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(2E,4R,5R,6S)-2-(4,5,6-Trihydroxycyclohex-2-en-1-ylidene)acetonitrile

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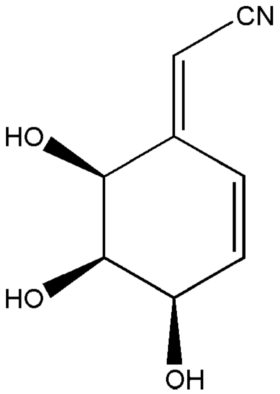
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.002 Å; R factor = 0.026; wR factor = 0.071; data-to-parameter ratio = 10.4.

The crystal structure of the title compound, $C_8H_9NO_3$, is characterized by a complex three-dimensional hydrogen-bond network in which every molecule is connected to six symmetry-related neighbours.

Related literature

For the isolation of this natural product, see: Hua *et al.* (2004). For previous phytochemical and biological studies of the stem bark of *Thecacoris annobonae*, see: Kuete *et al.* (2010).



Experimental

Crystal data

$C_8H_9NO_3$
M_r = 167.16
Monoclinic, $P2_1$
a = 4.8159 (5) Å
b = 10.2482 (5) Å
c = 8.3573 (9) Å
β = 102.842 (4)°
V = 402.15 (6) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.90 mm^{-1}
T = 193 K
0.60 × 0.06 × 0.06 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
2174 measured reflections
1514 independent reflections
1501 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.021
3 standard reflections every 60 min intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.071
S = 1.08
1514 reflections
146 parameters
1 restraint
All H-atom parameters refined
$\Delta\rho_{\rm max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.12 e Å^{-3}
Absolute structure: Flack, (1983)
Flack parameter: −0.04 (16)

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7···O9$^{\rm i}$	0.79 (2)	1.93 (2)	2.6885 (14)	160 (2)
O8—H8···N12$^{\rm ii}$	0.77 (2)	2.18 (2)	2.9138 (16)	160 (2)
O9—H9···O7$^{\rm iii}$	0.78 (3)	2.02 (2)	2.7944 (15)	170 (2)

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+1$; (ii) $x+1, y, z+1$; (iii) $-x+1, y+\frac{1}{2}, -z+1$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

We thank Dr J. C. Liermann (Mainz) for performing the NMR spectroscopy.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2287).

References

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supporting information

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(2*E*,4*R*,5*R*,6*S*)-2-(4,5,6-Trihydroxycyclohex-2-en-1-ylidene)acetonitrile

Alphonsine N. Guedem, Louis P. Sandjo, Till Opatz, Dieter Schollmeyer and Bonaventure T. Ngadjui

S1. Comment

Previous phytochemical and biological studies of the stem bark of Thecacoris annobonae (Euphorbiaceae) led to several bioactive secondary metabolites: Kuete *et al.* (2010). In the continuation of this investigation, the title compound was isolated from the leaves of the same plant using chromatographic methods and characterized by single crystal X-ray diffraction. It should be noted that this natural product was previously obtained from the root of Semiaquilegia adoxoides (Ranunculaceae): Hua *et al.* (2004).

In the crystal structure of the title compound the six membered ring adopts an envelope conformation in which C(3) is 0.678 (1) Å below the ring plane (Fig. 1). The acrylonitrile group is nearly coplanar to the least square plane of the ring system. The packing is characterized by a complex three-dimensional network formed by hydrogen bonds. Every molecule interacts by hydrogen bonds with six symmetry related molecules. While the hydroxyl groups O7 and O9 are both donor and acceptor of hydrogen bonds, O8 only interacts with N12 *via* hydrogen bonding (Fig. 2 and Table 1).

S2. Experimental

Air-dried powder of leaves of Thecacoris annobonae (1.37 kg) was successively macerated with hexane, ethyl acetate and methanol for two days each. Three fractions H (30 g), E (45 g), and *M* (61 g) were collected. The Methanol fraction *M* was subjected to a silica gel column chromatography eluted with CH_2Cl_2 to MeOH gradient yielding 7 mg of this secondary metabolite. It crystallized as needles in three of the fractions eluted with the mixture CH_2Cl_2/MeOH in a ratio of 97:3.

S3. Refinement

All hydrogen atoms were located from a difference Fourier map and refined with isotropic displacement parameters. The absolute structure was determined on the basis of 705 Friedel pairs.

