## **Electronic Supplementary Information (ESI)**

## New triterpenoid saponin glycosides from the fruit fibers of *Trichosanthes cucumerina* L.

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Figure S1. Structures of known compounds 6–16



Figure S2. Structures of compounds 1a-4a and 1b-4b

Position	1b	2b	3b	4b		
1	1.48 m	1.32 m	1.43 m	1.45 m		
	1.00 <sup>a</sup>	2.31 dd (11.6, 4.4)	0.90 m	0.90 m		
2	1.95 dd (11.9, 3.5)	4.24 dd (11.6, 3.9)	1.83 <sup>a</sup>	1.27ª		
	2.29 dd (11.9, 3.5)		2.26 dd (11.8, 3.7)			
3	4.32 dd (11.9, 4.4)	4.28 d (11.6)	3.42 dd (11.8, 5.3)	4.21 dd (11.8, 4.4)		
5	1.76 m	1.87 m	0.81 m	1.36 m		
6	1.3 m	1.38 m	1.31ª	1.83 <sup>a</sup>		
	1.73 m	1.74 <sup>a</sup>	1.50 m	2.23 m		
7	1.28 m	1.29ª	1.46 <sup>a</sup>	1.20 m		
	1.62 m	1.64 m	2.04 dd (13.8, 4.1)	1.45 m		
9	1.68 m	1.90 t (9.8)	1.65 t (9.1)	1.70 m		
11	1.93 m	1.94 m	2.15 m	2.11ª		
12	5.49 brt (3.4)	5.46 brt (3.4)	5.50 brt (3.3)	5.48 brt (3.2)		
15	1.15 m	1.12 m	1.22 m	1.15 m		
	2.15 m	2.15 m	2.16 m	2.11ª		
16	2.06 dd (13.8, 3.1)	2.01 m	1.92 dd (13.8, 3.8)	1.89 m		
			1.99 m	1.95 m		
18	3.30 dd (13.5, 3.8)	3.39 dd (13.5, 3.8)	3.32 dd (13.7, 4.0)	3.31 dd (14.0, 4.0)		
19	1.28 m	1.29ª	1.31 <sup>a</sup>	1.29ª		
	1.79 m	1.74 <sup>a</sup>	1.83 <sup>a</sup>	1.80 m		
21	1.19 m	1.16 m	1.22 m	1.15 m		
	1.45 dd (13.9, 3.7)	1.43 m	1.46 <sup>a</sup>	1.42 m		
22	1.83 m	1.82 m	1.26 m	1.83 <sup>a</sup>		
	2.03 dd (13.9, 3.7)	2.06 m		2.04 dd (14.2, 4.5)		
23	3.75 d (10.8)	3.72 d (10.8)	1.01 s	9.79 s		
	4.40 d (10.8)	4.58 d (10.8)				
24	0.99 s	1.02 s	1.34 s	1.33 s		
25	0.92 s	1.01 s	0.83 s	0.81 s		
26	1.03 s	1.03 s	1.01 s	0.96 s		
27	1.25 s	1.21 s	1.32 s	1.29 s		
29	0.93 s	0.93 s	0.97 s	0.97 s		
30	1.00 s	1.00 s	1.02 s	1.02 s		
	3-Glc'	3-Glc'	3-Glc'	3-Glc'		
1′	5.18 d (7.8)	5.18 <sup>a</sup>	4.98 d (7.8)	4.88 d (7.7)		
2'	4.08 t (8.3)	4.15 m	4.08 t (8.2)	3.96 t (8.3)		
3'	4.21 t (8.9)	4.16 m	4.31 t (8.8)	4.23 m		
4'	4.29 t (9.2)	4.28 t (9.4)	4.27 t (8.8)	4.23 m		
5'	3.94 ddd (9.4, 4.6, 2.3)	3.95 ddd (9.5, 4.9, 2.0)	4.05 m	3.99 m		
6'	4.43 dd (11.9, 4.9)	4.35 dd (11.8, 5.4)	4.45 dd (11.7, 5.4)	4.41 dd (11.5, 5.2)		
-	4.56 dd (11.9, 2.0)	4.56 dd (11.8, 1.8)	4.63 dd (11.7, 2.4)	4.61 dd (11.5, 1.6)		
<sup>a</sup> Signals overlapped.						

