Crystal structure of (–)-hardwickiic acid, $C_{19}H_{27}OCOOH$

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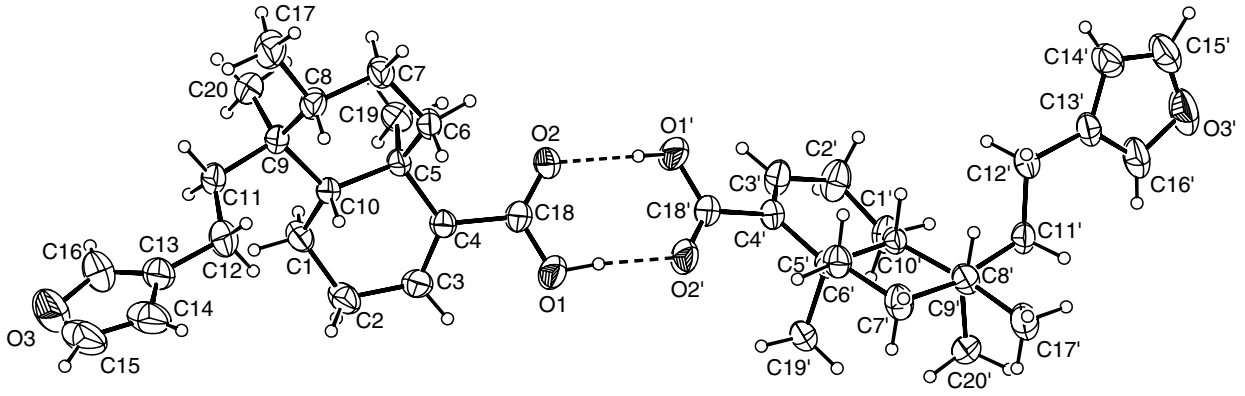

Abstract

$C_{20}H_{28}O_3$, monoclinic, $P2_1$ (no. 4),
a = 10.0279(2) Å, b = 11.1076(3) Å, c = 17.0856(4) Å,
β = 105.522(1)°, V = 1833.7 Å^3, Z = 4,
$R_{gt}(F)$ = 0.058, $wR_{ref}(F^2)$ = 0.159, T = 293 K.

Source of material

The title compound was isolated from stem bark of *Croton oblongifolius Roxb*. A single crystal of the title compound was obtained by recrystallization from ethyl acetate, m.p. 104 °C – 105 °C and $[\alpha]^{25}_a = -114.8°$ (c = 1, MeOH).

Experimental details

All hydrogen atoms were refined using the riding model except those bound to oxygen atoms. The two hydroxyl H atoms were found from difference Fourier maps and refined with restraints for U_{iso}. Their bond distances to the O atoms were restrained to be approximately 0.89 Å. A disorder of the free 3-furyl group on the C12 atom did not need to be resolved. The respective U_{ij} values are large, but the bond geometry is acceptable.

Discussion

Hardwickiic acid has been isolated from many plants, e.g. *Hardwickia pinnata* [1], *Solidago juncea* [2], *Solidago arguta* [3], *Grangea maderaspatana* [4], *Baccharis macraei* [5], *Clerodendrum neriifolium* [6], *Croton oblongifolius* [7], *Croton aromaticus* [8], *Croton sonderianus* [9]. It exhibits insecticidal activity against *Aphis craccivora* [8], and antimicrobial activity [9]. The identity of the title compound was deduced from spectroscopic data, but the crystal structure has never been reported.

The crystal has two independent hardwickiic acid molecules in the asymmetric unit. The two molecules form an asymmetric intermolecular hydrogen bonded dimer. The O1···O2′ and O1′···O2 distances are 2.679(3) Å and 2.669(2) Å, and the ∠O1–H1O···O2′ and ∠O1′–H1′O···O2 angles are 172° and 160°, respectively. For the intermolecular hydrogen bonding between the two carboxyl groups, the carboxylic planes connected to the C4 and C4′ are twisted from the characteristic of sp^2 double bond plane of C4=C3 and C4′=C3′ with the ∠O1–C18–C4–C3 and ∠O1′–C18′–C4′–C3′ torsion angles of −28.8(4)° and –27.0(4)°, respectively. The twist might be due to the steric effect of the C19 methyl group. The distances of 1.332(3) Å, 1.339(4) Å, 1.223(3) Å and 1.221(3) Å, respectively, confirm the double bond character of the C3=C4, C3′=C4′, C18=O2 and C18′=O2′ bonds. Two independent molecules occurring in the asymmetric unit may be deduced from different packing, resulting in slight conformational differences on both the twistable $-CH_2-CH_2-$ group and the attached furyl unit.

