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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

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Electronic supplementary information for

Anti Hepatitis B Virus Activities and Absolute

Configurations of Sesquiterpenoid Glycosides from

Phyllanthus emblica

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Table o 1.	of contents Figure S1 HRESIMS of compound 1	5
2.	Figure S2 ¹ H NMR (500 MHz) spectrum of phyllaemblicins G1 (1) in CD₃OD	6
3.	Figure S3 ¹³ C NMR (125 MHz) spectrum of phyllaemblicins G1 (1) in CD₃OD	7
4.	Figure S4 HSQC spectrum of phyllaemblicins G1 (1) in CD₃OD	8
5.	Figure S5 HMBC spectrum of phyllaemblicins G1 (1) in CD₃OD	9
6.	Figure S6 ¹ H- ¹ H COSY spectrum of phyllaemblicins G1 (1) in CD₃OD	10
7.	Figure S7 ROESY spectrum of phyllaemblicins G1 (1) in CD₃OD	11
8.	Figure S8 HRESIMS of phyllaemblicins G2 (2)	12
9.	Figure S9 ¹ H NMR (800 MHz) spectrum of phyllaemblicins G2 (2) in CD₃OD	13
10.	Figure S10 13 C NMR (125 MHz) spectrum of phyllaemblicins G2 (2) in CD ₃ OD	14
11.	Figure S11 HSQC spectrum of phyllaemblicins G2 (2) in CD₃OD	15
12.	Figure S12 HMBC spectrum of phyllaemblicins G2 (2) in CD₃OD	16
13.	Figure S13 ¹ H- ¹ H COSY spectrum of phyllaemblicins G2 (2) in CD ₃ OD	17
14.	Figure S14 ROESY spectrum of phyllaemblicins G2 (2) in CD ₃ OD	18
15.	Figure S15 HETLOC spectrum of phyllaemblicins G2 (2) in CD ₃ OD	19
16.	Figure S16 HETLOC spectrum of phyllaemblicins G2 (2) in CD ₃ OD	20
17.	Figure S17 ${}^{3}J_{H10,C14}$ calculation using HETLOC spectrum of phyllaemblicins G2 (2) in CD ₃ OD	21
18.	Figure S18 $^{2}J_{H11,C10}$ calculation using HETLOC spectrum of phyllaemblicins G2 (2) in CD ₃ OD	22
19.	Figure S19 ${}^{3}\!J_{H11,C9}$ calculation using TOCSY and HETLOC spectrum of phyllaemblicins G2 (2) in CD ₃ OD	23
20.	Figure S20 ${}^{3}J_{H10,C12}$ calculation using TOCSY and HETLOC spectrum of phyllaemblicins G2 (2) in CD ₃ OD	24
21.	Figure S21 HSQC-TOCSY spectrum of phyllaemblicins G2 (2) in CD₃OD	25
22.	Figure S22 HRESIMS of compound 2A	26
23.	Figure S23 ¹ H NMR (800 MHz) spectrum of compound 2A in DMSO- d_{6}	27
24.	Figure S24 ¹³ C NMR (800 MHz) spectrum of compound 2A in CH ₃ OD	28
25.	Figure S25 HSQC spectrum of compound 2A in DMSO- d_6	29
26.	Figure S26 HMBC spectrum of compound 2A in DMSO- d_{ϕ}	30
27.	Figure S27 ¹ H- ¹ H COSY spectrum of compound 2A in DMSO- d_6	31
28.	Figure S28 HRESIMS of phyllaemblicins G3 (3)	32
29.	Figure S29 ¹ H NMR (600 MHz) spectrum of phyllaemblicins G3 (3) in CD ₃ OD	33
30.	Figure S30 13 C NMR (150 MHz) spectrum of phyllaemblicins G3 (3) in CD ₃ OD	34
31.	Figure S31 HSQC spectrum of phyllaemblicins G3 (3) in CD₃OD	35
32.	Figure S32 HMBC spectrum of phyllaemblicins G3 (3) in CD ₃ OD	36
33.	Figure S33 ¹ H- ¹ H COSY spectrum of phyllaemblicins G3 (3) in CD ₃ OD	37
34.	Figure S34 ROESY spectrum of phyllaemblicins G3 (3) in CD₃OD	38

