Supporting Information

Caeruleanone A, a Rotenoid with a New Arrangement of the D-ring from the Fruits of *Millettia caerulea*

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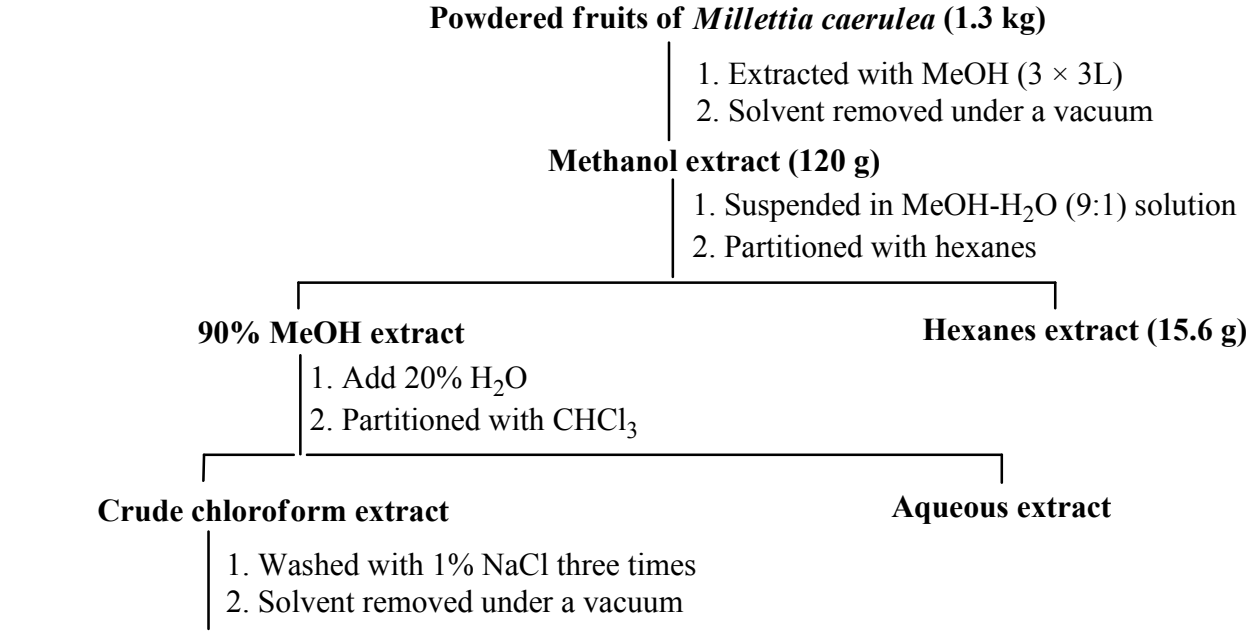
S1. General experimental procedures.

Melting point was obtained in a Fisher Scientific melting point device and is uncorrected. Specific rotations were measured on a Perkin-Elmer 343 automatic polarimeter. UV spectra measurements were performed using a Hitachi U-2910 UV/vis spectrometer. ECD spectra were measured with a JASCO J-810 spectropolarimeter. IR spectra were obtained on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. NMR spectra were run at room temperature on Bruker Avance DRX-400 MHz spectrometer and the data were processed using MestReNova 6.0 software (Mestrelab Research SL, Santiago de Compostela, Spain). Accurate mass values were recorded on a Micromass Q-Tof II ESI spectrometer. Sodium iodide was used for mass calibration for a calibration range of *m/z* 100-2000. Column chromatography (CC) was carried out using silica gel (65-250 or 230-400 mesh; Sorbent Technologies, Atlanta, GA) and Sephadex LH-20 (Sigma-Aldrich, St. Louis, MO). Analytical TLC was conducted on precoated 200 μm thickness silica gel UV_{254} aluminum-backed plates (Sorbent Technologies). Waters XBridge® analytical (4.6 × 150 mm), semi-preparative (10 × 150 mm), and preparative (19 x 150 mm) OBD C_{18} (5 μm) columns were used for HPLC, as conducted on a Waters system composed of a 600 controller, a 717 Plus autosampler, and a 2487 dual wavelength absorbance detector.

S2. Plant material.

The fruits of *M. caerulea* were collected on July 28, 2011 at Nui Chua National Park (11^o 37.998'; 109^o 09.633' E Alt.: 70 masl.) in Southern Vietnam by D. D. Soejarto, T. N. Ninh and B. V. Thanh. D. D. Soejarto identified this plant and a voucher specimen (DDS 14879) was deposited in the John G. Searle Herbarium of the Field Museum of Natural History, Chicago, Illinois.

S3. Extraction scheme



S4. Characterization of new compounds **1-3**.

Caeruleanone A (**1**): colorless prisms; mp 148-151°C; $[\alpha]^{20}_D$ 0 (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 208 (4.47) nm; 220 (sh, 4.27) nm; 304 (4.14) nm; 360 (3.61) nm; IR (film) ν_{max} 2968, 2911, 1663, 1629, 1483, 1420, 1413, 1340, 1312, 1192, 1160, 1055, 1043, 938, 913, 862, 837, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) data, see Tables 1 and 2 in manuscript; HRESIMS *m/z* 501.1890 $[M + Na]^+$ (calcd for $C_{28}H_{30}O_7Na$, 501.1889).

Caeruleanone B (**2**): colorless solid; $[\alpha]^{20}_D$ 0 (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 205 (4.50) nm; 220 (sh, 4.31) nm; 279 (3.81) nm; 346 (3.40) nm; IR (film) ν_{max} 3424, 2958, 2851, 1733, 1673, 1600, 1502, 1471, 1464, 1432, 1375, 1325, 1280, 1261, 1207, 1169, 1097, 1036, 799, 758, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) data, see Tables 1 and 2 in manuscript; HRESIMS *m/z* 517.1844 $[M + Na]^+$ (calcd for $C_{28}H_{30}O_8Na$, 517.1838).

Caeruleanone C (**3**): white powder; $[\alpha]^{20}_D$ +17.0 (*c* 0.15, acetone); UV (MeOH) λ_{max} (log ε) 211 (4.45) nm; 240 (sh, 4.10) nm; 293 (3.99) nm; 342 (3.66) nm; ECD (MeOH) 311 ($\Delta\epsilon$ 1.62), 359 (-0.86) nm; IR (film) ν_{max} 3433, 2917, 1667, 1600, 1480, 1467, 1435, 1334, 1287, 1249, 1201, 1169, 1090, 1081, 1055, 1040, 935, 908, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) data, see Tables 1 and 2 in manuscript; HRESIMS *m/z* 449.1216 $[M + Na]^+$ (calcd for $C_{23}H_{22}O_8Na$, 449.1212).

S5. X-ray crystallographic details of **1**.

The data collection crystal was a colorless plate, which had been cut from a much larger plate. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a monoclinic crystal system. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. The data collection strategy was set up to measure a quadrant of reciprocal space with a redundancy factor of 4.6, which means that 90% of these reflections were measured at least 4.6 times. Phi and omega scans with a frame width of 1.0˚ were used. Data integration was done with Denzo,[1] and scaling and merging of the data was done with Scalepack.[1] Merging the data and averaging the symmetry equivalent reflections resulted in an Rint value of 0.045.

The structure was solved by the direct methods procedure in SHELXS-97.[2] Full-matrix least-squares refinements based on F^2 were performed in SHELXL-97,[3] as incorporated in the WinGX package.[4] There are two independent molecules in the asymmetric unit.

For the methyl groups, the hydrogen atoms were added at calculated positions using a riding model with U(H) = 1.5 * Ueq(bonded carbon atom). The torsion angle, which defines the orientation of the methyl group about the C-O or C-C bond, was refined. The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with U(H) = 1.2 * Ueq(bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion.[5]

References:

(1) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307-326.
(2) SHELXS-97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.
(3) SHELXL-97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.
(4) WinGX-Version 1.70.01: Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837-838.
(5) International Tables for Crystallography (1992). Volume C. Dordrecht: Kluwer Academic Publishers.

Table 1. Crystallographic details for 1.

Formula	$C_{28}\ H_{30}O_7$
Formula weight	478.52
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.6740(2) Å
	b = 18.0944(3) Å
	c = 21.0316(3) Å
	β= 92.142(1)°
Volume	4819.77(13) $Å^3$
Z	8
Density (calculated)	1.319 Mg/m^3
Absorption coefficient	0.094 mm^{-1}
F(000)	2032
Crystal size	0.12 x 0.31 x 0.38 mm^3
Theta range for data collection	1.49 to 25.03°
Index ranges	-15<=h<=15, -21<=k<=21, -25<=l<=25
Reflections collected	81260
Independent reflections	8509 [R(int) = 0.045]
Completeness to theta = 25.03°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8509 / 0 / 641
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.1012
R indices (all data)	R1 = 0.0725, wR2 = 0.1140
Largest diff. peak and hole	0.250 and -0.185 $e/Å^3$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	4678(1)	2397(1)	5109(1)	68(1)
O(3)	6513(1)	2362(1)	5130(1)	70(1)
O(5)	6809(1)	1838(1)	7364(1)	41(1)
O(7)	5739(1)	594(1)	7645(1)	31(1)
O(9)	5203(1)	-1753(1)	6708(1)	36(1)
O(10)	3186(1)	-1514(1)	6449(1)	39(1)
O(12)	2775(1)	1247(1)	7074(1)	38(1)
C(1)	4516(2)	2033(1)	6234(1)	41(1)
C(1A)	5087(1)	1882(1)	6804(1)	34(1)
C(2)	5064(2)	2206(1)	5709(1)	48(1)
C(2A)	5581(2)	2406(2)	4725(1)	78(1)
C(3)	6156(2)	2205(1)	5726(1)	50(1)
C(4)	6741(2)	2081(1)	6270(1)	47(1)
C(4A)	6187(1)	1937(1)	6819(1)	38(1)
C(6)	6262(1)	1786(1)	7948(1)	38(1)
C(6A)	5322(1)	1294(1)	7867(1)	32(1)
C(7A)	5070(1)	130(1)	7335(1)	27(1)
C(8)	5589(1)	-598(1)	7204(1)	27(1)
C(9)	4854(1)	-1147(1)	6857(1)	29(1)
C(10)	3751(1)	-944(1)	6718(1)	31(1)
C(11)	3395(1)	-262(1)	6848(1)	30(1)
C(11A)	4066(1)	302(1)	7146(1)	28(1)
C(12)	3686(1)	1060(1)	7204(1)	30(1)
C(12A)	4527(1)	1623(1)	7390(1)	32(1)
C(13)	2099(1)	-1382(1)	6285(1)	44(1)
C(1')	6553(1)	-465(1)	6779(1)	32(1)
C(2')	6320(1)	-53(1)	6173(1)	36(1)
C(3')	6483(1)	-282(1)	5586(1)	40(1)
C(4')	6884(2)	-1038(1)	5429(1)	54(1)
C(5')	6328(2)	229(2)	5025(1)	65(1)
C(1")	5988(1)	-960(1)	7838(1)	32(1)
C(2")	5138(1)	-1049(1)	8305(1)	32(1)
C(3")	5056(1)	-703(1)	8859(1)	36(1)
C(4")	4132(2)	-835(1)	9270(1)	49(1)
C(5")	5840(2)	-160(1)	9132(1)	53(1)
O(2B)	2051(1)	1522(1)	11102(1)	64(1)
O(3B)	564(1)	2226(1)	11245(1)	66(1)
O(5B)	268(1)	2978(1)	9053(1)	42(1)
O(7B)	337(1)	1842(1)	8174(1)	35(1)
O(9B)	-907(1)	-501(1)	7491(1)	39(1)
O(10B)	886(1)	-1165(1)	7787(1)	42(1)

O(12B)	3164(1)	955(1)	8760(1)	42(1)
C(1B)	2142(2)	1754(1)	9943(1)	41(1)
C(1C)	1639(1)	2117(1)	9422(1)	33(1)
C(2B)	1732(2)	1844(1)	10529(1)	46(1)
C(2C)	1486(2)	1920(1)	11565(1)	65(1)
C(3B)	848(2)	2268(1)	10616(1)	47(1)
C(4B)	349(2)	2643(1)	10130(1)	46(1)
C(4C)	779(2)	2571(1)	9528(1)	36(1)
C(6B)	808(2)	3052(1)	8472(1)	41(1)
C(6C)	1247(1)	2324(1)	8264(1)	35(1)
C(7C)	526(1)	1109(1)	8124(1)	29(1)
C(8B)	-406(1)	705(1)	7837(1)	30(1)
C(9B)	-201(1)	-117(1)	7726(1)	31(1)
C(10B)	830(1)	-427(1)	7920(1)	32(1)
C(11B)	1588(1)	-4(1)	8194(1)	32(1)
C(11C)	1450(1)	782(1)	8306(1)	29(1)
C(12C)	2044(1)	2021(1)	8756(1)	33(1)
C(12B)	2297(1)	1216(1)	8612(1)	33(1)
C(13B)	1791(2)	-1549(1)	8041(1)	51(1)
C(1'B)	-1356(1)	773(1)	8283(1)	35(1)
C(2'B)	-1213(1)	402(1)	8915(1)	39(1)
C(3'B)	-1405(1)	680(1)	9481(1)	40(1)
C(4'B)	-1792(2)	1452(1)	9580(1)	66(1)
C(5'B)	-1310(2)	220(2)	10077(1)	61(1)
C(1"B)	-726(1)	1050(1)	7179(1)	34(1)
C(2"B)	142(1)	1007(1)	6718(1)	34(1)
C(3"B)	145(2)	635(1)	6175(1)	38(1)
C(4"B)	1082(2)	654(1)	5763(1)	49(1)
C(5"B)	-739(2)	164(2)	5920(1)	77(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

O(2)-C(2)	1.381(2)
O(2)-C(2A)	1.425(3)
O(3)-C(3)	1.377(2)
O(3)-C(2A)	1.433(3)
O(5)-C(4A)	1.379(2)
O(5)-C(6)	1.434(2)
O(7)-C(7A)	1.344(2)
O(7)-C(6A)	1.457(2)
O(9)-C(9)	1.229(2)
O(10)-C(10)	1.367(2)
O(10)-C(13)	1.428(2)
O(12)-C(12)	1.224(2)
C(1)-C(2)	1.362(3)
C(1)-C(1A)	1.404(3)
C(1)-H(1)	0.9500
C(1A)-C(4A)	1.398(2)
C(1A)-C(12A)	1.518(2)
C(2)-C(3)	1.384(3)
C(2A)-H(2A1)	0.9900
C(2A)-H(2A2)	0.9900
C(3)-C(4)	1.360(3)
C(4)-C(4A)	1.398(3)
C(4)-H(4)	0.9500
C(6)-C(6A)	1.492(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6A)-C(12A)	1.518(2)
C(6A)-H(6A1)	1.0000
C(7A)-C(11A)	1.356(2)
C(7A)-C(8)	1.503(2)
C(8)-C(9)	1.528(2)
C(8)-C(1")	1.552(2)
C(8)-C(1')	1.559(2)
C(9)-C(10)	1.465(2)
C(10)-C(11)	1.345(2)
C(11)-C(11A)	1.455(2)
C(11)-H(11)	0.9500
C(11A)-C(12)	1.459(2)
C(12)-C(12A)	1.516(2)
C(12A)-H(12A)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(1')-C(2')	1.496(2)