The conformation of the rings A (C1 to C10) and B (C10 to C9) were analyzed by calculating the ring-puckering parameters [10] using the PARST program [11]. The ring A is a half-chair conformation $^1H_6$ with the puckering parameters Q = 0.539(2) Å and θ = 52.15(3)°. The ring B adopts a chair conformation with the puckering parameters Q = 0.556(2) Å and θ = 3.94(2)°. The methyl C19 and C20 groups are located on the same side. Therefore, the configurations of C5, C8 and C10 (sp^3) chiral centres induce the *R,* and C9 the *S* configuration, resp. The absolute configuration agrees with that reported for (–)-hardwickiic acid obtained by [1]. Interestingly, the moieties of the furan chains connected to C9 and C9′ are nearly planar, even though C11—C12 and C11′—C12′ are both single bonds. The deviation of the mean plane for both furan chains (C9, C11 to C16, O3 and C9′, C11′ to

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C16′, O3′) are 0.101 Å and 0.021 Å. The C11–C12–C13–C16 torsion angle of 19.4(5)° is larger than that of C11′–C12′–C13′–C16′ at 5.2(5)°. This difference in torsion angles is probably due to a C–H···O hydrogen bond between C17–H···O3′(x–2, y, z–1). The C17···O3′ distance is 3.436(3) Å. However, there is only van der Waals contact between C17′–H···O3. In addition, the mean planes of both furan side chains connected to C9 and C9′ are nearly perpendicular to rings A and A′, respectively. The dihedral angles between the furan mean planes and ring A and ring A′ are 83.9(1)° and 89.4(1)°, respectively. The molecules build non-polar layers parallel to the *ac* plane.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.10 × 0.45 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.75 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω
$2\theta_{max}$:	61°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13598, 9331
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6221
$N(param)_{refined}$:	421
Programs:	SHELXS-97 [12], SHELXL-97 [13]

