SUPPLEMENTARY MATERIAL

An unambiguous and practical synthesis of Oroxylin A – a commonly misidentified flavone

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Abstract:

Oroxylin A, a major flavonoid in the extracts of *Oroxylum indicum* as well as *Scutellaria baicalensis* possesses useful medicinal properties. Many of the published routes claiming the synthesis of Oroxylin A (**1**) have in fact led to a regioisomer Negletein (**3**) that was misinterpreted as Oroxylin A (**1**). In the present work, we describe a novel, straight-forward and scalable semi-synthetic approach for rapid access to the title compound, the structure of which is unambiguously secured by NMR and X-ray crystallographic analysis of a derivative. This work also encompasses the synthesis of a glycosylated derivative of Oroxylin A *viz* OAGME (**2**), which has marked pharmacological importance.

Keywords: Oroxylin A; Negletein; *Oroxylum indicum; Scutellaria baicalensis;* semi-synthesis

6,7-Dimethylbaicalein (5): ^{1}H NMR (300 MHz, DMSO-d6)δ ppm: 12.76 (s, 1H, 5-OH), 8.08-8.11 (m, 2H, Ar), 7.57-7.59 (m, 3H, Ar), 7.04 (s, 1H), 6.98 (s, 1H), 3.92 (s, 3H, OMe), 3.72 (s, 3H, OMe). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.8-7.9 (m, 2H, Ar), 7.51-7.55 (m, 3H, Ar), 6.67 (s, 1H), 6.56 (s, 1H), 3.96 (s, 3H, OMe), 3.92 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$, 75 MHz) ppm: 182.70, 163.95, 158.89, 153.31, 153.00, 131.84, 131.26, 129.08, 126.23, 105.59, 90.64, 60.87, 56.34.

Negletein (3): ^{1}H NMR (300 MHz, DMSO-d6) δ ppm: 12.48 (s, 1H, 5-OH), 8.76 (s, 1H, 6-OH), 8.05-8.08 (m, 2H, Ar), 7.55-7.57 (m, 3H, Ar), 6.97 (s, 1H), 6.93 (s, 1H), 3.90 (s, 3H, OMe).

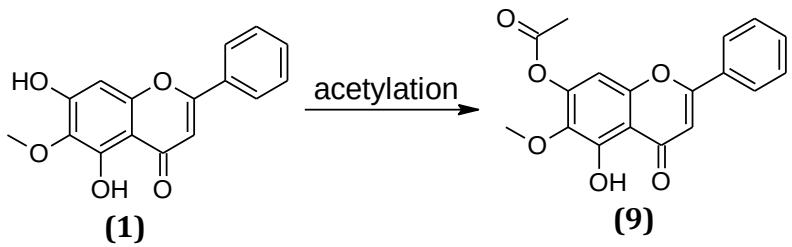
Table S1. Summary of publications misidentifying Oroxylin A (**1**) for Negletein (**3**) and *vice-versa*.

Sl. No	**Starting material/process**	**Claimed product**	**Actual outcome***	**Ref**
1	5,6,7-trimethyl baicalein (**4**) $\xrightarrow[\text{reflux}]{\text{HBr}}$	Oroxylin A (**1**)	Negletein (**3**)	Pham 2012, Huang 2003, Shaw 2004
2	5,6,7-trimethyl baicalein (**4**) $\xrightarrow[\text{reflux}]{\text{HBr}}$	Oroxylin A (**1**)	NMR data does not match	Tan 2015
3	Isolation from *Scutellaria oblanga* extract	Negletein (**3**)	Oroxylin A (**1**)	Rajendran 2016
4	Baicalin (**6**) or Baicalein (**8**) $\xrightarrow[\text{trasnformation}]{\text{Microbial}}$	Oroxylin A (**1**)	Negletein (**3**)	Kostzewa-Suslow 2007

5	Baicalein (**8**) $\xrightarrow{\text{E. coli}}$	Oroxylin A (**1**) and Negletein (**3**)	NMR assignments interchanged	Han 2016

*based on ^{1}H NMR data found in the respective publications

Preparation of 7-*O*-acetyl Oroxylin A (9)



Scheme S1. Preparation of 7-*O*-acetyl Oroxylin A (**9**)

To a solution of **1** (1 mmol) in 10 mL DMF, K_2CO_3 (2 mmol) and acetyl chloride (1.5 mmol) were added. After completion of the reaction, the product was worked up and isolated by a simple column chromatography as pale yellow solid (**9**) which was crystallized in acetone. ^{1}H NMR (300 MHz, DMSO-d6) δ ppm: 13.06 (s, 1H, 5-OH), 8.0 (m, 2H, Ar), 7.59 (m, 3H, Ar), 7.14 (s, 1H, H-8), 7.11 (s, 1H, H-3), 3.78 (s, 3H, OCH_3), 2.34 (s, 3H, $COCH_3$); ^{13}C NMR (DMSO-d6, 75MHz) δ ppm: 183.46, 168.69, 164.74, 153.22, 151.57, 149.48, 135.73, 132.87, 130.82, 129.62, 127.06, 109.63, 105.52, 102.47, 60.59, 20.88; melting range: 158-159 °C.

NMR of 7-*O*-acetyl Oroxylin A (natural): ^{1}H NMR (300 MHz, DMSO-d6) δ ppm: 13.06 (s, 1H, 5-OH), 8.0 (q, 2H, Ar), 7.59 (t, 3H, Ar), 7.15 (s, 1H, H-8), 7.11 (s, 1H, H-3), 3.78 (s, 3H, OCH_3), 2.34 (s, 3H, $COCH_3$); ^{13}C NMR (DMSO-d6, 75MHz) δ ppm: 183.48, 168.71, 164.74, 153.20, 151.59, 149.48, 135.73, 132.88, 130.82, 129.63, 127.06, 109.98, 109.63, 105.52, 102.48, 60.59, 20.88.

Figure S1. ORTEP diagram of 7-*O*-acetyl Oroxylin A (**9**).

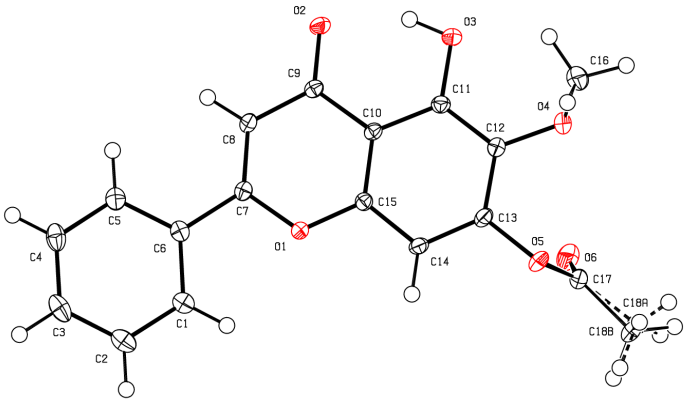


Figure S2. ^{1}H NMR spectrum of Baicalin methyl ester (**7**)

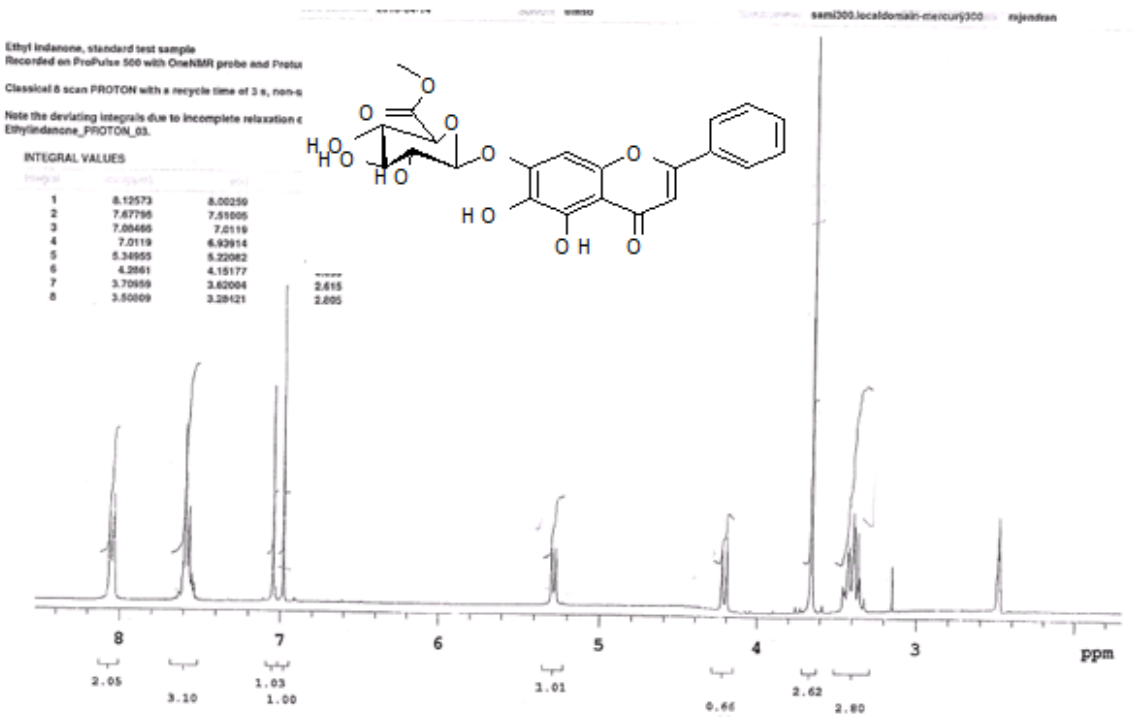


Figure S3. ^{13}C NMR spectrum of Baicalin methyl ester (**7**)