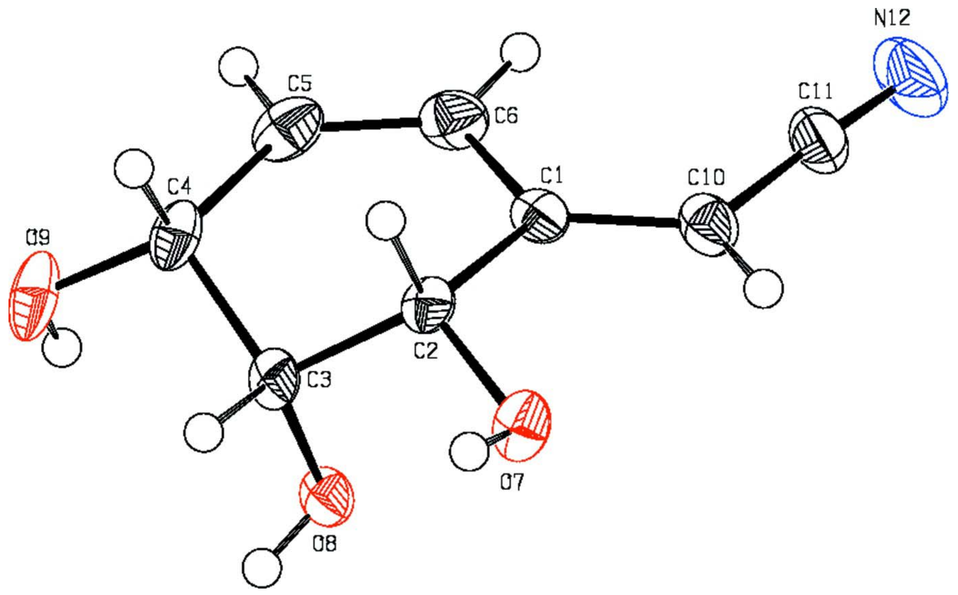

Figure 1

Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 50% probability level.

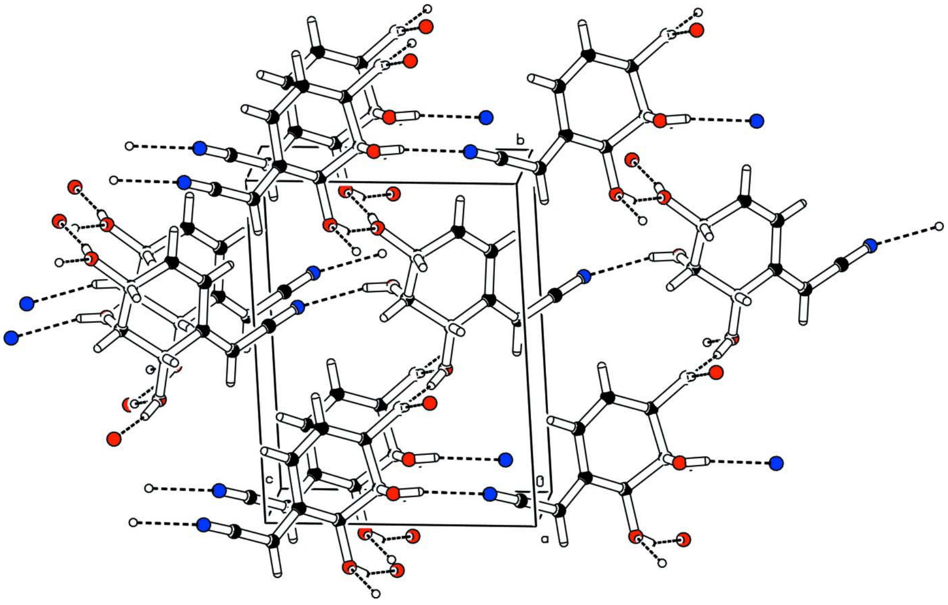

Figure 2

Crystal structure of the title compound with view along the a-axis. For calrity only H-atoms involved in hydrogen bonds are shown. Intermolecular hydrogen bonding is represented as dashed lines.

(2*E*,4*R*,5*R*,6*S*)-2-(4,5,6-Trihydroxycyclohex-2-en-1- ylidene)acetonitrile

Crystal data

$C_8H_9NO_3$
M_r = 167.16
Monoclinic, $P2_1$
Hall symbol: P 2yb
a = 4.8159 (5) Å
b = 10.2482 (5) Å
c = 8.3573 (9) Å
β = 102.842 (4)°
V = 402.15 (6) Å^3
Z = 2

$F(000) = 176$
$D_x = 1.380$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 35$–46°
$\mu = 0.90$ mm^{-1}
$T = 193$ K
Needle, colourless
0.60 × 0.06 × 0.06 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: rotating anode
Graphite monochromator
$\omega/2\theta$ scans
2174 measured reflections
1514 independent reflections
1501 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\rm max} = 70.0°$, $\theta_{\rm min} = 5.4°$
$h = -5 \rightarrow 5$
$k = -12 \rightarrow 12$
$l = -10 \rightarrow 10$
3 standard reflections every 60 min
intensity decay: 5%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.071$
$S = 1.08$
1514 reflections
146 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.0306P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.018 (3)
Absolute structure: Flack, (1983)
Absolute structure parameter: −0.04 (16)