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

Atom	Site	x	y	z	U_{iso}
H(12A)	2*a*	–0.8001	0.3747	0.2274	0.099
H(12B)	2*a*	–0.8884	0.2593	0.2307	0.099
H(15)	2*a*	–1.0467	0.2999	–0.0547	0.156
H(16)	2*a*	–1.0903	0.5036	0.1226	0.154
H(17A)	2*a*	–1.0938	0.2244	0.3341	0.152
H(17B)	2*a*	–1.0890	0.2633	0.4230	0.152
H(17C)	2*a*	–1.0333	0.1365	0.4067	0.152
H(19A)	2*a*	–0.7763	0.5134	0.5368	0.106
H(19B)	2*a*	–0.6731	0.6051	0.5149	0.106
H(19C)	2*a*	–0.6206	0.5146	0.5870	0.106
H(2′1)	2*a*	0.1557	0.5211	0.9654	0.099
H(2′2)	2*a*	0.1638	0.6346	0.9123	0.099
H(15′)	2*a*	0.5500	0.2415	1.3195	0.121
H(16′)	2*a*	0.6871	0.3578	1.1394	0.108
H(17D)	2*a*	0.6277	0.1262	0.9248	0.122
H(17E)	2*a*	0.6134	0.1575	0.8335	0.122
H(17F)	2*a*	0.5513	0.0371	0.8563	0.122
H(19A)	2*a*	0.3454	0.4070	0.7217	0.107
H(19B)	2*a*	0.2659	0.5215	0.7385	0.107
H(19C)	2*a*	0.1914	0.4283	0.6723	0.107
H(1A)	2*a*	–0.785(3)	0.575(2)	0.296(2)	0.062(7)
H(1O)	2*a*	–0.190(5)	0.373(5)	0.574(3)	0.16(2)
H(3)	2*a*	–0.375(3)	0.528(2)	0.414(2)	0.065(7)
H(6A)	2*a*	–0.611(3)	0.294(3)	0.563(2)	0.077(8)
H(6B)	2*a*	–0.624(3)	0.255(2)	0.475(2)	0.053(7)
H(7A)	2*a*	–0.820(3)	0.178(3)	0.505(2)	0.10(1)
H(8)	2*a*	–0.852(3)	0.228(3)	0.363(2)	0.088(9)
H(10)	2*a*	–0.699(2)	0.381(2)	0.356(1)	0.057(6)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12′)	2*a*	0.346(3)	0.320(3)	1.036(2)	0.073(8)
H(14′)	2*a*	0.373(3)	0.194(2)	1.190(1)	0.053(7)
H(20A)	2*a*	–0.959(3)	0.575(3)	0.394(2)	0.076(9)
H(20B)	2*a*	–0.974(3)	0.472(3)	0.460(2)	0.09(1)
H(20C)	2*a*	–1.076(3)	0.484(3)	0.380(2)	0.086(9)
H(14)	2*a*	–0.892(3)	0.209(3)	0.074(2)	0.071(9)
H(2B)	2*a*	–0.549(3)	0.655(3)	0.333(2)	0.077(8)
H(11B)	2*a*	–1.055(3)	0.386(2)	0.262(1)	0.059(6)
H(11A)	2*a*	–0.979(3)	0.504(3)	0.255(2)	0.072(8)
H(11C)	2*a*	0.604(3)	0.269(2)	1.001(1)	0.064(7)
H(10′)	2*a*	0.252(2)	0.331(2)	0.912(1)	0.044(5)
H(11D)	2*a*	0.546(2)	0.405(3)	1.006(2)	0.063(7)
H(1D)	2*a*	0.374(3)	0.521(2)	0.959(2)	0.062(7)
H(8′)	2*a*	0.387(3)	0.139(3)	0.905(2)	0.071(7)
H(1C)	2*a*	0.332(3)	0.562(3)	0.868(2)	0.076(9)
H(20D)	2*a*	0.653(3)	0.358(3)	0.888(2)	0.071(7)
H(12D)	2*a*	0.397(3)	0.195(3)	1.032(2)	0.067(8)
H(3′)	2*a*	–0.035(3)	0.524(2)	0.849(1)	0.063(7)
H(7C)	2*a*	0.387(3)	0.222(3)	0.737(2)	0.088(9)
H(20E)	2*a*	0.533(3)	0.370(3)	0.803(2)	0.084(9)
H(20F)	2*a*	0.538(3)	0.464(4)	0.871(2)	0.09(1)
H(6C)	2*a*	0.145(3)	0.182(3)	0.810(2)	0.089(9)
H(6D)	2*a*	0.149(3)	0.223(3)	0.720(2)	0.072(8)
H(7D)	2*a*	0.318(3)	0.081(3)	0.766(2)	0.087(9)
H(1′O)	2*a*	–0.245(4)	0.386(3)	0.702(2)	0.10(1)
H(1B)	2*a*	–0.724(3)	0.627(3)	0.385(2)	0.069(8)
H(7B)	2*a*	–0.861(3)	0.319(3)	0.527(2)	0.10(1)
H(2F)	2*a*	–0.564(4)	0.533(4)	0.283(2)	0.13(1)

