## Barrigenol triterpenes from the husks of *Xanthoceras sorbifolia* Bunge and their antitumor activities

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# Figure S4. HMBC Spectrum of 3-*O*-(3'-*O*-angeloyl)-*b*-*D*-glucopyranosyl-28-*O*- [ $\alpha$ -*L*-rhamnopyranosyl(1 $\rightarrow$ 2)]-*b*-*D*-glucopyranosyl-3*b*, 21*b*, 22 $\alpha$ , 28-tetrahydroxy-olean-12-ene (1) in C<sub>5</sub>D<sub>5</sub>N.



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Figure S6. NOESY Spectrum of 3-O-(3'-O-angeloyl)- $\beta$ -D-glucopyranosyl-28-O- [ $\alpha$ -L-rhamnopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucopyranosyl-3 $\beta$ , 21 $\beta$ , 22 $\alpha$ , 28-tetrahydroxy-olean-12-ene (1) in C<sub>5</sub>D<sub>5</sub>N.





Figure S7. IR Spectrum of 3-*O*-(3'-*O*-angeloyl)-*B*-*D*-glucopyranosyl-28-*O*- [ $\alpha$ -*L*-rhamnopyranosyl(1 $\rightarrow$ 2)]-*B*-*D*-glucopyranosyl-3*B*, 21*B*, 22 $\alpha$ , 28-tetrahydroxy-olean-12-ene (1).

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# Figure S8. <sup>1</sup>H-NMR Spectrum of 3-*O*-[ $\alpha$ -*L*-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -*D*-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -*D*- $\delta'$ - *n*-butyl-glucuronic acid-21-*O*-epoxyangeloyl-22-*O*-angeloyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (2) in C<sub>5</sub>D<sub>5</sub>N.

Figure S9. <sup>13</sup>C-NMR Spectrum of 3-*O*-[ $\alpha$ -*L*-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -*D*-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -*D*- $\beta$ '- *n*-butyl-glucuronic acid-21-*O*-epoxyangeloyl-22-*O*-angeloyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (2)in C<sub>5</sub>D<sub>5</sub>N.

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50 240 230 220	210 200 190 180	170 160	150 140	130 f1 (m	, 120 m)	110	100	90	80	70	60	50	40	1 , 30 2	0 10	

Figure S10. HR-ESI-MS Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D- $\delta$ '- n-butyl-glucuronic acid-21-O-epoxyangeloyl-22-O-angeloyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (2).

	Mass S	pectrum Mol	lecular Fo	rmula Repo	ort		
Analysis Info				Acquisition Date	4/28/2	013 9:16:41	AM
Analysis Name	D:\Data\20130428\16.	.5d					
Method	MA250-550POS.m			Operator	Bruker	Customer	
Sample Name	16.5-	10 Ol 11		Instrument / Ser	# micrO	TOF-Q 12	25
Comment		· · · · ·					
Acquisition Par	ameter						
Source Type	ESI	ion Polarity	Positive	Set Nebuliz	287	0.3 Bar	
Focus	Not active	Set Capillary	4500 V	Set Dry He	ater	180 °C	
Scan Begin Scan End	3000 m/z	Set Collision Cell R	= 1000.0 Vpp	Set Divert 1	valve	Source	
Generate Molec	ular Formula Paramet	er					
Formula, min.	C61H96O23Na				_22		
Measured miz	1219 62	Tolerance	4 mDa	Charge	1		
Check Valence	00	Minimum	0	Maximur	mÖ		
Nirogen Rule	no	Electron Cor	figuration both				
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Figure S11. HMBC Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D- $\beta$ '- n-butyl-glucuronic acid-21-O-epoxyangeloyl-22-O-angeloyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (2) in C<sub>5</sub>D<sub>5</sub>N.







Figure S13. NOESY Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D- $\delta'$ - n-butyl-glucuronic acid-21-O-epoxyangeloyl-22-O-angeloyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (2) in C<sub>5</sub>D<sub>5</sub>N.





Figure S14. IR Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D- $\delta'$ -n-butyl-glucuronic acid-21-O-epoxyangeloyl-22-O-angeloyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (2).

