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Biomimetic total synthesis of (+)-himbacine.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **18**, **14**, **20**, **21**, **3**, **4**, **22**; ^1H NMR of synthetic and natural (+)-himbacine **1**. Tables of crystal data, fractional coordinates and thermal parameters, and interatomic distances with standard deviation for the himandravine derivative **22**.

6.82

88.86

Single-crystal X-ray diffraction report for $C_{28}H_{35}N_3O_7$ (CCDC 255393)

Crystals of **CCDC 255393** were grown by slow evaporation of a solution in ethyl acetate. A single crystal having dimensions approximately 0.18 x 0.18 x 0.38 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package¹.

Examination of the systematic absences of the intensity data showed the space group to be either $P 2_1$ or $P 2_1/m$. The structure was solved in the space group $P 2_1$ using the direct-methods program SIR92², which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite³. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R = 0.0302$, $wR = 0.0331$.

Attached is a thermal ellipsoid plot (ORTEP-3⁴) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

References:

- 1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.
- 2 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.* 1994, **27**, 435.
- 3 CRYSTALS Issue 12, P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487
- 4 ORTEP-3 v. 1.0.2, C. K. Johnson and M. K. Burnett, 1998.

Table 1: Crystal data and refinement details

Crystal identification	CCDC 255393
Chemical formula	$C_{28}H_{35}N_3O_7$
Formula weight	525.60
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P 2_1$
a (Å)	6.1778(2)
b (Å)	19.7758(5)
c (Å)	11.2460(3)
α (°)	90
β (°)	97.6355(10)
γ (°)	90
Cell volume (Å ³)	1361.75(7)
Z	2
Calculated density (Mg/m ³)	1.282
Absorption coefficient (mm ⁻¹)	0.093
F_{000}	560
Crystal size (mm)	0.18 x 0.18 x 0.38
Description of crystal	Colourless prism
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.97, 0.98
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-8 \leq h \leq 7, 0 \leq k \leq 25, 0 \leq l \leq 14$
Reflections measured	15085
Unique reflections	3192
R_{int}	0.040
Observed reflections ($I > 3\sigma(I)$)	2427
Refinement method	Full-matrix least-squares on F
Parameters refined	343
Weighting scheme	Chebyshev 3-term polynomial
Goodness of fit	1.1343
R	0.0302
wR	0.0331
Residual electron density (min,max) (eÅ ⁻³)	-0.16, 0.13

Table 2: Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}
C(1)	0.8167(4)	0.48885(12)	0.3151(2)	0.0333
O(1)	0.6639(3)	0.48411(9)	0.38954(15)	0.0378
O(2)	0.9803(3)	0.45450(9)	0.33010(17)	0.0434
C(2)	0.4842(4)	0.53215(12)	0.3551(2)	0.0332
C(3)	0.5796(4)	0.58208(11)	0.2712(2)	0.0293
C(4)	0.4188(3)	0.62003(10)	0.17718(19)	0.0264
C(5)	0.3192(3)	0.57391(11)	0.07225(19)	0.0262
C(6)	0.1607(4)	0.61346(11)	-0.0187(2)	0.0310
C(7)	0.0793(4)	0.57179(13)	-0.1303(2)	0.0362
C(8)	0.2684(4)	0.54327(13)	-0.1888(2)	0.0378
C(9)	0.4203(4)	0.50143(12)	-0.0994(2)	0.0339
C(10)	0.5061(4)	0.54212(11)	0.01307(19)	0.0275
C(11)	0.6459(4)	0.49808(11)	0.1043(2)	0.0303
C(12)	0.7440(3)	0.53808(11)	0.2155(2)	0.0299
C(13)	0.4264(5)	0.56163(17)	0.4716(2)	0.0554
C(14)	0.2461(3)	0.65750(11)	0.23241(19)	0.0272
C(15)	0.2226(4)	0.72418(11)	0.23171(19)	0.0279
C(16)	0.0373(3)	0.76011(11)	0.28037(18)	0.0269
C(17)	-0.0474(4)	0.82045(12)	0.2031(2)	0.0320
C(18)	0.1054(4)	0.88093(11)	0.2205(2)	0.0341
C(19)	0.1363(4)	0.90150(12)	0.3527(2)	0.0359
C(20)	0.2281(4)	0.84387(11)	0.43510(19)	0.0294
C(21)	0.4703(4)	0.83152(13)	0.4308(2)	0.0395
N(1)	0.0966(3)	0.78173(9)	0.40711(15)	0.0254
C(22)	0.0555(4)	0.73711(11)	0.49253(19)	0.0295
O(3)	-0.0276(3)	0.68117(9)	0.47187(15)	0.0456
C(23)	0.1104(3)	0.75942(11)	0.62119(18)	0.0268
C(24)	0.2999(4)	0.73723(11)	0.6911(2)	0.0316
C(25)	0.3416(4)	0.75888(12)	0.8092(2)	0.0324
C(26)	0.2019(4)	0.80072(12)	0.86187(19)	0.0322
C(27)	0.0134(4)	0.81962(11)	0.79021(19)	0.0276
C(28)	-0.0359(3)	0.80032(11)	0.67167(19)	0.0269
N(2)	0.5458(3)	0.73696(12)	0.8817(2)	0.0471
O(4)	0.6689(3)	0.70025(12)	0.8344(2)	0.0641
O(5)	0.5804(3)	0.75713(13)	0.98602(19)	0.0637
N(3)	-0.1436(3)	0.86393(10)	0.84080(17)	0.0341
O(6)	-0.0831(3)	0.89155(9)	0.93703(15)	0.0485
O(7)	-0.3262(3)	0.86956(9)	0.78403(17)	0.0416

