Crystal structure of (1*R**,2*S**,5*S**,6*S**,7*R**)-6-(3,5-dinitrobenzoyloxy)methyl-2,7-dimethyl-tricyclo [5.2.2.0^{1,5}]undec-8-ene, $C_{21}H_{24}N_2O_6$

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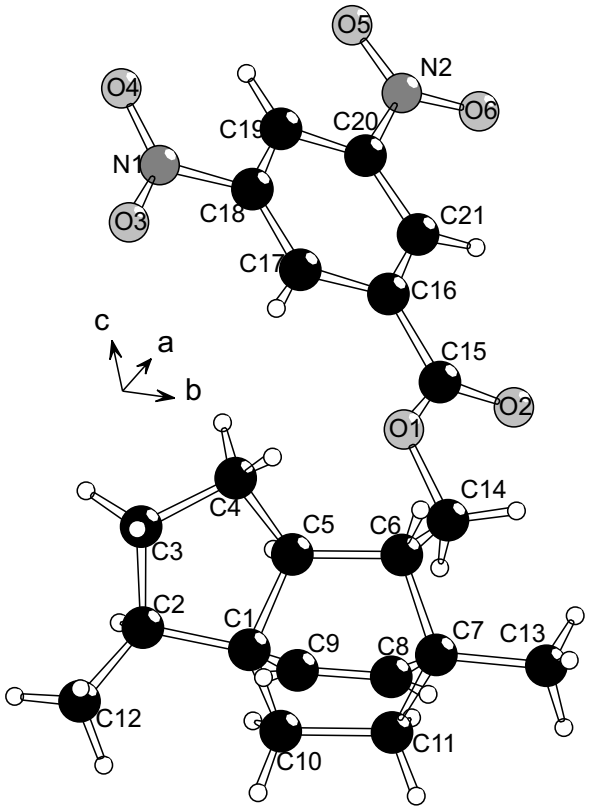

Abstract

$C_{21}H_{24}N_2O_6$, orthorhombic, $P2_12_12_1$ (No. 19), a = 6.285(2) Å, b = 9.044(4) Å, c = 35.52(2) Å, V = 2019.0 Å^3, Z = 4, $R(F)$ = 0.095, $wR_{ref}(F^2)$ = 0.279, T = 295 K.

Source of material

The title compound is a derivative of the corresponding (1*R**,2*S**,5*S**,6*S**,7*R**)-2,7-dimethyl-tricyclo[5.2.2.0^{1,5}]undec-8-en-6 carbaldehyde (**I**) formed by a two step procedure: a) reduction of aldehyde **I** with $LiAlH_4$ in Et_2O and b) esterification of the crude alcohol with 3,5- dinitrobenzoyl chloride, triethylamine and a catalytic amount of 4-dimethylaminopyridine (DMAP) in CH_2Cl_2. It was impossible to determine the absolute structure of the title compound, however, other derivatives of aldehyde I (*p*-bromobenzoate and *p*-bromosulfonate) could not be crystallized. Nor-sesquiterpene **I** is a minor constituent (0.24%) of Santalum spicatum (R. Br.) A. DC. (Santalaceae) [1]. It was isolated analogously to its enantiopure C-6-epimer (1*R*,2*S*,5*S*,6*R*,7*R*)-2,7-dimethyl-tricyclo[5.2.2.0^{1,5}] undec-8-en-6-carbaldehyde (**II**) [2]. Beside these two nor-helifolen-12-als, four other stereoisomers exist in Western Australian sandalwood oil in concentrations between 0.05% and 0.4%.

Experimental details

The crystal material was very poorly crystallized, resulting in broad reflection profiles and in a large number of 'unobserved' reflections, even below 2θ = 40° and hence in a low $N(hkl)_{gt}/N(param)$ ratio. Extension of the data collection was checked but found useless and considered unreasonable.