**Table S1.** <sup>1</sup>H NMR data of compounds **1b–4b** in pyridine- $d_5$  at 400 MHz ( $\delta$  in ppm, J in Hz)

Position	1b	2b	3b	4b
1	39.1	47.7	39.2	38.5
2	26.4	67.5	27.1	30.5
3	82.6	89.0	89.3	82.1
4	43.9	45.2	40.0	56.0
5	48.6	47.7	56.3	48.0
6	18.6	18.7	19.0	25.5
7	33.3	33.2	33.7	34.7
8	40.2	40.2	40.2	40.4
9	48.1	48.6	48.5	48.4
10	37.4	38.3	37.5	36.6
11	24.3	24.1	24.2	24.2
12	123.0	123.0	123.0	122.7
13	145.3	145.3	145.3	145.4
14	42.6	42.7	42.6	42.7
15	28.8	28.8	28.7	28.7
16	24.1	24.4	24.2	24.1
17	47.1	47.1	47.2	47.1
18	42.4	42.4	42.5	42.4
19	46.8	46.8	46.9	47.1
20	31.4	31.4	31.5	31.4
21	34.6	34.7	34.7	33.0
22	33.3	33.7	30.5	33.6
23	65.1	64.3	17.5	207.4
24	14.2	15.3	28.7	10.9
25	16.6	17.8	15.9	16.0
26	17.9	18.0	17.9	17.8
27	26.6	26.6	26.7	26.6
28	180.7	180.7	180.7	179.2
29	33.3	33.7	33.8	33.8
30	24.3	24.2	24.2	24.2
	3-Glc'	3-Glc'	3-Glc'	3-Glc'
1′	106.4	106.3	107.4	105.3
2'	76.4	76.0	76.3	75.9
3'	79.2	79.1	79.3	79.1
4'	72.1	71.9	72.3	72.0
5'	78.9	79.0	78.8	79.1
6'	63.2	62.8	63.5	63.4
-				

**Table S2.** <sup>13</sup>C NMR data of compounds **1b–4b** in pyridine- $d_5$  at 100 MHz ( $\delta$  in ppm)



Figure S3. <sup>1</sup>H NMR spectra of compound 1a recorded in pyridine- $d_5$ 



Figure S4. <sup>13</sup>C NMR spectra of compound 1a recorded in pyridine- $d_5$ 



Figure S5. <sup>1</sup>H NMR spectra of compound 2a recorded in pyridine-*d*<sub>5</sub>



Figure S6. <sup>13</sup>C NMR spectra of compound 2a recorded in pyridine- $d_5$ 



Figure S7. <sup>1</sup>H NMR spectra of compound 3a recorded in pyridine- $d_5$ 



Figure S8. <sup>13</sup>C NMR spectra of compound 3a recorded in pyridine- $d_5$ 



Figure S9. <sup>1</sup>H NMR spectra of compound 4a recorded in pyridine- $d_5$ 



Figure S10. <sup>13</sup>C NMR spectra of compound 4a recorded in pyridine- $d_5$ 



Figure S11. <sup>1</sup>H NMR spectra of compound 1b recorded in pyridine-*d*<sub>5</sub>



Figure S12. <sup>13</sup>C NMR spectra of compound 1b recorded in pyridine- $d_5$ 



Figure S13. <sup>1</sup>H NMR spectra of compound 2b recorded in pyridine-*d*<sub>5</sub>



Figure S14. <sup>13</sup>C NMR spectra of compound 2b recorded in pyridine-*d*<sub>5</sub>