C(1')-H(1'1)	0.9900
C(1')-H(1'2)	0.9900
C(2')-C(3')	1.327(2)
C(2')-H(2')	0.9500
C(3')-C(4')	1.502(3)
C(3')-C(5')	1.505(3)
C(4')-H(4'1)	0.9800
C(4')-H(4'2)	0.9800
C(4')-H(4'3)	0.9800
C(5')-H(5'1)	0.9800
C(5')-H(5'2)	0.9800
C(5')-H(5'3)	0.9800
C(1")-C(2")	1.493(2)
C(1")-H(1"1)	0.9900
C(1")-H(1"2)	0.9900
C(2")-C(3")	1.331(2)
C(2")-H(2")	0.9500
C(3")-C(5")	1.497(3)
C(3")-C(4")	1.500(3)
C(4")-H(4"1)	0.9800
C(4")-H(4"2)	0.9800
C(4")-H(4"3)	0.9800
C(5")-H(5"1)	0.9800
C(5")-H(5"2)	0.9800
C(5")-H(5"3)	0.9800
O(2B)-C(2B)	1.385(2)
O(2B)-C(2C)	1.426(3)
O(3B)-C(3B)	1.388(2)
O(3B)-C(2C)	1.436(3)
O(5B)-C(4C)	1.383(2)
O(5B)-C(6B)	1.430(2)
O(7B)-C(7C)	1.353(2)
O(7B)-C(6C)	1.452(2)
O(9B)-C(9B)	1.224(2)
O(10B)-C(10B)	1.367(2)
O(10B)-C(13B)	1.426(2)
O(12B)-C(12B)	1.225(2)
C(1B)-C(2B)	1.365(3)
C(1B)-C(1C)	1.410(3)
C(1B)-H(1B)	0.9500
C(1C)-C(4C)	1.390(3)
C(1C)-C(12C)	1.519(2)
C(2B)-C(3B)	1.375(3)
C(2C)-H(2C1)	0.9900
C(2C)-H(2C2)	0.9900
C(3B)-C(4B)	1.362(3)

C(4B)-C(4C)	1.403(3)
C(4B)-H(4B)	0.9500
C(6B)-C(6C)	1.502(3)
C(6B)-H(6B1)	0.9900
C(6B)-H(6B2)	0.9900
C(6C)-C(12C)	1.520(2)
C(6C)-H(6C)	1.0000
C(7C)-C(11C)	1.354(2)
C(7C)-C(8B)	1.497(2)
C(8B)-C(9B)	1.529(3)
C(8B)-C(1"B)	1.557(2)
C(8B)-C(1'B)	1.558(2)
C(9B)-C(10B)	1.466(2)
C(10B)-C(11B)	1.342(2)
C(11B)-C(11C)	1.453(3)
C(11B)-H(11B)	0.9500
C(11C)-C(12B)	1.460(2)
C(12C)-C(12B)	1.525(3)
C(12C)-H(12C)	1.0000
C(13B)-H(13D)	0.9800
C(13B)-H(13E)	0.9800
C(13B)-H(13F)	0.9800
C(1'B)-C(2'B)	1.494(3)
C(1'B)-H(1'3)	0.9900
C(1'B)-H(1'4)	0.9900
C(2'B)-C(3'B)	1.323(2)
C(2'B)-H(2'B)	0.9500
C(3'B)-C(4'B)	1.498(3)
C(3'B)-C(5'B)	1.505(3)
C(4'B)-H(4'4)	0.9800
C(4'B)-H(4'5)	0.9800
C(4'B)-H(4'6)	0.9800
C(5'B)-H(5'4)	0.9800
C(5'B)-H(5'5)	0.9800
C(5'B)-H(5'6)	0.9800
C(1"B)-C(2"B)	1.495(2)
C(1"B)-H(1"3)	0.9900
C(1"B)-H(1"4)	0.9900
C(2"B)-C(3"B)	1.327(2)
C(2"B)-H(2"B)	0.9500
C(3"B)-C(5"B)	1.491(3)
C(3"B)-C(4"B)	1.496(3)
C(4"B)-H(4"4)	0.9800
C(4"B)-H(4"5)	0.9800
C(4"B)-H(4"6)	0.9800
C(5"B)-H(5"4)	0.9800

C(5"B)-H(5"5)	0.9800
C(5"B)-H(5"6)	0.9800
C(2)-O(2)-C(2A)	104.88(18)
C(3)-O(3)-C(2A)	105.09(17)
C(4A)-O(5)-C(6)	116.10(14)
C(7A)-O(7)-C(6A)	117.95(12)
C(10)-O(10)-C(13)	117.31(14)
C(2)-C(1)-C(1A)	118.32(18)
C(2)-C(1)-H(1)	120.8
C(1A)-C(1)-H(1)	120.8
C(4A)-C(1A)-C(1)	119.19(17)
C(4A)-C(1A)-C(12A)	119.99(17)
C(1)-C(1A)-C(12A)	120.74(16)
C(1)-C(2)-O(2)	128.6(2)
C(1)-C(2)-C(3)	121.3(2)
O(2)-C(2)-C(3)	110.03(18)
O(2)-C(2A)-O(3)	108.92(18)
O(2)-C(2A)-H(2A1)	109.9
O(3)-C(2A)-H(2A1)	109.9
O(2)-C(2A)-H(2A2)	109.9
O(3)-C(2A)-H(2A2)	109.9
H(2A1)-C(2A)-H(2A2)	108.3
C(4)-C(3)-O(3)	127.8(2)
C(4)-C(3)-C(2)	122.34(19)
O(3)-C(3)-C(2)	109.9(2)
C(3)-C(4)-C(4A)	116.81(19)
C(3)-C(4)-H(4)	121.6
C(4A)-C(4)-H(4)	121.6
O(5)-C(4A)-C(1A)	123.29(17)
O(5)-C(4A)-C(4)	114.93(17)
C(1A)-C(4A)-C(4)	121.76(19)
O(5)-C(6)-C(6A)	110.58(14)
O(5)-C(6)-H(6A)	109.5
C(6A)-C(6)-H(6A)	109.5
O(5)-C(6)-H(6B)	109.5
C(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	108.1
O(7)-C(6A)-C(6)	104.93(13)
O(7)-C(6A)-C(12A)	111.67(14)
C(6)-C(6A)-C(12A)	110.42(16)
O(7)-C(6A)-H(6A1)	109.9
C(6)-C(6A)-H(6A1)	109.9
C(12A)-C(6A)-H(6A1)	109.9
O(7)-C(7A)-C(11A)	124.56(15)
O(7)-C(7A)-C(8)	111.29(14)

C(11A)-C(7A)-C(8)	124.12(15)
C(7A)-C(8)-C(9)	113.14(14)
C(7A)-C(8)-C(1")	110.14(13)
C(9)-C(8)-C(1")	108.05(13)
C(7A)-C(8)-C(1')	109.05(14)
C(9)-C(8)-C(1')	107.61(13)
C(1")-C(8)-C(1')	108.74(13)
O(9)-C(9)-C(10)	121.51(16)
O(9)-C(9)-C(8)	118.92(15)
C(10)-C(9)-C(8)	119.57(15)
C(11)-C(10)-O(10)	127.07(16)
C(11)-C(10)-C(9)	120.93(16)
O(10)-C(10)-C(9)	112.00(15)
C(10)-C(11)-C(11A)	122.43(16)
C(10)-C(11)-H(11)	118.8
C(11A)-C(11)-H(11)	118.8
C(7A)-C(11A)-C(11)	119.46(16)
C(7A)-C(11A)-C(12)	120.03(16)
C(11)-C(11A)-C(12)	120.38(15)
O(12)-C(12)-C(11A)	123.58(16)
O(12)-C(12)-C(12A)	121.26(16)
C(11A)-C(12)-C(12A)	114.99(15)
C(12)-C(12A)-C(6A)	110.48(15)
C(12)-C(12A)-C(1A)	110.08(14)
C(6A)-C(12A)-C(1A)	109.80(14)
C(12)-C(12A)-H(12A)	108.8
C(6A)-C(12A)-H(12A)	108.8
C(1A)-C(12A)-H(12A)	108.8
O(10)-C(13)-H(13A)	109.5
O(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(2')-C(1')-C(8)	115.63(14)
C(2')-C(1')-H(1'1)	108.4
C(8)-C(1')-H(1'1)	108.4
C(2')-C(1')-H(1'2)	108.4
C(8)-C(1')-H(1'2)	108.4
H(1'1)-C(1')-H(1'2)	107.4
C(3')-C(2')-C(1')	127.28(17)
C(3')-C(2')-H(2')	116.4
C(1')-C(2')-H(2')	116.4
C(2')-C(3')-C(4')	123.69(18)
C(2')-C(3')-C(5')	121.24(19)
C(4')-C(3')-C(5')	114.99(18)

C(3')-C(4')-H(4'1)	109.5
C(3')-C(4')-H(4'2)	109.5
H(4'1)-C(4')-H(4'2)	109.5
C(3')-C(4')-H(4'3)	109.5
H(4'1)-C(4')-H(4'3)	109.5
H(4'2)-C(4')-H(4'3)	109.5
C(3')-C(5')-H(5'1)	109.5
C(3')-C(5')-H(5'2)	109.5
H(5'1)-C(5')-H(5'2)	109.5
C(3')-C(5')-H(5'3)	109.5
H(5'1)-C(5')-H(5'3)	109.5
H(5'2)-C(5')-H(5'3)	109.5
C(2")-C(1")-C(8)	112.97(14)
C(2")-C(1")-H(1"1)	109.0
C(8)-C(1")-H(1"1)	109.0
C(2")-C(1")-H(1"2)	109.0
C(8)-C(1")-H(1"2)	109.0
H(1"1)-C(1")-H(1"2)	107.8
C(3")-C(2")-C(1")	127.39(17)
C(3")-C(2")-H(2")	116.3
C(1")-C(2")-H(2")	116.3
C(2")-C(3")-C(5")	124.91(17)
C(2")-C(3")-C(4")	121.22(18)
C(5")-C(3")-C(4")	113.87(16)
C(3")-C(4")-H(4"1)	109.5
C(3")-C(4")-H(4"2)	109.5
H(4"1)-C(4")-H(4"2)	109.5
C(3")-C(4")-H(4"3)	109.5
H(4"1)-C(4")-H(4"3)	109.5
H(4"2)-C(4")-H(4"3)	109.5
C(3")-C(5")-H(5"1)	109.5
C(3")-C(5")-H(5"2)	109.5
H(5"1)-C(5")-H(5"2)	109.5
C(3")-C(5")-H(5"3)	109.5
H(5"1)-C(5")-H(5"3)	109.5
H(5"2)-C(5")-H(5"3)	109.5
C(2B)-O(2B)-C(2C)	104.11(16)
C(3B)-O(3B)-C(2C)	103.41(17)
C(4C)-O(5B)-C(6B)	116.21(14)
C(7C)-O(7B)-C(6C)	117.18(13)
C(10B)-O(10B)-C(13B)	116.49(14)
C(2B)-C(1B)-C(1C)	118.09(18)
C(2B)-C(1B)-H(1B)	121.0
C(1C)-C(1B)-H(1B)	121.0
C(4C)-C(1C)-C(1B)	118.95(17)
C(4C)-C(1C)-C(12C)	120.64(16)

C(1B)-C(1C)-C(12C)	120.41(16)
C(1B)-C(2B)-C(3B)	121.70(19)
C(1B)-C(2B)-O(2B)	128.8(2)
C(3B)-C(2B)-O(2B)	109.42(18)
O(2B)-C(2C)-O(3B)	107.18(16)
O(2B)-C(2C)-H(2C1)	110.3
O(3B)-C(2C)-H(2C1)	110.3
O(2B)-C(2C)-H(2C2)	110.3
O(3B)-C(2C)-H(2C2)	110.3
H(2C1)-C(2C)-H(2C2)	108.5
C(4B)-C(3B)-C(2B)	122.45(18)
C(4B)-C(3B)-O(3B)	127.8(2)
C(2B)-C(3B)-O(3B)	109.72(19)
C(3B)-C(4B)-C(4C)	116.45(18)
C(3B)-C(4B)-H(4B)	121.8
C(4C)-C(4B)-H(4B)	121.8
O(5B)-C(4C)-C(1C)	123.19(16)
O(5B)-C(4C)-C(4B)	114.57(16)
C(1C)-C(4C)-C(4B)	122.24(18)
O(5B)-C(6B)-C(6C)	111.05(15)
O(5B)-C(6B)-H(6B1)	109.4
C(6C)-C(6B)-H(6B1)	109.4
O(5B)-C(6B)-H(6B2)	109.4
C(6C)-C(6B)-H(6B2)	109.4
H(6B1)-C(6B)-H(6B2)	108.0
O(7B)-C(6C)-C(6B)	105.33(14)
O(7B)-C(6C)-C(12C)	112.11(14)
C(6B)-C(6C)-C(12C)	111.25(15)
O(7B)-C(6C)-H(6C)	109.4
C(6B)-C(6C)-H(6C)	109.4
C(12C)-C(6C)-H(6C)	109.4
O(7B)-C(7C)-C(11C)	124.07(16)
O(7B)-C(7C)-C(8B)	111.76(14)
C(11C)-C(7C)-C(8B)	124.17(16)
C(7C)-C(8B)-C(9B)	113.55(14)
C(7C)-C(8B)-C(1"B)	109.78(14)
C(9B)-C(8B)-C(1"B)	107.15(14)
C(7C)-C(8B)-C(1'B)	109.50(14)
C(9B)-C(8B)-C(1'B)	107.94(14)
C(1"B)-C(8B)-C(1'B)	108.81(13)
O(9B)-C(9B)-C(10B)	121.67(17)
O(9B)-C(9B)-C(8B)	119.22(16)
C(10B)-C(9B)-C(8B)	119.09(16)
C(11B)-C(10B)-O(10B)	127.14(16)
C(11B)-C(10B)-C(9B)	121.07(16)
O(10B)-C(10B)-C(9B)	111.79(15)

C(10B)-C(11B)-C(11C)	122.67(16)
C(10B)-C(11B)-H(11B)	118.7
C(11C)-C(11B)-H(11B)	118.7
C(7C)-C(11C)-C(11B)	119.36(16)
C(7C)-C(11C)-C(12B)	120.26(16)
C(11B)-C(11C)-C(12B)	120.38(15)
C(1C)-C(12C)-C(6C)	110.32(14)
C(1C)-C(12C)-C(12B)	111.89(14)
C(6C)-C(12C)-C(12B)	110.44(15)
C(1C)-C(12C)-H(12C)	108.0
C(6C)-C(12C)-H(12C)	108.0
C(12B)-C(12C)-H(12C)	108.0
O(12B)-C(12B)-C(11C)	122.87(17)
O(12B)-C(12B)-C(12C)	120.78(16)
C(11C)-C(12B)-C(12C)	116.33(15)
O(10B)-C(13B)-H(13D)	109.5
O(10B)-C(13B)-H(13E)	109.5
H(13D)-C(13B)-H(13E)	109.5
O(10B)-C(13B)-H(13F)	109.5
H(13D)-C(13B)-H(13F)	109.5
H(13E)-C(13B)-H(13F)	109.5
C(2'B)-C(1'B)-C(8B)	115.45(14)
C(2'B)-C(1'B)-H(1'3)	108.4
C(8B)-C(1'B)-H(1'3)	108.4
C(2'B)-C(1'B)-H(1'4)	108.4
C(8B)-C(1'B)-H(1'4)	108.4
H(1'3)-C(1'B)-H(1'4)	107.5
C(3'B)-C(2'B)-C(1'B)	127.57(18)
C(3'B)-C(2'B)-H(2'B)	116.2
C(1'B)-C(2'B)-H(2'B)	116.2
C(2'B)-C(3'B)-C(4'B)	123.47(19)
C(2'B)-C(3'B)-C(5'B)	121.82(19)
C(4'B)-C(3'B)-C(5'B)	114.61(18)
C(3'B)-C(4'B)-H(4'4)	109.5
C(3'B)-C(4'B)-H(4'5)	109.5
H(4'4)-C(4'B)-H(4'5)	109.5
C(3'B)-C(4'B)-H(4'6)	109.5
H(4'4)-C(4'B)-H(4'6)	109.5
H(4'5)-C(4'B)-H(4'6)	109.5
C(3'B)-C(5'B)-H(5'4)	109.5
C(3'B)-C(5'B)-H(5'5)	109.5
H(5'4)-C(5'B)-H(5'5)	109.5
C(3'B)-C(5'B)-H(5'6)	109.5
H(5'4)-C(5'B)-H(5'6)	109.5
H(5'5)-C(5'B)-H(5'6)	109.5
C(2"B)-C(1"B)-C(8B)	112.45(14)

