# Design and synthesis of coumarin-glyoxal hybrids for spermicidal and antimicrobial actions: A dual approach to contraception.

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## **Supporting Information**

1. Scan data of compounds 2a-2h	S2-S13
2. Scan data of compounds 3a-3h	S14-25
3. Scan data of compounds 4a-4h	S25-S37
4. Scan data of compounds 5a-5f	S37-S46
5. HPLC data of all compounds	S47-S56
6. Mass and NMR spectra of dicoumarol	S56-S58

# Copies of <sup>1</sup>H, <sup>13</sup>C NMR and HRMS spectra of compounds:



## <sup>1</sup>H NMR spectrum of compound 2a:

#### <sup>13</sup>C NMR spectrum of compound 2a:



HRMS spectra of compound 2a:



<sup>1</sup>H NMR spectra of compound 2b:





#### HRMS spectra of compound 2b:



## <sup>1</sup>H NMR spectra of compound 2c:



## <sup>13</sup>C NMR spectra of compound 2c:



#### HRMS spectra of compound 2c:



#### <sup>1</sup>H NMR spectra of compound 2d:



#### <sup>13</sup>C NMR spectra of compound 2d:



#### HRMS spectra of compound 2d:





## 13C NMR spectra of compound 2e:



#### HRMS spectra of compound 2e:

Inj Vol Data Filename	1 50-400-42-075-4	InjPosition	vial 10		SampleType	Instrument 1 Sample	User Name IRM Calibration Status	Success
×10.4 +E	SI Scan (0.6 min)	Frag=150.0	ISO-DEC.n	1	Comment		Acquired Time	4/23/2015 10:49:22 A
1.8-			152					
17			398.1					
1.0								
1.0								
1.5-								
1.4								
1.3								
1.2								0.000
1.1-								
1.								
0.9								
0.8								
0.7				1139				
0.0				400				
0.0	~		50					
0.5			9.118					
0.4			33					
0.3				12	50			
0.2 16				01.11	322			86
0.1				4	40			415.2
0					1 11 11			

<sup>1</sup>H NMR spectra of compound 2f:



## <sup>13</sup>C NMR spectra of compound 2f:



# HRMS spectra of compound 2f:

>	SG-23 #5	RT: 0.12 AV: 1 5	B: 9 0.74-0.9	0, 0.01-0.	06 NL: 1.7	9E6						
	T: FTMS +	c ESI Full ms [100.	00-1500.00]									
	100	570	1090									
	95											
	90											
	85											
	80											
	75											
	70											
	65											
	8 60											
	Lep 55		378.5299									
	unq 50											
	0 45											
	elati											
	œ 40											
	35											
	30		379 172	2								
	25			-								
	20											
	15											
	10											
	5	377.9174		380.1752	204 4700							
	0	077 070	The		381.1783		383.0831		385.1698	386.6	3094	388.177
	376	3// 378	379	380	381	382	383	384	385	386	387	388



## <sup>13</sup>C NMR spectra of compound 2g:



#### HRMS spectra of compound 2g:

Sample Name Inj Vol Data Filename	Dr. A.K.DWIVEDI/SWAT 1 SG-AKD-31B-122.d	Position InjPosition ACQ Method	Vial 14 ISO-DEC.m	Instrument Name SampleType Comment	Instrument 1 Sample	User Name IRM Calibration Status	Some Ions Missed
x10 5 +E	SI Scan (0.5 min) Fr	ag=150.0V S	3-AKD-31B-1	22.d		Acquired Time	3/31/2015 11:34:52 AM
3.			51				
2.9			0.16				
2.8			410				
2.7							
2.6							
2.5							
2.4							
2.3							
21							
2							
1.9							
1.8						•	
1.7							
1.6-							
1.5							
1.4							200
1.3-							
1.2-							
1.1-							
1-				-			
0.9				164			
0.8				÷.			
0.6				4			No. I Alacha Maria I.
0.5							
0.4							
0.3				88			
0.2				2.16			
0.1-				14			

## <sup>1</sup>H NMR spectra of compound 2h:



<sup>13</sup>C NMR spectra of compound 2h:



## HRMS spectra of compound 2h:



#### <sup>1</sup>H NMR spectra of compound 3a:



# <sup>13</sup>C NMR spectra of compound 3a:



#### HRMS spectra of compound 3a:



## <sup>1</sup>H NMR spectra of compound 3b:



## <sup>13</sup>C NMR spectra of compound 3b:



## <sup>1</sup>H NMR spectra of compound 3c:





#### HRMS spectra of compound 3c:



## <sup>1</sup>H NMR spectra of compound 3d:



## <sup>13</sup>C NMR spectra of compound 3d:



#### HRMS spectra of compound 3d:



## <sup>1</sup>H NMR spectra of compound 3e:





#### HRMS spectra of compound 3e:



## <sup>1</sup>H NMR spectra of compound 3f:



## <sup>13</sup>C NMR spectra of compound 3f:



#### HRMS spectra of compound 3f:

>	Sample Name Inj Vol Data Filename	Dr. DWIVED	d	Pos	sition jPositio O Meth	n od 1	Nal 10	TC.m		Ins San Cor	npleT	ent Nam 'ype nt	ie	Instru Sampl	ment 1 le		I	Iser Name RM Calibra couired Ti	ation Stat	us	Si 1	uccess	5 11:55:	45 AM
	x10 5 +E	SI Scan (	0.4-0.6	s min,	, 14 S	cans)	Frag=	150.	ov s	G-6	9-15	3.d S	ubtr	act		_					-			
	1.1-													1003	200									
	1.05													ASS	ž									
	1-																							
	0.95-																							
	0.9-																							
	0.85																							
	0.8																							
	0.75																							
	0.7																							
	0.65																							
	0.6-																							
	0.55																							
	0.5																							
	0.45																							
	0.4-																							
	0.35																							
	0.3-																	906						
	0.25																	111						
	0.2 -																							
	0.15-										-										53			
	0.1	9	805	Ξ	06	17 39	82	75	100	75	660.	530	20	67		51	337	827	692	9	93.0	E	4	
	0.05	8.25	93.1	98.9	0.40	00:00	0.05	000	29.07	3.09	431	2.00	9.08	3.12		2.06	90.99	174.0	82.0	9.18	4	0.66	5.08	
	0	8		63	4	4	4	4	4	4	11.	4 4	4	4	L.L.	49	4	litel	4 4	84	14	4	50	

## <sup>1</sup>H NMR spectra of compound 3g:





#### HRMS spectra of compound 3g:



#### <sup>1</sup>H NMR spectra of compound 3h:



#### <sup>13</sup>C NMR spectra of compound 3h:



#### HRMS spectra of compound 3h:



<sup>1</sup>H NMR spectra of compound 4a:



#### <sup>13</sup>C NMR spectra of compound 4a:



#### HRMS spectra of compound 4a:





<sup>13</sup>C NMR spectra of compound 4b:



#### HRMS spectra of compound 4b:

Data Filen	ame S	G-72-141.d	InjPosition ACO Method	ISOCRATIC.m	SampleType	Sample	User Name IRM Calibration Status	Success
×10 5	+ESI	Scan (0.4-0.8	3 min, 28 Sca	ns) Frag=150.	0V SG-72-141.d		Augurea rune	11/24/2013 2.11.46 P
1.3	-			537				
1.25	-			54.1				
1.2	-			e				
1.15	-							
1.1	-							
1.05	-							
1	-							
0.95	-							
0.9	-							
0.85	-							
0.8	-							
0.75	-							
0.7	-							
0.65	-							
0.6	-							
0.55	-							100
0.5	-							
0.45	-							
0.4	-			267				
0.35	-			192				
0.3	-			ě		,		
0.25	-							
0.2	-							
0.15	-				1596			
0.1	-				366.			
0.05	1							

## <sup>1</sup>H NMR spectra of compound 4c:



<sup>13</sup>C NMR spectra of compound 4c:



#### HRMS spectra of compound 4c:



<sup>1</sup>H NMR spectra of compound 4d:



<sup>13</sup>C NMR spectra of compound 4d:



#### HRMS spectra of compound 4d:

Inj Vol Data Filename	1 SG-80-119.d	InjPosition ACO Method	Vial 15	Instrument Name SampleType Comment	Instrument 1 Sample	User Name IRM Calibration Status Acquired Time	Success
×10 5 +E	SI Scan (0.4 min)	Frag=150.0	V SG-80-119.d			, indian on Linio	14/24/2015 12:30:10
3-			68				
2.9			0.14				
2.8-			<b></b>				
2.7-							1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
2.6							
2.5							
2.4 -			1.1.2				
2.3			L N L Dere				
2.2-							
2.1-							
2-							
1.9-							
1.8-							
1.7-							
1.6-							
1.5-			1.1.2.1.2.2.				
1.4			SUL ICA ST				
1.3-							
1.2-							
1.11							
0.0]							
0.8			210				
0.7			31.1				
0.6			8	*			
0.5							
0.4							
0.3			220				
			2.1				
0.2			39				
			382.1				

## <sup>1</sup>H NMR spectra of compound 4e:



#### <sup>13</sup>C NMR spectra of compound 4e:



## HRMS spectra of compound 4e:



#### <sup>1</sup>H NMR spectra of compound 4f:



## <sup>13</sup>C NMR spectra of compound 4f:



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

#### HRMS spectra of compound 4f:

Sample Name Inj Vol	Dr. DWIVEDI/SWATI 1 SG-71-142 d	Position InjPosition ACO Method	Vial 38	Instrument Name SampleType Comment	Instrument 1 Sample	User Name IRM Calibration Status Acquired Time	Success 11/24/2015 2:15:32 P
Data Filename	SI Scan (0.4-0.7	min, 18 Scan	ns) Frag=150.0	/ SG-71-142.d			
x10 • -			Ŧ				
1.4-			41.4				
1.35 -			39				
1.3-							
1.25-							
1.2							+ C
1.15-							
1.1-							
1.05							
0.95							
0.9-							
0.85-							
0.8							
0.75							
0.7-							
0.65							
0.6							31 m 1 m 2
0.55							
0.5							
0.45				1572			
0.4							
0.35				e. ,			
0.25							3
0.2				10			
0.15				160			
0.1-				366.			
0.05							
	359 360	361 362	363 364 C	365 366 367 ounts vs. Mass-to-(	7 368 369 Charge (m/z)	370 371 372 3	373 374

## <sup>1</sup>H NMR spectra of compound 4g:



<sup>13</sup>C NMR spectra of compound 4g:



#### HRMS spectra of compound 4g:



#### <sup>1</sup>H NMR spectra of compound 4h:



#### <sup>13</sup>C NMR spectra of compound 4h:



HRMS spectra of compound 4h:



<sup>1</sup>H NMR spectra of compound 5a:



<sup>13</sup>C NMR spectra of compound 5a:



#### HRMS spectra of compound 5a:



<sup>1</sup>H NMR spectra of compound 5b:



<sup>13</sup>C NMR spectra of compound 5b:



#### HRMS spectra of compound 5b:



<sup>1</sup>H NMR spectra of compound 5c:





# HRMS spectra of compound 5c:





<sup>13</sup>C NMR spectra of compound 5d:



#### HRMS spectra of compound 5d:



# <sup>1</sup>H NMR spectra of compound 5e:





200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

## HRMS spectra of compound 5e:



#### <sup>1</sup>H NMR spectra of compound 5f:



## <sup>13</sup>C NMR spectra of compound 5f:



#### HRMS spectra of compound 5f:



#### HPLC purity determination assay

Purity of compounds was determined by Reverse phase HPLC method using RP-18 Lichrocart <sup>®</sup>, Merck column (5  $\mu$ m, 250 X 4.0 mm, id) under low pressure gradient condition using mobile phase Acetonitrile/water with 0.5% glacial acetic acid in the ratio between 10 :90 to 90:10, %v/vat a flow rate of 1.0 mL/min. The HPLC system (Shimadzu, Kyoto, Japan) equipped with Photo Diode Array detector (SPD-M20A), a pump (LC-20AD), controller (CBM-20A),Rheodyne (Cotati, CA, USA) model 7125 injector with a 20  $\mu$ l loop. Data was acquired in LC solution software (Shimadzu,Japan).compounds were monitored at 274 nm with a UV-Vis multiple wavelength detector.Mobile phase was filtered through 0.22- $\mu$ m Millipore filter (Billerica, USA) and degassed using ultrasonicator for 15 min before use.