Figure S15. <sup>1</sup>H NMR spectra of compound 3b recorded in pyridine-*d*<sub>5</sub>



Figure S16. <sup>13</sup>C NMR spectra of compound 3b recorded in pyridine- $d_5$ 



Figure S17. <sup>1</sup>H NMR spectra of compound 4b recorded in pyridine-*d*<sub>5</sub>



Figure S18. <sup>13</sup>C NMR spectra of compound 4b recorded in pyridine- $d_5$ 



Figure S19. <sup>1</sup>H NMR spectra of compound 1 recorded in pyridine-*d*<sub>5</sub>



Figure S20. Expansion of <sup>1</sup>H NMR spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S21. Expansion of <sup>1</sup>H NMR spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S22. Expansion of <sup>1</sup>H NMR spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S23. <sup>13</sup>C NMR and DEPT spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S24. Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S25. Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S26. <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S27. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S28. Expansion of  $^{1}H^{-1}H$  COSY spectra of compound 1 recorded in pyridine- $d_{5}$ 



Figure S29. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S30. HMQC spectrum of compound 1 recorded in pyridine-d<sub>5</sub>



Figure S31. Expansion of HMQC spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S32. Expansion of HMQC spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S33. Expansion of HMQC spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S34. HMBC spectra of compound 1 recorded in pyridine-d<sub>5</sub>



Figure S35. Expansion of HMBC spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S36. Expansion of HMBC spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S37. Expansion of HMBC spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S38. Expansion of HMBC spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S39. NOESY spectra of compound 1 recorded in pyridine-*d*<sub>5</sub>



Figure S40. Expansion of NOESY spectra of compound 1 recorded in pyridine- $d_5$ 



Figure S41. Expansion of NOESY spectra of compound 1 recorded in pyridine-d<sub>5</sub>



Figure S42. Expansion of NOESY spectra of compound 1 recorded in pyridine- $d_5$ 







Figure S44. <sup>1</sup>H NMR spectra of compound 2 recorded in pyridine-*d*<sub>5</sub>



Figure S45. Expansion of <sup>1</sup>H NMR spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S46. Expansion of <sup>1</sup>H NMR spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S47. Expansion of <sup>1</sup>H NMR spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S48. <sup>13</sup>C NMR and DEPT spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S49. Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S50. Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S51. <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S52. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S53. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S54. HMQC spectra of compound 2 recorded in pyridine-*d*<sub>5</sub>



Figure S55. Expansion of HMQC spectra of compound 2 recorded in pyridine-d<sub>5</sub>



Figure S56. Expansion of HMQC spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S57. Expansion of HMQC spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S58. HMBC spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S59. Expansion of HMBC spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S60. Expansion of HMBC spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S61. Expansion of HMBC spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S62. Expansion of HMBC spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S63. Expansion of HMBC spectra of compound 2 recorded in pyridine-d<sub>5</sub>



Figure S64. NOESY spectra of compound 2 recorded in pyridine-d<sub>5</sub>


Figure S65. Expansion of NOESY spectra of compound 2 recorded in pyridine- $d_5$ 



Figure S66. Expansion of NOESY spectra of compound 2 recorded in pyridine- $d_5$ 





Figure S67. ESI-TOF-MS of compound 2



Figure S68. <sup>1</sup>H NMR spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S69. Expansion of <sup>1</sup>H NMR spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S70. Expansion of <sup>1</sup>H NMR spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S71. Expansion of <sup>1</sup>H NMR spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S72. <sup>13</sup>C NMR and DEPT spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S73. Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S74. Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S75. <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S76. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S77. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S78. HMQC spectra of compound 3 recorded in pyridine-d<sub>5</sub>



Figure S79. Expansion of HMQC spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S80. Expansion of HMQC spectra of compound 3 recorded in pyridine-d<sub>5</sub>