C(2"B)-C(1"B)-H(1"3)	109.1
C(8B)-C(1"B)-H(1"3)	109.1
C(2"B)-C(1"B)-H(1"4)	109.1
C(8B)-C(1"B)-H(1"4)	109.1
H(1"3)-C(1"B)-H(1"4)	107.8
C(3"B)-C(2"B)-C(1"B)	127.65(17)
C(3"B)-C(2"B)-H(2"B)	116.2
C(1"B)-C(2"B)-H(2"B)	116.2
C(2"B)-C(3"B)-C(5"B)	124.96(18)
C(2"B)-C(3"B)-C(4"B)	121.00(18)
C(5"B)-C(3"B)-C(4"B)	114.03(17)
C(3"B)-C(4"B)-H(4"4)	109.5
C(3"B)-C(4"B)-H(4"5)	109.5
H(4"4)-C(4"B)-H(4"5)	109.5
C(3"B)-C(4"B)-H(4"6)	109.5
H(4"4)-C(4"B)-H(4"6)	109.5
H(4"5)-C(4"B)-H(4"6)	109.5
C(3"B)-C(5"B)-H(5"4)	109.5
C(3"B)-C(5"B)-H(5"5)	109.5
H(5"4)-C(5"B)-H(5"5)	109.5
C(3"B)-C(5"B)-H(5"6)	109.5
H(5"4)-C(5"B)-H(5"6)	109.5

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	78(1)	83(1)	44(1)	11(1)	-2(1)	-29(1)
O(3)	78(1)	82(1)	51(1)	-3(1)	15(1)	-36(1)
O(5)	29(1)	38(1)	56(1)	-4(1)	-3(1)	-4(1)
O(7)	27(1)	28(1)	38(1)	-8(1)	-4(1)	2(1)
O(9)	39(1)	29(1)	40(1)	-4(1)	1(1)	-1(1)
O(10)	35(1)	33(1)	49(1)	-4(1)	-8(1)	-7(1)
O(12)	25(1)	41(1)	49(1)	1(1)	-2(1)	4(1)
C(1)	40(1)	39(1)	44(1)	0(1)	-1(1)	-9(1)
C(1A)	33(1)	26(1)	42(1)	-4(1)	0(1)	-4(1)
C(2)	58(1)	46(1)	39(1)	1(1)	-5(1)	-16(1)
C(2A)	97(2)	94(2)	45(2)	-2(1)	9(2)	-30(2)
C(3)	58(1)	47(1)	46(1)	-4(1)	16(1)	-22(1)
C(4)	38(1)	43(1)	59(1)	-11(1)	6(1)	-16(1)
C(4A)	36(1)	28(1)	49(1)	-6(1)	1(1)	-5(1)
C(6)	35(1)	34(1)	45(1)	-11(1)	-4(1)	6(1)
C(6A)	30(1)	30(1)	38(1)	-9(1)	0(1)	6(1)
C(7A)	29(1)	29(1)	24(1)	-1(1)	1(1)	-5(1)
C(8)	25(1)	27(1)	30(1)	-1(1)	1(1)	2(1)
C(9)	34(1)	29(1)	24(1)	1(1)	5(1)	-2(1)
C(10)	32(1)	30(1)	29(1)	0(1)	-1(1)	-6(1)
C(11)	24(1)	35(1)	31(1)	2(1)	-1(1)	-4(1)
C(11A)	25(1)	29(1)	29(1)	0(1)	2(1)	1(1)
C(12)	27(1)	36(1)	27(1)	0(1)	1(1)	1(1)
C(12A)	27(1)	29(1)	39(1)	-7(1)	0(1)	4(1)
C(13)	33(1)	46(1)	53(1)	-3(1)	-10(1)	-8(1)
C(1')	27(1)	34(1)	35(1)	-4(1)	3(1)	-2(1)
C(2')	34(1)	33(1)	41(1)	2(1)	10(1)	2(1)
C(3')	32(1)	50(1)	38(1)	4(1)	8(1)	-4(1)
C(4')	66(2)	55(1)	42(1)	-13(1)	13(1)	-12(1)
C(5')	57(1)	90(2)	48(1)	20(1)	15(1)	6(1)
C(1")	36(1)	29(1)	30(1)	-2(1)	-3(1)	5(1)
C(2")	35(1)	29(1)	32(1)	2(1)	-2(1)	1(1)
C(3")	40(1)	35(1)	32(1)	1(1)	-2(1)	5(1)
C(4")	57(1)	54(1)	37(1)	0(1)	9(1)	1(1)
C(5")	63(1)	57(1)	39(1)	-12(1)	-1(1)	-6(1)
O(2B)	107(1)	55(1)	30(1)	1(1)	-6(1)	13(1)
O(3B)	102(1)	59(1)	38(1)	-4(1)	21(1)	3(1)
O(5B)	44(1)	40(1)	42(1)	0(1)	1(1)	10(1)
O(7B)	34(1)	32(1)	40(1)	-1(1)	-4(1)	2(1)
O(9B)	36(1)	39(1)	42(1)	-4(1)	-3(1)	0(1)
O(10B)	43(1)	33(1)	48(1)	-6(1)	-6(1)	9(1)

O(12B)	30(1)	49(1)	48(1)	-5(1)	-4(1)	6(1)
C(1B)	47(1)	37(1)	39(1)	-2(1)	-6(1)	4(1)
C(1C)	35(1)	31(1)	34(1)	-2(1)	-1(1)	-3(1)
C(2B)	68(2)	38(1)	32(1)	-1(1)	-4(1)	1(1)
C(2C)	109(2)	53(2)	34(1)	1(1)	2(1)	-2(1)
C(3B)	70(2)	38(1)	34(1)	-6(1)	11(1)	-6(1)
C(4B)	50(1)	42(1)	45(1)	-7(1)	9(1)	6(1)
C(4C)	40(1)	31(1)	38(1)	0(1)	-2(1)	-1(1)
C(6B)	44(1)	35(1)	42(1)	6(1)	-1(1)	-3(1)
C(6C)	36(1)	36(1)	34(1)	4(1)	0(1)	-3(1)
C(7C)	32(1)	30(1)	25(1)	1(1)	4(1)	5(1)
C(8B)	27(1)	33(1)	29(1)	-2(1)	-1(1)	5(1)
C(9B)	30(1)	37(1)	25(1)	1(1)	3(1)	-1(1)
C(10B)	35(1)	34(1)	27(1)	-3(1)	3(1)	5(1)
C(11B)	30(1)	38(1)	29(1)	2(1)	2(1)	9(1)
C(11C)	28(1)	35(1)	25(1)	-1(1)	2(1)	3(1)
C(12C)	30(1)	34(1)	35(1)	0(1)	1(1)	-4(1)
C(12B)	29(1)	42(1)	27(1)	2(1)	4(1)	2(1)
C(13B)	57(1)	35(1)	60(1)	-4(1)	-10(1)	16(1)
C(1'B)	28(1)	41(1)	38(1)	-6(1)	2(1)	4(1)
C(2'B)	38(1)	41(1)	39(1)	1(1)	11(1)	7(1)
C(3'B)	28(1)	54(1)	39(1)	-3(1)	7(1)	0(1)
C(4'B)	83(2)	63(2)	52(1)	-15(1)	13(1)	6(1)
C(5'B)	53(1)	90(2)	41(1)	10(1)	15(1)	8(1)
C(1"B)	33(1)	37(1)	32(1)	-1(1)	-2(1)	5(1)
C(2"B)	33(1)	36(1)	32(1)	3(1)	-2(1)	-2(1)
C(3"B)	40(1)	41(1)	33(1)	1(1)	0(1)	1(1)
C(4"B)	53(1)	57(1)	39(1)	4(1)	7(1)	12(1)
C(5"B)	76(2)	102(2)	51(2)	-30(1)	10(1)	-35(2)

Table 5. Calculated hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **1**.

	x	y	z	U(eq)
H(1)	3766	2015	6215	49
H(2A1)	5590	2867	4472	94
H(2A2)	5555	1982	4427	94
H(4)	7491	2092	6277	56
H(6A)	6034	2285	8079	46
H(6B)	6745	1587	8287	46
H(6A1)	4988	1222	8286	39
H(11)	2680	-145	6741	36
H(12A)	4181	2058	7589	38
H(13A)	1738	-1212	6662	66
H(13B)	1770	-1841	6128	66
H(13C)	2042	-1003	5953	66
H(1'1)	7097	-188	7031	38
H(1'2)	6859	-951	6672	38
H(2')	6023	426	6214	43
H(4'1)	7647	-1015	5369	81
H(4'2)	6526	-1216	5036	81
H(4'3)	6742	-1378	5778	81
H(5'1)	6006	691	5164	97
H(5'2)	5865	-7	4701	97
H(5'3)	7014	335	4844	97
H(1"1)	6290	-1451	7746	38
H(1"2)	6560	-651	8032	38
H(2")	4594	-1392	8193	38
H(4"1)	3677	-1218	9077	73
H(4"2)	3729	-376	9309	73
H(4"3)	4386	-997	9693	73
H(5"1)	6410	-91	8836	79
H(5"2)	6134	-346	9539	79
H(5"3)	5488	315	9201	79
H(1B)	2748	1455	9889	49
H(2C1)	1932	2319	11752	78
H(2C2)	1279	1585	11911	78
H(4B)	-257	2938	10196	55
H(6B1)	1392	3413	8532	49
H(6B2)	314	3245	8136	49
H(6C)	1595	2388	7849	42
H(11B)	2241	-227	8320	39
H(12C)	2710	2313	8727	40
H(13D)	2431	-1327	7876	76
H(13E)	1751	-2069	7915	76

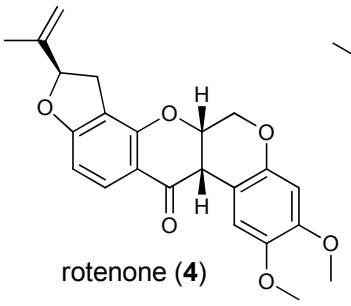
H(13F)	1813	-1513	8506	76
H(1'3)	-1496	1304	8355	43
H(1'4)	-1989	562	8061	43
H(2'B)	-953	-90	8910	47
H(4'4)	-1642	1753	9207	99
H(4'5)	-1432	1664	9958	99
H(4'6)	-2555	1444	9640	99
H(5'4)	-1032	-270	9974	91
H(5'5)	-2007	166	10258	91
H(5'6)	-829	463	10387	91
H(1"3)	-1354	788	6999	41
H(1"4)	-922	1574	7240	41
H(2"B)	764	1279	6827	40
H(4"4)	1640	954	5969	74
H(4"5)	877	871	5350	74
H(4"6)	1341	150	5701	74
H(5"4)	-1276	117	6242	115
H(5"5)	-468	-327	5816	115
H(5"6)	-1055	393	5536	115

S6. Isolation of known compounds **4-14**.

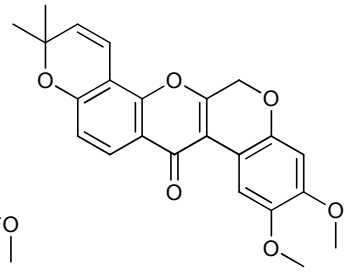
A precipitate, rotenone (**4**, 1.2 g) was obtained in pure form in Fr. 1.4 and a further impure precipitate in Fr. 1.3. Fr. 1.3 precipitate (17.6 mg) was purified using HPLC preparative RP-18 column with CH_3CN-H_2O (65:35) as solvent system to afford 6a,12a-dehydrodeguelin (**5**, 5.5 mg) and 11-hydroxy-6a,12a-dehydrodeguelin (**6**, 1.4 mg). Fr. 1.4 soluble fraction (6.3 g) was chromatographed over a silica gel column with hexanes/acetone (10:1 to 1:1) solvent mixtures to yield seven subfractions (Fr. 2.1-2.7) and a precipitate in pure form in Fr. 2.2 corresponding to additional amounts of **4** (219.0 mg). Fr. 2.2 soluble fraction (1.1 g) was chromatographed over a Sephadex LH-20 column using MeOH-H_2O (9:1) as solvent system to afford four subfractions (Fr. 3.1-3.4). Fr. 2.3 (3.1 g) was chromatographed on a silica gel column using hexanes-acetone (10:1 to 0:1) as solvent system to give ten subfractions (Fr. 4.1-4.10). Fr. 4.4 (509.1 mg) was purified by preparative RP-18 HPLC using CH_3CN-H_2O (65:35) as solvent mixtures to yield *cis*-(6a*β*,12a*β*)-hydroxyrotenone (**7**, 12.8 mg) and tephrosin (**8**, 54.7 mg). A fraction (49.6 mg) collected during the previous HPLC isolation experiment was further purified in a separate semipreparative RP-18 HPLC experiment using MeOH-H_2O (55:45) to afford additional amounts of **4** (5.3 mg) and 11-hydroxytephrosin (**9**, 1.3 mg). Fr. 3.3 (477.7 mg) was subjected to RP-18 HPLC using gradient solvent systems consisting of CH_3CN-H_2O (45:55 for 20 min., then 31:69 for 50 min.) to afford five subfractions (Fr. 5.1-5.5). Fr. 5.2 (3.1 mg) was purified by Sephadex LH-20 using MeOH as solvent to yield 12a-hydroxyisomillettone (**10**, 2.9 mg). Fr. 5.3 (7.4 mg) was further purified in a semipreparative RP-18 HPLC experiment using MeOH-H_2O (50:50) as solvent mixtures to afford further amounts of **10** (1.4 mg) and millettosin (**11**, 2.6 mg). Fr. 5.5 (34.7 mg) was purified by RP-18 HPLC using CH_3CN-H_2O (33:67) as solvent system to yield deguelin (**12**, 7.3 mg). Fr. 1.5 (1.7 g) was chromatographed over a silica gel column using

$CHCl_3$-acetone in a gradient solvent system to afford five subfractions (Fr. 6.1-.6.5). Fr. 6.2 (755.5 mg) was further chromatographed on a Sephadex LH-20 column using MeOH-H_2O (1:1) as solvent system to give four subfractions (Fr. 7.1-7.4). Fr. 7.2 (234.1 mg) was purified by preparative RP-18 HPLC using MeOH-H_2O in a gradient fashion (55:45 for 25 min., then 47:53 for 69 min.) as solvent system to give 12a-hydroxyerythynone (**13**, 7.3 mg), erythynone (**14**, 2.4 mg), and additional amounts of **8** (5.5 mg).

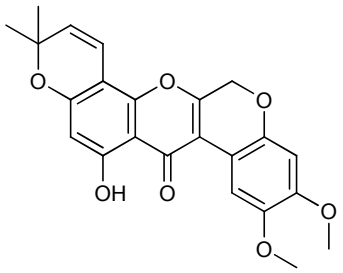
S7. Structures of known compounds **4-14** isolated from *M. caerulea*.



