′)–C(17′)	1.352(17)	1.357	1.417	1.377	2.029
C(4′)–C(18′)	1.527(9)	1.528	1.528	1.527	1.735
C(18′)–O(21′)	1.241(6)	1.254	1.292	1.247	1.597
C(18′)–O(22′)	1.254(8)	1.257	1.304	1.260	1.596

a) The observed distances between a pair of atomic positions. b) Assuming rigid-body motion of non-hydrogen of the molecule. c) Assuming internal motions of rigid groups about specific bounds. d) Involving hydrogen.

Table 7. The Geometry of Hydrogen-Bonds and C–H···O Contacts

D[a]···A[b]	D···A (Å)	H	D–H (Å)	A–H (Å)	∠D–H···A (deg)
O(22)···O(21′)^{i}	2.622(8)	H(22)	0.91(6)	1.756(57)	159(5)
O(22′)···O(21)^{i}	2.635(8)	H(22′)	1.13(5)	1.535(52)	160(4)
C(5)···O(21)^{i}	2.784(8)	H(5)	1.03(4)	2.325(36)	106(2)
C(19)···O(22)^{i}	2.655(10)	H(19a)	1.01(5)	2.383(51)	94(3)
C(5′)···O(21′)^{i}	2.911(7)	H(5′)	1.03(4)	2.469(42)	105(3)
C(19′)···O(22′)^{i}	2.657(10)	H(19′c)	0.98(4)	2.557(48)	85(3)

a) D=donor. b) A=acceptor. The Roman numeral as superscripts refers to the equivalent position relative to the reference molecule at x, y, z. i: x, y, z.

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