35.	Figure S35 HRESIMS of phyllaemblicin G4 (4)	39
36.	Figure S36 ¹ H NMR (400 MHz) spectrum of phyllaemblicins G4 (4) in CD ₃ OD	40
37.	Figure S37 ¹³ C NMR (100 MHz) spectrum of phyllaemblicins G4 (4) in CD ₃ OD	41
38.	Figure S38 HSQC spectrum of phyllaemblicins G4 (4) in CD₃OD	42
39.	Figure S39 HMBC spectrum of phyllaemblicins G4 (4) in CD ₃ OD	43
40.	Figure S40 ¹ H- ¹ H COSY spectrum of phyllaemblicins G4 (4) in CD ₃ OD	44
41.	Figure S41 ROESY spectrum of phyllaemblicins G4 (4) in CD₃OD	45
42.	Figure S42 HSQC-TOCSY spectrum of phyllaemblicins G4 (4) in CD ₃ OD	46
43.	Figure S43 HRESIMS of phyllaemblicin G5 (5)	47
44.	Figure S44 1 H NMR (500 MHz) spectrum of phyllaemblicin G5 (5) in CD ₃ OD	48
45.	Figure S45 ¹³ C NMR (125 MHz) spectrum of phyllaemblicin G5 (5) in CD ₃ OD	49
46.	Figure S46 HSQC spectrum of phyllaemblicin G5 (5) in CD₃OD	50
47.	Figure S47 HMBC spectrum of phyllaemblicin G5 (5) in CD₃OD	51
48.	Figure S48 ¹ H- ¹ H COSY spectrum of phyllaemblicin G5 (5) in CD ₃ OD	52
49.	Figure S49 ROESY spectrum of phyllaemblicin G5 (5) in CD₃OD	53
50.	Figure S50 HRESIMS of phyllaemblicin G6 (6)	54
51.	Figure S51 ¹ H NMR (500 MHz) spectrum of phyllaemblicin G6 (6) in CD ₃ OD	55
52.	Figure S52 13 C NMR (125 MHz) spectrum of phyllaemblicin G6 (6) in CD ₃ OD	56
53.	Figure S53 HSQC spectrum of phyllaemblicin G6 (6) in CD₃OD	57
54.	Figure S54 HMBC spectrum of phyllaemblicin G6 (6) in CD₃OD	58
55.	Figure S55 ¹ H- ¹ H COSY spectrum of phyllaemblicin G6 (6) in CD ₃ OD	59
56.	Figure S56 ROESY spectrum of phyllaemblicin G6 (6) in CD₃OD	60
57.	Figure S57 HRESIMS of phyllaemblicin G7 (7)	61
58.	Figure S58 ¹ H NMR (500 MHz) spectrum of phyllaemblicin G7 (7) in CD ₃ OD	62
59.	Figure S59 ¹³ C NMR (100 MHz) spectrum of phyllaemblicin G7 (7) in CD ₃ OD	63
60.	Figure S60 HSQC spectrum of phyllaemblicin G7 (7) in CD₃OD	64
61.	Figure S61 HMBC spectrum of phyllaemblicin G7 (7) in CD₃OD	65
62.	Figure S62 ¹ H- ¹ H COSY spectrum of phyllaemblicin G7 (7) in CD ₃ OD	66
63.	Figure S63 ROESY spectrum of phyllaemblicin G7 (7) in CD₃OD	67
64.	Figure S64 HRESIMS of phyllaemblicin G8 (8)	68
65.	Figure S65 ¹ H NMR (800 MHz) spectrum of phyllaemblicin G8 (8) in CD ₃ OD	69
66.	Figure S66 ¹³ C NMR (100 MHz) spectrum of phyllaemblicin G8 (8) in CD ₃ OD	70
67.	Figure S67 HSQC spectrum of phyllaemblicin G8 (8) in CD₃OD	71
68.	Figure S68 HMBC spectrum of phyllaemblicin G8 (8) in CD ₃ OD	72
69.	Figure S69 ¹ H- ¹ H COSY spectrum of phyllaemblicin G8 (8) in CD ₃ OD	73
70.	Figure S70 ROESY spectrum of phyllaemblicin G8 (8) in CD₃OD	74