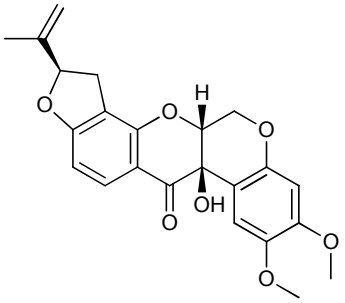
rotenone (**4**)



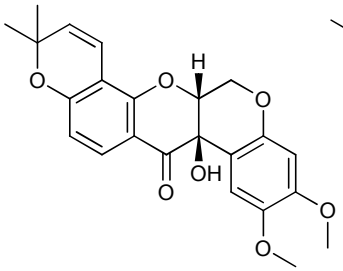
6a,12a-dehydrodeguelin (**5**)



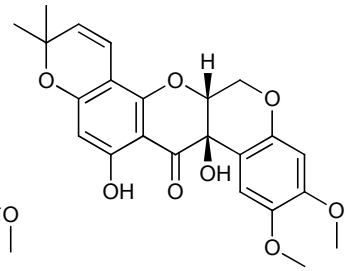
11-hydroxy-6a,12a-dehydrodeguelin (**6**)



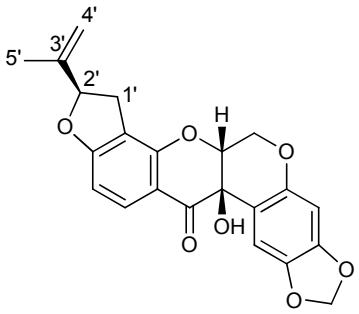
cis-(6aβ,12aβ)-hydroxyrotenone (**7**)



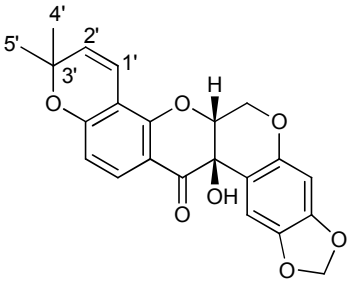
tephrosin (**8**)



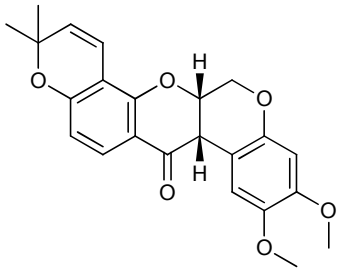
11-hydroxytephrosin (**9**)



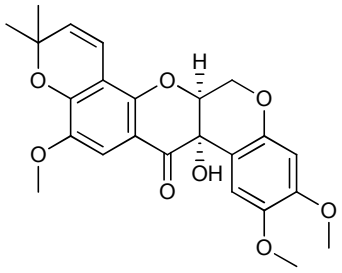
12a-hydroxyisomillettone (**10**)



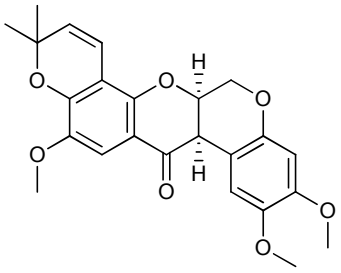
millettosin (**11**)



deguelin (**12**)



12a-hydroxyerythynone (**13**)



erythynone (**14**)

S8. Characterization of known compounds **10-11** and **13-14**.

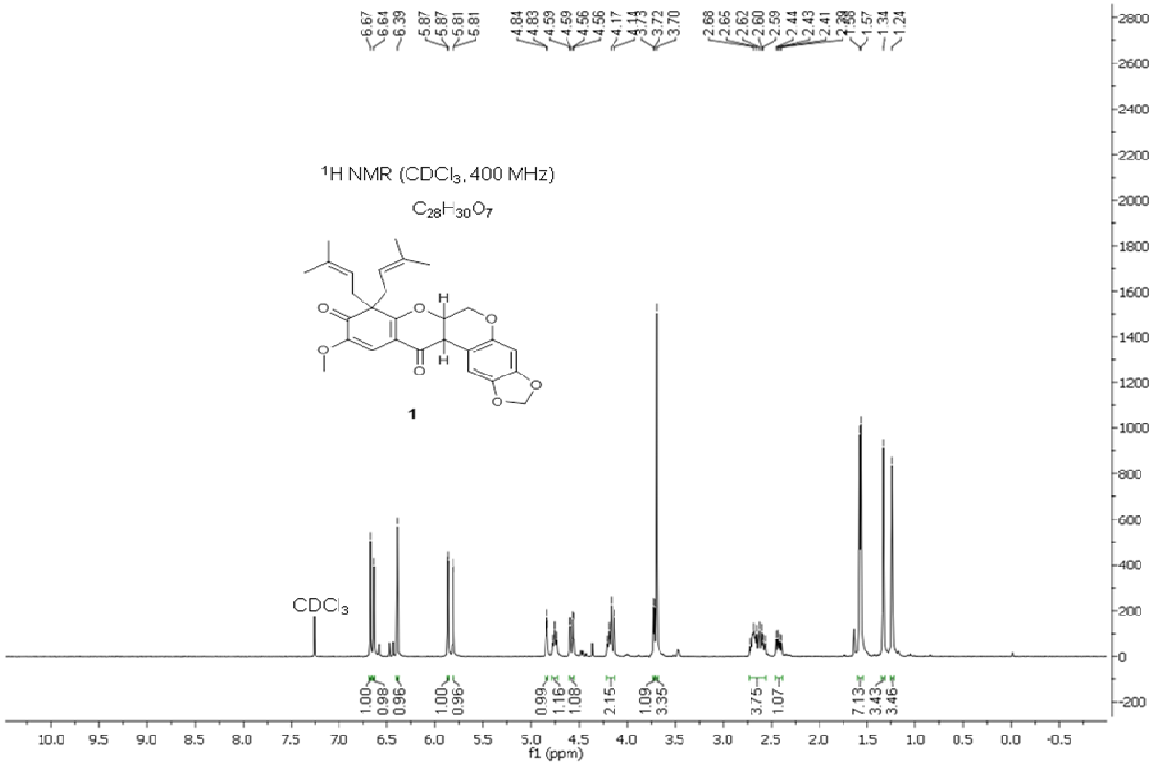
12a-hydroxyisomillettone (**10**): pale yellow powder; $[\alpha]^{20}_{D}$ -108.0 (*c* 0.08, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 209 (4.49) nm; 240 (sh, 4.10) nm; 296 (4.10) nm; ECD (MeOH) 245 ($\Delta\epsilon$ 4.39), 277 (-2.20), 299 (2.34), 322 (-7.26) nm; IR (film) ν_{max} 3462, 3019, 2917, 2848, 1676, 1610, 1480, 1454, 1363, 1334, 1296, 1245, 1217, 1169, 1087, 1040, 941, 910, 758, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 6.53[a] (H-1), 5.84 (br d, *J* = 8.3 Hz, H-2a), 6.45 (s, H-4), 4.57[a] (H-6ax), 4.47[a] (H-6eq), 4.57[a] (H-6a), 6.53[a] (H-10), 7.81 (d, *J* = 8.5 Hz, H-11), 2.93 (dd, *J* = 15.9, 8.5 Hz, H-1□a), 3.29 (dd, *J* = 15.7, 9.7 Hz, H-1□b), 5.24 (t, *J* = 8.8 Hz, H-2□), 4.94 (s, H-4□a), 5.06 (s, H-4□b), 1.76 (s, H-5□), 4.47[a] (OH-12a), and ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 106.2 (C-1), 110.2 (C-1a), 142.7 (C-2), 101.7 (C-2a), 149.8 (C-3), 99.4 (C-4), 149.7 (C-4a), 64.2 (C-6), 76.2 (C-6a), 158.0 (C-7a), 113.6 (C-8), 168.4 (C-9), 105.7 (C-10), 130.5 (C-11), 112.0 (C-11a), 191.3 (C-12), 68.1 (C-12a), 31.5 (C-1□), 88.4 (C-2□), 143.3 (C-3□), 113.1 (C-4□), 17.5 (C-5□); HRESIMS *m/z* 417.0937 $[M + Na]^+$ (calcd for $C_{22}H_{18}O_7Na$, 417.0950). [a]Overlapping signals.

milletosin (**11**): pale yellow powder; $[\alpha]^{20}_{D}$ -118.0 (*c* 0.09, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 204 (4.40) nm; 271 (4.20) nm; 304 (3.88) nm; ECD (MeOH) 240 ($\Delta\epsilon$ -4.62), 274 (3.77), 301 (0.80), 330 (-5.41) nm; IR (film) ν_{max} 3452, 2924, 2850, 1676, 1600, 1578, 1505, 1480, 1375, 1331, 1274, 1211, 1166, 1112, 1084, 1033, 995, 891, 837, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 6.54 (s, H-1), 5.85 (dd, *J* = 7.6, 1.2 Hz, H-2a), 6.46[a] (H-4), 4.61 (dd, 12.1, 2.3 Hz, H-6ax), 4.47 (d, 12.1 Hz, H-6eq), 4.54 (d, 1.5 Hz, H-6a), 6.46[a] (H-10), 7.71 (d, *J* = 8.7 Hz, H-11), 6.59 (d, *J* = 9.9 Hz, H-1□), 5.56 (d, *J* = 10.1 Hz, H-2□), 1.40 (s, H-4□), 1.45 (s, H-5□), 4.42 (s, OH-12a), and ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 106.2 (C-1), 110.1 (C-1a), 142.6 (C-2), 101.7 (C-2a), 149.9 (C-3), 99.5 (C-4), 149.7 (C-4a), 64.3 (C-6), 76.4 (C-6a), 157.0 (C-7a), 109.5 (C-8), 161.2 (C-9), 112.3 (C-10), 129.0 (C-11), 111.4 (C-11a), 191.6 (C-12), 68.0 (C-12a), 115.8 (C-1□), 129.3 (C-2□), 78.4 (C-3□), 28.7 (C-4□), 28.9 (C-5□); HRESIMS *m/z* 417.0941 $[M + Na]^+$ (calcd for $C_{22}H_{18}O_7Na$, 417.0950). [a]Overlapping signals.

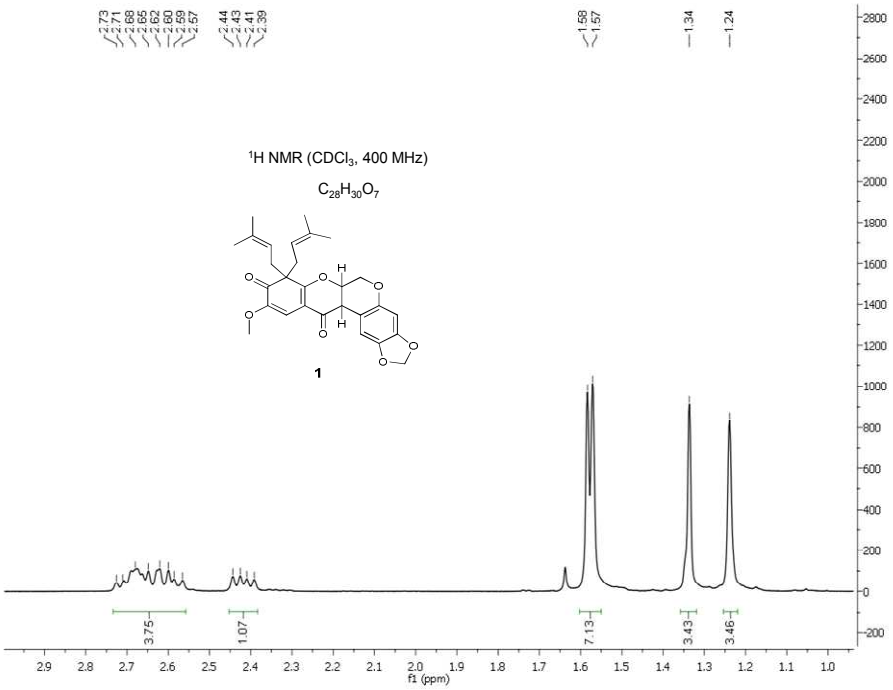
12a-hydroxyerythynone (**13**): pale yellow powder; $[\alpha]^{20}_{D}$ +34.0 (*c* 0.09, MeOH); UV (MeOH) λ_{max} (log ε) 207 (4.55) nm; 255 (4.31) nm; 320 (3.83) nm; ECD (MeOH) 233 ($\Delta\epsilon$ -3.08), 246 (2.64), 287 (2.82), 335 (1.19), 372 (-2.02) nm; IR (film) ν_{max} 3440, 2927, 2857, 1673, 1638, 1597, 1511, 1470, 1394, 1378, 1331, 1277, 1214, 1154, 1109, 1043, 888, 758, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 6.59[a] (H-1), 6.48 (s, H-4), 4.61 (dd, 12.1, 2.4 Hz, H-6ax), 4.48 (d, 12.0 Hz, H-6eq), 4.55 (d, 1.4 Hz, H-6a), 7.23 (s, H-11), 6.59[a] (H-1□), 5.57 (d, *J* = 10.1 Hz, H-2□), 1.43 (s, H-4□), 1.51 (s, H-5□), 3.74 (s, OMe-2), 3.81 (s, OMe-3), 3.85 (s, OMe-10), 4.37 (br s, OH-12a), and ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 109.9[a] (C-1), 109.2 (C-1a), 144.4 (C-2), 151.5 (C-3), 101.5 (C-4), 148.9 (C-4a), 64.3 (C-6), 76.9 (C-6a), 152.4 (C-7a), 110.6 (C-8), 151.2 (C-9), 144.9 (C-10), 108.1 (C-11), 109.9[a] (C-11a), 191.7 (C-12), 68.0 (C-12a), 116.1 (C-1□), 129.3 (C-2□), 78.9 (C-3□), 28.5 (C-4□), 28.9 (C-5□), 56.8[a] (OMe-2), 56.3 (OMe-3), 56.8[a] (OMe-10); HRESIMS *m/z* 463.1366 $[M + Na]^+$ (calcd for $C_{24}H_{24}O_8Na$, 463.1369). [a]Overlapping signals.

erythynone (**14**): pale yellow powder; $[\alpha]^{20}_{D}$ +12.0 (*c* 0.09, MeOH); UV (MeOH) λ_{max} (log ε) 206 (4.50) nm; 255 (4.19) nm; 320 (3.76) nm; ECD (MeOH) 233 ($\Delta\epsilon$ -1.00), 247 (1.34), 289 (1.54), 336 (1.00), 370 (-1.29) nm; IR (film) ν_{max} 2927, 2857, 1667, 1638, 1597, 1511, 1467, 1391, 1378, 1350, 1274, 1207, 1173, 1131, 1100, 1090, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.82 (s, H-1), 6.46 (s, H-4), 4.63 (dd, J = 12.0, 3.1 Hz, H-6ax), 4.18 (d, 12.1 Hz, H-6eq), 4.89 (t, 3.4 Hz, H-6a), 7.28 (s, H-11), 3.85[a] (H-12a), 6.64 (d, J = 10.1 Hz, H-1□), 5.58 (d, J = 10.0 Hz, H-2□), 1.44 (s, H-4□), 1.52 (s, H-5□), 3.78 (s, OMe-2), 3.81 (s, OMe-3), 3.85[a] (OMe-10), and ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 110.7 (C-1), 105.2 (C-1a), 144.2 (C-2), 149.8 (C-3), 101.3 (C-4), 147.8 (C-4a), 66.8 (C-6), 73.0 (C-6a), 152.6 (C-7a), 110.6 (C-8), 150.4 (C-9), 144.6 (C-10), 108.2 (C-11), 111.6 (C-11a), 189.7 (C-12), 44.8 (C-12a), 116.4 (C-1□), 129.2 (C-2□), 78.6 (C-3□), 28.4 (C-4□), 28.8 (C-5□), 56.7[a] (OMe-2), 56.3 (OMe-3), 56.7[a] (OMe-10); HRESIMS *m/z* 447.1436 $[M + Na]^+$ (calcd for $C_{24}H_{24}O_7Na$, 447.1420). [a]Overlapping signals.