Table 3: Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(21)	0.3449	0.5137	0.3117	0.0403
H(31)	0.6439	0.6220	0.3177	0.0349
H(41)	0.5084	0.6548	0.1414	0.0319
H(51)	0.2323	0.5370	0.1041	0.0317
H(61)	0.2372	0.6545	-0.0440	0.0372
H(62)	0.0321	0.6275	0.0209	0.0372
H(71)	-0.0117	0.6014	-0.1894	0.0427
H(72)	-0.0118	0.5335	-0.1066	0.0427
H(81)	0.3527	0.5815	-0.2184	0.0454
H(82)	0.2090	0.5139	-0.2579	0.0454
H(91)	0.5473	0.4859	-0.1390	0.0413
H(92)	0.3385	0.4612	-0.0750	0.0413
H(101)	0.5977	0.5794	-0.0136	0.0335
H(111)	0.7676	0.4782	0.0654	0.0371
H(112)	0.5529	0.4609	0.1303	0.0371
H(121)	0.8605	0.5666	0.1870	0.0360
H(131)	0.3044	0.5948	0.4535	0.0674
H(132)	0.5570	0.5850	0.5152	0.0674
H(133)	0.3797	0.5244	0.5228	0.0674
H(141)	0.1408	0.6302	0.2728	0.0326
H(151)	0.3336	0.7522	0.1971	0.0336
H(161)	-0.0830	0.7261	0.2776	0.0322
H(171)	-0.1930	0.8340	0.2250	0.0378
H(172)	-0.0638	0.8066	0.1169	0.0378
H(181)	0.0409	0.9195	0.1703	0.0404
H(182)	0.2499	0.8686	0.1958	0.0404
H(191)	0.2397	0.9406	0.3638	0.0425
H(192)	-0.0083	0.9154	0.3755	0.0425
H(201)	0.2164	0.8576	0.5196	0.0348
H(211)	0.5217	0.7935	0.4860	0.0463
H(212)	0.5544	0.8734	0.4564	0.0463
H(213)	0.4936	0.8195	0.3470	0.0463
H(241)	0.4038	0.7063	0.6570	0.0382
H(261)	0.2358	0.8163	0.9469	0.0381
H(281)	-0.1746	0.8155	0.6230	0.0319