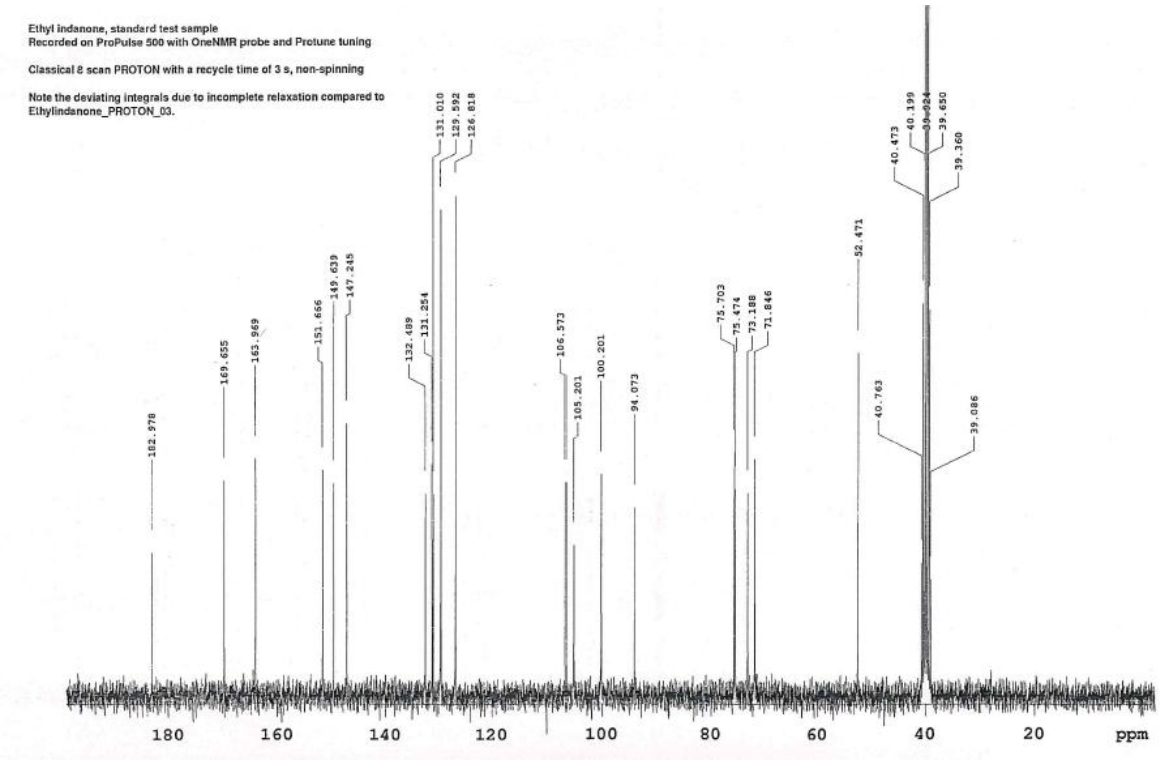


Figure S4. HRMS spectrum of Baicalin methyl ester (**7**)

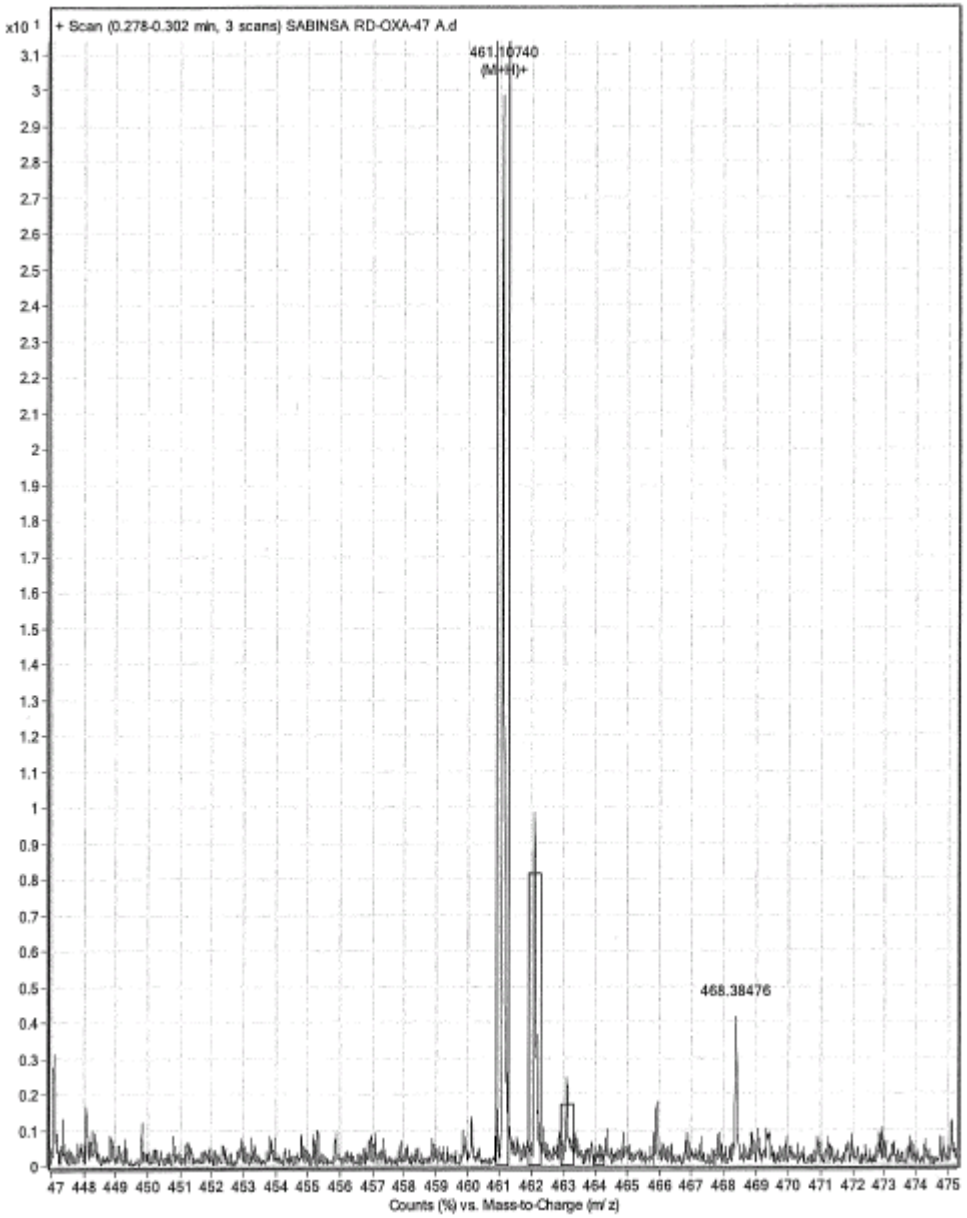


Figure S5. ^{1}H NMR spectrum of OAGME (**2**)

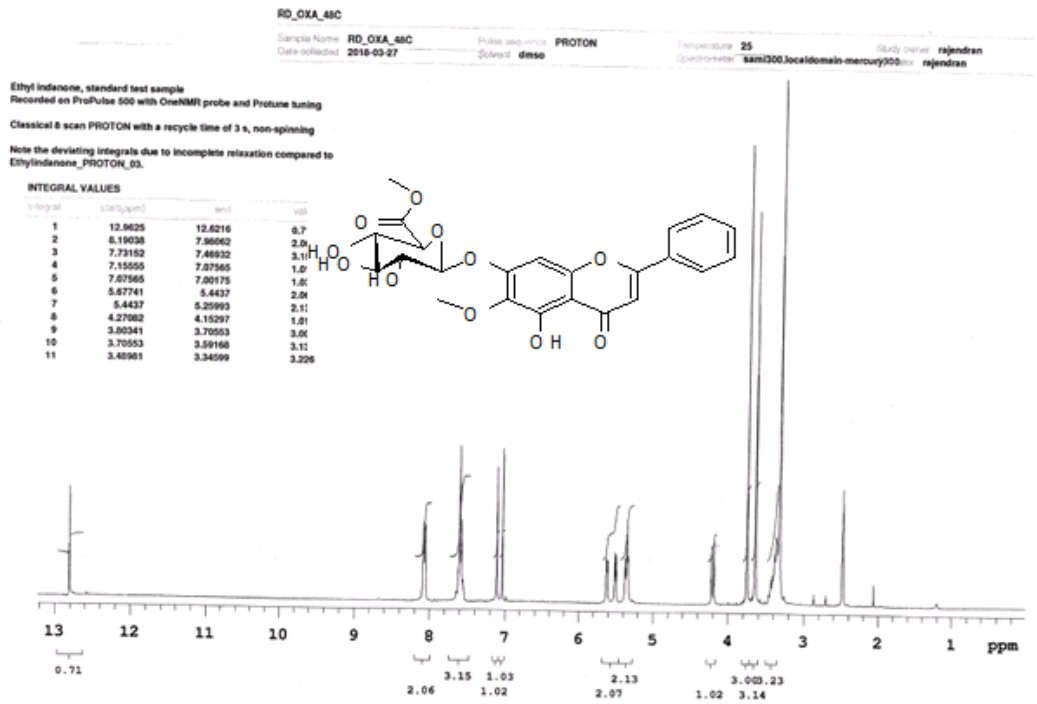


Figure S6. ^{13}C NMR spectrum of OAGME (**2**)