### Figure S15. <sup>1</sup>H-NMR Spectrum of 6'-methylester-O-Xanifolia-Y5 (3) in $C_5D_5N$ .



## Figure S16. <sup>13</sup>C-NMR Spectrum of 6'-methylester-O-Xanifolia-Y5 (3) in C<sub>5</sub>D<sub>5</sub>N.

-167.79	-167.39 -143.39 -137.06 -136.14 -128.79	-128.60 -125.06 -106.82 -104.97 -88.80 -83.39 -78.26 -77.14	76.61 -76.39 -74.60	74.36 -73.25 -73.04	-72.33 -69.23 -67.18	-62.80	-51.74 -48.05	46.79	-41.15 -40.66 -39.20	-38.63 -36.62	736.03	27.70	23.66	-20.68 -20.32 -19.89	-18.44 -17.23	-16.44 -15.58 -15.50 -15.35	-550
	Parameter	Value															ł
1 Cot	mment																-500
2 Ori	igin	Bruker BioSpin GmbH															
3 Ow	mer	nmr															1
4 Site	e																-450
5 Spe	ectrometer	spect															
6 Sol	vent	Pvr															1082
7 Ter	mperature	298.8															-40
8 Pul	lse Sequence	zepe30															-
9 Ext	periment	1D															002
10 Nut	mber of Scans	4035															-35
11 Rec	ceiver Gain	175															÷
12 Rel	laxation Delay	2.0000															20
13 Pul	lse Width	11.5500		1													Fou
14 Acc	ouisition Time	0.9044															÷
15 Acc	guisition Date	2014-06-24T19:55:31															-25
16 Mo	dification Date	2015-06-24T19:37:27															100
17 Spe	ectrometer Frequenc	w 150.90		I													ł
18 Spe	ectral Width	36231.9		I													-20
19 Los	west Frequency	-3041.0															1.00
20 Nu	cleus	13C		1													t
21 Acc	ovired Size	32768															-18
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### Figure S17. HR-ESI-MS Spectrum of 6'-methylester-O-Xanifolia-Y5 (3).

#### Mass Spectrum Molecular Formula Report Analysis Info Acquisition Date 11/18/2015 12:21:31 PM D:\Data\20151118CEYANG\WD-12\_1-a,5\_01\_5982.d Analysis Name Method 20131026\_ceyang.m Operator micrOTOF-Q Sample Name WD-12 Instrument / Ser# Bruker Customer 125 Comment Acquisition Parameter Source Type ESI Ion Polarity Positive Set Nebulizer 1.2 Bar Focus Active Set Capillary 4500 V Set Dry Heater 180 °C Scan Begin 50 m/z Set End Plate Offset -500 V Set Dry Gas 8.0 Vmin Scan End 3000 m/z Set Collision Cell RF 400.0 Vpp Set Divert Valve Source Generate Molecular Formula Parameter Formula, min. C53H82O19Na Formula, max. Measured m/z 1045.53 5 ppm Charge Tolerance Check Valence Minimum 0 Maximum 0 no Electron Configuration both Nirogen Rule no Filter H/C Ratio Minimum 0 Maximum 3 no Estimate Carbon yes Intens. +MS, 0.4min #26 5000-4000-1045.5294 3000-2000-1031.5084 1040.5685 1000-1093.4896 1006.6851 1061.5120 1077.5133 مستعيديالاس فالمعالم فيعيارة 0-14 1060 1000 1010 1020 1030 1040 1050 1070 1080 1090 m/z Sum Formula Sigma Err [ppm] Mean Err [ppm] Err [mDa] rdb N Rule m/z e 1045.5343 C 53 H 82 Na 1 O 19 0.039 4.87 12.50 4.66 7.66 ok even

Figure S18. HMBC Spectrum of 6'-methylester-O-Xanifolia-Y5 (3) in C<sub>5</sub>D<sub>5</sub>N.



Figure S19. HSQC Spectrum of 6'-methylester-O-Xanifolia-Y5 (3) in C<sub>5</sub>D<sub>5</sub>N.