Table 4: Anisotropic thermal parameters ($\text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.0326(12)	0.0307(12)	0.0353(12)	-0.0036(10)	0.0002(9)	0.0016(10)
O(1)	0.0411(9)	0.0371(9)	0.0357(9)	0.0074(7)	0.0066(7)	0.0094(8)
O(2)	0.0378(9)	0.0412(10)	0.0493(10)	-0.0014(8)	-0.0016(7)	0.0116(8)
C(2)	0.0337(11)	0.0351(12)	0.0318(11)	0.0070(10)	0.0080(9)	0.0102(10)
C(3)	0.0338(11)	0.0240(10)	0.0295(11)	-0.0033(9)	0.0019(9)	-0.0007(9)
C(4)	0.0308(10)	0.0185(10)	0.0304(11)	-0.0009(8)	0.0059(8)	-0.0005(8)
C(5)	0.0290(10)	0.0211(10)	0.0292(10)	-0.0007(8)	0.0068(8)	-0.0020(8)
C(6)	0.0344(11)	0.0271(11)	0.0314(12)	-0.0020(9)	0.0036(9)	0.0000(9)
C(7)	0.0391(13)	0.0366(12)	0.0309(12)	-0.0058(10)	-0.0019(9)	0.0024(11)
C(8)	0.0426(13)	0.0402(13)	0.0307(12)	-0.0063(10)	0.0053(10)	-0.0032(11)
C(9)	0.0394(13)	0.0332(12)	0.0306(12)	-0.0051(9)	0.0098(10)	-0.0015(10)
C(10)	0.0294(10)	0.0245(10)	0.0298(11)	-0.0016(8)	0.0089(8)	-0.0015(8)
C(11)	0.0308(11)	0.0275(11)	0.0344(12)	-0.0016(9)	0.0106(9)	0.0015(9)
C(12)	0.0273(10)	0.0283(11)	0.0344(12)	-0.0005(9)	0.0050(9)	-0.0012(9)
C(13)	0.0688(19)	0.066(2)	0.0335(14)	0.0054(13)	0.0149(13)	0.0276(16)
C(14)	0.0276(10)	0.0252(10)	0.0288(10)	-0.0016(8)	0.0038(8)	-0.0034(8)
C(15)	0.0343(11)	0.0259(11)	0.0237(10)	-0.0042(8)	0.0046(8)	-0.0029(9)
C(16)	0.0299(10)	0.0264(10)	0.0242(10)	-0.0056(8)	0.0023(8)	-0.0025(9)
C(17)	0.0345(12)	0.0340(12)	0.0260(11)	-0.0035(9)	-0.0017(8)	0.0031(9)
C(18)	0.0466(13)	0.0264(11)	0.0280(11)	0.0033(9)	0.0000(9)	0.0022(10)
C(19)	0.0488(14)	0.0247(11)	0.0327(12)	-0.0016(9)	-0.0002(10)	0.0006(10)
C(20)	0.0363(11)	0.0263(10)	0.0244(10)	-0.0017(8)	-0.0004(8)	-0.0054(9)
C(21)	0.0330(12)	0.0422(14)	0.0406(13)	0.0056(11)	-0.0054(10)	-0.0102(11)
N(1)	0.0299(9)	0.0238(9)	0.0220(8)	-0.0036(7)	0.0017(7)	-0.0010(7)
C(22)	0.0327(11)	0.0278(11)	0.0283(11)	-0.0032(9)	0.0057(9)	0.0009(9)
O(3)	0.0702(12)	0.0319(9)	0.0365(9)	-0.0053(7)	0.0134(8)	-0.0166(9)
C(23)	0.0291(10)	0.0268(10)	0.0244(10)	0.0030(8)	0.0028(8)	-0.0004(9)
C(24)	0.0279(11)	0.0298(11)	0.0377(12)	0.0093(9)	0.0071(9)	0.0023(9)
C(25)	0.0252(10)	0.0350(12)	0.0348(12)	0.0143(10)	-0.0039(8)	-0.0065(9)
C(26)	0.0363(12)	0.0375(12)	0.0214(10)	0.0044(9)	-0.0014(9)	-0.0129(10)
C(27)	0.0312(11)	0.0263(10)	0.0260(10)	-0.0002(8)	0.0068(8)	-0.0038(9)
C(28)	0.0266(10)	0.0277(11)	0.0253(10)	-0.0003(8)	-0.0002(8)	0.0000(8)
N(2)	0.0310(11)	0.0522(14)	0.0539(14)	0.0282(11)	-0.0095(10)	-0.0108(10)
O(4)	0.0338(10)	0.0731(15)	0.0835(15)	0.0294(12)	0.0004(10)	0.0140(10)
O(5)	0.0525(12)	0.0814(16)	0.0488(12)	0.0215(11)	-0.0236(10)	-0.0189(11)
N(3)	0.0432(11)	0.0299(10)	0.0316(10)	-0.0010(8)	0.0140(8)	-0.0049(8)
O(6)	0.0687(13)	0.0487(11)	0.0307(9)	-0.0113(8)	0.0161(8)	-0.0100(9)
O(7)	0.0363(9)	0.0385(9)	0.0521(11)	-0.0026(8)	0.0136(8)	0.0025(8)

Table 5: Bond lengths (Å)