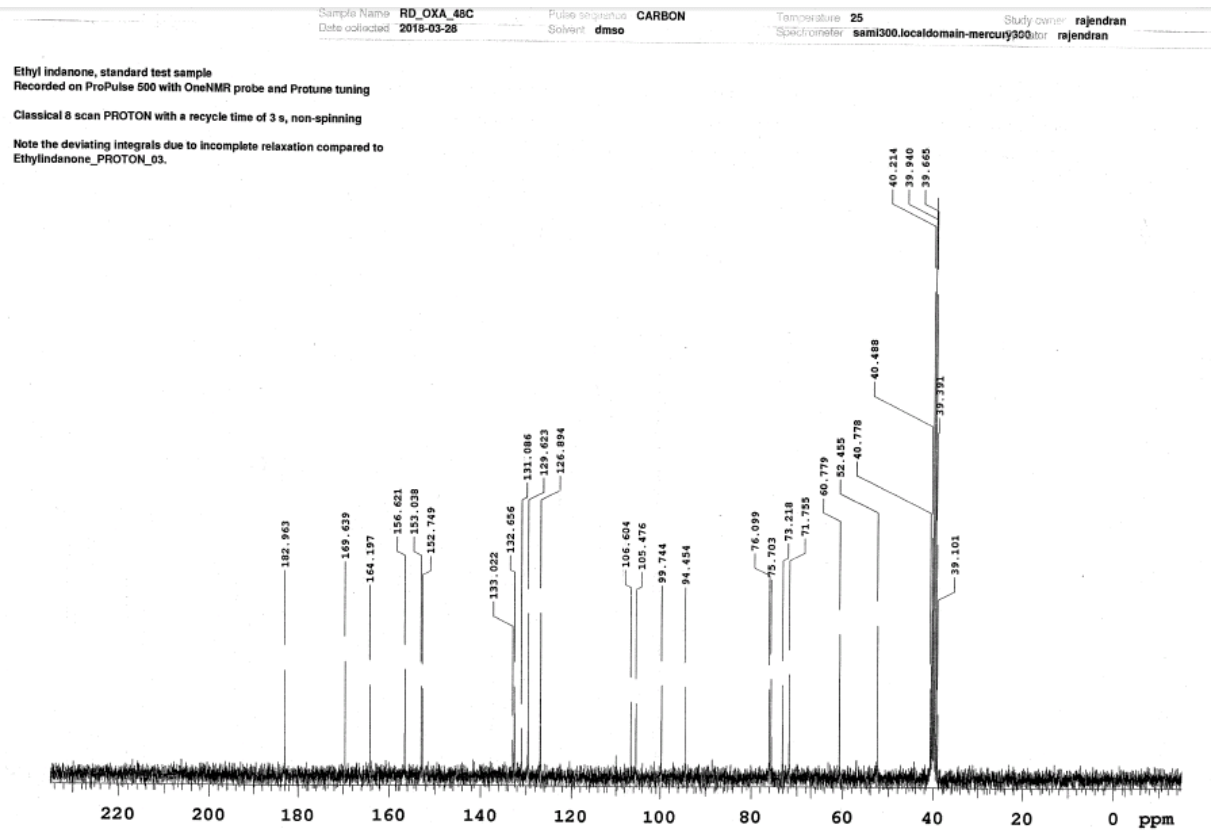


Figure S7. Mass spectrum of OAGME (**2**)

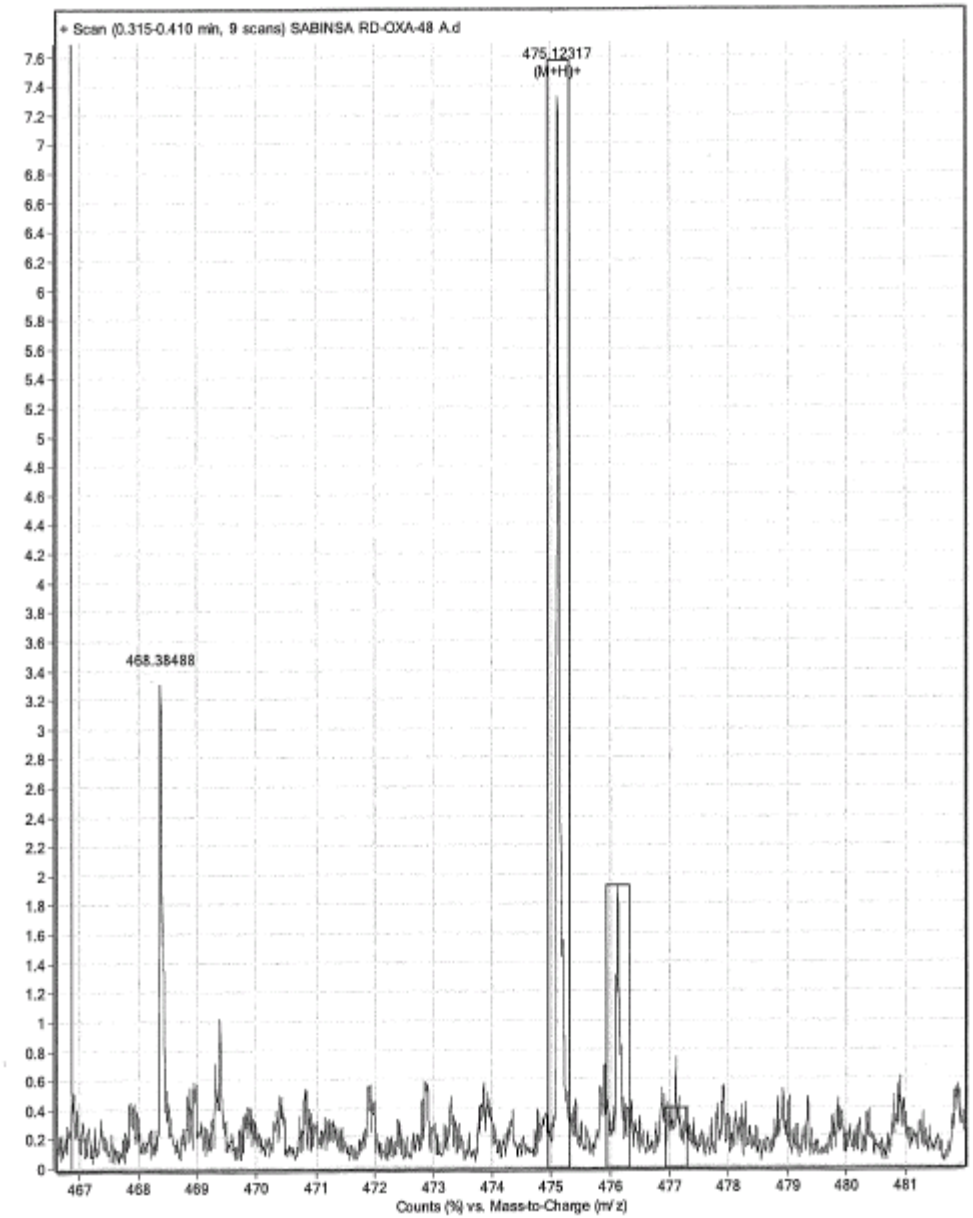


Figure S8. ^{1}H NMR spectrum of Oroxylin A (**1**)

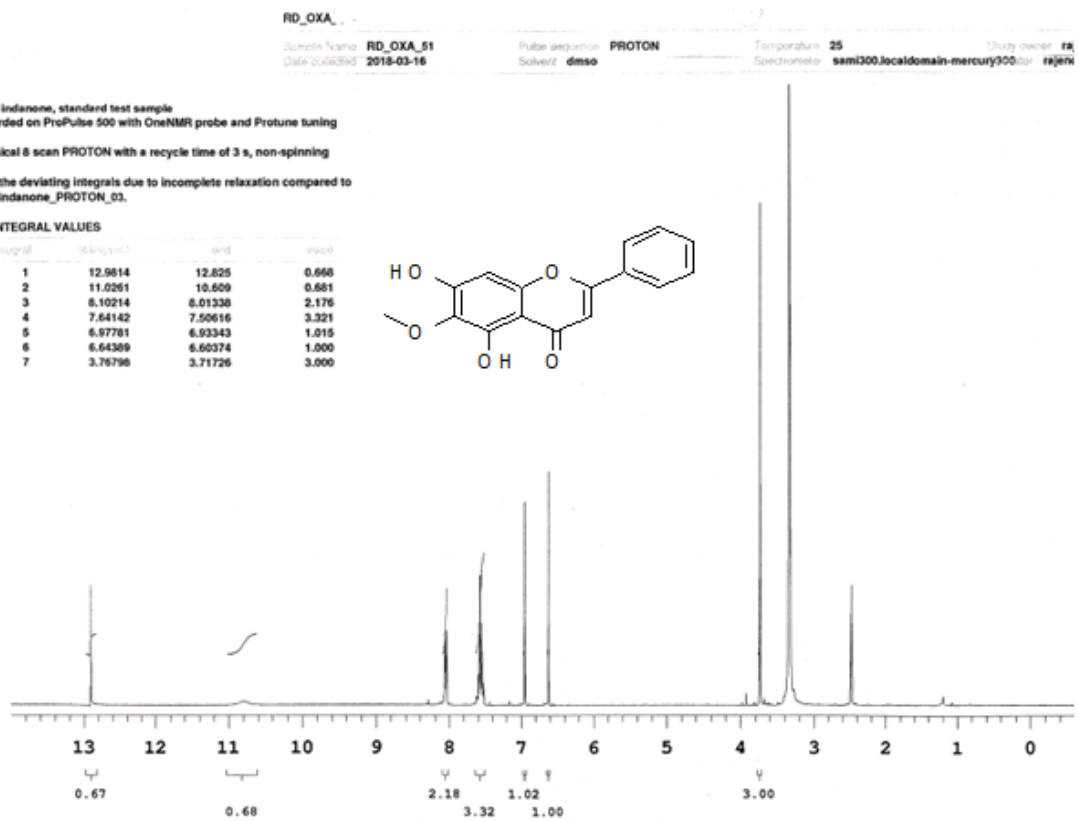


Figure S9. ^{13}C NMR spectrum of Oroxylin A (**1**)