Special details

Experimental. ^{1}H–, ^{13}C– and two-dimensional-NMR spectra were recorded on Bruker AVANCE II-400 MHz s pectrometer equipped with a 5 mm observe probe and a *z*-gradient coil using standard pulse sequences. HR-ESI-MS was carried out on a Waters Q-TOF Ultima III mass spectrometer. HR-ESI-MS m/*z* 190.0470 (calcd. for $[C_8H_9NO_3+Na]^+$ 190.0475); NMR (^{1}H-NMR, 400 MHz, acetone-d$_6$): 6.55 (1*H*, dd, J = 2.5, 10.1 Hz, H-2), 6.04 (1*H*, dd, J = 1.8, 10.1 Hz, H-3), 4.11–4.16 (1*H*, m, H-4), 4.40–4.44 (1*H*, m, H-5), 4.44–4.50 (1*H*, m, H-6), 5.63 (1*H*, s, H-7), 4.60 (1*H*, d, J = 7.9 Hz, OH-5), 4.16–4.18 (2*H*, m, OH-4 and 6); (^{13}C-NMR, 100 MHz, acetone-d$_6$): 159.7 (C-1), 124.0 (C-2), 139.6 (C-3), 74.5 (C-4), 69.6 (C-5), 71.9 (C-6),93.7 (C-7), 117.6 (C-8).

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}*/U_{\rm eq}$
C1	0.4167 (3)	0.60278 (13)	0.16499 (15)	0.0204 (3)
C2	0.6543 (3)	0.54538 (12)	0.29376 (15)	0.0193 (3)
H2	0.822 (3)	0.5471 (15)	0.2490 (18)	0.014 (3)*

C3	0.7220 (3)	0.63193 (13)	0.44623 (15)	0.0195 (3)
H3	0.881 (4)	0.5923 (17)	0.525 (2)	0.023 (4)*
C4	0.8147 (3)	0.76563 (13)	0.39626 (17)	0.0244 (3)
H4	0.992 (4)	0.7516 (17)	0.364 (2)	0.023 (4)*
C5	0.6001 (3)	0.81945 (14)	0.2530 (2)	0.0291 (3)
H5	0.591 (4)	0.911 (2)	0.238 (2)	0.041 (5)*
C6	0.4214 (3)	0.74407 (14)	0.14727 (17)	0.0277 (3)
H6	0.289 (4)	0.7814 (18)	0.059 (2)	0.023 (4)*
O7	0.5884 (2)	0.41531 (9)	0.32843 (12)	0.0246 (2)
H7	0.730 (5)	0.381 (2)	0.375 (2)	0.038 (5)*
O8	0.47685 (18)	0.64281 (10)	0.51340 (11)	0.0221 (2)
H8	0.530 (4)	0.644 (2)	0.607 (3)	0.031 (5)*
O9	0.8700 (2)	0.85292 (10)	0.53125 (14)	0.0320 (3)
H9	0.730 (5)	0.870 (2)	0.559 (3)	0.045 (6)*
C10	0.2197 (3)	0.52459 (15)	0.07211 (16)	0.0252 (3)
H10	0.220 (4)	0.431 (2)	0.0850 (19)	0.024 (4)*
C11	−0.0065 (3)	0.57476 (17)	−0.05275 (17)	0.0316 (3)
N12	−0.1938 (3)	0.61195 (18)	−0.15135 (17)	0.0451 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0145 (6)	0.0289 (7)	0.0186 (5)	0.0032 (5)	0.0053 (4)	0.0007 (5)
C2	0.0106 (6)	0.0241 (6)	0.0233 (6)	0.0012 (5)	0.0043 (5)	0.0010 (5)
C3	0.0086 (5)	0.0255 (6)	0.0227 (5)	0.0031 (4)	−0.0001 (4)	0.0005 (5)
C4	0.0128 (6)	0.0260 (7)	0.0344 (7)	−0.0030 (5)	0.0054 (5)	−0.0046 (5)
C5	0.0271 (8)	0.0222 (7)	0.0391 (8)	−0.0003 (5)	0.0098 (6)	0.0065 (5)
C6	0.0229 (7)	0.0318 (8)	0.0273 (6)	0.0039 (6)	0.0034 (5)	0.0097 (6)
O7	0.0167 (5)	0.0204 (5)	0.0340 (5)	0.0034 (4)	−0.0001 (4)	0.0022 (4)
O8	0.0134 (4)	0.0328 (5)	0.0197 (4)	0.0006 (4)	0.0030 (3)	−0.0018 (4)
O9	0.0135 (5)	0.0332 (6)	0.0489 (6)	−0.0054 (4)	0.0060 (4)	−0.0162 (5)
C10	0.0186 (6)	0.0354 (7)	0.0212 (6)	0.0016 (5)	0.0034 (5)	−0.0014 (5)
C11	0.0250 (7)	0.0477 (9)	0.0208 (6)	−0.0052 (6)	0.0024 (6)	−0.0037 (6)
N12	0.0319 (7)	0.0705 (11)	0.0269 (6)	0.0011 (7)	−0.0064 (5)	0.0055 (6)