C(1) - O(1)	1.346(3)	C(16) - N(1)	1.486(3)
C(1) - O(2)	1.211(3)	C(17) - C(18)	1.520(3)
C(1) - C(12)	1.507(3)	C(18) - C(19)	1.529(3)
O(1) - C(2)	1.473(3)	C(19) - C(20)	1.529(3)
C(2) - C(3)	1.536(3)	C(20) - C(21)	1.523(3)
C(2) - C(13)	1.519(3)	C(20) - N(1)	1.484(3)
C(3) - C(4)	1.546(3)	N(1) - C(22)	1.353(3)
C(3) - C(12)	1.533(3)	C(22) - O(3)	1.229(3)
C(4) - C(5)	1.553(3)	C(22) - C(23)	1.508(3)
C(4) - C(14)	1.500(3)	C(23) - C(24)	1.392(3)
C(5) - C(6)	1.533(3)	C(23) - C(28)	1.389(3)
C(5) - C(10)	1.542(3)	C(24) - C(25)	1.386(3)
C(6) - C(7)	1.530(3)	C(25) - C(26)	1.384(3)
C(7) - C(8)	1.523(3)	C(25) - N(2)	1.474(3)
C(8) - C(9)	1.525(4)	C(26) - C(27)	1.377(3)
C(9) - C(10)	1.533(3)	C(27) - C(28)	1.381(3)
C(10) - C(11)	1.524(3)	C(27) - N(3)	1.476(3)
C(11) - C(12)	1.534(3)	N(2) - O(4)	1.223(3)
C(14) - C(15)	1.327(3)	N(2) - O(5)	1.230(3)
C(15) - C(16)	1.510(3)	N(3) - O(6)	1.226(3)
C(16) - C(17)	1.527(3)	N(3) - O(7)	1.225(3)

Note – H atoms have been excluded

Table 6: Bond angles (°)

O(1) - C(1) - O(2)	121.0(2)	C(15) - C(16) - N(1)	112.37(17)
O(1) - C(1) - C(12)	110.06(19)	C(17) - C(16) - N(1)	110.05(17)
O(2) - C(1) - C(12)	128.8(2)	C(16) - C(17) - C(18)	112.46(18)
C(1) - O(1) - C(2)	110.95(17)	C(17) - C(18) - C(19)	109.24(19)
O(1) - C(2) - C(3)	103.82(17)	C(18) - C(19) - C(20)	112.28(19)
O(1) - C(2) - C(13)	106.01(19)	C(19) - C(20) - C(21)	112.8(2)
C(3) - C(2) - C(13)	115.9(2)	C(19) - C(20) - N(1)	109.91(17)
C(2) - C(3) - C(4)	117.91(18)	C(21) - C(20) - N(1)	111.87(19)
C(2) - C(3) - C(12)	102.43(17)	C(16) - N(1) - C(20)	120.00(17)
C(4) - C(3) - C(12)	113.33(18)	C(16) - N(1) - C(22)	116.59(17)
C(3) - C(4) - C(5)	112.87(17)	C(20) - N(1) - C(22)	122.60(18)
C(3) - C(4) - C(14)	112.61(17)	N(1) - C(22) - O(3)	124.5(2)
C(5) - C(4) - C(14)	111.89(17)	N(1) - C(22) - C(23)	116.81(18)
C(4) - C(5) - C(6)	111.15(17)	O(3) - C(22) - C(23)	118.7(2)
C(4) - C(5) - C(10)	108.87(17)	C(22) - C(23) - C(24)	121.02(19)
C(6) - C(5) - C(10)	111.64(17)	C(22) - C(23) - C(28)	119.15(18)
C(5) - C(6) - C(7)	112.57(19)	C(24) - C(23) - C(28)	119.76(19)
C(6) - C(7) - C(8)	111.48(19)	C(23) - C(24) - C(25)	118.6(2)
C(7) - C(8) - C(9)	110.90(19)	C(24) - C(25) - C(26)	123.2(2)
C(8) - C(9) - C(10)	111.96(19)	C(24) - C(25) - N(2)	118.4(2)
C(5) - C(10) - C(9)	111.93(18)	C(26) - C(25) - N(2)	118.4(2)
C(5) - C(10) - C(11)	109.40(17)	C(25) - C(26) - C(27)	116.0(2)
C(9) - C(10) - C(11)	111.01(18)	C(26) - C(27) - C(28)	123.4(2)
C(10) - C(11) - C(12)	112.40(17)	C(26) - C(27) - N(3)	118.92(19)

C(1) - C(12) - C(3)	102.18(18)	C(28) - C(27) - N(3)	117.66(19)
C(1) - C(12) - C(11)	108.59(18)	C(23) - C(28) - C(27)	118.92(19)
C(3) - C(12) - C(11)	114.48(17)	C(25) - N(2) - O(4)	118.0(2)
C(4) - C(14) - C(15)	124.90(19)	C(25) - N(2) - O(5)	117.4(2)
C(14) - C(15) - C(16)	123.6(2)	O(4) - N(2) - O(5)	124.6(2)
C(15) - C(16) - C(17)	112.36(18)	C(27) - N(3) - O(6)	117.8(2)

Note – H atoms have been excluded