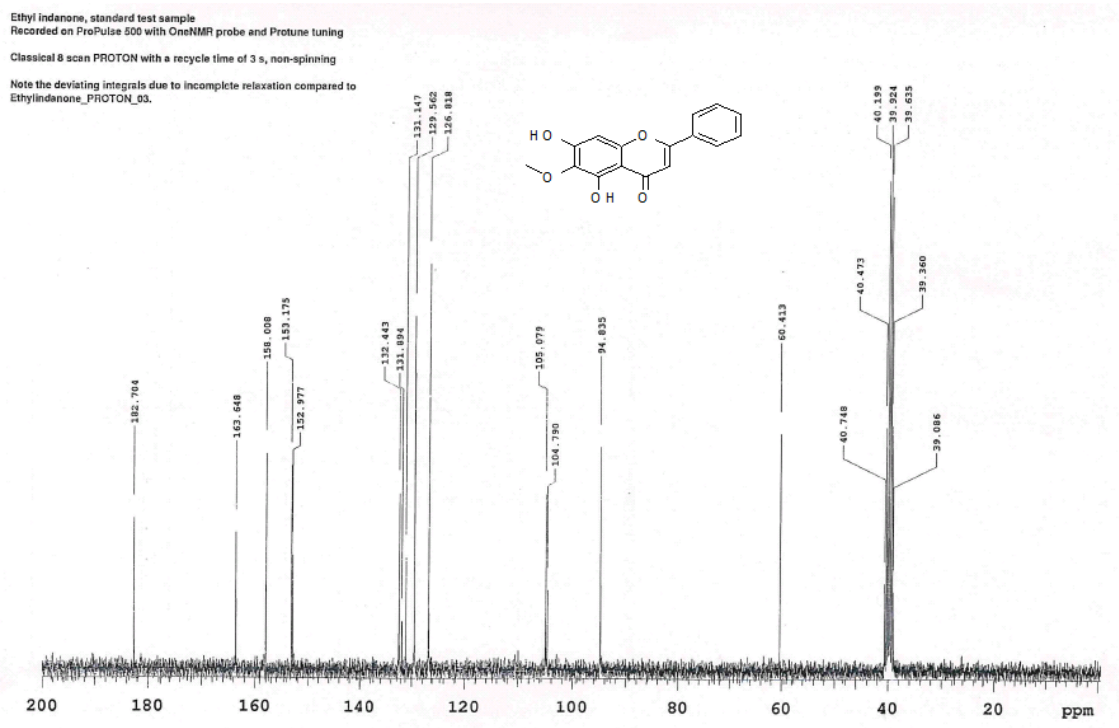


Figure S10. HRMS spectrum of Oroxylin A (**1**)

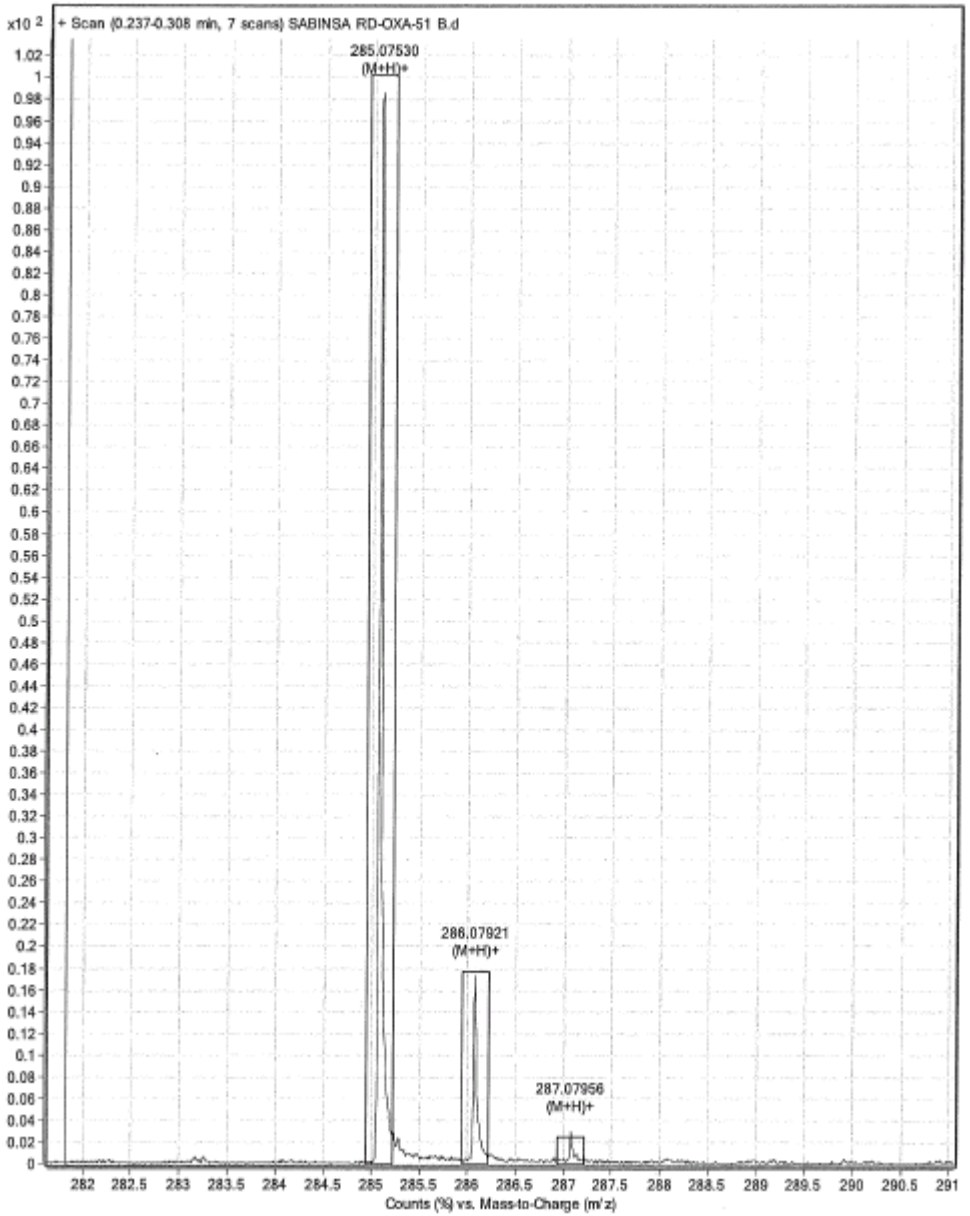
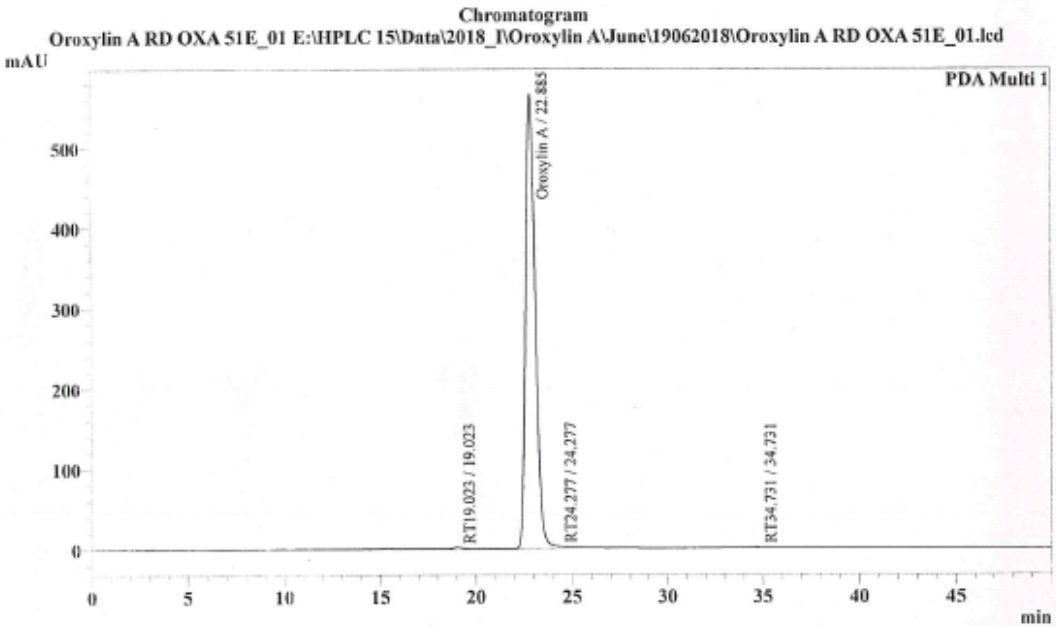


Figure S11. HPLC chromatogram of Oroxylin A (**1**)



PeakTable E:\HPLC 15\Data\2018_I\Oroxylin A\June\19062018\Oroxylin A RD OXA 51E_01.lcd
PDA Ch1 267nm 8nm

Peak#	Ret. Time	Name	Area	Area %
1	19.023	RT19.023	42891	0.216
2	22.885	Oroxylin A	19691429	99.231
3	24.277	RT24.277	95873	0.483
4	34.731	RT34.731	13804	0.070
Total			19843997	100.000

Figure S12. ^{1}H NMR spectrum of Oroxylin A (Natural)