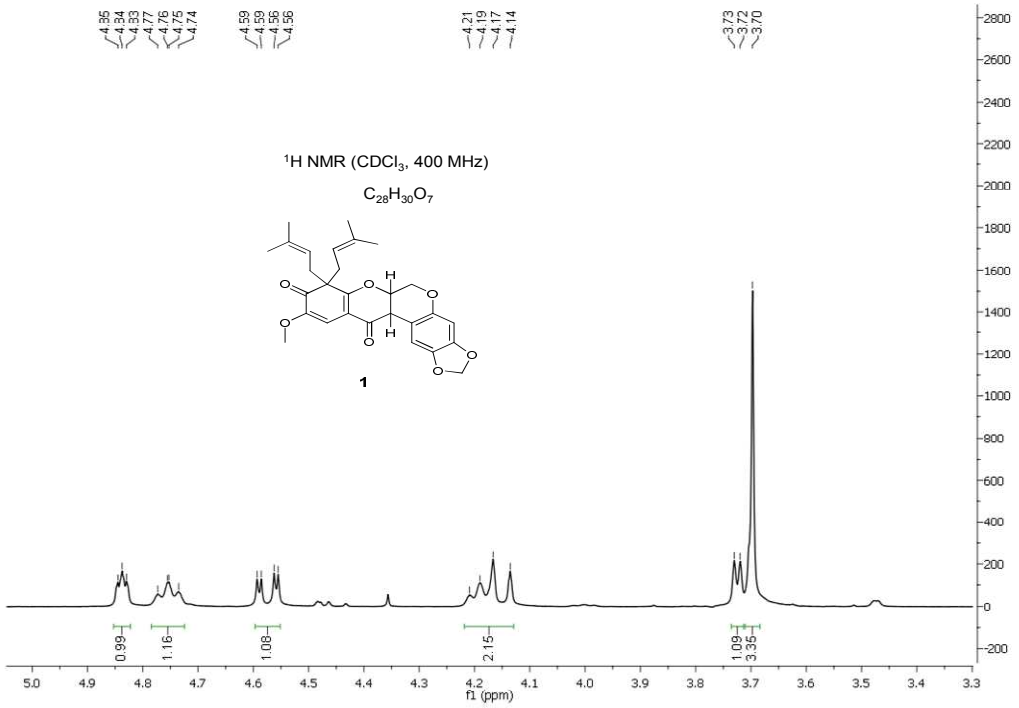
S9. ^{1}H NMR spectrum of **1** from -1.0 to 10.0 ppm ($CDCl_3$, 400 MHz).



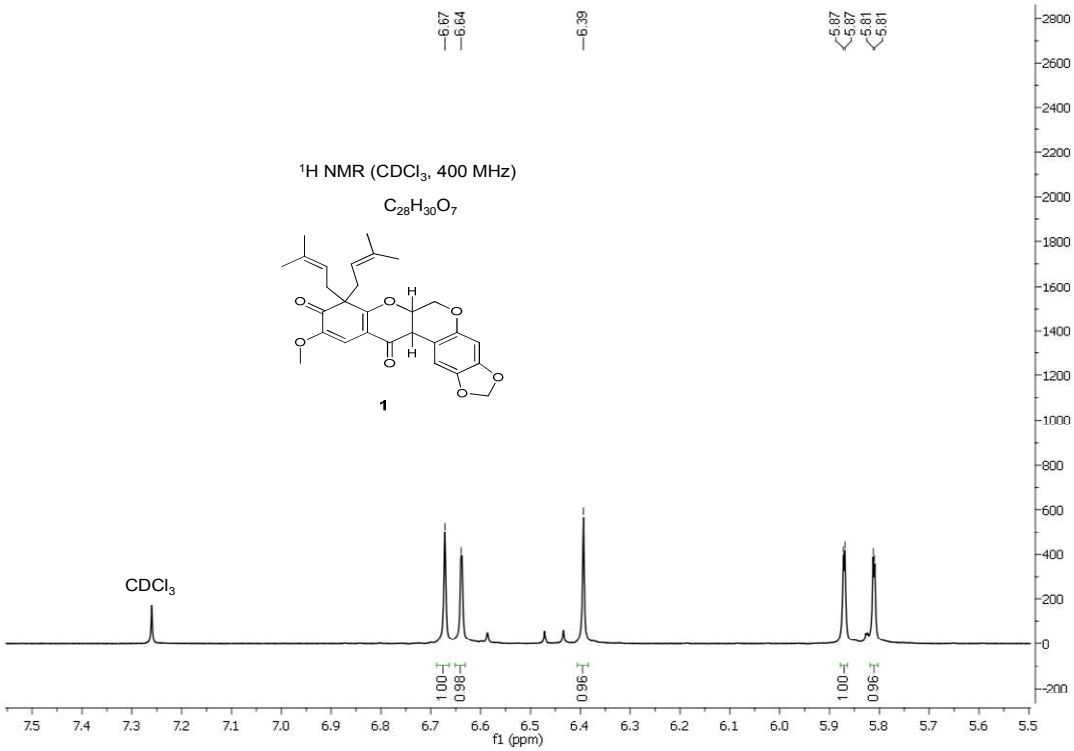
S10. Amplification of region 1.0-3.0 ppm of ^{1}H NMR spectrum of **1** ($CDCl_3$, 400 MHz).



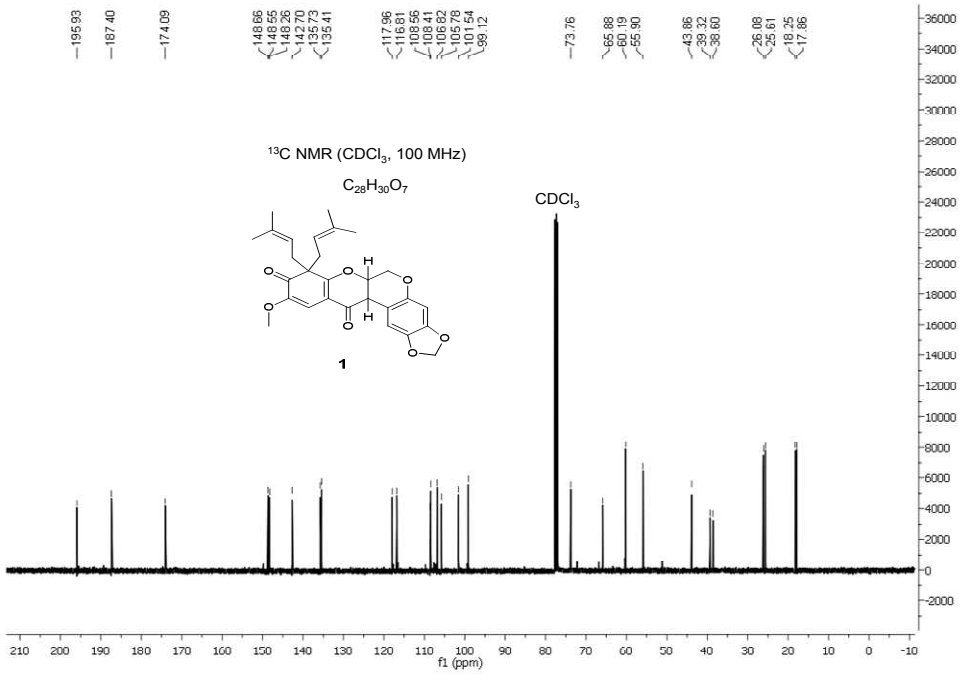
S11. Amplification of region 3.3-5.0 ppm of ^{1}H NMR spectrum of **1** ($CDCl_3$, 400 MHz).



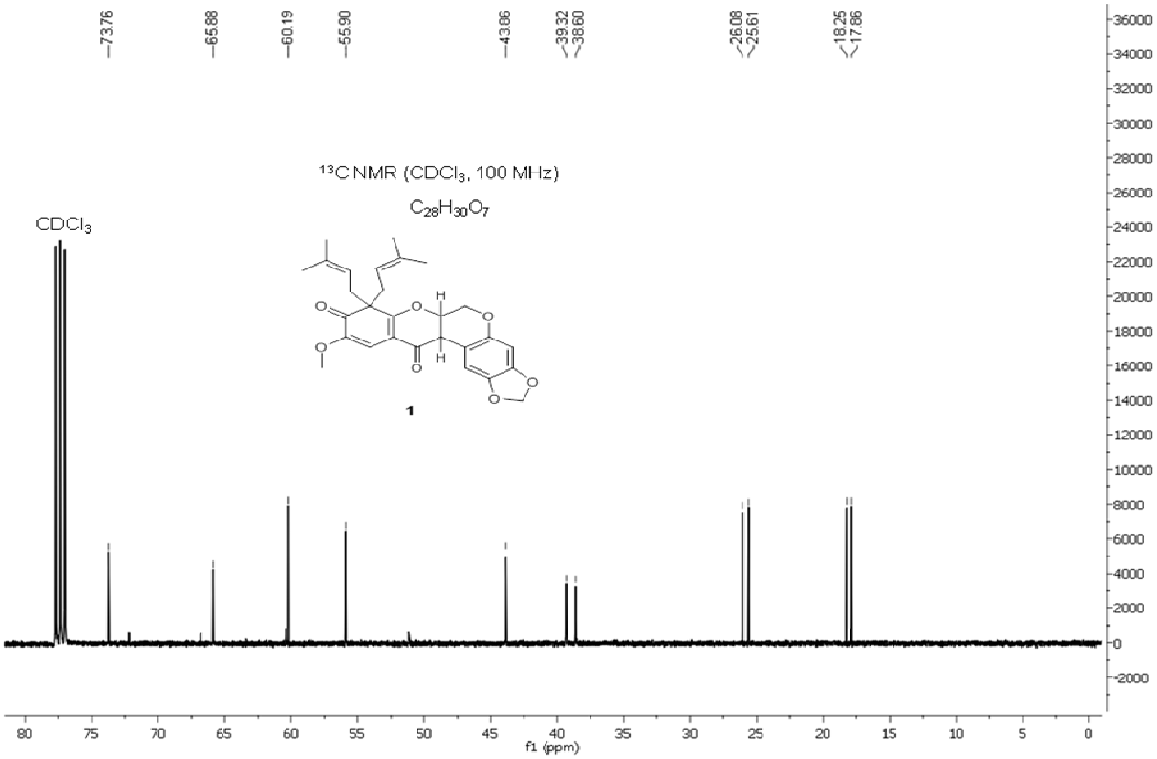
S12. Amplification of region 5.5-7.5 ppm of ^{1}H NMR spectrum of **1** ($CDCl_3$, 400 MHz).



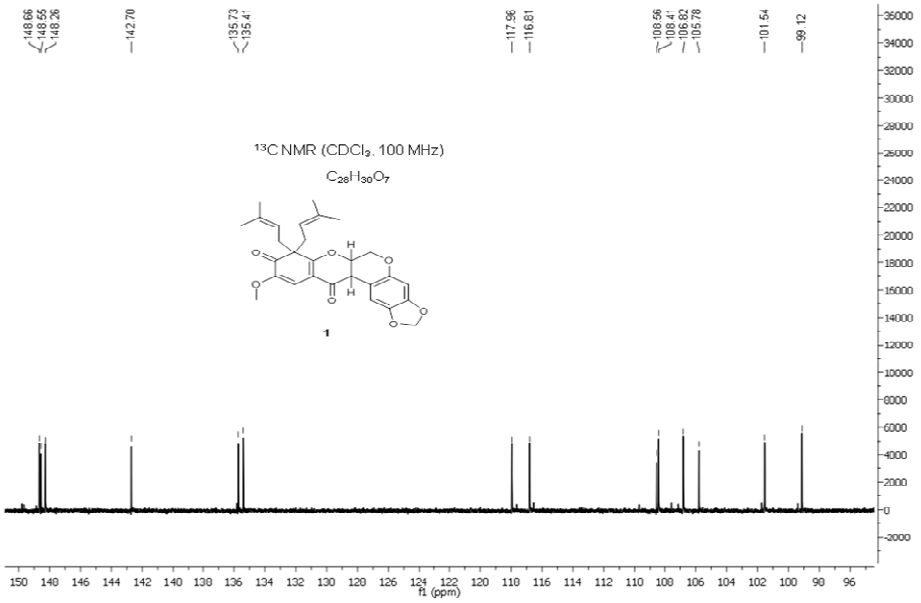
S13. ^{13}C NMR spectrum of **1** from -10.0 to 210 ppm ($CDCl_3$, 100 MHz).



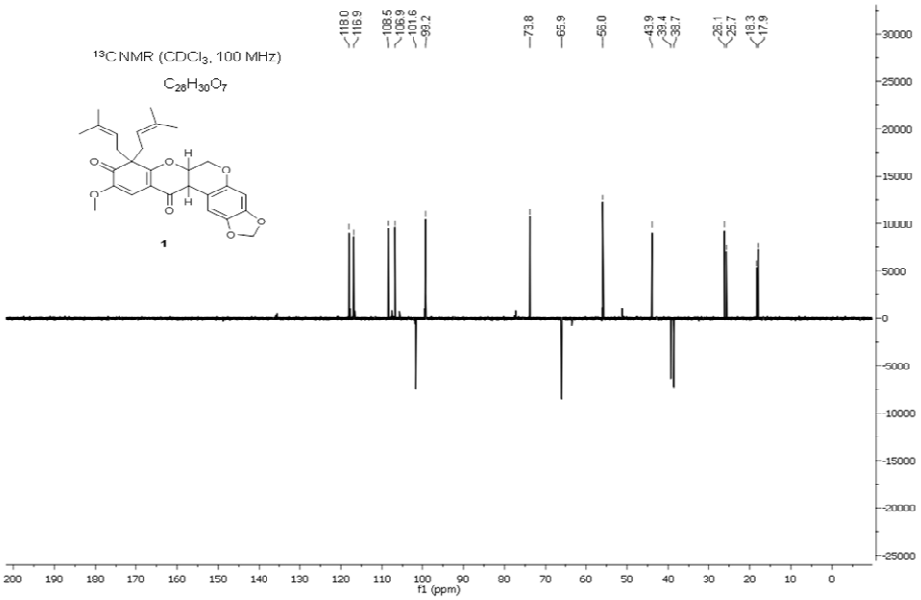
S14. Amplification of region 0 - 80.0 ppm ^{13}C NMR spectrum of **1** ($CDCl_3$, 100 MHz).



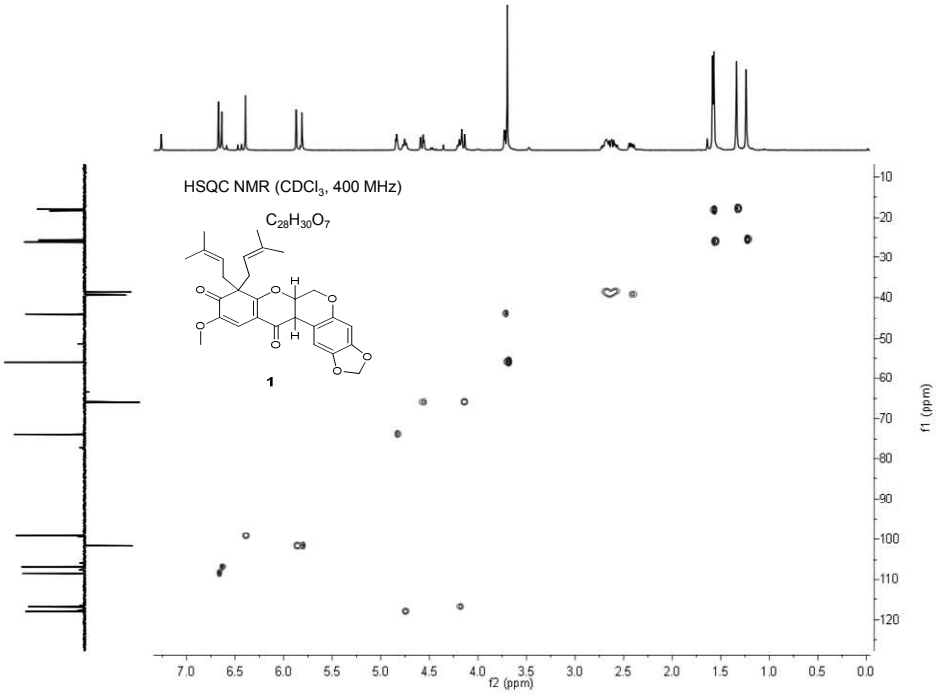
S15. Amplification of region 95.0 - 150.0 ppm ^{13}C NMR spectrum of **1** ($CDCl_3$, 100 MHz).