Geometric parameters (Å, º)

C1—C10	1.3479 (19)	C4—H4	0.963 (18)
C1—C6	1.4563 (19)	C5—C6	1.334 (2)
C1—C2	1.5054 (16)	C5—H5	0.94 (2)
C2—O7	1.4151 (15)	C6—H6	0.943 (18)
C2—C3	1.5272 (17)	O7—H7	0.79 (2)
C2—H2	0.962 (16)	O8—H8	0.77 (2)
C3—O8	1.4200 (16)	O9—H9	0.78 (3)
C3—C4	1.5277 (18)	C10—C11	1.426 (2)
C3—H3	0.981 (17)	C10—H10	0.96 (2)
C4—O9	1.4178 (17)	C11—N12	1.144 (2)
C4—C5	1.5019 (19)		

C10—C1—C6	123.87 (12)	C5—C4—C3	110.86 (10)
C10—C1—C2	120.34 (12)	O9—C4—H4	107.3 (10)
C6—C1—C2	115.77 (11)	C5—C4—H4	109.1 (10)
O7—C2—C1	110.18 (11)	C3—C4—H4	105.9 (10)
O7—C2—C3	113.10 (10)	C6—C5—C4	122.94 (13)
C1—C2—C3	110.92 (10)	C6—C5—H5	119.0 (12)
O7—C2—H2	110.0 (10)	C4—C5—H5	118.1 (12)
C1—C2—H2	106.6 (9)	C5—C6—C1	122.05 (12)
C3—C2—H2	105.8 (9)	C5—C6—H6	120.6 (11)
O8—C3—C2	109.47 (10)	C1—C6—H6	117.4 (11)
O8—C3—C4	110.90 (11)	C2—O7—H7	108.3 (16)
C2—C3—C4	108.30 (10)	C3—O8—H8	106.5 (14)
O8—C3—H3	111.0 (10)	C4—O9—H9	111.1 (17)
C2—C3—H3	108.2 (10)	C1—C10—C11	122.16 (14)
C4—C3—H3	108.9 (10)	C1—C10—H10	123.0 (10)
O9—C4—C5	112.14 (12)	C11—C10—H10	114.9 (10)
O9—C4—C3	111.28 (11)	N12—C11—C10	177.70 (18)

C10—C1—C2—O7	−16.29 (16)	O8—C3—C4—C5	−68.05 (13)
C6—C1—C2—O7	165.07 (11)	C2—C3—C4—C5	52.09 (14)
C10—C1—C2—C3	−142.30 (13)	O9—C4—C5—C6	−149.07 (14)
C6—C1—C2—C3	39.06 (15)	C3—C4—C5—C6	−24.01 (19)
O7—C2—C3—O8	−63.88 (13)	C4—C5—C6—C1	1.4 (2)
C1—C2—C3—O8	60.49 (13)	C10—C1—C6—C5	172.38 (14)
O7—C2—C3—C4	175.09 (9)	C2—C1—C6—C5	−9.0 (2)
C1—C2—C3—C4	−60.54 (13)	C6—C1—C10—C11	−0.6 (2)
O8—C3—C4—O9	57.48 (13)	C2—C1—C10—C11	−179.10 (12)
C2—C3—C4—O9	177.62 (10)	C1—C10—C11—N12	−141 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7···O9^{i}	0.79 (2)	1.93 (2)	2.6885 (14)	160 (2)
O8—H8···N12^{ii}	0.77 (2)	2.18 (2)	2.9138 (16)	160 (2)
O9—H9···O7^{iii}	0.78 (3)	2.02 (2)	2.7944 (15)	170 (2)

Symmetry codes: (i) −*x*+2, *y*−1/2, −*z*+1; (ii) *x*+1, *y*, *z*+1; (iii) −*x*+1, *y*+1/2, −*z*+1.