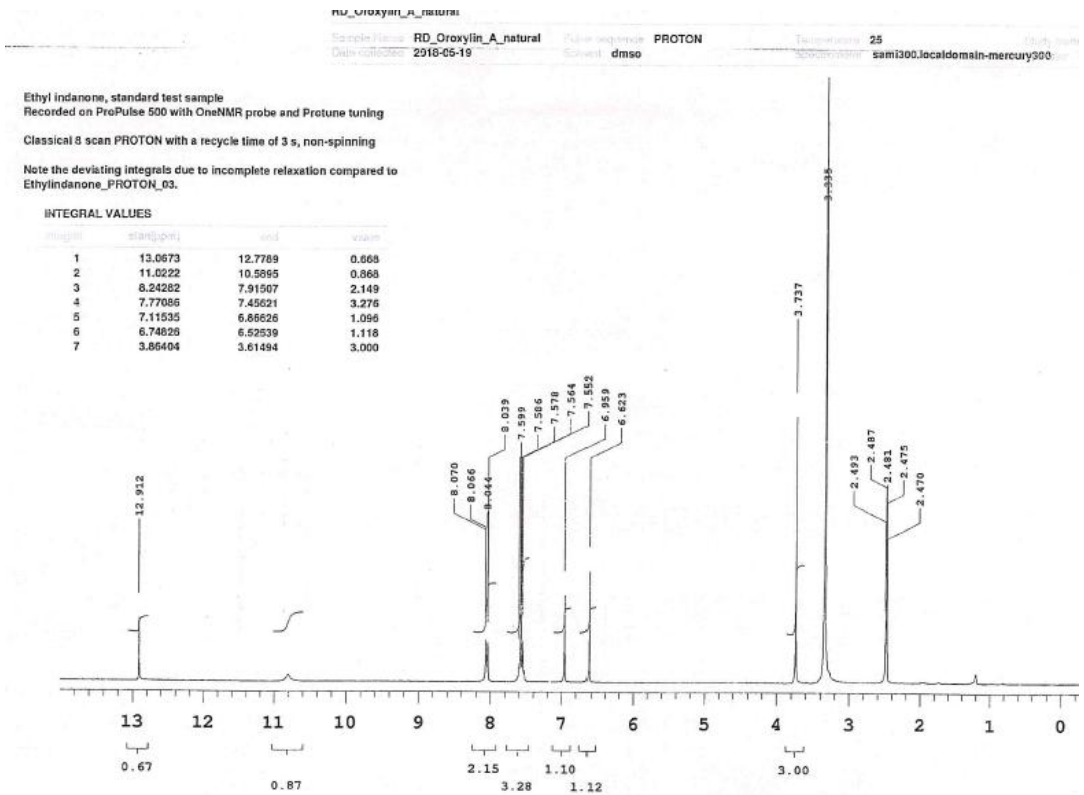


Figure S13. ^{13}C NMR spectrum of Oroxylin A (Natural)

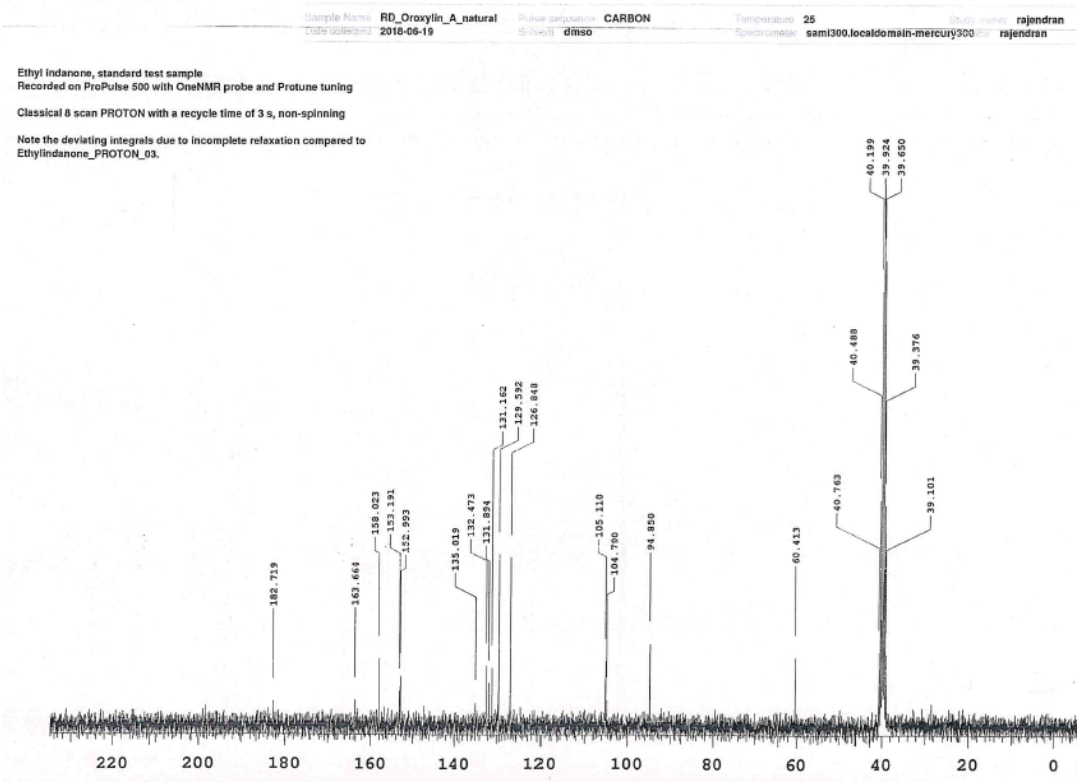


Figure S14. ^{1}H NMR spectra of Negletein (**3**)

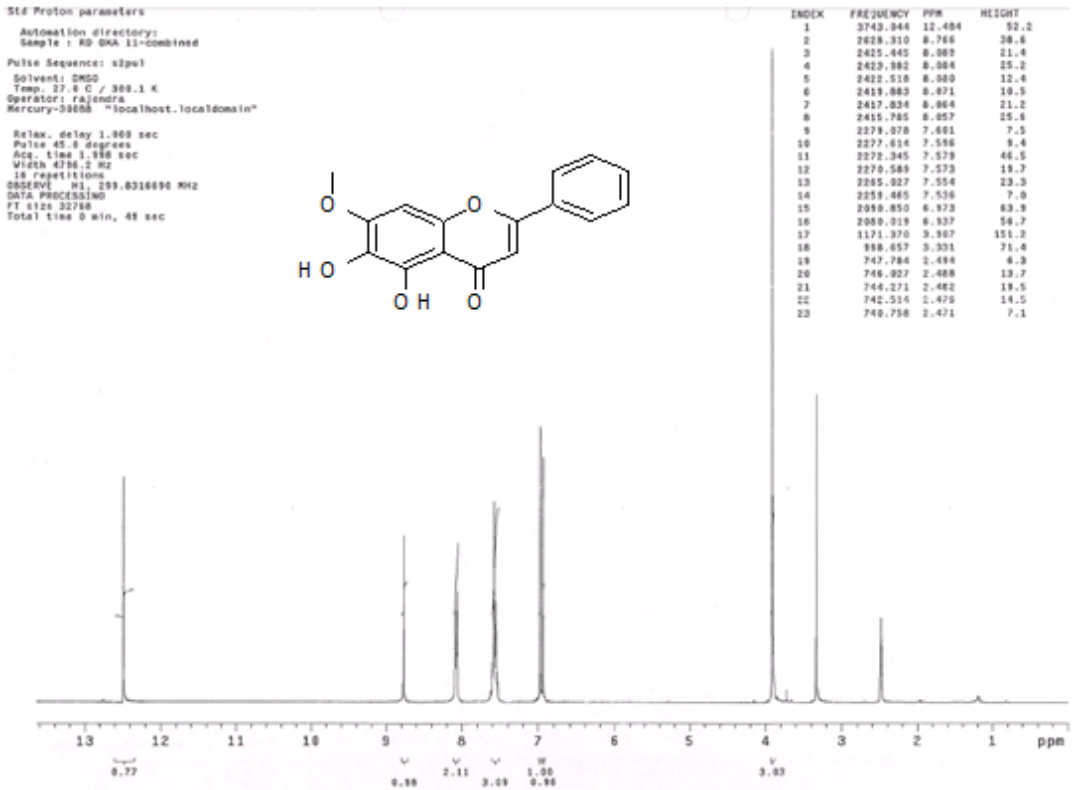


Figure S15. ^{13}C NMR spectrum of Negletein (**3**)