Figure S81. Expansion of HMQC spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S82. HMBC spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S83. Expansion of HMBC spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S84. Expansion of HMBC spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S85. Expansion of HMBC spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S86. Expansion of HMBC spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S87. NOESY spectra of compound 3 recorded in pyridine-d<sub>5</sub>



Figure S88. Expansion of NOESY spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S89. Expansion of NOESY spectra of compound 3 recorded in pyridine- $d_5$ 



Figure S90. Expansion of NOESY spectra of compound 3 recorded in pyridine- $d_5$ 









Figure S92. <sup>1</sup>H NMR spectra of compound 4 recorded in pyridine-*d*<sub>5</sub>



Figure S93. Expansion of <sup>1</sup>H NMR spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S94. Expansion of <sup>1</sup>H NMR spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S95. Expansion of <sup>1</sup>H NMR spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S96. <sup>13</sup>C NMR and DEPT spectra of compound 4 recorded in pyridine- $d_5$ 



**Figure S97.** Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 4 recorded in pyridine- $d_5$ 



**Figure S98.** Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S99. <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S100. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S101. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 4 recorded in pyridine-*d*<sub>5</sub>



Figure S102. HMQC spectra of compound 4 recorded in pyridine-*d*<sub>5</sub>



Figure S103. Expansion of HMQC spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S104. Expansion of HMQC spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S105. Expansion of HMQC spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S106. HMBC spectra of compound 4 recorded in pyridine-*d*<sub>5</sub>



Figure S107. Expansion of HMBC spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S108. Expansion of HMBC spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S109. Expansion of HMBC spectra of compound 4 recorded in pyridine-d<sub>5</sub>



Figure S110. Expansion of HMBC spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S111. Expansion of HMBC spectra of compound 4 recorded in pyridine-d<sub>5</sub>



Figure S112. Expansion of HMBC spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S113. NOESY spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S114. Expansion of NOESY spectra of compound 4 recorded in pyridine- $d_5$ 



**Figure S115.** Expansion of NOESY spectra of compound 4 recorded in pyridine- $d_5$ 



Figure S116. ESI-TOF-MS of compound 4



Figure S117. <sup>1</sup>H NMR spectra of compound 5 recorded in pyridine-*d*<sub>5</sub>



Figure S118. Expansion of <sup>1</sup>H NMR spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S119. Expansion of <sup>1</sup>H NMR spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S120. Expansion of <sup>1</sup>H NMR spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S121. Expansion of <sup>1</sup>H NMR spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S122. <sup>13</sup>C NMR and DEPT spectra of compound 5 recorded in pyridine-*d*<sub>5</sub>



Figure S123. Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S124. Expansion of <sup>13</sup>C NMR and DEPT spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S125. Expansion of <sup>13</sup>C NMR spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S126. <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 5 recorded in pyridine-*d*<sub>5</sub>



Figure S127. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S128. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 5 recorded in pyridine-*d*<sub>5</sub>



Figure S129. Expansion of <sup>1</sup>H-<sup>1</sup>H COSY spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S130. HMQC spectra of compound 5 recorded in pyridine-*d*<sub>5</sub>



Figure S131. Expansion of HMQC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S132. Expansion of HMQC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S133. Expansion of HMQC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S134. HMBC spectra of compound 5 recorded in pyridine-*d*<sub>5</sub>



Figure S135. Expansion of HMBC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S136. Expansion of HMBC spectra of compound 5 recorded in pyridine- $d_5$


Figure S137. Expansion of HMBC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S138. Expansion of HMBC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S139. Expansion of HMBC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S140. Expansion of HMBC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S141. Expansion of HMBC spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S142. NOESY spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S143. Expansion of NOESY spectra of compound 5 recorded in pyridine- $d_5$ 



Figure S144. Expansion of NOESY spectra of compound 5 recorded in pyridine-d<sub>5</sub>



Figure S145. ESI-TOF-MS of compound 5