## Figure S21. <sup>1</sup>H-NMR Spectrum of 16-*O*-acetyl-aesculioside G12 (4) in $C_5D_5N$ .

6.3260 6.3086 6.0736 6.0735 6.0703 6.0103	5.7233 5.5594 5.4227 5.3676 5.3676 4.9984 4.9984 4.9987	4.9871	4.8814	4.8254	4.6231-	4.5019	4.4636	4.3707	4.3288	4.3136	4.2174	3.7696 3.6280	2.0824	2.0800	2.0679	2.0495	1.9859	1.8521	1.4747	1.2947	1.11661	0.7809 0.7469
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1 Receiver Gain	128					I .											11		11			
2 Relaxation Delay	1.0000				1	I .							21				11		11			
3 Pulse Width	11.1000					I .							11				11					
4 Acquisition Time	2.7263					I .											11		11			
5 Acquisition Date	2013-03-20T17:23:20					1											11		11			
6 Modification Date	2013-03-20T17:23:00					I .											11		11			
7 Spectrometer Frequen	cy 600.13					I .											11		11			
8 Spectral Width	12019.2					I .											1		11		a.	
9 Lowest Frequency	-2377.2					1													11			
0 Nucleus	1H					I .			1										11			
1 Acquired Size	32768					I .			1				11						11			
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12.5 12.0 11.5	11.0 10.5 10.0 9.5	9.0	8.5	8.0	7.5	7.0	6.5 fl	6.0 (ppm)	5. 5	5.0	4.	5 4.0	3.	5 3	.0 2	. 5	2.0	1.5	1.0	0.	5 0. (	0 -0

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				1 11 11111		<b>1 1 1 1</b>	AL THEFT

85 45 485

### Figure S22 <sup>13</sup>C-NMR Spectrum of 16-*O*-acetyl-aesculioside G12 (4) in C-D-N



	N	lass	Spectr	um Mo	lecular F	ormula	Repo	ort		
Analysis Info						Acquis	ition Date	4/10/2	013 3:09:3	5 PM
Analysis Name	D:\Data\Z	L-M.d								
Method	LIU 250-5	50POS.r	m			Operat	tor	Bruke	r Custome	r
Sample Name	ZL-M					Instrum	nent / Ser	# micrO	TOF-Q	125
Comment										
Acquisition Pa	arameter		22							,
Source Type	ESI		Ion P	olarity	Positive		Set Nebuliz	zer	0.3 Bar	
Focus	Not act	ive	Set C	apillary	4500 V		Set Dry Hea	ater	180 °C	
Scan Begin	50 m/z	i	Set E	nd Plate Offs	et -500 V		Set Dry Ga	S	4.0 l/mir	1
Scan End	3000 m	1/z	Set C	Collision Cell R	RF 500.0 Vpp		Set Divert \	Valve	Source	
Generate Mol	ecular Formu	la Para	meter							
Formula, min.	C60H92O	23Na					0.4			
Formula, max.	1000 50			Telerance	5 000		Charge	1		
Measured m/z	1203.59			Minimum	0		Maximur	m 0		
Lirogen Rule	10			Electron Co	ofiguration both		TVID.XIIII GI			
Filter H/C Ratio	00			Minimum	0		Maximur	m 3		
Estimate Carbon	yes									
				1.					-MC	0.6min #2/
v104-									+MO.	0.00000 #34
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15										
1.5					22					
1 .	1203.5925									
10										
1.01										
1	11									
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0.57										
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	Sum Formula	Sigma	m/z	Err [pom]	Mean Err (ppm)	Err (mDal	rdb	N Kule	e	
C 60 H	Sum Formula 92 Na 1 O 23	Sigma 0.036	m/z 1203.5922	-0.29	Mean Err [ppm] 0.59	-0.35	14.50	ok	even	



Figure S24. HMBC Spectrum of 16-O-acetyl-aesculioside G12 (4) in C<sub>5</sub>D<sub>5</sub>N.

Figure S25. HSQC Spectrum of 16-O-acetyl-aesculioside G12 (4) in C<sub>5</sub>D<sub>5</sub>N.



Figure S26. NOESYS pectrum of 16-O-acetyl-aesculioside G12 (4) in  $C_5D_5N$ .





Figure S28. <sup>1</sup>H-NMR Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D-6'-methyl-glucuronic acid-21-O-(3'''',4''''-O-diangeloyl)- $\beta$ -D-fucopyranosyl-28-O-acetyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (5) in C<sub>5</sub>D<sub>5</sub>N.





Figure S29. <sup>13</sup>C-NMR Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D-6'-methyl-glucuronic acid-21-O-(3''',4''''-O-diangeloyl)- $\beta$ -D-fucopyranosyl-28-O-acetyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (5) in C<sub>5</sub>D<sub>5</sub>N.



Figure S30. HR-ESI-MS Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D-6'-methyl-glucuronic acid-21-O-(3'''',4''''-O-diangeloyl)- $\beta$ -D-fucopyranosyl-28-O-acetyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (5).