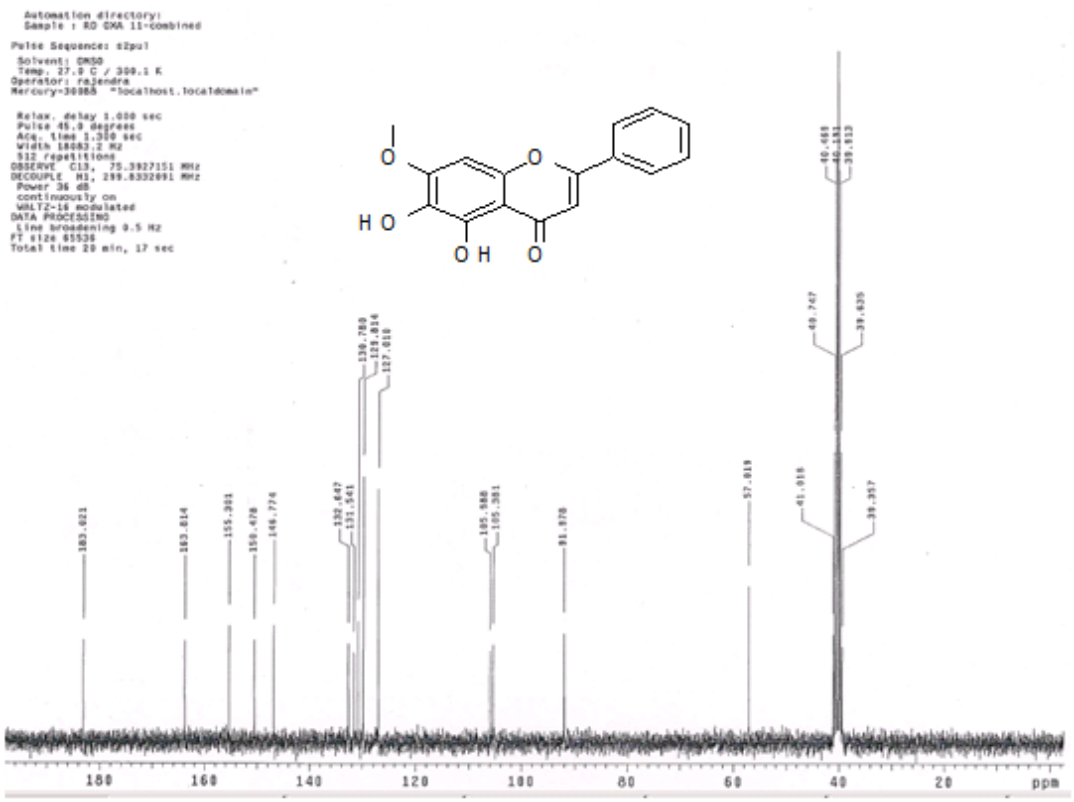


Figure S16. ^{1}H NMR spectrum of 6,7-dimethyl baicalein (**5**) (DMSO-d6)

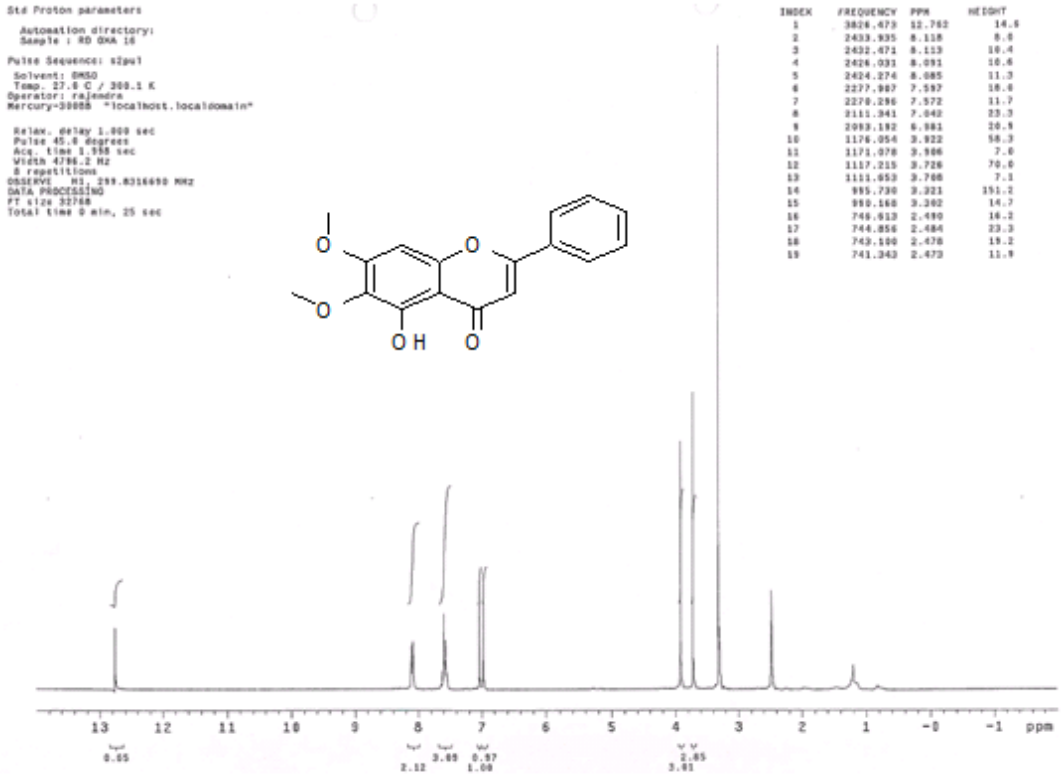


Figure S17. ^{1}H NMR spectrum of 6,7-dimethyl baicalein (**5**) ($CDCl_3$)

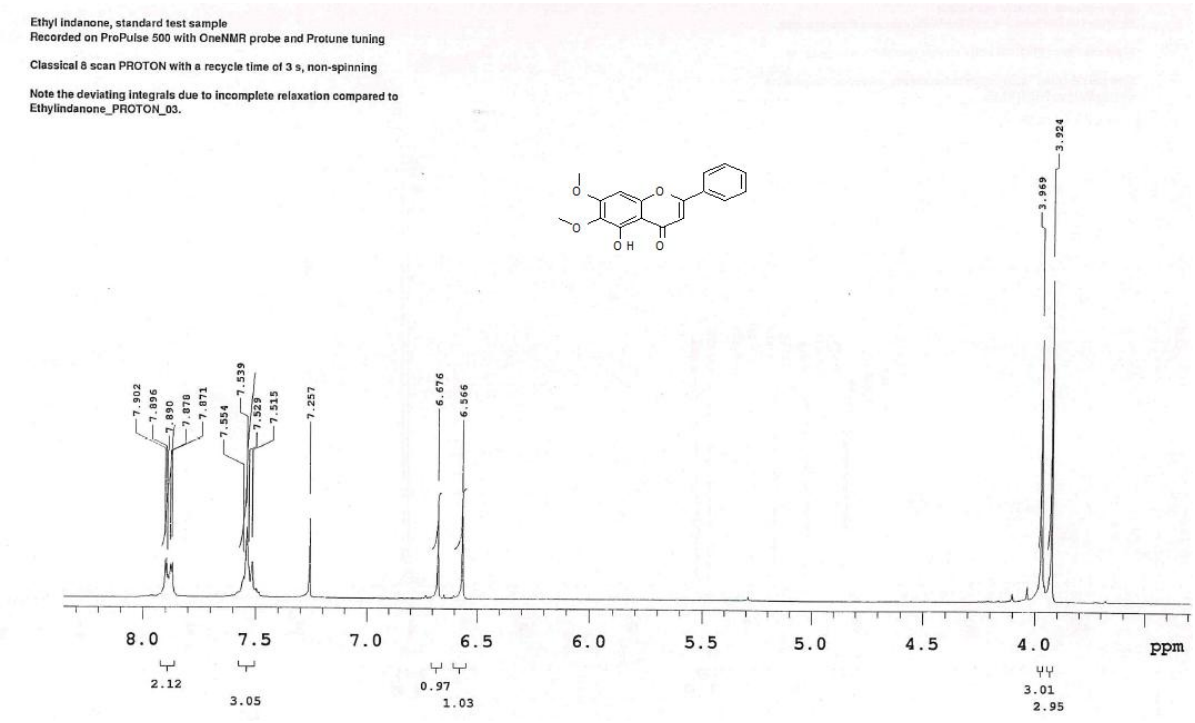


Figure S18. ^{13}C NMR spectrum of 6,7-dimethyl baicalein (**5**) ($CDCl_3$)

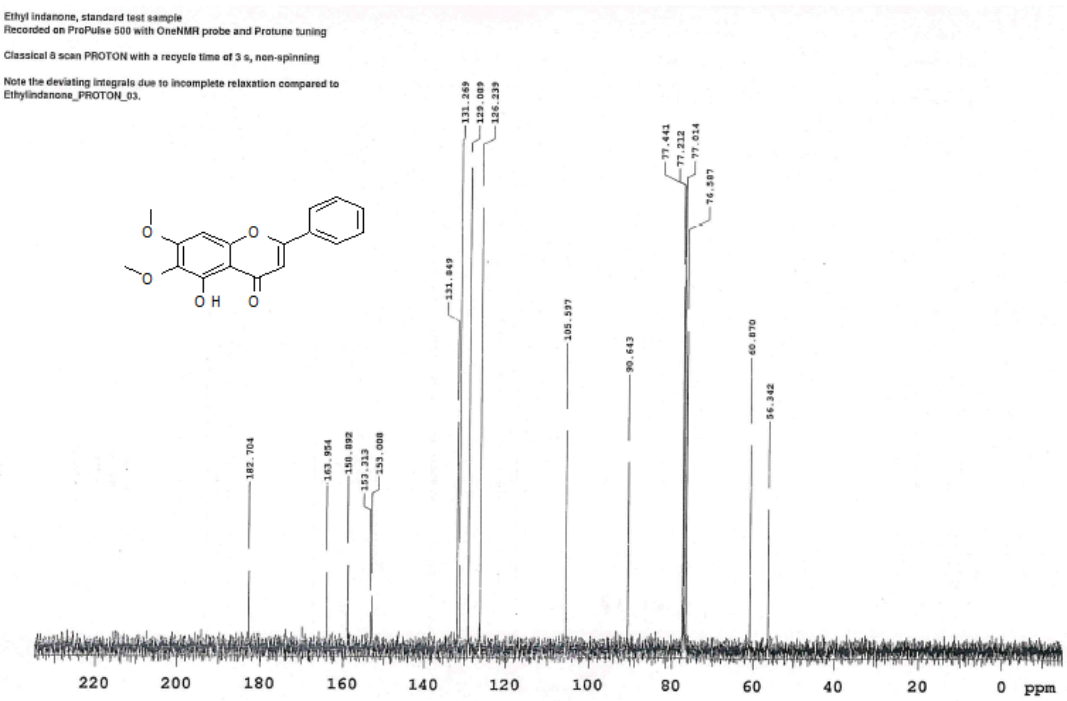
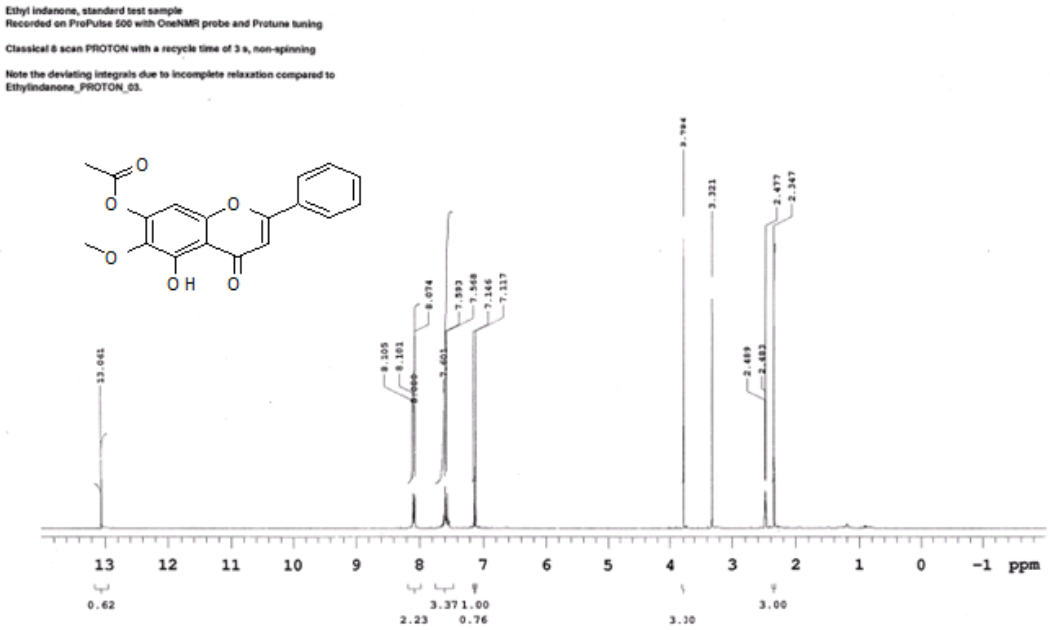