Discussion

The space group of this molecule crystal was assigned to $P2_12_12_1$, in spite of some extinction violations. The structure consists of one molecule per asymmetric unit and is held together by van der Waals forces. All intramolecular bond lengths are normal. The best fit results were obtained for a structure model with one methyl group (C13) assumed ideally disordered, i.e. with two positions rotated by 60°. The main and planar part of the molecule consists of the atoms C14, C15, C16, C17, C18, C19, C20, C21, N1, N2, O1, O2, O3, O4, O5, O6, H17, H19, H21, with an rms value of the deviations from the least squares plane of 0.050 Å. The fact, that the NO_2 groups are aligned to the aromatic ring plane can be attributed to intramolecular electrostatic interactions between the oxygen and the hydrogen atoms (d(O···H) = 2.37 – 2.59 Å), whereas the next intermolecular O···H distances exceed 2.66 Å (O5···H12A). The packing scheme of the molecules is characterized by stacking of molecular planes normal to [100], where the shortest distances are approximately $a_o/2$ due to the 2_1 screw axis.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.18 × 0.65 × 0.65 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	0.97 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-6R, ω
$2\theta_{max}$:	40.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2191, 1887
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1342
$N(param)_{refined}$:	277
Programs:	SHELXS-97 [3], SHELXL-97 [4], DIAMOND [5]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2)	4*a*		0.3865	–0.3491	–0.1452	0.07
H(3A)	4*a*		0.7866	–0.4789	–0.1517	0.17
H(3B)	4*a*		0.6317	–0.4806	–0.1168	0.17
H(4A)	4*a*		0.7844	–0.2771	–0.0945	0.19
H(4B)	4*a*		0.9445	–0.2787	–0.1286	0.19
H(5)	4*a*		0.5599	–0.1233	–0.1226	0.11
H(6)	4*a*		0.9517	–0.0303	–0.1448	0.04
H(8)	4*a*		0.9405	–0.0843	–0.2315	0.14
H(9)	4*a*		0.7990	–0.3104	–0.2165	0.07
H(10A)	4*a*		0.3017	–0.1002	–0.1721	0.13
H(10B)	4*a*		0.3567	–0.1467	–0.2136	0.13
H(11A)	4*a*		0.4583	0.1157	–0.1803	0.08
H(11B)	4*a*		0.4962	0.0742	–0.2227	0.08
H(12A)	4*a*		0.3354	–0.5452	–0.1809	0.21
H(12B)	4*a*		0.5548	–0.5297	–0.2015	0.21
H(12C)	4*a*		0.3662	–0.4238	–0.2119	0.21
H(13A)	4*a*	0.50	0.9037	0.2361	–0.1791	0.10
H(13B)	4*a*	0.50	0.7800	0.2324	–0.2174	0.10
H(13C)	4*a*	0.50	1.0041	0.1574	–0.2141	0.10
H(13D)	4*a*	0.50	0.8882	0.1812	–0.2280	0.10
H(13E)	4*a*	0.50	1.0119	0.1849	–0.1897	0.10
H(13F)	4*a*	0.50	0.7878	0.2599	–0.1929	0.10
H(14A)	4*a*		0.8489	0.1959	–0.1255	0.07
H(14B)	4*a*		0.6075	0.1507	–0.1262	0.07
H(17)	4*a*		0.7713	–0.1253	–0.0336	0.07
H(19)	4*a*		0.7616	–0.0821	0.0784	0.13
H(21)	4*a*		0.7444	0.2795	0.0126	0.12