71.	Figure S71 HSQC-TOCSY spectrum of phyllaemblicin G8 (8) in CD ₃ OD	75
72.	Figure S72 ¹ H NMR (800 MHz) spectrum of glucose (hydolysis product of 7) in pyridine- d_{δ}	76
73.	Figure S73 ECD calculations of phyllaemblicin G1 (1)	77
74.	Figure S74 ECD calculations of phyllaemblicin G2 (2)	79
75.	Figure S75 ECD calculations of compound 3	81
76.	Figure S76 ECD calculations of compound 10	83

1. Figure S1 HRESIMS of compound 1

Min Max Val. Min Max Elmt Val. Min Max Elmt Val. Val. Min Max Elmt Elmt Use Adduct P н 0 100 N 3 0 0 3 0 Br 0 н 1 0 1 0 0 30 В 3 0 2 0 s 2 0 0 3 0 HCOO 0 0 Т С 4 0 60 F 1 0 0 CI 1 0 0 Error Margin (mDa): 20.0 DBE Range: 0.0 - 30.0 Electron lons: both HC Ratio: unlimited Apply N Rule: no Use MSn Info: yes Max Isotopes: all Isotope RI (%): 1.00 Isotope Res: 10000 MSn Iso RI (%): 75.00 MSn Logic Mode: OR Max Results: 800

Data File: D:\分子量测定\2013-01-24\gca40_TLJ1814C_28.lcd

Event#: 2 MS(E-) Ret. Time : 0.240 -> 0.540 - 1.110 -> 2.359 Scan# : 50 -> 110 - 224 -> 474





2. Figure S2 ¹H NMR (500 MHz) spectrum of phyllaemblicins G1 (1) in CD_3OD



3. Figure S3 13 C NMR (125 MHz) spectrum of phyllaemblicins G1 (1) in CD₃OD







5. Figure S5 HMBC spectrum of phyllaemblicins G1 (1) in CD₃OD



6. Figure S6 1 H- 1 H COSY spectrum of phyllaemblicins G1 (1) in CD₃OD

fl (ppm)



8. Figure S8 HRESIMS of phyllaemblicins G2 (2)

Formula Predictor Report - gca40_TLJ1664_29.lcd

Data File: D:\分子量测定\2013-01-24\gca40_TLJ1664_29.lcd

Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	N	3	0	0	P	3	0	0	Br	1	0	0	H
В	3	0	0	0	2	0	30	S	2	0	0	- I	3	0	0	HCOO
С	4	0	60	F	1	0	0	CI	1	0	0					
Error Margin (mDa): 20.0 HC Ratio: unlimited Max Isotopes: all MSn Iso RI (%): 75.00						Di App Isoto MSn Lo	BE Ran ply N Ri ppe RI (pgic Mo	ge: 0.0 - ule: no %): 1.00 de: OR	30.0			Electro Use MS Isotop Max R	n lons: Sn Info: e Res: esults:	both yes 1000(800	D	

Event#: 2 MS(E-) Ret. Time : 0.250 -> 0.550 Scan# : 52 -> 112



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9. Figure S9 ¹H NMR (800 MHz) spectrum of phyllaemblicins G2 (2) in CD_3OD



10. Figure S10¹³C NMR (125 MHz) spectrum of phyllaemblicins G2 (2) in CD₃OD



11. Figure S11 HSQC spectrum of phyllaemblicins G2 (2) in CD₃OD





13. Figure S13 ¹H-¹H COSY spectrum of phyllaemblicins G2 (**2**) in CD₃OD

fl (ppm)