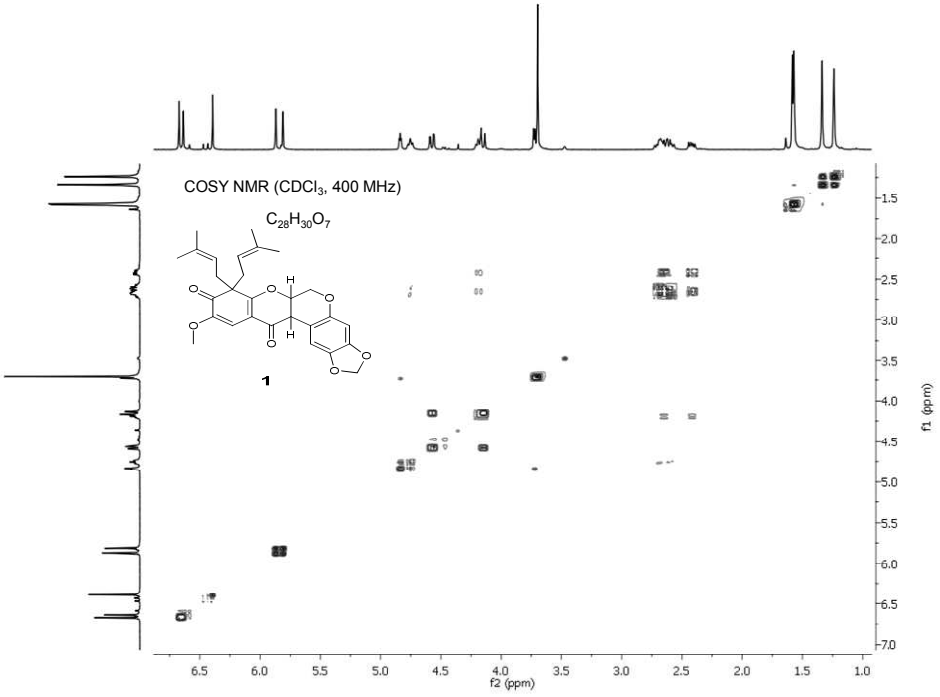
S16. ^{13}C DEPT 135 NMR spectrum of **1** ($CDCl_3$, 100 MHz).



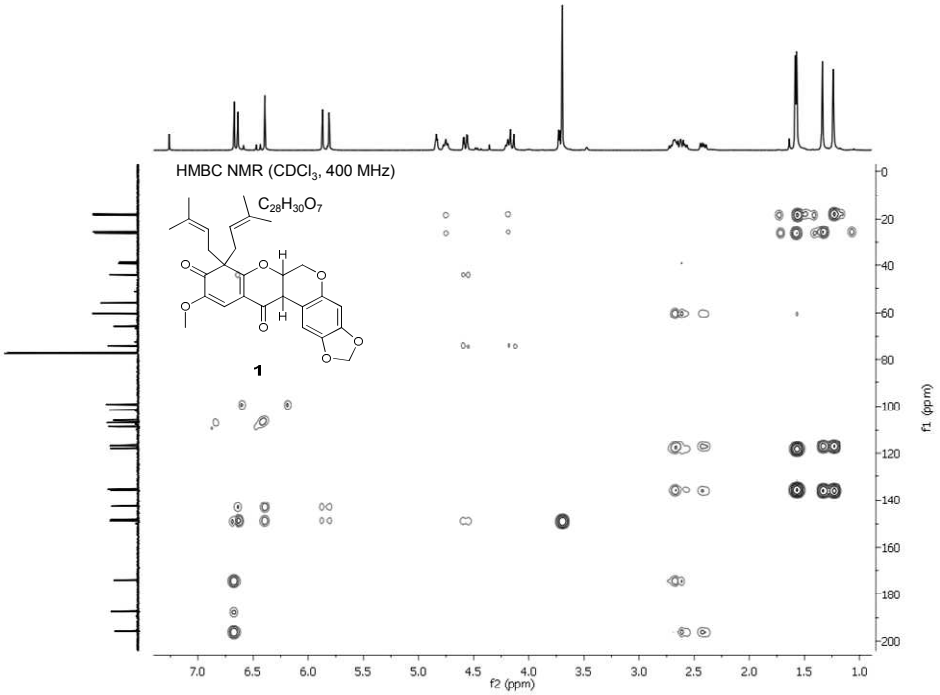
S17. HSQC NMR spectrum of **1** ($CDCl_3$, 400 MHz).



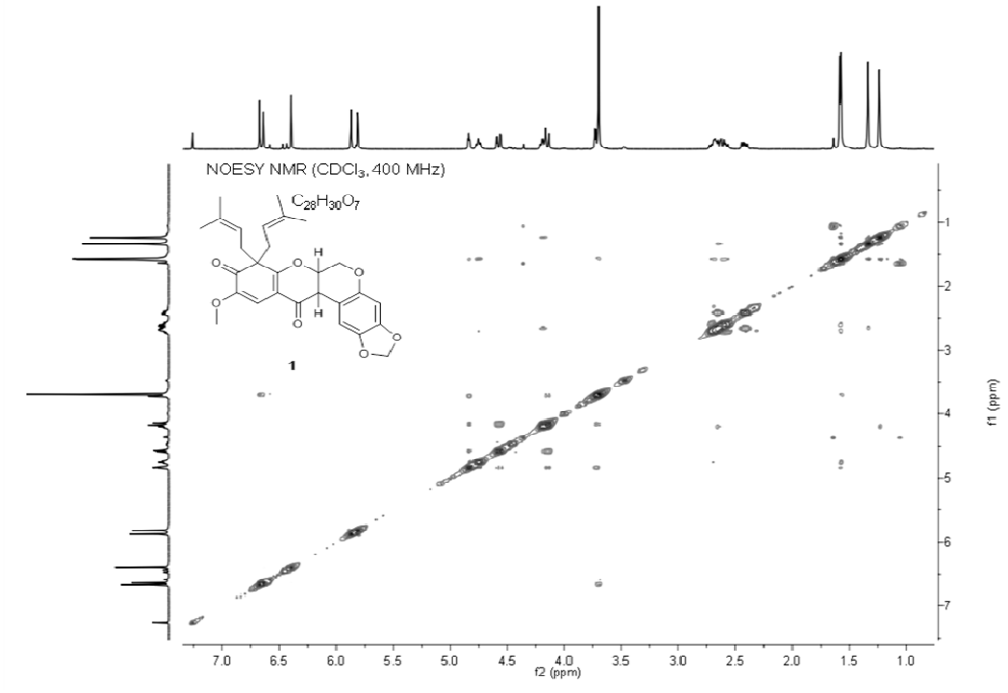
S18. ^{1}H-^{1}H COSY NMR spectrum of **1** ($CDCl_3$, 400 MHz).



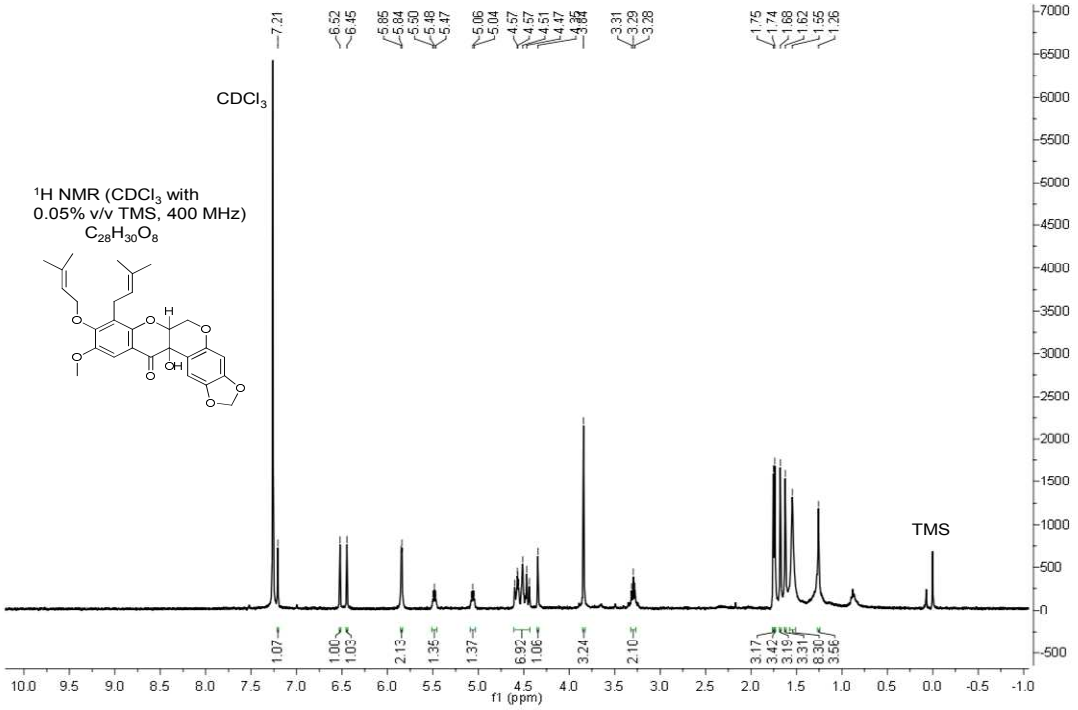
S19. HMBC NMR spectrum of **1** ($CDCl_3$, 400 MHz).



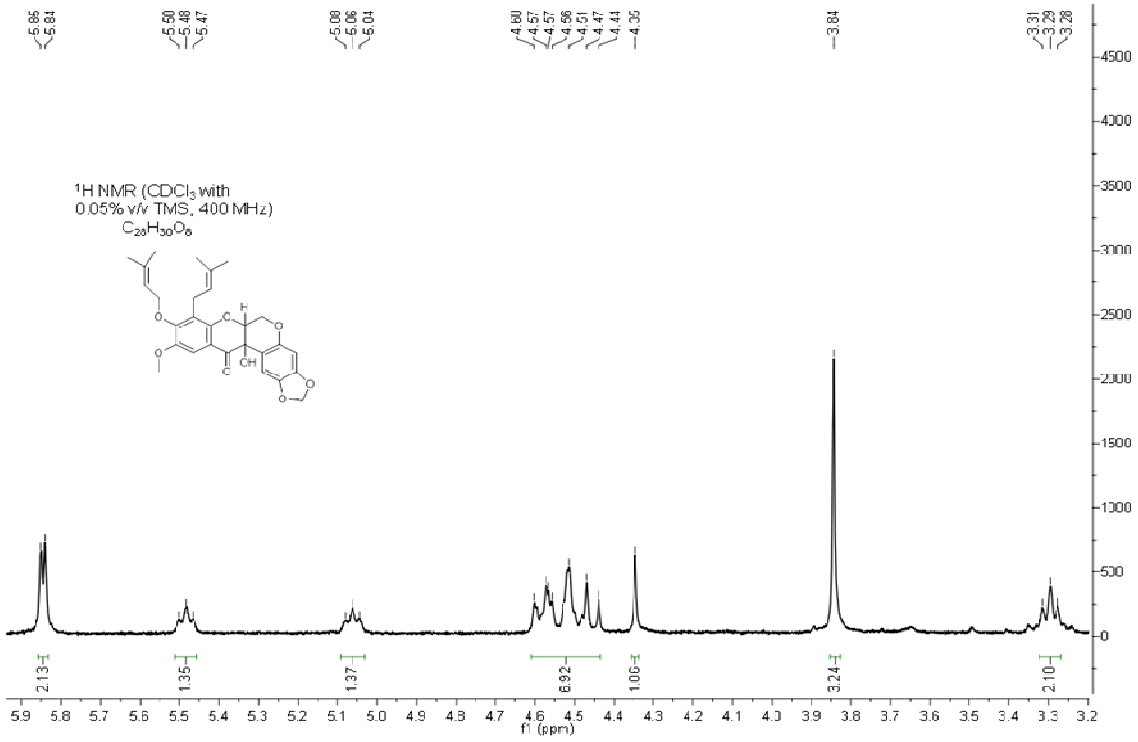
S20. NOESY NMR spectrum of **1** ($CDCl_3$, 400 MHz).



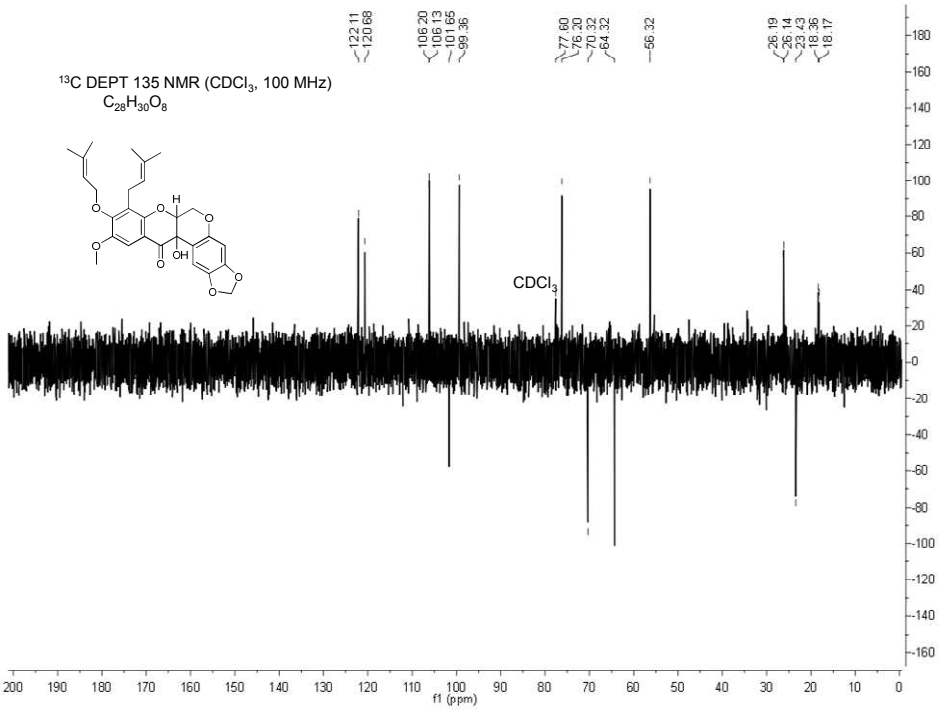
S21. ^{1}H NMR spectrum of **2** from -1.0 to 10.0 ppm ($CDCl_3$ with 0.05% v/v TMS, 400 MHz).



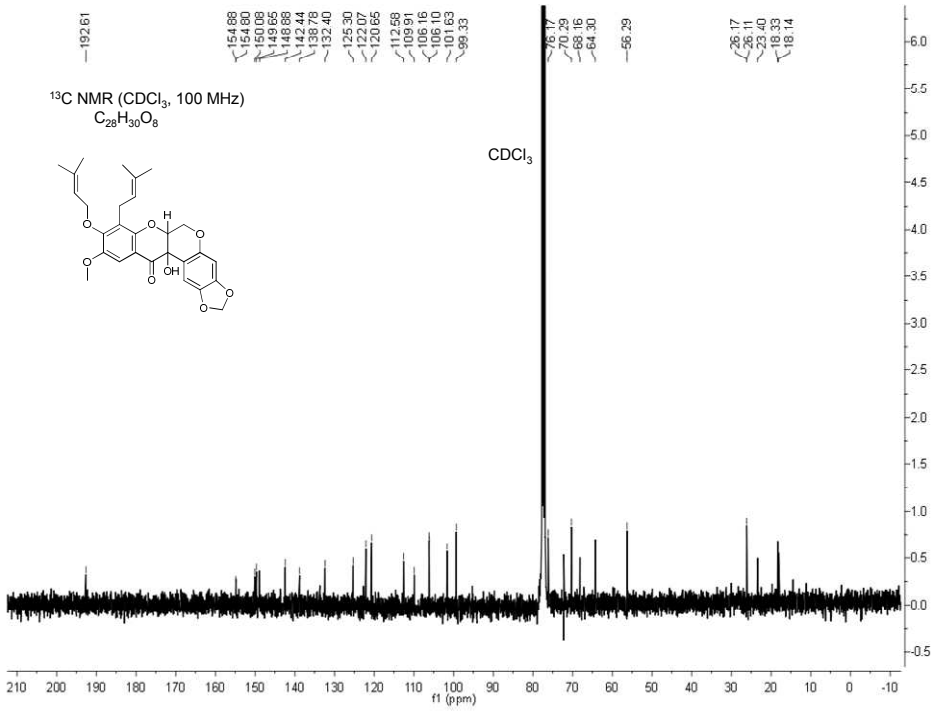
S22. Amplification of region 3.2 – 5.9 ppm ^{1}H NMR spectrum of **2** ($CDCl_3$ with 0.05% v/v TMS, 400 MHz).