#### HPLC Chromatogram of compound 2a:



#### HPLC Chromatogram of compound 2b:



Peak no.	Retention time	Area%
1.	14.271	100

## HPLC Chromatogram of compound 2c:



Peak no.	Retention time	Area%
1.	12.471	99.3582
2.	13.869	0.6418

## HPLC Chromatogram of compound 2d:



Peak no.	Retention time	Area%
1.	12.914	4.2882
2.	14.166	95.7118

# HPLC Chromatogram of compound 2e:



Peak no.	Retention time	Area%
1.	12.999	0.8738
2.	13.766	0.4368
3.	14.587	98.6893

## HPLC Chromatogram of compound 2f:



Peak no.	Retention time	Area%
1.	13.376	4.3516
2.	14.961	95.6484

HPLC Chromatogram of compound 2g:



Peak no.	Retention time	Area%
1.	12.995	98.3201
2.	14.141	0.2342
3.	14.712	1.1983

# HPLC Chromatogram of compound 2h:



Peak no.	Retention time	Area%
1.	12.383	1.0086
2.	13.23	97.4742
3.	14.562	1.5172

## HPLC Chromatogram of compound 3a:



Peak no.	Retention time	Area%
1.	11.339	98.8874
2.	14.656	1.1126

#### HPLC Chromatogram of compound 3b:



Peak no.	Retention time	Area%
1.	13.062	100

## HPLC Chromatogram of compound 3c:



Peak no.	Retention time	Area%
1.	11.339	98.8874
2.	14.656	1.1126

#### HPLC Chromatogram of compound 3d:



Peak no.	Retention time	Area%
1.	11.325	2.384
2.	11.689	97.616

## HPLC Chromatogram of compound 3e:



Peak	Retention time	Area%
no.		
1.	14.095	98.3623
2.	15.359	1.6377

## HPLC Chromatogram of compound 3f:



Peak no.	Retention time	Area%
1.	11.478	1.701
2.	13.376	3.1184
3.	13.888	95.1806

## HPLC Chromatogram of compound 3g:



Peak no.	Retention time	Area%
1.	11.993	99.6571
2.	13.578	0.3429

HPLC Chromatogram of compound 3h:



Peak no.	Retention time	Area%
1.	13.062	100

## HPLC Chromatogram of compound 4a:



Peak no.	Retention time	Area%
1.	12.027	98.9693
2.	14.035	1.0307

HPLC Chromatogram of compound 4b:



Peak no.	Retention time	Area%
1.	12.94	2.1801
2.	13.578	97.8199

HPLC Chromatogram of compound 4c:



Peak no.	Retention time	Area%
1.	12.115	100

## HPLC Chromatogram of compound 4d:



Peak no.	Retention time	Area%
1.	13.299	96.2584
2.	14.28	3.7416

## HPLC Chromatogram of compound 4e:



Peak no.	Retention time	Area%
1.	13.286	95.2063
2.	14.541	4.7937

## HPLC Chromatogram of compound 4f:



Peak no.	<b>Retention time</b>	Area%
1.	13.118	4.465
2.	14.282	95.535

## HPLC Chromatogram of compound 4g:



Peak no.	Retention time	Area%
1.	12.027	98.9693
2.	14.035	1.0307

## HPLC Chromatogram of compound 4h:



Peak no.	Retention time	Area%
1.	11.774	3.6956
2.	12.631	96.3044

## HPLC Chromatogram of compound 5a:



Peak no.	Retention time	Area%
1.	10.584	1.3536
2.	11.718	98.6464

## HPLC Chromatogram of compound 5b:



Peak no.	Retention time	Area%
1.	11.95	3.2661
2.	12.605	96.7339

HPLC Chromatogram of compound 5c:



Peak no.	<b>Retention time</b>	Area%
1.	12.681	2.0039
2.	13.868	95.0504
3.	16.965	2.0446
4.	19.01	0.9011

HPLC Chromatogram of compound 5d:



Peak no.	Retention time	Area%
1.	7.61	2.7642
2.	12.394	1.6246
3.	13.338	0.5484
4.	15.444	95.0628

HPLC Chromatogram of compound 5e:



Peak no.	Retention time	Area%
1.	12.343	3.024
2.	12.824	96.976

#### HPLC Chromatogram of compound 5f:



Peak no.	<b>Retention time</b>	Area%
1.	14.186	95.2955
2.	16.184	0.3994
3.	17.237	3.0847
4.	19.225	1.2205



<sup>13</sup>C NMR spectra of dicoumarol:



## Mass spectra of dicoumarol:

