The Structure of an Abietic Acid Dimer

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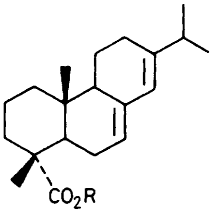
The first *X*-ray structural determination of an acid-catalysed dimer of abietic acid is reported.

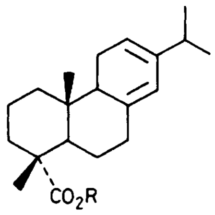
The acid-catalysed dimerisation of abietic acid (**1**, R = H) and related acids from pine colophony has been in use for about five decades as a source of industrially useful products.[1] However, the structure of such dimers has remained elusive, in spite of the active interest of several research groups.[2—4] We report here the molecular structure of a dimer isolated from toluene-*p*-sulphonic acid-catalysed dimerisation of methyl levopimarate (**2**, R = Me) in chloroform at room temperature.

A very fast isomerisation of (**2**, R = Me) into (**1**, R = Me) (monitored by ^{1}H n.m.r. spectroscopy; $t_{\frac{1}{2}}$ <5 min) was observed, followed by a slow dimerisation to yield (**3**, R = 13αH/13βH) (10%). These dimers were isolated as a crystalline material† after chromatographic purification. A single crystal *X*-ray analysis‡ (Figure 1) reveals that only one new C–C bond, between C(7) and C(30), has been formed. The two monomer fragments are twisted into an almost normal relationship to each other, with a resulting short 7-H-37-H contact of 2.01 Å. This structure differs from other proposed structures for abietic acid dimers,[2—4] which involve the formation of two new C–C bonds upon dimerisation. This conformation of (**3**) is also indicated in solution by the observation of a strong (>10%) nuclear Overhauser enhancement between 7-H and 37-H in the 250 MHz ^{1}H n.m.r. spectrum of (**3**).

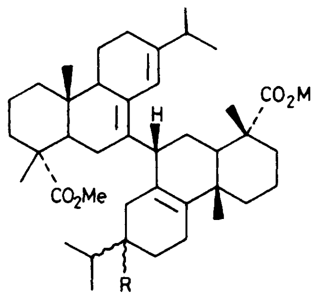
Dimerisation results in the creation of two new chiral centres, at C(7) and C(13), and the loss of one at C(9), in one abietic acid component only. The C(13) centre was found to be disordered in the *X*-ray analysis; indeed there is notable thermal anisotropy with characteristic associated artificial bond shortening, in all atoms between C(11) and C(14) in this ring and also the isopropyl group, with the principal axes of vibration being normal to the plane of the ring. This could be consistent with either the presence in the crystal of unequal



(**1**) R = H
R = Me



(**2**) R = H
R = Me



(**3**) R = 13-β-H
R = 13-β-H

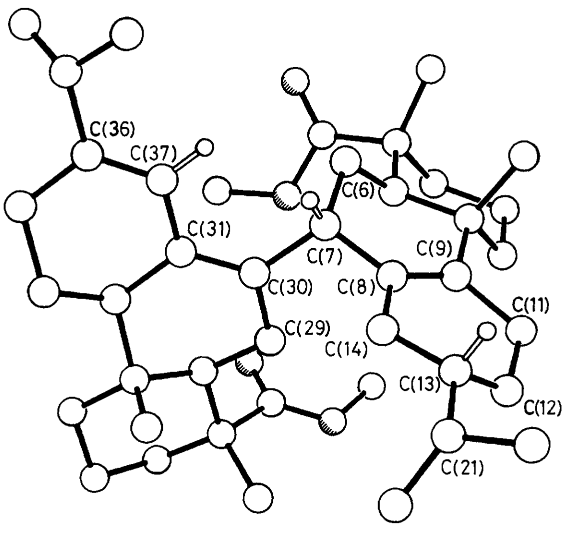


Figure 1. The molecular structure of (**3**) (with crystallographic numbering). There are C–C double bonds between C(8)–C(9), C(30)–C(31), and C(36)–C(37). The H(7)–C(7)–C(30)–C(31) torsion angle is 29°.

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† M.p. 185—188 °C (from MeOH); $\nu_{\text{max.}}$ (CCl_4) 1725 cm^{-1}; $\lambda_{\text{max.}}$ (EtOH) (ε), 251 (21 200), 256 (21 200) nm; *m/z* (%), 632 (M^+) (37), 572 (18), 317 (34), 316 (35), 315 (70), 257 (85), 255 (100), 243 (16), 241 (77).

‡ *Crystal data:* $C_{42}H_{64}O_4$, orthorhombic, a = 10.160(2), b = 18.391(5), c = 20.428(6) Å, U = 3817 Å^3, space group $P2_12_12_1$, Z = 4, M = 632.9, D_c = 1.06 g cm^{-3}, μ(Cu-K_α) = 5 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using ω scans. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters U(H) = 1.2 $U_{\text{eq.}}$(C) and allowed to ride on their parent carbon atoms. Refinement converged to give R 0.070, R_w 0.080 for 2438 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leqslant 58°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

amounts of two epimers at C(13) in which the isopropyl group is equatorial in both cases, or with partial occupancy in the crystal of a closely related compound with a C(13)–C(14) double bond. It was not possible to resolve the obvious disorder present in this region in the crystal structure into discrete partial occupancy alternative ring configurations. However, the ^1H n.m.r. spectrum supports the epimeric interpretation. Two pairs of ester peaks (at δ 3.59, 3.60 and 3.69, 3.70) in spectra obtained from single crystals of this material indicate the presence in the crystal of two closely related isomers. The exact ratio of these isomers varied according to the batch and the preparative conditions, indicating the two compounds are *not* in equilibrium in $CDCl_3$ solution, and that therefore this is *not* a conformational phenomenon. Peaks at δ 6.13 and 6.09 in the same ratio indicate the presence of only *one* vinylic proton (due to 14-H) in each isomer, whilst a broad doublet at δ 3.15 due to 7-H shows a coupling constant ($J < 7$ Hz) which is consistent with this proton being *equatorial* in both isomers. The chiral centre at C(7) must therefore be formed stereospecifically, whereas that at C(13) is not.

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