15. Figure S15 HETLOC spectrum of phyllaemblicins G2 (2) in CD₃OD



16. Figure S16 HETLOC spectrum of phyllaemblicins G2 (2) in CD_3OD

17. Figure S17 ${}^{3}J_{H10,C14}$ calculation using HETLOC spectrum of phyllaemblicins G2 (2) in CD₃OD



18. Figure S18 ${}^{2}J_{H11,C10}$ calculation using HETLOC spectrum of phyllaemblicins G2 (2) in CD₃OD





19. Figure S19 ${}^{3}J_{H11,C9}$ calculation using TOCSY and HETLOC spectrum of phyllaemblicins G2 (2) in CD₃OD



20. Figure S20 ${}^{3}J_{H10,C12}$ calculation using TOCSY and HETLOC spectrum of phyllaemblicins G2 (2) in CD₃OD



21. Figure S21 HSQC-TOCSY spectrum of phyllaemblicins G2 (2) in CD₃OD

22.Figure S22 HRESIMS of compound **2A**

Data Filename	140709ESINA1.d	Sample Name	YLJ1664AG
Sample Type	Sample	Position	
Instrument Name	Agilent G6230 TOF N	4S User Name	KIB
Acq Method	ESIN.m	Acquired Time	7/9/2014 10:51:30 AM
IRM Calibration Statu	s Success	DA Method	ESIN.m
Comment			
Sample Group		Info.	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)		

User Spectra

Fragmentor Voltage Collision En 200 0			nergy	Ionization Mode ESI			
×10 4 -ESI So	an (O	0.844 min) F	rag=200.0	V 140709ESIN	NA1.d		
8-					347.1347		
6-							
4-							
2-							
o <u>!</u> ;	347.1	13455 347	.1346 3	47.13465 34 Counts vs. Ma	17.1347 347.1347 ass-to-Charge (m/z)	75 347.1348 3	347.13485
Peak List							
m/z 1	z Al	bund]				
1033.9881 1	1 16	4102.28	l				
Formula Calcula	ator	Element Lir	nits				
C Prement Pr		0 200	{				
		0 200	{				
n 0		0 400	{				
U Formula Calcula	ator	1 10 Regulte	1				
Formula	ICa	alculatedMa	355	Mz	Diff.(mDa)	Diff. (ppm)	DBE
C15 H23 O9			347.1342	347.1347	-0.5	1	.4 4.5

--- End Of Report ---



23.Figure S23 ¹H NMR (800 MHz) spectrum of compound **2A** in DMSO- d_6



24. Figure S24 13 C NMR (800 MHz) spectrum of compound **2A** in CH₃OD







26. Figure S26 HMBC spectrum of compound **2A** in DMSO- d_6



27. Figure S27 ¹H-¹H COSY spectrum of compound **2A** in DMSO- d_6

28.Figure S28 HRESIMS of phyllaemblicins G3 (3)

Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125.1)	

User Spectra



	0	100
0	8	10
Na	1	1

Formula Calculator Results

Formula	Calculated Mass	Measured Mass	Diff. (mDa)	Diff. (ppm)	DBE
C22 H28 Na O9	459.1631	459.1642	-1.1	-2.4	8.5



29.Figure S29 ¹H NMR (600 MHz) spectrum of phyllaemblicins G3 (**3**) in CD₃OD

-3 -2 entennet versteller attente versteller versteller versteller versteller versteller versteller versteller verste rahangkalar din pada karangkalan karang pana palan karang baran karang baran karang barang barang barang barang Nicht Ware and Cold With

80 75 f1 (ppm)

70 65

95 90 85

30.Figure S30¹³C NMR (150 MHz) spectrum of phyllaemblicins G3 (**3**) in CD₃OD

<u>4</u>П








f1 (ppm)



35.Figure S35 HRESIMS of phyllaemblicin G4 (4)