Figure S31. HMBC Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D-6'-methyl-glucuronic acid-21-O-(3''',4''''-O-diangeloyl)- $\beta$ -D-fucopyranosyl-28-O-acetyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (5) in C<sub>5</sub>D<sub>5</sub>N.



Figure S32. HSQC Spectrum of 3-O-[ $\alpha$ -L-arabinofuranosyl(1 $\rightarrow$ 3)]- $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)- $\beta$ -D-6'-methyl-glucuronic acid-21-O-(3''',4''''-O-diangeloyl)- $\beta$ -D-fucopyranosyl-28-O-acetyl-3 $\beta$ , 16 $\alpha$ , 21 $\beta$ , 22 $\alpha$ , 28-pentahydroxy-olean-12-ene (5) in C<sub>5</sub>D<sub>5</sub>N.







Figure S34. <sup>1</sup>H-NMR Spectrum of 6'-methylester-O-Xanifolia-Y2 (6) in  $C_5D_5N$ .

69.78 69.78 67.70 37.41 36.47	25.08 25.20 25.20 04.73 04.73 03.92 03.92 5.35 5.35	3.64 8.55 8.40	8.21 7.47	5.46	3.30	9.48 7.46	3.08	5.89	233	7.68	6.86 6.86	3.58	0.95	8.59 6.79	6.50	6.33 9.49	6.56	2.17	00.1	0.19	8.79	5.90	-8000
<u> </u>		866		60	111	- 6 6	6.6	9 19	N. C	1 4 4	14	4 4	14	n n	E C	19 W	22	23	100	12			-7500
Parameter	Value																						-7000
1 Origin	Bruker BioSpin GmbH																						
2 Owner	av600		1																				-6500
3 Site			1																				
4 Spectrometer	spect																						- 6000
5 Solvent	Pyr		1																				-0000
6 Temperature	294.9																						5500
7 Pulse Sequence	zgpg30																						-5500
8 Experiment	1D																						6000
9 Number of Scans	7594																						-5000
10 Receiver Gain	13000																						1.000
11 Relaxation Delay	2.0000																						-4500
12 Pulse Width	6.0000																						İ
13 Acquisition Time	0.7209		1																				-4000
14 Acquisition Date	2013-02-17T09:21:35																						1.000
15 Modification Date	2013-02-17T15:09:00																						-3500
16 Spectrometer Freque	ney 150.90																						1
17 Spectral Width	45454.5																						-3000
18 Lowest Frequency	-7602.7																						-
19 Nucleus	13C																						-2500
20 Acquired Size	32768																						ł
21 Spectral Size	65536																						-2000
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## Figure S35. <sup>13</sup>C-NMR Spectrum of 6'-methylester-O-Xanifolia-Y2 (6) in $C_5D_5N$ .

Figure S36. HR-ESI-MS Spectrum of 6'-methylester-O-Xanifolia-Y2 (6).

	Ι	Mass	Spect	trum M	oled	cular F	ormul	a Rep	ort			
Analysis Info							Acqu	isition Date	3/12	/2014 7	32:01 F	PM
Analysis Name Method Sample Name Comment	D:\Data\2 tune_higt ZL-9	0140312 1_pos.m	2ceyang\ZL	-9.d			Oper	rator ument / Ser	Bruk # micr	er Custo	omer 2 125	
Acquisition Par Source Type Focus Scan Begin Scan End	ESI Active 50 m/z 3000 n	r n/z	lon Set Set	Polarity Capillary End Plate Off Collision Cell	set RF	Positive 4500 V -500 V 1000.0 Vpp		Set Nebuliz Set Dry He Set Dry Ga Set Divert	zer ater is Valve	0.3 180 4.0 Sou	Bar )°C Vmin urce	
Generate Molec Formula, min. Formula, max. Measured m/z Check Valence Nirogen Rule Filter H/C Ratio Estimate Carbon	C58H90O 1193.57 no no ves	ula Para 124Na	meter	Tolerance Minimum Electron C Minimum	5 0 Configu 0	ppm ration both		Charge Maximur Maximur	m 1 m 3			
ntens. x104 1.5 1.0				1	193.57	'19					+MS, 0.	2min #9
0.5	1128,0600	) 1140	1160	1180		200	1220	1240	1260		1280	, m/z
C 58 H 90	m Formula Na 1 O 24	Sigma 0.073	m/z	Err [ppm] -0.42	Mean	-0.30	Err [mDa -0.5	] rdb   0 13.50	N Rule ok	even		



## Figure S37. HMBC Spectrum of 6'-methylester-O-Xanifolia-Y2 (6) in $C_5D_5N$ .



Figure S38. HSQC Spectrum of 6'-methylester-O-Xanifolia-Y2 (6) in C<sub>5</sub>D<sub>5</sub>N.