Figure S19. ^{1}H NMR spectrum of 7-*O*-acetyl-Oroxylin A (**9**)



Crystal Structure Report for PDJORA1a

A specimen of $C_{18}H_{14}O_6$, approximate dimensions 0.082 mm x 0.220 mm x 0.326 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table S1: Data collection details for PDJORA1a.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temp/K
Omega	33.976	15.71	-150.29	-157.80	54.74	0.50	303	25.00	0.71073	50	1.0	100.0
Omega	33.976	15.71	-150.29	-67.35	54.74	0.50	303	25.00	0.71073	50	1.0	100.0
Omega	33.976	15.71	-150.29	-0.93	54.74	0.50	303	25.00	0.71073	50	1.0	100.0
Phi	33.976	16.61	-149.58	-212.00	54.74	0.50	418	25.00	0.71073	50	1.0	100.0

A total of 1327 frames were collected. The total exposure time was 9.22 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 34796 reflections to a maximum θ angle of 30.50° (0.70 Å resolution), of which 4599 were independent (average redundancy 7.566, completeness = 100.0%, R_{int} = 3.30%, R_{sig} = 1.94%) and 3850 (83.71%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.4147(8) Å, b = 6.8644(3) Å, c = 13.5165(6) Å, β = 98.3683(16)°, volume = 1506.78(12) $Å^3$, are based upon the refinement of the XYZ-centroids of 9452 reflections above 20 σ(I) with 5.016° < 2θ < 62.03°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.948. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9650 and 0.9910.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{18}H_{14}O_6$. The final anisotropic full-matrix least-squares refinement on F^2 with 234 variables converged at R1 = 4.60%, for the observed data and wR2 = 12.92% for all data. The goodness-of-fit was 1.050.

Table S2. Sample and crystal data for PDJORA1a.

Identification code	PDJORA1a	
Chemical formula	$C_{18}H_{14}O_6$	
Formula weight	326.29 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.082 x 0.220 x 0.326 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 16.4147(8) Å	α = 90°
	b = 6.8644(3) Å	β = 98.3683(16)°
	c = 13.5165(6) Å	γ = 90°
Volume	1506.78(12) $Å^3$	
Z	4	
Density (calculated)	1.438 g/cm^3	
Absorption coefficient	0.109 mm^{-1}	
F(000)	680	

Table S3. Data collection and structure refinement for PDJORA1a.

Theta range for data collection	2.51 to 30.50°
Index ranges	-22<=h<=23, -9<=k<=9, -19<=l<=18
Reflections collected	34796
Independent reflections	4599 [R(int) = 0.0330]
Coverage of independent reflections	100.0%
Absorption correction	multi-scan
Max. and min. transmission	0.9910 and 0.9650
Structure solution technique	direct methods
Structure solution program	SHELXT (Sheldrick, 2016)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4599 / 12 / 234
Goodness-of-fit on F^2	1.050
Δ/σ_{max}	0.001
Final R indices	3850 data; $I>2\sigma(I)$ R1 = 0.0460, wR2 = 0.1216 all data R1 = 0.0566, wR2 = 0.1292
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0672P)^2+0.6727P$ where $P=(F_o^2+2Fc^2)/3$
Largest diff. peak and hole	0.569 and -0.211 eÅ^{-3}

R.M.S. deviation from mean	0.060 eÅ^{-3}
Largest diff. peak and hole	0.569 and -0.211 eÅ^{-3}

R.M.S. deviation from mean	0.060 eÅ^{-3}

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for PDJORA1a.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.42380(5)	0.38740(12)	0.68617(6)	0.01382(17)
C1	0.56983(7)	0.36709(16)	0.62219(9)	0.0161(2)
O2	0.38049(5)	0.39890(12)	0.97568(6)	0.01690(18)
C2	0.64487(8)	0.37216(17)	0.58602(10)	0.0198(2)
O3	0.22398(5)	0.42507(13)	0.91252(6)	0.01822(18)
C3	0.71768(7)	0.40062(17)	0.65078(10)	0.0215(3)
O4	0.09954(5)	0.43878(14)	0.74869(6)	0.01986(19)
C4	0.71586(7)	0.42112(17)	0.75267(10)	0.0207(2)
O5	0.14133(5)	0.41355(13)	0.55920(6)	0.01963(19)
C5	0.64106(7)	0.41496(16)	0.78975(9)	0.0168(2)
O6	0.10706(6)	0.10530(14)	0.59471(7)	0.0265(2)
C6	0.56736(7)	0.38878(15)	0.72484(8)	0.0134(2)
C7	0.48759(6)	0.38783(15)	0.76241(8)	0.0124(2)
C8	0.47541(6)	0.38923(16)	0.85953(8)	0.0134(2)

C9	0.39372(6)	0.39679(15)	0.88652(8)	0.0125(2)
C10	0.32695(6)	0.40456(15)	0.80380(8)	0.0120(2)
C11	0.24360(7)	0.41834(16)	0.81909(8)	0.0137(2)
C12	0.18112(7)	0.42566(17)	0.73752(8)	0.0153(2)
C13	0.20305(7)	0.40841(16)	0.64171(8)	0.0150(2)
C14	0.28327(7)	0.39288(16)	0.62370(8)	0.0140(2)
C15	0.34462(6)	0.39574(15)	0.70608(8)	0.0123(2)
C16	0.07703(8)	0.6260(2)	0.78538(10)	0.0245(3)
C17	0.09580(7)	0.2451(2)	0.54174(9)	0.0213(3)
C18A	0.0309(5)	0.2455(11)	0.4561(6)	0.0190(12)
C18B	0.0377(4)	0.2825(11)	0.4435(4)	0.0210(10)

Table S5. Bond lengths (Å) for PDJORA1a.

O1-C7	1.3580(13)	O1-C15	1.3662(12)
C1-C2	1.3901(15)	C1-C6	1.4020(15)
C1-H1	0.95	O2-C9	1.2552(13)
C2-C3	1.3887(18)	C2-H2	0.95
O3-C11	1.3486(13)	O3-H3A	0.91(2)
C3-C4	1.3891(19)	C3-H3	0.95
O4-C12	1.3721(13)	O4-C16	1.4446(16)
C4-C5	1.3927(16)	C4-H4	0.95
O5-C17	1.3786(15)	O5-C13	1.3938(13)
C5-C6	1.3987(16)	C5-H5	0.95
O6-C17	1.1953(17)	C6-C7	1.4717(14)
C7-C8	1.3564(15)	C8-C9	1.4409(14)
C8-H8	0.95	C9-C10	1.4483(14)
C10-C15	1.3944(14)	C10-C11	1.4162(14)
C11-C12	1.3931(15)	C12-C13	1.3987(15)
C13-C14	1.3776(15)	C14-C15	1.3885(14)
C14-H14	0.95	C16-H16A	0.98
C16-H16B	0.98	C16-H16C	0.98
C17-C18A	1.454(7)	C17-C18B	1.539(6)
C18A-H18A	0.98	C18A-H18B	0.98
C18A-H18C	0.98	C18B-H18D	0.98
C18B-H18E	0.98	C18B-H18F	0.98

Table S6. Bond angles (°) for PDJORA1a.