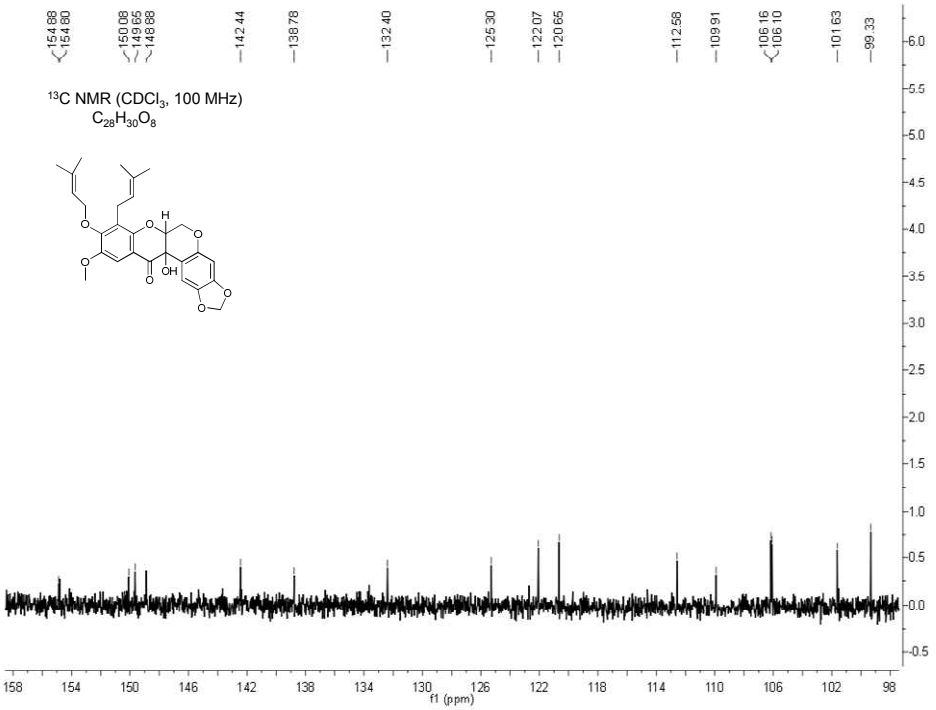
S23. ^{13}C DEPT 135 NMR spectrum of **2** ($CDCl_3$, 100 MHz).



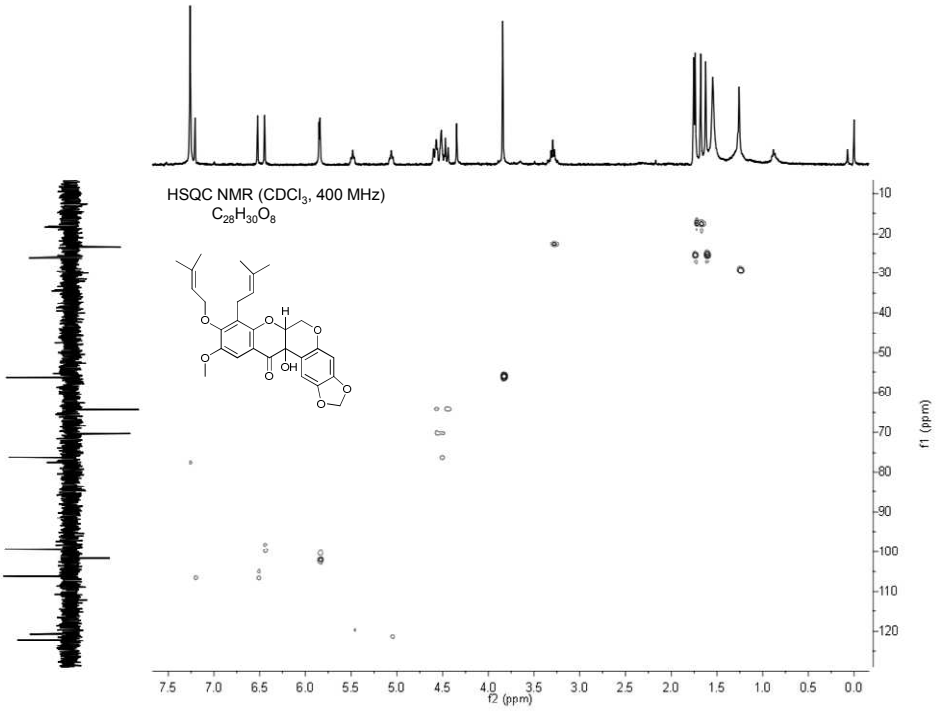
S24. ^{13}C NMR spectrum of **2** ($CDCl_3$, 100 MHz).



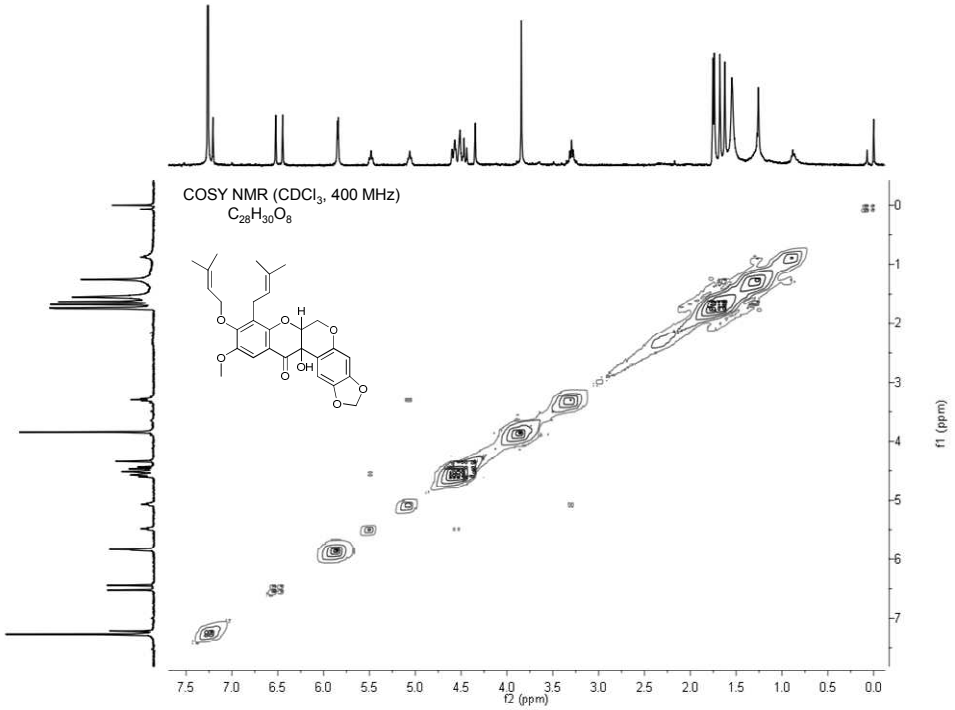
S25. Amplification of region 98.0 – 158.0 ppm ^{13}C NMR spectrum of **2** ($CDCl_3$, 100 MHz).



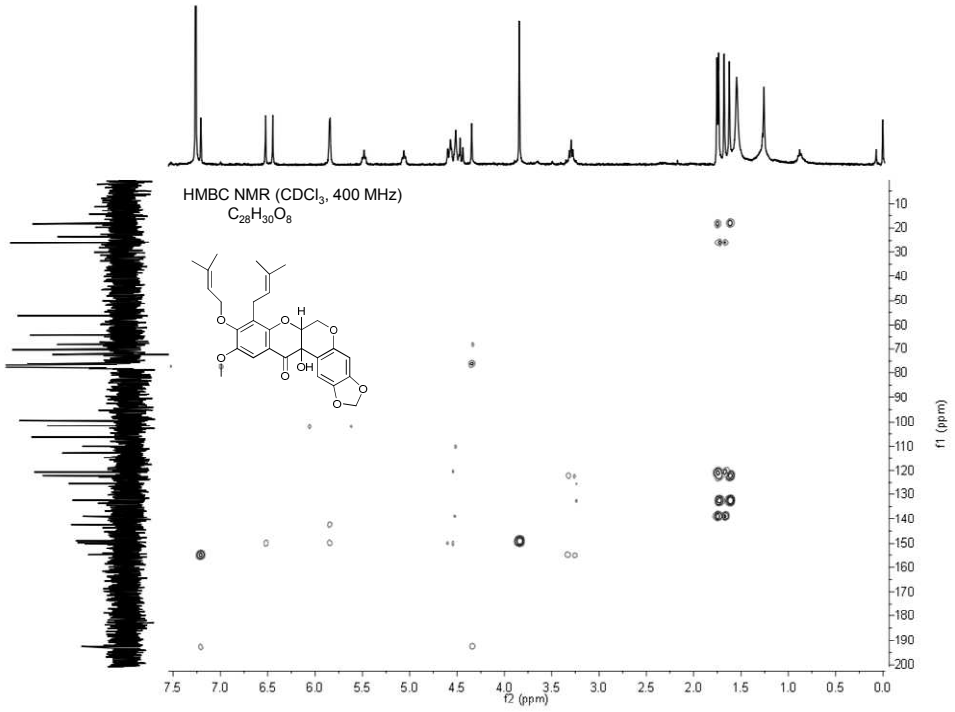
S26. HSQC NMR spectrum of **2** ($CDCl_3$, 400 MHz).



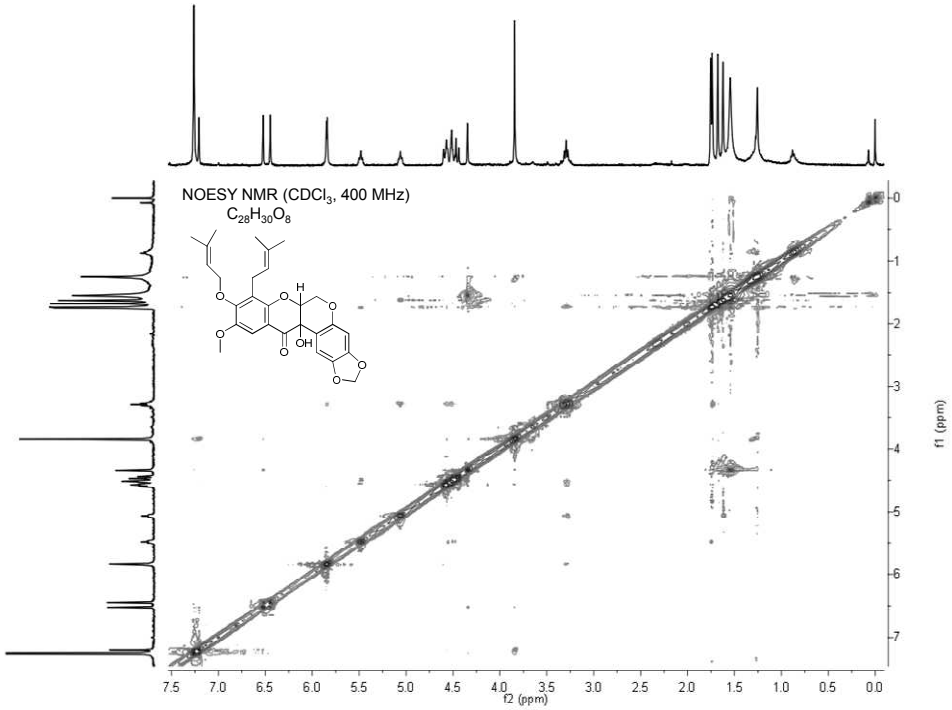
S27. ^{1}H-^{1}H COSY NMR spectrum of **2** ($CDCl_3$, 400 MHz).



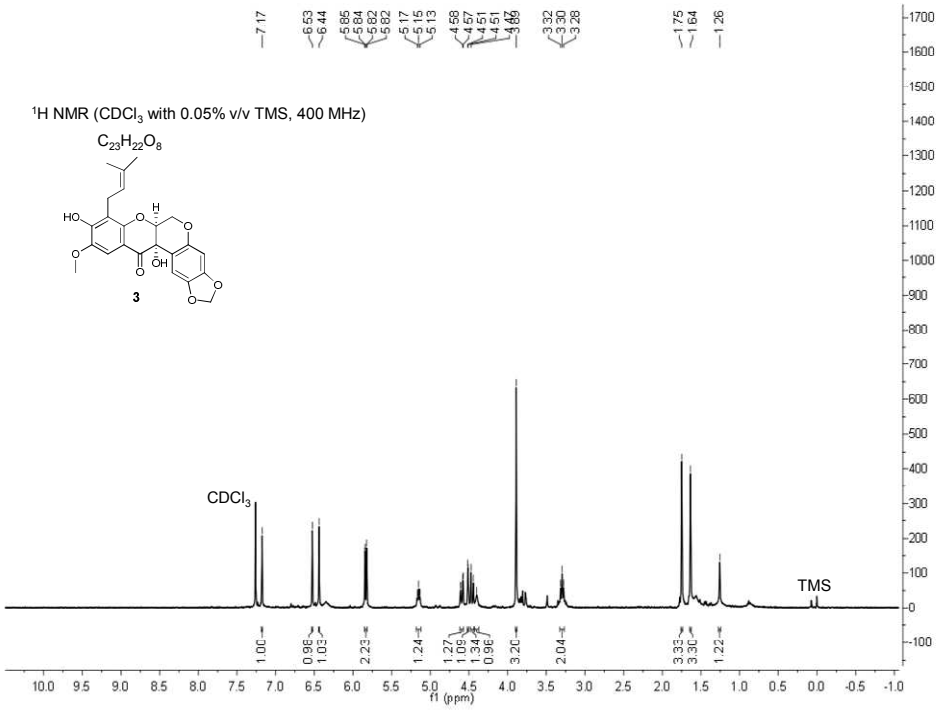
S28. HMBC NMR spectrum of **2** ($CDCl_3$, 400 MHz).



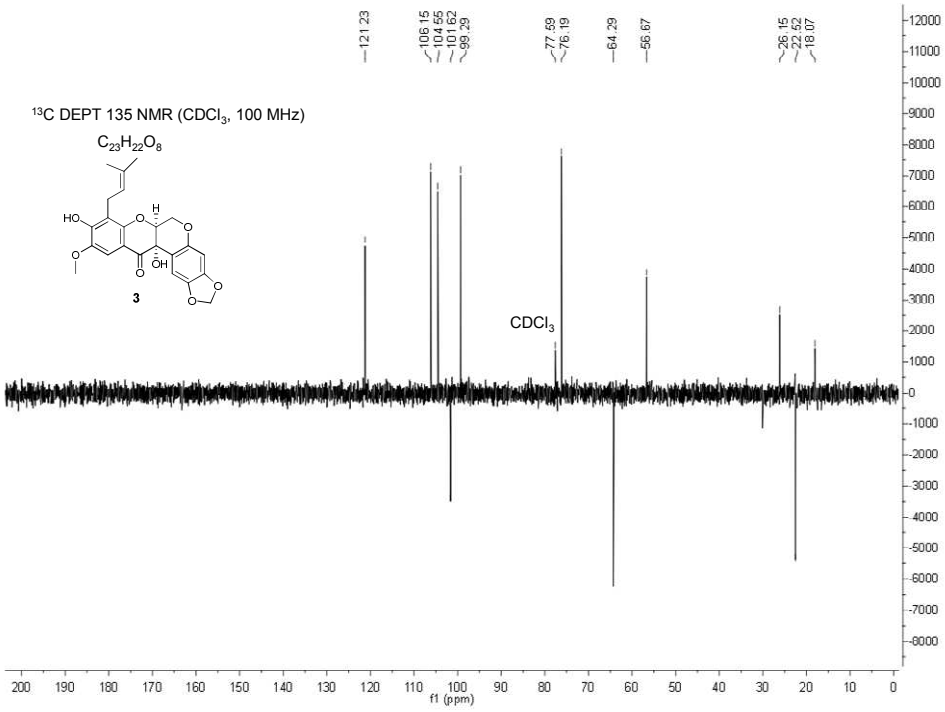
S29. NOESY NMR spectrum of **2** ($CDCl_3$, 400 MHz).