Figure S39. IR Spectrum of 6'-methylester-O-Xanifolia-Y2 (6).





-169.77 -168.10 -167.67 -142.72 -137.22 -137.08	-128.93 -124.11 -123.50 -111.21 -103.89 -91.57 -85.26 -85.41 -85.41 -85.41 -85.41 -85.41 -85.41 -85.41 -85.41 -78.70	71.76 77.76 77.47	-76.37 -73.52	-69.47 -68.57	-63.50 -63.17	-61.18 -56.05	-52.33	-47.15	43.62	r40.01	38.38	36.35	134.77	133.08	-27.48	-26.49	-22.24	-21.01	-20.26	-18.42	-15.88	-15.78 15.53	-65000
Parameter	Value																						-60000
1 Origin	Bruker BioSpin GmbH																						-
2 Owner	av600																						- 55000
3 Site		1	I																				-
4 Spectrometer	spect																						- 50000
5 Solvent	Pyr																						
6 Temperature	673.2																						-45000
7 Pulse Sequence	zgpg30																						
8 Experiment	1D																						4000
9 Number of Scans	5802																						-4000
10 Receiver Gain	13000																						1
11 Relaxation Delay	2.0000																						-35000
12 Pulse Width	6.0000																						1
13 Acquisition Time	0.7209																						- 3000
14 Acquisition Date	2013-04-15T22:04:35																						
15 Modification Date	2013-04-15T22:04:00																						-25000
16 Spectrometer Frequer	ney 150.90																						
17 Spectral Width	45454.5																						-2000
18 Lowest Frequency	-7776.6																						2000
19 Nucleus	13C																						1500
20 Acquired Size	32768																						- 1500
21 Spectral Size	65536																						- 1000
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240 230 220 21	10 200 190 180 170 160	150 140	130	120 11	0 100 fl(pp	90 () 90 (m)	80	70	60	50	40	3	0	20	10	0	'.	10	-20	-30	40	) <mark>-</mark> 5	۲ 0

## Figure S41. <sup>13</sup>C-NMR Spectrum of 6'-methylester-O-Xanifolia-Y8 (7) in C<sub>5</sub>D<sub>5</sub>N.

Figure S42. HR-ESI-MS Spectrum of 6'-methylester-O-Xanifolia-Y8 (7).

	Iviass op			inula Repu	L	
Analysis Info				Acquisition Date	3/12/2014	7:28:36 PM
Analysis Name Method Sample Name Comment	D:\Data\20140312ceyan tune_high_pos.m ZL-10	ıg\ZL-10.d		Operator Instrument / Ser#	Bruker Ci micrOTO	ustomer F-Q 125
Acquisition Par	ameter	101.14200.0020.004	Constant and the second		~ *	12 017 TO 4010
Source Type Focus Scan Begin Scan End	ESI Active 50 m/z 3000 m/z	Ion Polarity Set Capillary Set End Plate Offset Set Collision Cell RF	Positive 4500 V -500 V 1000.0 Vpp	Set Nebulizer Set Dry Heate Set Dry Gas Set Divert Va	ar Ive	0.3 Bar 180 °C 4.0 Vmin Source
Generate Molec Formula, min. Formula, max.	ular Formula Parameter C58H90O23Na					
Aeasured m/z	1177.58	Tolerance	5 ppm	Charge	1	
heck Valence	no	Minimum	0	Maximum	0	
liter H/C Ratio	00	Electron Config Minimum	0	Maximum	3	
stimate Carbon	yes	10000000000	304	Constant of the second	1920	
1000						+MS, 0.5min #3
2500						
2000			1177.5	5759		
1500						
1000-						
500						
	1045.5328				7 93	20 829-0
1000	1050	1100	1150	1200	1250	m



Figure S43. HMBC Spectrum of 6'-methylester-O-Xanifolia-Y8 (7) in C<sub>5</sub>D<sub>5</sub>N.