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}
C(1)	2*a*	–0.7165(3)	0.5658(3)	0.3502(2)	0.069(2)	0.064(2)	0.048(1)	–0.006(1)	0.006(1)	0.012(1)
C(2)	2*a*	–0.5699(3)	0.5727(3)	0.3434(2)	0.076(2)	0.092(2)	0.057(2)	–0.031(2)	0.007(1)	0.019(2)
C(3)	2*a*	–0.4677(3)	0.5158(3)	0.4124(1)	0.054(1)	0.092(2)	0.051(1)	–0.025(1)	0.011(1)	–0.006(1)
C(4)	2*a*	–0.4989(2)	0.4545(2)	0.4719(1)	0.048(1)	0.068(2)	0.041(1)	–0.011(1)	0.0052(9)	–0.005(1)
C(5)	2*a*	–0.6483(2)	0.4321(2)	0.4746(1)	0.045(1)	0.061(1)	0.039(1)	–0.003(1)	0.0041(8)	0.0028(9)
C(6)	2*a*	–0.6632(2)	0.3041(3)	0.5039(2)	0.046(1)	0.069(2)	0.061(2)	–0.006(1)	0.001(1)	0.019(1)
C(7)	2*a*	–0.8127(3)	0.2639(3)	0.4899(2)	0.055(1)	0.078(2)	0.072(2)	–0.010(1)	0.003(1)	0.031(2)
C(8)	2*a*	–0.8960(2)	0.2736(3)	0.4003(2)	0.044(1)	0.070(2)	0.071(2)	–0.010(1)	0.003(1)	0.013(1)
C(9)	2*a*	–0.8952(2)	0.4040(2)	0.3681(1)	0.041(1)	0.068(2)	0.054(1)	0.003(1)	0.0059(9)	0.012(1)
C(10)	2*a*	–0.7406(2)	0.4434(2)	0.3852(1)	0.041(1)	0.057(1)	0.041(1)	–0.0020(9)	0.0066(8)	0.003(1)
C(11)	2*a*	–0.9642(2)	0.4092(3)	0.2750(2)	0.042(1)	0.090(2)	0.059(1)	–0.003(1)	–0.002(1)	0.014(1)
C(12)	2*a*	–0.8939(3)	0.3446(3)	0.2179(2)	0.072(2)	0.107(2)	0.057(1)	–0.002(2)	–0.003(1)	–0.002(2)
C(13)	2*a*	–0.9679(3)	0.3605(4)	0.1296(2)	0.065(2)	0.139(3)	0.055(2)	–0.031(2)	0.004(1)	0.004(2)
C(14)	2*a*	–0.9521(4)	0.2879(5)	0.0646(2)	0.105(3)	0.147(4)	0.069(2)	–0.054(3)	0.026(2)	–0.009(2)
C(15)	2*a*	–1.0360(5)	0.3325(6)	–0.0032(2)	0.126(4)	0.203(6)	0.055(2)	–0.076(4)	0.017(2)	–0.008(3)
C(16)	2*a*	–1.0593(4)	0.4431(6)	0.0941(2)	0.103(3)	0.207(5)	0.063(2)	0.005(3)	–0.002(2)	0.018(3)
C(17)	2*a*	–1.0419(3)	0.2193(4)	0.3901(2)	0.060(2)	0.123(3)	0.107(2)	–0.033(2)	–0.004(2)	0.033(2)
C(18)	2*a*	–0.3816(2)	0.4145(3)	0.5411(1)	0.047(1)	0.081(2)	0.053(1)	–0.010(1)	0.0021(9)	–0.005(1)
C(19)	2*a*	–0.6829(3)	0.5252(3)	0.5340(2)	0.073(2)	0.092(2)	0.048(1)	0.003(1)	0.018(1)	–0.004(1)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(20)	2*a*	–0.9822(3)	0.4895(4)	0.4056(2)	0.058(2)	0.100(3)	0.074(2)	0.021(2)	0.019(1)	0.015(2)
O(1)	2*a*	–0.2646(2)	0.3954(3)	0.5224(1)	0.0493(9)	0.150(2)	0.062(1)	0.007(1)	0.0043(8)	–0.008(1)
O(2)	2*a*	–0.3918(2)	0.4010(2)	0.6103(1)	0.0519(9)	0.142(2)	0.0479(9)	–0.007(1)	–0.0013(7)	0.012(1)
O(3)	2*a*	–1.1036(3)	0.4311(5)	0.0123(2)	0.123(2)	0.273(5)	0.071(2)	–0.019(3)	–0.005(2)	0.036(2)