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*a*	0.775(2)	–0.284(1)	0.0267(3)	0.059(5)	0.102(9)	0.101(8)	–0.015(7)	–0.008(6)	0.006(7)
N(2)	4*a*	0.738(2)	0.206(1)	0.0826(3)	0.083(7)	0.124(9)	0.060(7)	0.019(9)	–0.009(6)	–0.006(7)
O(1)	4*a*	0.767(1)	0.0627(8)	–0.0830(2)	0.066(5)	0.099(5)	0.065(5)	0.001(5)	0.004(4)	0.000(4)
O(2)	4*a*	0.733(2)	0.291(1)	–0.0602(2)	0.114(6)	0.106(6)	0.060(4)	–0.003(7)	0.004(5)	–0.005(4)
O(3)	4*a*	0.765(2)	–0.3580(9)	–0.0015(3)	0.086(6)	0.094(5)	0.112(6)	0.011(5)	–0.017(6)	–0.008(5)
O(4)	4*a*	0.790(2)	–0.332(1)	0.0589(3)	0.20(1)	0.120(7)	0.101(6)	0.021(8)	–0.008(8)	0.038(6)
O(5)	4*a*	0.723(2)	0.151(1)	0.1138(2)	0.154(8)	0.142(7)	0.056(5)	0.042(7)	–0.006(6)	–0.001(5)
O(6)	4*a*	0.742(2)	0.340(1)	0.0786(2)	0.122(7)	0.120(6)	0.080(5)	0.017(8)	–0.012(6)	–0.021(5)
C(1)	4*a*	0.584(2)	–0.218(1)	–0.1754(3)	0.066(7)	0.088(8)	0.054(6)	–0.006(7)	–0.001(5)	–0.001(6)
C(2)	4*a*	0.508(2)	–0.367(2)	–0.1618(3)	0.084(8)	0.11(1)	0.073(8)	0.000(8)	0.004(7)	–0.001(8)
C(3)	4*a*	0.686(2)	–0.420(1)	–0.1372(3)	0.11(1)	0.076(8)	0.095(8)	0.000(7)	–0.015(9)	0.016(6)
C(4)	4*a*	0.795(3)	–0.280(1)	–0.1217(3)	0.13(1)	0.11(1)	0.067(7)	0.01(1)	–0.016(8)	0.017(7)
C(5)	4*a*	0.679(2)	–0.149(1)	–0.1392(2)	0.070(7)	0.100(8)	0.037(5)	0.010(7)	0.013(5)	0.002(5)
C(6)	4*a*	0.800(2)	–0.008(1)	–0.1479(2)	0.036(5)	0.095(8)	0.054(6)	0.011(5)	0.005(4)	–0.005(6)
C(7)	4*a*	0.767(2)	0.032(1)	–0.1894(3)	0.052(6)	0.083(7)	0.062(6)	–0.004(6)	0.013(6)	0.003(5)
C(8)	4*a*	0.840(2)	–0.096(2)	–0.2125(3)	0.062(8)	0.12(1)	0.057(7)	0.011(7)	–0.002(6)	0.005(8)
C(9)	4*a*	0.756(2)	–0.223(2)	–0.2048(3)	0.083(8)	0.106(9)	0.045(6)	0.015(9)	–0.001(6)	–0.001(6)
C(10)	4*a*	0.416(2)	–0.110(1)	–0.1902(3)	0.052(6)	0.12(1)	0.084(8)	0.004(7)	–0.013(6)	0.007(8)
C(11)	4*a*	0.521(2)	0.043(2)	–0.1970(3)	0.064(7)	0.12(1)	0.070(8)	0.028(7)	–0.006(5)	0.006(7)
C(12)	4*a*	0.434(3)	–0.477(2)	–0.1918(3)	0.17(2)	0.14(1)	0.072(8)	–0.05(1)	–0.008(9)	–0.015(9)
C(13)	4*a*	0.874(2)	0.178(2)	–0.2011(3)	0.093(8)	0.13(1)	0.063(7)	0.000(9)	–0.001(6)	0.000(7)
C(14)	4*a*	0.750(2)	0.115(1)	–0.1215(2)	0.072(7)	0.104(7)	0.042(6)	–0.021(7)	0.001(6)	0.005(6)
C(15)	4*a*	0.750(2)	0.157(1)	–0.0553(3)	0.055(6)	0.082(8)	0.070(8)	–0.009(7)	0.006(6)	–0.009(7)
C(16)	4*a*	0.758(2)	0.094(1)	–0.0173(2)	0.043(5)	0.087(7)	0.051(6)	–0.008(6)	–0.005(5)	0.004(5)
C(17)	4*a*	0.766(1)	–0.063(1)	–0.0128(3)	0.026(5)	0.113(9)	0.059(7)	–0.004(7)	–0.008(5)	–0.005(7)
C(18)	4*a*	0.767(2)	–0.119(1)	0.0225(3)	0.041(5)	0.102(9)	0.050(7)	–0.002(7)	–0.003(5)	–0.003(6)
C(19)	4*a*	0.758(2)	–0.039(1)	0.0547(3)	0.040(6)	0.111(9)	0.062(8)	–0.009(7)	–0.004(6)	0.011(7)
C(20)	4*a*	0.743(2)	0.114(1)	0.0495(2)	0.057(6)	0.114(9)	0.036(6)	0.005(7)	–0.005(6)	–0.011(6)
C(21)	4*a*	0.748(2)	0.177(2)	0.0146(3)	0.060(6)	0.12(1)	0.049(7)	–0.001(8)	–0.011(6)	–0.007(6)

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