Figure S44. HSQC Spectrum of 6'-methylester-O-Xanifolia-Y8 (7) in C<sub>5</sub>D<sub>5</sub>N.



Figure S45. IR Spectrum of 6'-methylester-O-Xanifolia-Y8 (7).



## Figure S46. <sup>1</sup>H-NMR Spectrum of Xanifolia Y (8) in C<sub>5</sub>D<sub>5</sub>N.

/172.02
/168.10
/167.73 143.67 137.40 /111.19
/105.21
/104.86 -129.13 -1 25.44 89.87 85.48 83.63 69.77 67.52 67.52 61.84 48.38 47.72 73.36 73.36 Parameter Value Comment -1700 Origin Bruker BioSpin GmbH -1600 Owner nmr Site -1500 Spectrometer spect -1400 Solvent Pyr Temperature 295.9 -1300 Pulse Sequence zgpg30 -1200 Experiment 1D Number of Scans 1376 -1100 Receiver Gain 203 Relaxation Delay 2.0000 -1000 Pulse Width 9,4000 -900 Acquisition Time 1.1010 Acquisition Date 2013-11-18T12:18:18 -800 Modification Date 2013-11-18 T00:00:00 -700 Spectrometer Frequency 100.61 Spectral Width 29761.9 -600 -4795.2 Lowest Frequency -500 Nucleus 13C Acquired Size 32768 -400 Spectral Size 65536 -300 -200 -100 . A STATE OF THE AND A STATE OF THE a district and a state of a state of the second state of the secon -0 ANALY MANAL AND ALK ANALAND A -100 -200 -300 -400 -500 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 fl (ppm)

## Figure S47. <sup>13</sup>C-NMR Spectrum of Xanifolia Y (8) in $C_5D_5N$ .



Figure S48. <sup>1</sup>H-NMR Spectrum of Xanifolia ACH-Y (9) in  $C_5D_5N$ .



Figure S49. <sup>13</sup>C-NMR Spectrum of Xanifolia ACH-Y (9) in  $C_5D_5N$ .

--200

-- 300



## Figure S50. <sup>1</sup>H-NMR Spectrum of Xanifolia Y2 (10) in $C_5D_5N$ .



Figure S51. <sup>13</sup>C-NMR Spectrum of Xanifolia Y2 (10) in  $C_5D_5N$ .

Figure S52. HR-ESI-MSSpectrum of Xanifolia Y2 (10) in C<sub>5</sub>D<sub>5</sub>N.

	N	lass S	Spectr	um Mol	ec	ular Fo	ormula	Repo	ort					
Analysis Info Analysis Name Method Sample Name Comment	alysis Info alysis Name D:\Data\20150605CEYANG\wd-15_1-a,7 20131026_ceyang.m imple Name wd-15 omment						Acquisiti Operato Instrume	Acquisition Date 5/6 Operator m Instrument / Ser# Bru			/6/2015 12:37:12 PM nicrOTOF-Q ruker Customer 125			
Acquisition Par Source Type Focus Scan Begin Scan End	ESI Active 50 m/z 3000 m/	z	Ion Pr Set C Set E Set C	olarity apillary nd Plate Offset ollision Cell RF		Positive 4500 V -500 V 600.0 Vpp	S S S	et Nebuliz et Dry He et Dry Ga et Divert \	ter ater s /alve	1.2 Ba 180 °C 8.0 Vn Sourc	ir Diin e			
Generate Molect Formula, min. Formula, max. Measured m/z Check Valence Nirogen Rule Filter H/C Ratio Estimate Carbon	cular Formul C66H102O 1349.64 no no no yes	a Parame 27Na	iter	Tolerance Minimum Electron Con Minimum	6 0 figun 0	ppm ation both		Charge Maximur Maximur	n 0 n 3					
1.5- 1.0- 1.5- 1.0-	272.6346			1327.6526	1349	0.6426	1384.6	378	×14	+M 117.6215	S, 0.6min #35			
0.0 1260 St C 66 H 102	1280 um Formula 2 Na 1 O 27	1300 Sigma 0.018	13 m/z 1349.6501	20 134 Err [ppm] 5.54	0 Mea	1360 n Err [ppm] 7,44	1380 Err (mDa) 7,47	140 rdb 15.50	N Rule	1420 e <sup>-</sup>	1440 m/z			