C(1′)	2*a*	0.3069(3)	0.5074(3)	0.9068(2)	0.058(1)	0.058(2)	0.069(2)	–0.001(1)	–0.005(1)	–0.010(1)
C(2′)	2*a*	0.1677(3)	0.5473(3)	0.9135(2)	0.068(2)	0.078(2)	0.086(2)	0.012(2)	–0.004(1)	–0.025(2)
C(3′)	2*a*	0.0516(3)	0.4985(3)	0.8467(2)	0.051(1)	0.082(2)	0.068(2)	0.013(1)	0.001(1)	–0.005(1)
C(4′)	2*a*	0.0664(2)	0.4190(2)	0.7907(1)	0.046(1)	0.069(2)	0.044(1)	0.001(1)	0.0007(8)	0.002(1)
C(5′)	2*a*	0.2069(2)	0.3672(2)	0.7893(1)	0.047(1)	0.054(1)	0.042(1)	–0.0022(9)	0.0046(8)	0.0027(9)
C(6′)	2*a*	0.1949(3)	0.2327(2)	0.7679(2)	0.061(1)	0.066(2)	0.049(1)	–0.002(1)	–0.001(1)	–0.012(1)
C(7′)	2*a*	0.3369(3)	0.1745(3)	0.7783(2)	0.076(2)	0.071(2)	0.055(1)	0.015(1)	0.004(1)	–0.009(1)
C(8′)	2*a*	0.4313(3)	0.1846(2)	0.8655(1)	0.066(1)	0.061(2)	0.048(1)	0.012(1)	0.012(1)	0.002(1)
C(9′)	2*a*	0.4486(2)	0.3167(2)	0.8958(1)	0.044(1)	0.061(1)	0.045(1)	–0.001(1)	0.0061(8)	0.004(1)
C(10′)	2*a*	0.3026(2)	0.3770(2)	0.8773(1)	0.043(1)	0.050(1)	0.041(1)	–0.0030(9)	0.0042(8)	0.0023(9)
C(11′)	2*a*	0.5159(2)	0.3182(3)	0.9898(1)	0.046(1)	0.066(2)	0.050(1)	0.006(1)	–0.0006(9)	0.002(1)
C(12′)	2*a*	0.4313(3)	0.2717(3)	1.0443(1)	0.059(2)	0.082(2)	0.045(1)	–0.000(1)	0.002(1)	0.005(1)
C(13′)	2*a*	0.5057(3)	0.2765(2)	1.1338(1)	0.069(2)	0.070(2)	0.045(1)	0.025(1)	0.004(1)	0.002(1)
C(14′)	2*a*	0.4563(4)	0.2336(3)	1.1992(2)	0.093(2)	0.100(2)	0.056(2)	0.027(2)	0.023(2)	0.003(2)
C(15′)	2*a*	0.5555(5)	0.2602(4)	1.2674(2)	0.128(3)	0.121(3)	0.048(2)	0.048(3)	0.015(2)	0.008(2)
C(16′)	2*a*	0.6300(3)	0.3240(3)	1.1683(2)	0.086(2)	0.112(3)	0.055(2)	0.011(2)	–0.012(1)	0.005(2)
C(17′)	2*a*	0.5688(3)	0.1203(3)	0.8705(2)	0.085(2)	0.096(2)	0.057(2)	0.036(2)	0.008(1)	0.003(1)
C(18′)	2*a*	–0.0587(2)	0.3911(3)	0.7236(2)	0.047(1)	0.088(2)	0.054(1)	–0.001(1)	0.004(1)	0.003(1)
C(19′)	2*a*	0.2572(3)	0.4377(3)	0.7243(1)	0.063(1)	0.094(2)	0.053(1)	–0.001(1)	0.008(1)	0.022(1)
C(20′)	2*a*	0.5498(3)	0.3856(4)	0.8580(2)	0.052(1)	0.092(2)	0.069(2)	–0.006(1)	0.015(1)	0.013(2)
O(1′)	2*a*	–0.1769(2)	0.4053(3)	0.7423(1)	0.0450(9)	0.196(3)	0.058(1)	–0.005(1)	0.0008(8)	–0.007(1)
O(2′)	2*a*	–0.0549(2)	0.3616(2)	0.6554(1)	0.0526(9)	0.128(2)	0.054(1)	0.007(1)	–0.0036(7)	–0.014(1)
O(3′)	2*a*	0.6633(3)	0.3171(3)	1.2510(1)	0.113(2)	0.144(2)	0.060(1)	0.022(2)	–0.018(1)	–0.002(1)

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