C7-O1-C15	120.07(8)	C2-C1-C6	120.01(11)
C2-C1-H1	120.0	C6-C1-H1	120.0
C3-C2-C1	120.48(11)	C3-C2-H2	119.8
C1-C2-H2	119.8	C11-O3-H3A	105.0(13)
C2-C3-C4	119.89(11)	C2-C3-H3	120.1
C4-C3-H3	120.1	C12-O4-C16	113.49(9)
C3-C4-C5	120.07(11)	C3-C4-H4	120.0
C5-C4-H4	120.0	C17-O5-C13	115.38(9)
C4-C5-C6	120.37(11)	C4-C5-H5	119.8
C6-C5-H5	119.8	C5-C6-C1	119.17(10)
C5-C6-C7	121.06(10)	C1-C6-C7	119.76(10)
C8-C7-O1	121.89(9)	C8-C7-C6	126.71(10)
O1-C7-C6	111.39(9)	C7-C8-C9	121.27(10)
C7-C8-H8	119.4	C9-C8-H8	119.4
O2-C9-C8	122.75(10)	O2-C9-C10	121.56(9)
C8-C9-C10	115.69(9)	C15-C10-C11	118.67(9)
C15-C10-C9	119.43(9)	C11-C10-C9	121.90(9)
O3-C11-C12	119.42(10)	O3-C11-C10	120.41(10)
C12-C11-C10	120.17(10)	O4-C12-C11	122.22(10)
O4-C12-C13	119.62(10)	C11-C12-C13	118.07(10)
C14-C13-O5	117.56(10)	C14-C13-C12	123.48(10)
O5-C13-C12	118.92(10)	C13-C14-C15	117.23(10)
C13-C14-H14	121.4	C15-C14-H14	121.4
O1-C15-C14	116.18(9)	O1-C15-C10	121.56(9)
C14-C15-C10	122.25(10)	O4-C16-H16A	109.5
O4-C16-H16B	109.5	H16A-C16-H16B	109.5
O4-C16-H16C	109.5	H16A-C16-H16C	109.5
H16B-C16-H16C	109.5	O6-C17-O5	122.56(10)
O6-C17-C18A	120.7(4)	O5-C17-C18A	116.8(3)
O6-C17-C18B	132.3(3)	O5-C17-C18B	105.1(3)

C17-C18A-H18A	109.5	C17-C18A-H18B	109.5
H18A-C18A-H18B	109.5	C17-C18A-H18C	109.5
H18A-C18A-H18C	109.5	H18B-C18A-H18C	109.5
C17-C18B-H18D	109.5	C17-C18B-H18E	109.5
H18D-C18B-H18E	109.5	C17-C18B-H18F	109.5
H18D-C18B-H18F	109.5	H18E-C18B-H18F	109.5

Table S7. Torsion angles (°) for PDJORA1a.

C6-C1-C2-C3	-0.66(17)	C1-C2-C3-C4	1.03(17)
C2-C3-C4-C5	-0.59(17)	C3-C4-C5-C6	-0.21(17)
C4-C5-C6-C1	0.57(16)	C4-C5-C6-C7	-178.14(10)
C2-C1-C6-C5	-0.14(16)	C2-C1-C6-C7	178.59(10)
C15-O1-C7-C8	2.44(15)	C15-O1-C7-C6	-176.93(8)
C5-C6-C7-C8	-7.78(17)	C1-C6-C7-C8	173.52(11)
C5-C6-C7-O1	171.56(9)	C1-C6-C7-O1	-7.14(14)
O1-C7-C8-C9	-2.06(16)	C6-C7-C8-C9	177.21(9)
C7-C8-C9-O2	-179.76(10)	C7-C8-C9-C10	-0.57(15)
O2-C9-C10-C15	-178.03(10)	C8-C9-C10-C15	2.77(14)
O2-C9-C10-C11	1.12(16)	C8-C9-C10-C11	-178.08(9)
C15-C10-C11-O3	179.29(10)	C9-C10-C11-O3	0.13(16)
C15-C10-C11-C12	-0.91(15)	C9-C10-C11-C12	179.94(10)
C16-O4-C12-C11	70.69(14)	C16-O4-C12-C13	-112.83(12)
O3-C11-C12-O4	-0.28(17)	C10-C11-C12-O4	179.92(10)
O3-C11-C12-C13	-176.81(10)	C10-C11-C12-C13	3.39(16)
C17-O5-C13-C14	105.56(12)	C17-O5-C13-C12	-76.55(13)
O4-C12-C13-C14	-179.46(10)	C11-C12-C13-C14	-2.84(17)
O4-C12-C13-O5	2.78(16)	C11-C12-C13-O5	179.40(10)
O5-C13-C14-C15	177.47(9)	C12-C13-C14-C15	-0.31(17)
C7-O1-C15-C14	-179.45(9)	C7-O1-C15-C10	-0.09(15)
C13-C14-C15-O1	-177.66(9)	C13-C14-C15-C10	2.99(16)

C11-C10-C15-O1	178.28(9)	C9-C10-C15-O1	-2.54(15)
C11-C10-C15-C14	-2.40(16)	C9-C10-C15-C14	176.78(10)
C13-O5-C17-O6	1.55(16)	C13-O5-C17-C18A	-179.9(4)
C13-O5-C17-C18B	-175.6(2)		

Table S8. Anisotropic atomic displacement parameters ($Å^2$) for PDJORA1a.

The anisotropic atomic 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}
O1	0.0119(3)	0.0180(4)	0.0114(3)	-0.0011(3)	0.0011(3)	-0.0009(3)
C1	0.0184(5)	0.0131(5)	0.0174(5)	0.0013(4)	0.0046(4)	0.0000(4)
O2	0.0172(4)	0.0231(4)	0.0102(4)	0.0007(3)	0.0012(3)	-0.0026(3)
C2	0.0238(6)	0.0143(5)	0.0235(6)	0.0017(4)	0.0108(5)	0.0006(4)
O3	0.0158(4)	0.0281(5)	0.0109(4)	-0.0001(3)	0.0027(3)	-0.0016(3)
C3	0.0184(5)	0.0148(5)	0.0337(7)	0.0013(5)	0.0120(5)	0.0003(4)
O4	0.0115(4)	0.0291(5)	0.0189(4)	-0.0030(3)	0.0017(3)	0.0001(3)
C4	0.0145(5)	0.0149(5)	0.0327(7)	-0.0018(5)	0.0035(4)	-0.0007(4)
O5	0.0165(4)	0.0276(5)	0.0130(4)	-0.0011(3)	-0.0042(3)	0.0012(3)
C5	0.0155(5)	0.0134(5)	0.0213(5)	-0.0020(4)	0.0023(4)	0.0000(4)
O6	0.0206(4)	0.0311(5)	0.0264(5)	-0.0034(4)	-0.0013(4)	-0.0063(4)
C6	0.0140(5)	0.0089(4)	0.0176(5)	0.0003(4)	0.0034(4)	-0.0001(3)
C7	0.0127(4)	0.0097(4)	0.0144(5)	-0.0003(4)	0.0005(4)	-0.0008(3)
C8	0.0121(4)	0.0144(5)	0.0131(5)	0.0005(4)	-0.0005(4)	-0.0012(4)
C9	0.0144(5)	0.0111(4)	0.0117(5)	0.0002(4)	0.0008(4)	-0.0018(3)
C10	0.0129(4)	0.0114(4)	0.0113(5)	-0.0003(3)	0.0007(4)	-0.0015(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	0.0146(5)	0.0148(5)	0.0117(5)	0.0000(4)	0.0024(4)	-0.0015(4)
C12	0.0127(5)	0.0189(5)	0.0141(5)	-0.0010(4)	0.0010(4)	-0.0013(4)
C13	0.0141(5)	0.0176(5)	0.0121(5)	-0.0004(4)	-0.0019(4)	-0.0005(4)
C14	0.0155(5)	0.0160(5)	0.0099(4)	-0.0010(4)	0.0005(4)	-0.0009(4)
C15	0.0121(4)	0.0116(4)	0.0130(5)	-0.0008(4)	0.0017(4)	-0.0010(3)
C16	0.0184(5)	0.0318(7)	0.0234(6)	-0.0016(5)	0.0036(4)	0.0064(5)
C17	0.0125(5)	0.0324(7)	0.0183(5)	-0.0093(5)	0.0004(4)	0.0011(4)
C18A	0.0178(17)	0.0187(18)	0.0191(18)	0.0016(13)	-0.0027(12)	-0.0008(13)
C18B	0.0173(13)	0.0279(17)	0.0158(14)	-0.0031(12)	-0.0040(10)	-0.0006(12)

Table S9. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for PDJORA1a.

	x/a	y/b	z/c	U(eq)
H1	0.5202	0.3489	0.5773	0.019
H2	0.6463	0.3560	0.5165	0.024
H3	0.7687	0.4061	0.6254	0.026
H3A	0.2729(14)	0.417(3)	0.9535(16)	0.048(6)
H4	0.7657	0.4394	0.7971	0.025
H5	0.6401	0.4286	0.8595	0.02
H8	0.5216	0.3851	0.9107	0.016
H14	0.2961	0.3807	0.5577	0.017
H16A	0.0912	0.7288	0.7406	0.037
H16B	0.1070	0.6474	0.8527	0.037

	x/a	y/b	z/c	U(eq)
H16C	0.0177	0.6286	0.7878	0.037
H18A	-0.0098	0.3456	0.4654	0.029
H18B	0.0042	0.1176	0.4499	0.029
H18C	0.0548	0.2736	0.3952	0.029
H18D	0.0637	0.2361	0.3870	0.031
H18E	0.0267	0.4224	0.4361	0.031
H18F	-0.0142	0.2127	0.4448	0.031

Table S10. Hydrogen bond distances (Å) and angles (°) for PDJORA1a.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O3-H3A···O2	0.91(2)	1.75(2)	2.5927(12)	153.(2)
C8-H8···O2	0.95	2.53	3.3374(13)	142.5
C16-H16B···O3	0.98	2.49	3.0768(15)	117.9