Formula Predictor Report - gca40_TLJ1811_30.lcd

Data File: D:\分子量测定\2013-01-24\gca40_TLJ1811_30.lcd

Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	N	3	0	0	P	3	0	0	Br	1	0	0	Н
В	3	0	0	0	2	0	30	S	2	0	0	- I	3	0	0	HCOO
С	4	0	60	F	1	0	0	CI	1	0	0					
Error Ma	argin (r	mDa):	20.0			D	BE Ran	ige: 0.0 -	30.0			Electro	n lons:	both		
	HC	Ratio:	unlimite	ed		App	bly N R	ule: no				Use MS	in Info:	yes		
M	ax Isot	opes:	all			Isoto	pe RI (%): 1.00				Isotop	e Res:	10000)	
MSi	n Iso R	l (%):	75.00			MSn Lo	ogic Mo	de: OR				Max R	esults:	800		

Event#: 2 MS(E-) Ret. Time : 0.250 -> 0.540 Scan# : 52 -> 110





36.Figure S36 ¹H NMR (400 MHz) spectrum of phyllaemblicins G4 (4) in CD₃OD



37.Figure S37¹³C NMR (100 MHz) spectrum of phyllaemblicins G4 (**4**) in CD₃OD











40.Figure S40 ¹H-¹H COSY spectrum of phyllaemblicins G4 (**4**) in CD₃OD







42.Figure S42 HSQC-TOCSY spectrum of phyllaemblicins G4 (4) in CD₃OD

43.Figure S43 HRESIMS of phyllaemblicin G5 (**5**)

Data Filename	140115ESINA4.d	Sample Name	YWX1261
Sample Type	Sample	Position	
Instrument Name	Agilent G6230 TOF MS	User Name	KIB
Acq Method	ESIN.m	Acquired Time	1/15/2014 11:15:39 AM
IRM Calibration Statu	is Success	DA Method	demo1.m
Comment			
Sample Group	Ir	nfo.	
Acquisition SW	6200 series TOF/6500 series		
Version	Q-TOF B.05.01 (B5125.1)		

User Spectra





44.Figure S44 ¹H NMR (500 MHz) spectrum of phyllaemblicin G5 (**5**) in CD₃OD

45.Figure S45¹³C NMR (125 MHz) spectrum of phyllaemblicin G5 (5) in CD₃OD









47.Figure S47 HMBC spectrum of phyllaemblicin G5 (5) in CD₃OD



52

fl (ppm)





50.Figure S50 HRESIMS of phyllaemblicin G6 (6)

Formula Predictor Report - gca40_TLJ18851_20.lcd

Data File: D:\分子量测定\2013-01-24\gca40_TLJ18851_20.lcd

Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Elmt	Val.	Min	Max	Use Adduct
H	1	0	100	N	3	0	0	P	3	0	0	Br	1	0	0	н
В	3	0	0	0	2	0	30	s	2	0	0	- I	3	0	0	HCOO
С	4	0	60	F	1	0	0	CI	1	0	0					
Error Ma M MSi	argin (r HC I ax Isot n Iso R	mDa): Ratio: topes: {I(%):	20.0 unlimite all 75.00	ed		D App Isoto MSn Lo	BE Ran ply N Ru ope RI (' ogic Mo	ge: 0.0 - ıle: no %): 1.00 de: OR	30.0			Electro Use MS Isotop Max R	n lons: In Info: e Res: esults:	both yes 10000 800)	

Event#: 2 MS(E-) Ret. Time : 0.250 -> 0.660 Scan# : 52 -> 134





51.Figure S51 ¹H NMR (500 MHz) spectrum of phyllaemblicin G6 (**6**) in CD₃OD

52.Figure S52 ¹³C NMR (125 MHz) spectrum of phyllaemblicin G6 (6) in CD₃OD











57.Figure S57 HRESIMS of phyllaemblicin G7 (**7**)

Data Filename Sample Type	140115ESINA1.d Sample		Sample Name Position	YLJ18952
Instrument Name Acq Method	Agilent G6230 TOF ESIN.m	MS	User Name Acquired Time	KIB 1/15/2014 10:32:12 AM
IRM Calibration Statu Comment	s Success		DA Method	demo1.m
Sample Group Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)	Info.		