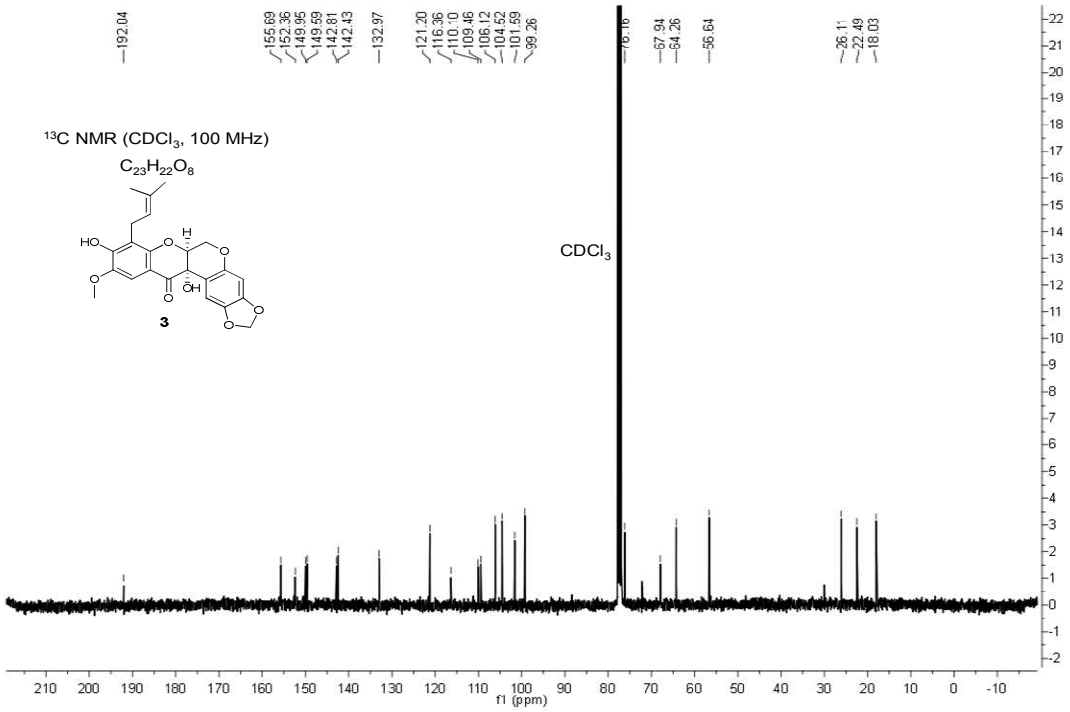
S30. ^{1}H NMR spectrum of **3** from -1.0 to 10.0 ppm ($CDCl_3$ with 0.05% v/v TMS, 400 MHz).



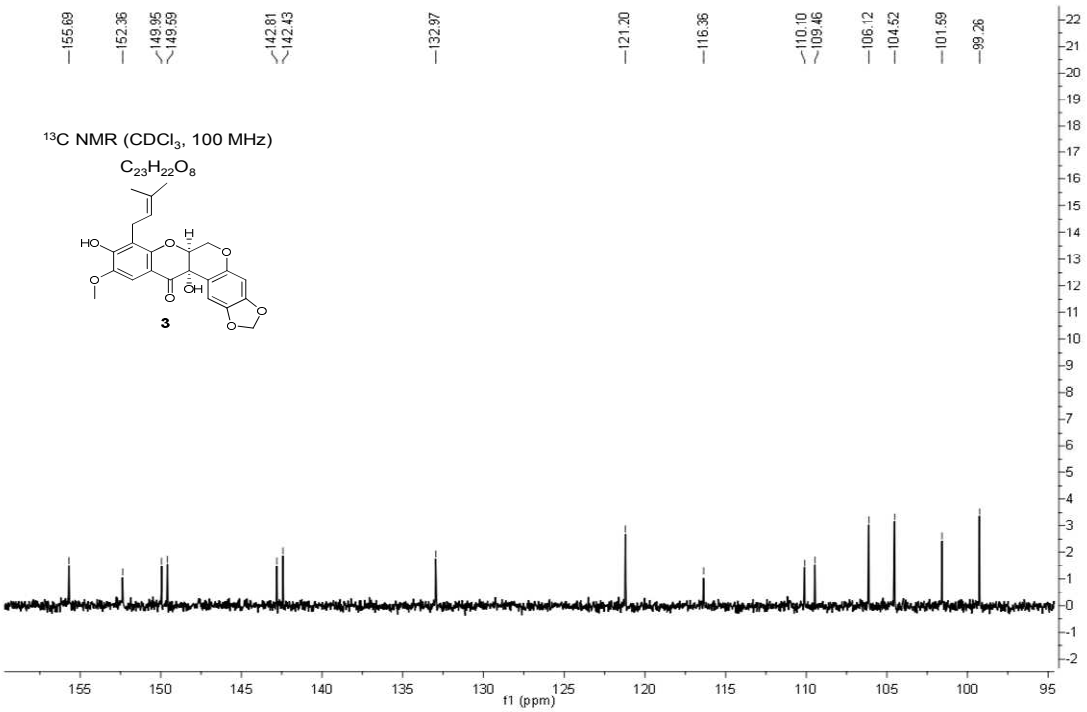
S31. ^{13}C DEPT 135 NMR spectrum of **3** ($CDCl_3$, 100 MHz).



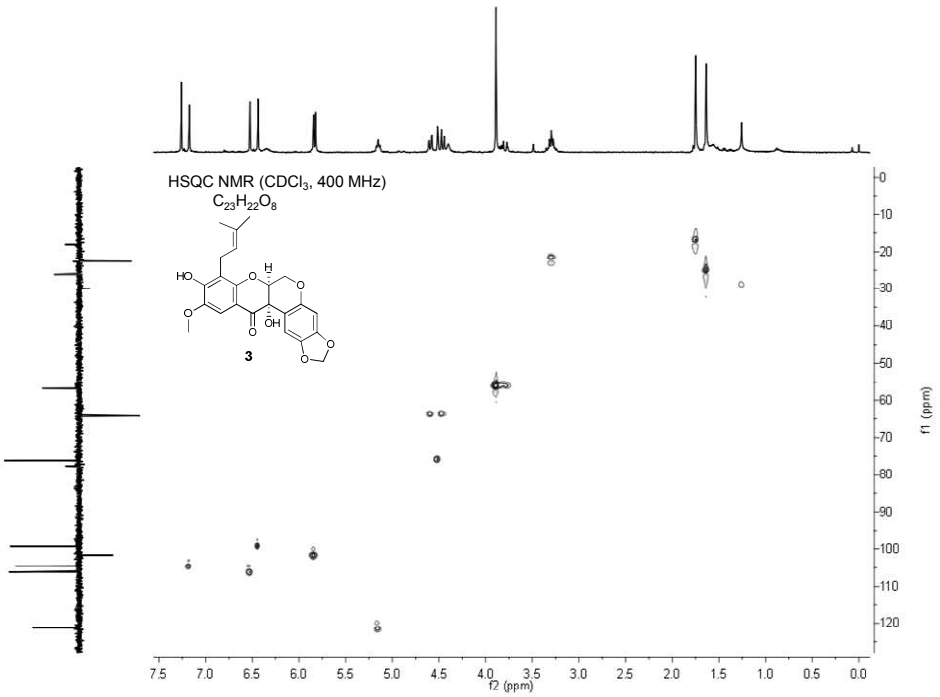
S32. ^{13}C NMR spectrum of **3** ($CDCl_3$, 100 MHz).



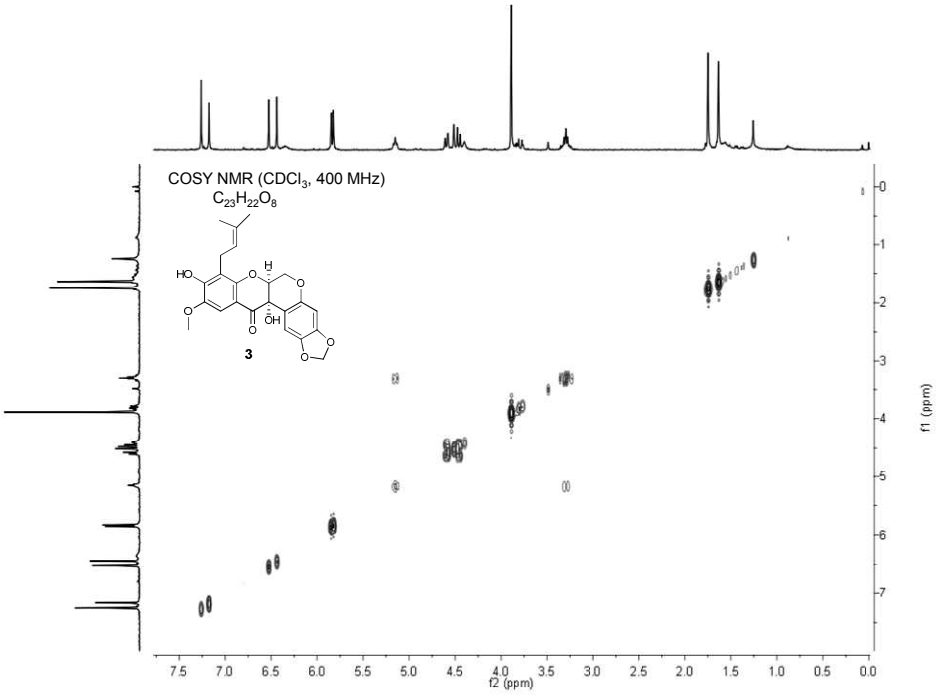
S33. Amplification of region 95.0 – 160.0 ppm ^{13}C NMR spectrum of **3** ($CDCl_3$, 100 MHz).



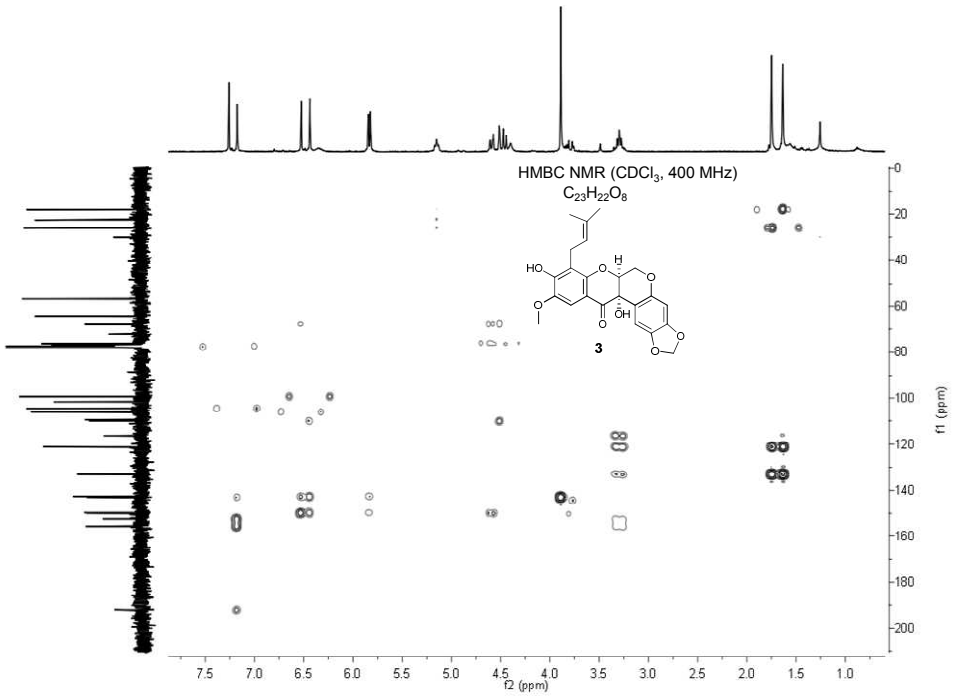
S34. HSQC NMR spectrum of **3** ($CDCl_3$, 400 MHz).



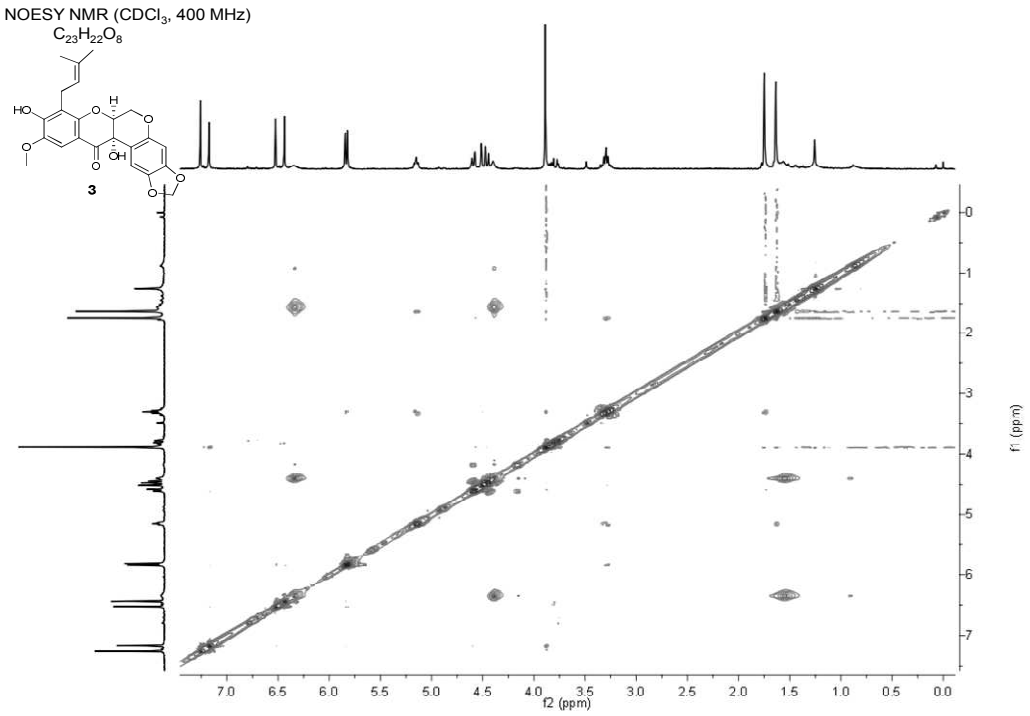
S35. ^{1}H-^{1}H COSY NMR spectrum of **3** ($CDCl_3$, 400 MHz).



S36. HMBC NMR spectrum of **3** ($CDCl_3$, 400 MHz).



S37. NOESY NMR spectrum of **3** ($CDCl_3$, 400 MHz).



S38. Procedures used for in vitro testing of isolates.

Quinone reductase induction assay. The quinone reductase induction assay was performed using Hepa 1c1c7 murine hepatoma cells, according to a standard procedure.[1,2] L-Sulforaphane was used as the positive control.

Mitochondria transmembrane potential (MTP) assay. The MTP assay was performed using HT-29 human colon cancer cells, according to a standard protocol.[3] Staurosporine was used as a positive control.

Cytotoxicity assay. Sulforhodamine B (SRB) assay was used for cytotoxicity-guided fractionation and for testing the cytotoxicity of isolated compounds against HT-29 cells, according to a standard protocol.[4] Paclitaxel was used as the positive control.

References:

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(2) Prochaska, H. J.; Santamaria, A. B. *Anal. Biochem.* **1988**, *169*, 328-336.

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(4) Pan, L.; Kardono, L. B. S.; Riswan, S.; Chai, H. B.; Carcache de Blanco, E. J.; Pannell, C. M.; Soejarto, D. D.; McCloud, T. G.; Newman, D. J.; Kinghorn, A. D. *J. Nat. Prod.* **2010**, *73*, 1873-1878.