User Spectra





58.Figure S58 ¹H NMR (500 MHz) spectrum of phyllaemblicin G7 (7) in CD₃OD

59.Figure S59¹³C NMR (100 MHz) spectrum of phyllaemblicin G7 (**7**) in CD₃OD





60.Figure S60 HSQC spectrum of phyllaemblicin G7 (7) in CD₃OD



61.Figure S61 HMBC spectrum of phyllaemblicin G7 (7) in CD₃OD







67

64.Figure S64 HRESIMS of phyllaemblicin G8 (8)

Data Filename	140115ESINA2.d		Sample Name	YLJ18951
Sample Type	Sample		Position	
Instrument Name	Agilent G6230 TOF	MS	User Name	KIB
Acq Method	ESIN.m		Acquired Time	1/15/2014 10:47:25 AM
IRM Calibration Statu	s Success		DA Method	demo1.m
Comment				
Sample Group		Info.		
Acquisition SW	6200 series TOF/6500 series			
Version	Q-TOF B.05.01 (B5125.1)			

User Spectra

Frag	gmentor Voltage 230	Collision Energy 0	Ionization Mode ESI		
x10 4	-ESI Scan (3.043-3	.059 min, 2 Scans) Frag	=230.0V 140115ESINA2.d		
_		11	61,3660		
7-					
6-					
5-					
4-					
3-					
2-					
1-					
0-		1 1			
	1161.1	1161.2 1161.3 Counts v	1161.4 1161.5 s. Mass-to-Charge (m/z)	1161.6	1161.7



65.Figure S65 ¹H NMR (800 MHz) spectrum of phyllaemblicin G8 (8) in CD₃OD



66.Figure S66¹³C NMR (100 MHz) spectrum of phyllaemblicin G8 (**8**) in CD₃OD






69.Figure S69 ¹H-¹H COSY spectrum of phyllaemblicin G8 (**8**) in CD₃OD

73

fl (ppm)







71.Figure S71 HSQC-TOCSY spectrum of phyllaemblicin G8 (8) in CD₃OD

fil (ppm)



72.Figure S72 ¹H NMR (800 MHz) spectrum of glucose (hydolysis product of **7**) in pyridine- d_6

73. Figure S73 ECD calculations of phyllaemblicin G1 (1)



DFT optimized conformers of the aglycon of 1S,3S,5R,6R,7S,8S,10S,11R- phyllaemblicin G1 (1) at B3LYP/6-311G(d, p) level in methanol (IEFPCM),

with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.



Figure 3. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon 1*S*, 3*S*, 5*R*, 6*R*, 7*S*, 8*S*, 10*S*, 11*R*-phyllaemblicin G1 (1), with Gaussian band shape 0.3ev.

74. Figure S74 ECD calculations of phyllaemblicin G2 (2)



DFT optimized conformers of the aglycon of 1*S*, 3*S*, 5*R*, 6*S*, 7*S*, 8*R*, 10*S*, 11*R*-phyllaemblicin G2 (**2**) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.



Figure 5. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon 1*S*, 3*S*, 5*R*, 6*S*, 7*S*, 8*R*, 10*S*, 11*R*-phyllaemblicin G2 (**2**), with Gaussian band shape 0.3ev.

75.Figure S75 ECD calculations of compound 3



(IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.



Figure 7. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of 1*S*, 3*S*, 5*R*, 6*S*,7*R*, 8*S*, 10*S*, 11*R*-phyllaemblicin G3 (**3**), with Gaussian band shape 0.3ev.

76. Figure S76 ECD calculations of compound 10

DFT optimized conformers of the aglycon of 1S, 3S, 5R, 6R, 8S, 10S, 11R-phyllaemblic acid (10) at B3LYP/6-311G(d, p) level in methanol (IEFPCM),

with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.



TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon 1*S*, 3*S*, 5*R*, 6*R*, 8*S*, 10*S*, 11*R*-phyllaemblic acid (**10**), with Gaussian band shape 0.3ev.