Four new unusual pentacyclic triterpenoids from the roots of *Jasminum sambac* (L.) Ait

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Abstract: Four new unusual pentacyclic triterpenoids (**1-4**) were isolated from the roots of *Jasminum sambac* (L.) Ait. Their structures were elucidated by 1D and 2D NMR analysis, single crystal X-ray diffraction and HRESIMS.

Keywords: unusual pentacyclic triterpenoids; isolation; strtuctural elucidation; NMR;XRD.

Jasminum (Oleaceae) is a genus with over 200 species, which are native to Asia, Australia, Africa, and the southern Pacific Islands. [1] The phytochemical investigations on some of Jasminum species have revealed the presence of secoiridoids, lignans, triterpenoids, flavonoids, sesquiterpenoids. [2-9] The roots of *Jasminum sambac* (L.) Ait. is a traditional Chinese medicine with anesthetic and analgesic effects and used for the treatment of insomnia, headache, decayed tooth, and injuries from falls. It was recorded that the roots is thought to be one important ingredient of "Ma-Fei-San", which was created by Tuo Hua and used for surgeries due to its significant anesthetic and analgesic effects. So it is very essential to deeply study the ingredients of the roots of *Jasminum sambac* (L.) Ait.

In our previous work, we have isolated and confirmed some compounds (triterpenoid, sesquiterpenoids, lignans and glycoside) from the roots of *Jasminum sambac* (L.) Ait. [10,11]. Here, we report the isolation and elucidation of another four new unusual pentacyclic triterpenoids (**1-4**) (Structures were shown in **Figure 1**) from the roots of *Jasminum sambac* (L.) Ait..

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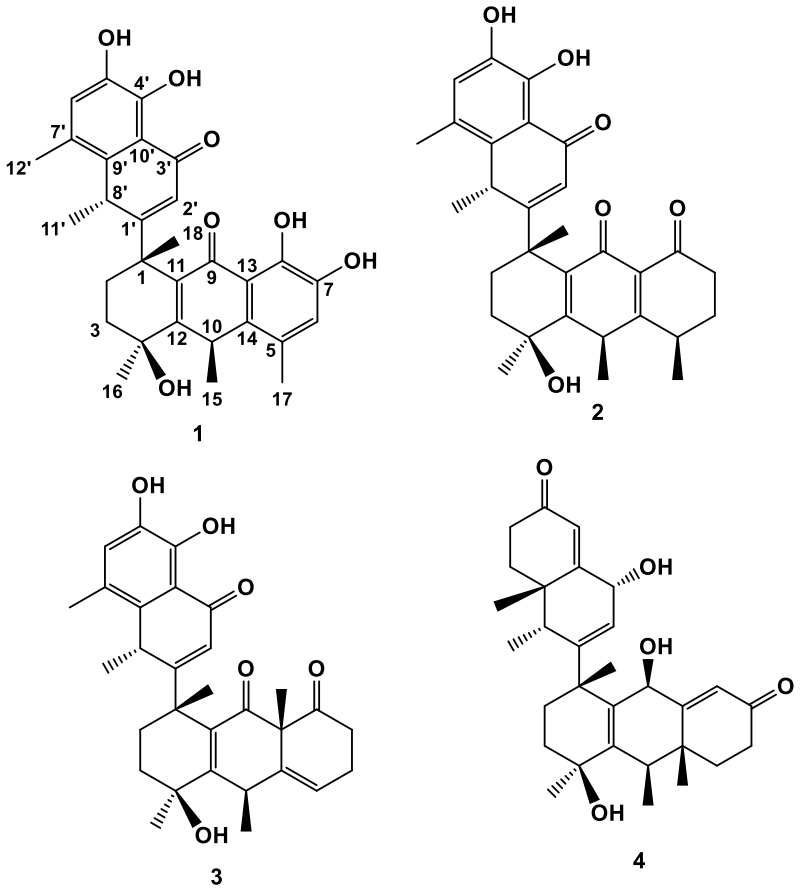

Figure 1. Structures of compounds (1-4).

Compound 1: Golden yellow solid, M.p 61-62 °C, HPLC purity: 96.596 %, retention time:17.067 min. Crystal Data: orthorhombic, space group P212121(no. 19), a=7.8148(3)Å, b=13.1614(6)Å, c=25.3786(11)Å, V=2610.28(19)Å^3, Z=4, T=272.00 K, μ(Mo Kα)= 0.091 mm^{-1}, Dcalc=1.284 g/cm^3, 22104 reflections measured (5.454° ≤ 2θ ≤ 54.36°), 5766 unique (Rint=0.0704, Rsigma=0.0650) which were used in all calculations. The final R_1 was 0.0536 (I > 2σ(I)) and wR_2 was 0.1512.

The molecular formula was confirmed as "$C_{30}H_{32}O_7$" through HRESIMS (m/z: found: 527.2040 [M+Na]+, calcd.: 527.2040). The ^{1}H NMR spectrum showed six methyl groups at [δH: 1.26 (d, *J*=4.4 Hz, H-12'), 1.32 (d, J=4.4 Hz, H-17), 1.45 (s, H-16), 1.72 (s, H-18), 2.24 (s, H-15), and2.31 (s, H-11')] ppm; two aromatic protons at [δH: 6.84 (s, H-6) and 6.93 (s, H-6')] ppm; five hydroxyl protons at [δH: 5.35 (s, 4-OH), 8.99 (s, 4'-OH), 9.10 (s, 8-OH), 11.78 (s, 7-OH), and 12.53 (s, 5'-OH)] ppm. The ^{13}C NMR toghether with DEPT spectra revealed the thirty signals, including: six methyls (C-15, C-16, C-17, C-18, C-11', and C-12'); two methylenes (C-2 and C-3); two methines (C-10 and C-8'); three olefinic methine (C-6, C-2', and C-6'), and seventeen quaternary carbons (C-1, C-4, C-5, C-7, C-8, C-9, C-11, C-12, C-13, C-14, C-1', C-3', C-4', C-5', C-7, C-9' and C-10). The HMBC correlations (**Figure 2**): from 4-OH (δH 5.35) to C-16 (δC 28.9), C-3 (δC 34.8), and C-4 (δC 71.1); from 8-OH (δH 9.10) to C-6 (δC 124.0) and C-8 (δC 148.3); from 7-OH (δH 11.78) to C-13 (δC 116.1), C-7 (δC 143.4), and C-8 (δC 148.3); from 4'-OH (δH 8.99) to C-6' (δC 123.9) and C-4' (δC 148.4); and from 5'-OH (δH 12.53) to C-10' (δC 114.8), C-5' (δC 143.6), and C-4' (δC 148.4), supported the "hydroxyl groups" at C-4, C-7, C-8, C-5' and C-4', respectively. 1H-1H COSY correlations (**Figure 2**): from H-6'/H-12' and H-8'/H-2'/H-11' coupled with the guidance of HMBC correlations: from H-2' (δH 5.69) to C-8' (δC 35.5) and C-10' (δC 114.8); from H-6' (δH 6.93) to C-9' (δC 137.2), C-5' (δC 143.5), and C-4' (δC 148.4); from H-11' (δH 2.31) to C-10' (δC 114.8), C-7' (δC 124.5), C-9' (δC 137.2), and C-4' (δC 148.4); and from H-12' (δH 1.26) to C-8' (δC 35.5) and C-9' (δC 137.2) indicated the presence of methylnaphthalen-1onyl group. Likewise, the correlations from H-10 (δH 4.01) to C-17 (δC

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28.1), C-4 (δC 71.1), and C-12 (δC 137.1); from H-15 (δH 2.24) to C-13 (δC 116.1), C-5 (δC 123.8), and C-14 (δC 136.9); from H-17 (δH 1.32) to C-10 (δC 33.1) and C-14 (δC 136.9); from H-16 (δH 1.45) to C-3 (δC 34.8) and C-4 (δC 71.1), accompanying with ^{1}H-^{1}H COSY correlations of H-6/H-17 and H-10/H-15/H-17, revealed the existence of hydroanthracen-9-onyl moiety. The methylnaphthalen-1-onyl and hydroanthracen-9-onyl groups of compound 1 were connected by analyzing HMBC correlation from H-2' (δH 5.69) to C-1 (δC 43.9), which was also supported by ^{1}H-^{1}H COSY correlation of H-2'/H-2/H-3. The ROESY correlations (**Figure 3**) showed that H-10α (δH 4.01) correlates with Me-16 (δH 1.45), Me-11' (δH 2.31), and H-8'β (δH 4.17) correlates with Me-15 (δH 2.24), Me-18 (δH 1.72) and 4-OH (δH 5.35), which indicated its relative configuration. The detailed 1H and ^{13}C NMR are shown in **Table 1**. The single-crystal X-ray diffraction analysis confidently confirmed its absolute configuration (CCDC 2259478, XRD structure is shown in **Figure 4**).

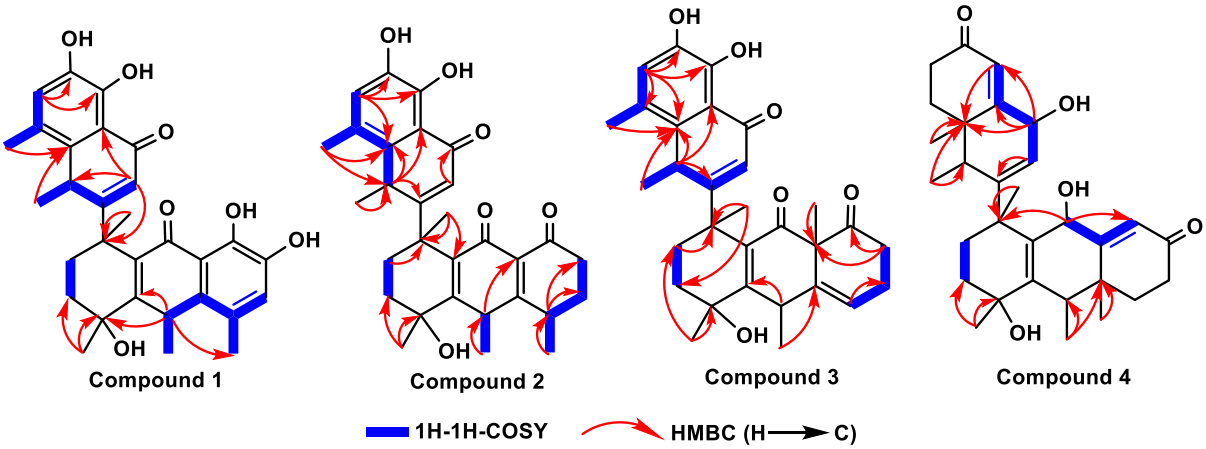

Figure 1. Structures with key ^{1}H-^{1}H COSY and HMBC correlations of the compounds 1 to 4.

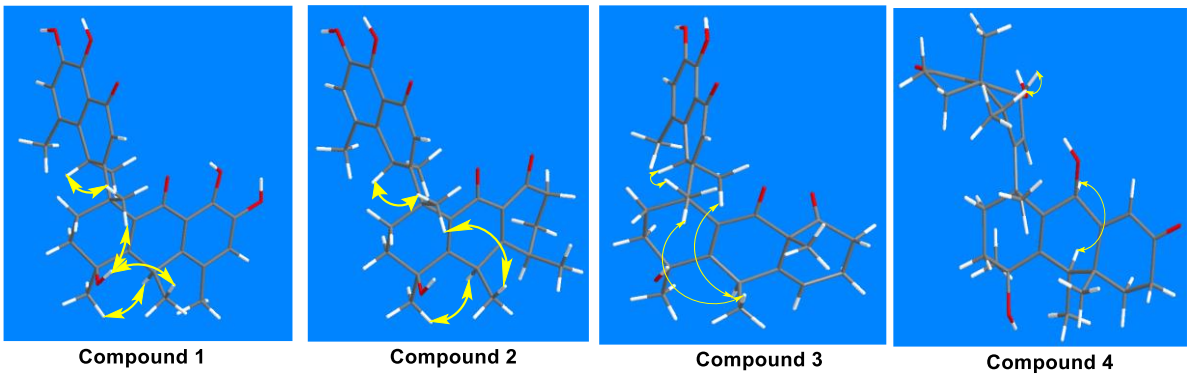

Figure 2. Key ROESY correlations of compounds 1 to 4.

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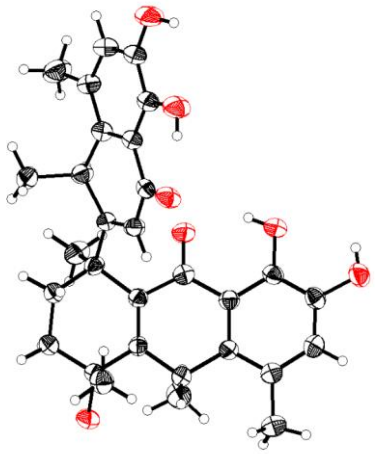

Figure 3. X-ray crystal structure for compound 1.

Compound 2: Yellow solid, M.p 58-59 °C, HPLC purity: 92.29%, retention time:18.807min. The molecular formula was confirmed as "$C_{30}H_{34}O_6$" through HRESIMS (m/z: 513.2247 [M+Na]+, calcd.: 513.2248). The ^{1}H and ^{13}C NMR data (**Table 1**) revealed six methyls at [δH 0.94 (d, J=4.4 Hz, H-17), δH 0.99 (s, H-15), δH 1.26 (d, J=4.5 Hz, H-12'), δH 1.51 (s, H-16), δH 1.58 (s, H-18), and δH 2.25 (s, H-11')] ppm; one aromatic proton at [δH 6.89 (s, H-6')] ppm; three hydroxyl protons at [δH 5.40 (s, 4-OH), δH 9.07 (1H, s, 4'-OH) and δH 12.23 (s, 5'-OH)] ppm; which are identical with those of compound 1.

Table 1. H-^{1}H COSY of H-17/H-5/H-6/H-7, H-15/H-10, H-16/H-15/H-3, H-18/H-11'/H-2, H-12'/H-6'/H-8 of compound 2 (**Figure 2**), guiding with HMBC correlations (**Figure 2**) from H-17 (δH 0.94) to C-5 (δC29.6) and C-7 (δC 42.4); from H-15 (δH 0.99) to C-6 (δC 38.3) and C-10 (δC 39.6); from H-12' (δH 1.26) to C-8' (δC 31.7) and C-9' (δC 137.4); from H-16 (δH 1.51) to C-3 (δC 35.0) and C-4 (δC 70.1); from H-18 (δH 1.58) to C-2 (δC 33.1), C-1 (δC 43.8), C-11 (δC 135.5); and from H-11' (δH 2.25) to C-8' (δC 31.7), C-7' (δC 123.6), C-9' (δC 137.4) are aided in assigning the positions of methyl groups. Also, the HMBC correlations from 4-OH (δH 5.40) to C-16 (δC 27.8), C-3 (δC 35.0) and C-4 (δC 70.1); from 4'-OH (δH 9.07) to C-6' (δC 123.9), C-5' (δC 143.5), and C-4' (δC 148.7), and from 5'-OH (δH 12.23) to C-10' (δC 115.8), C-5' (δC 143.5), C-4' (δC 148.7), indicated the positions of hydroxyl groups. The correlations from H-6' (δH 6.89) to C-11' (δC 17.7), C-9' (δC 137.4), C-5' (δC 143.5), C-4' (δC 148.7) revealed the position of aromatic protons. Its relative configuration of H-8β/Me-18/Me-15 and H-10α/H-5α/Me-16 is supported by ROSY correlations (**Figure 3**).

Compound 3: Yellow solid, M.p 73-74°C, HPLC purity: 96.67%, retention time:12.407min. The molecular formula was confirmed as "$C_{30}H_{34}O_6$" through HRESIMS (m/z: 513.2247 [M+Na]+, calcd.: 513.2248). The ^{1}H and ^{13}C NMR data are closely similar to those of compound 2, expect that the position of olefinic bond between C-13 and C-14 of compound 2 shifted to C-6 and C-14 of compound 3, which revealed the appearance of two peaks at δC 126.4 and δC 158.1 ppm for C-6 and C-14, respectively. This was also supported on the basis of HMBC correlations from H-5 (δH 6.47) to C-10 (δC 39.6), C-14 (δC 158.1), and C-9 (δC 187.8). The position of Me-17 of **compound 3** was assigned with the guidance of HMBC correlation from H-17 (δH 0.84) to C-13 (δC 39.6) and C-7 (δC 41.7) (**Figure 2**). The relative configuration of **compound 3** was similar to compound 2, which was determined by ROESY (**Figure 3**). The detailed ^{1}H and ^{13}C NMR are shown in Table 1.

Compound 4: Yellow solid, M.p 96-98°C, HPLC purity: 98.83%, retention time:21.400min. The molecular formula was confirmed as "$C_{30}H_{40}O_5$" through HRESIMS (m/z: 503.2771 [M+Na]+, calcd.: 503.2768). The ^{1}H NMR data showed four tertiary methyls at [δH 0.86 (s, H-17), δH 1.49 (s, H-16), δH 1.44 (s, H-18) and δH 0.93 (s, H-12')] ppm and two secondary methyls at [δH 0.97 (d, J=4.6 Hz, H-15) and δH 0.99 (d, J=2.9 Hz, H-11')] ppm. The ^{13}C NMR together with DEPT revealed 30 carbon signals, including: six methyls (C-15, C-16, C-17, C-18, C-11', and C-12'); six methylenes (C-2, C-3, C-5, C-6, C-6', and C-7'); two oxygenated methines (C-9 and C-3'); three olefinic methines (C-8, C-2', and C-4'); five sp^2 quaternary carbons (C-11, C-12, C-13, C-1', and C-10'); and six sp^3 quaternary carbons (C-1, C-4, C-14, C-9', C-7 and C-5'). The ^{1}H and ^{13}C NMR data(**Table 1**) were resembled with those of (1S*,5S*,10aR*)-1-[(8',8a'-dimethyl-4'-oxo-1',4',6',7',8',8a'-hexahydronaphthalene-2'-yl]-4-hydroxy-1,4,5,10atetramethyl-1,2,3,4,5,6,7,9,10,10a-decahydroanthracen-9-one[4] (which was isolated from the

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J. sambac roots), except that the two carbonyl groups of (1S*,5S*,10aR*)-1-[(8',8a'-dimethyl-4'-oxo-1',4',6',7',8',8a'-hexahydronaphthalene-2'-yl]-4-hydroxy-1, 4,5,10a tetramethyl-1,2,3,4,5,6,7,9,10,10a-decahydroanthracen-9-one were replaced with hydroxyl groups of compound 4, the hydroxyl groups of compound 4 were assigned according to HMBC correlations (**Figure 2**): from H-9 (δH 4.17) to C-17 (δC 18.1), C-1 (δC 41.9), C-4 (δC 68.8), C-13 (δC 139.1); and from H-3' (δH 4.51) to C-12' (δC 18.4), C-8' (δC 30.6), C-9' (δC 41.6), C-10' (δC 136.6), and C-4' (δC 139.2), which are accompanied by ^{1}H-^{1}H COSY correlations of H-9/H-15/H-8 and H-3'/H-2'/H-11'/H-4'. Also, the ^{13}C and DEPT spectra indicated the presence of two carbonyl groups, unlike those of (1S*,5S*,10aR*)-1-[(8',8a'-dimethyl-4'-oxo-1',4',6',7',8',8a'-hexahydronaphthalene-2'-yl]-4-hydroxy-1, 4,5,10a tetramethyl-1,2,3,4,5,6,7,9,10,10a-decahydroanthracen-9-one. The ROESY correlations of H-3'β/H-8'β/Me-15 and Me-11'/10α/H-9α/Me-16 (**Figure 3**) established its relative configuration.

Table 1. ^{1}H(400 MHz) and ^{13}C(100 MHz) NMR data for compounds **1, 2** in DMSO-*d*$_6$ and compounds **3** ,**4** in CD_3OD (δ in ppm and *J* in Hz).

No.	Compound 1		Compound 2		Compound 3		Compound 4	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1		43.9 C		43.8		44.4 C		41.9 C
2α	1.98, m	39.2 CH_2	1.90, m	33.1 CH_2	1.85, dt(3.4, 2.5)	34.0 CH_2	1.24, m	29.4 CH_2
2β	2.12, m		1.53, m		2.18, m			
3α	1.80, m	34.8 CH_2	1.61, m	35.0 CH_2	2.02, m	35.5 CH_2	1.76, m	33.7 CH_2
3β	2.15, m							
4		71.1 C		70.1 C		71.3 C		68.8 C
5		123.8 C	1.22, m	29.2 CH_2	6.47, s	126.4 CH	2.30, m	25.6 CH_2
6α	6.84	123.9 CH	2.56, m	38.3 CH_2	2.58, d(11.8)	38.5 CH_2	1.60, m	26.0 CH_2
6β			2.46					
7α		143.4 C	2.43, d(1.8)	42.4 CH_2	2.39, d(2.1)	41.7 CH_2		188.7 C
7β			2.21, m		2.27, m			
8		148.3 C		199.6 C		200.4 C	7.01, s	139.9 CH
9		191.9 C		191.9 C		187.8 C	4.17, s	67.9 CH
10	4.01, q(4.4)	33.1 CH	3.26, m	39.6 CH	3.76, m	39.9 CH	2.24	30.7 CH
11		137.1 C		135.5 C		136.7 C		
12		148.34		148.8 C		142.9 C		
13		116.1 C		135.6 C		39.6 C		139.1 C
14		136.9 C		157.7 C		158.1 C		42.8 C
15	2.24, s	17.7 CH_3	0.99, s	17.6 CH_3	1.04, s	16.8 CH_3	0.97, d(4.6)	14.0 CH_3
16	1.45, s	28.9 CH_3	1.51, s	27.8 CH_3	1.45, s	27.2 CH_3	1.49, s	26.3 CH_3
17	1.32, d(4.4)	28.1 CH_3	0.94, d(4.4)	15.3 CH_3	0.84, s	13.7 CH_3	0.86, s	18.1 CH_3
18	1.72, s	23.2 CH_3	1.58, s	25.6 CH_3	1.73, s	23.4 CH_3	1.44, s	23.1 CH_3
1'		168.9 C		167.5 C		168.8 C		138.5 C
2'	5.69, s	121.9 CH	6.27, d(0.7)	126.8 CH	6.89, s	122.9 CH	5.79, s	125.7 CH
3'		191.8 C		186.9 C		191.2 C	4.51, s	66.2 CH
4'		148.4 C		148.7 C		147.9 C	6.96, s	139.2 CH
5'		143.6 C		143.5 C		142.9 C		187.2 C
6'	6.93, s	124.0 CH	6.89, s	123.9 CH	6.90, s	122.4 CH	2.28, m	25.9 CH_2
7'		124.5 C		123.6 C		123.7 C	1.58, m	25.4 CH_2
8'	4.17, q(4.8)	35.5 CH	4.29, q(4.5)	31.7 CH	4.09, q(4.4)	33.1 CH	2.30	30.6 CH
9'		137.2 C		137.4 C		136.8 C		41.6 C
10'		114.8 C		115.8 C		115.2 C		136.6 C
11'	2.31, s	18.1 CH_3	2.25, s	17.7 CH_3	2.32, s	16.3 CH_3	0.99, d(2.9)	13.9 CH_3
12'	1.26, d(4.4)	24.4 CH_3	1.26, d(4.5)	27.9 CH_3	1.42, d(4.4)	26.7 CH_3	0.93, s	18.4 CH_3
4-OH	5.35, s		5.40, s					
7-OH	11.78,							
8-OH	9.10, s							
4'-OH	8.99, s		9.07, s					
5'-OH	12.53, s		12.23, s					

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In conclusion, we have isolated and confirmed four new unusual pentacyclic triterpenoids from the roots of *Jasminum sambac* (L.) Ait.. This work discovers new compounds from the roots of *Jasminum sambac* (L.) Ait., and also enriches the types of triterpenoids.

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References

1. Guo, Z.Y.; Li, P.; Huang,W.; Wang, J.J.; Liu, Y.J.; Liu, B.; Wang, Y.L.; Wu, S.B.; Kennelly, E.J.; Long, C.L. Antioxidant and anti-inflammatory caffeoyl phenylpro-panoid and secoiridoid glycosides from *Jasminum nervosum* stems, a Chinese folk medicine, Phytochem. 2014, 106, 124-133.
2. Lopez, H.; Perez, J. A.; Hernandez, J. M.; Trujillo, J. Secoiridoids from *Jasminum odoratissimum*. J. Nat. Prod. 1997, 60, 1334-1337.
3. Gallo, F.R.; Palazzino, G.; Federici, E.; Iurilli, R.; Monache, F. D.; Chifundera, K.; Galeffi, C. Oligomeric secoiridoid glucosides from *Jasminum abyssinicum*. Phytochemistry. 2006, 67, 504–510
4. Zeng, L.H.; Hu, M.; Yan, Y.M.; Lu, Q.; Cheng Y.X. Compounds from the roots of *Jasminum sambac*. Journal of Asian Natural Products Research. 2012, 14(12), 1180-1185.
5. Lou, L.L; Han, L.F.; Meng, D.L.; Li, N.; Li, X. Janceolaroside A and Janceoside A, Two New Compounds from the Stems and Roots of *Jasminum lanceolarium*. Natural Product Communications . 2011, 6 (6) , 749-752.
6. Lu, Y.; Han, Z.Z.; Zhang, C.G.; Ye, Z.; Wu, L.L.; Xu, H. Four new sesquiterpenoids with anti-inflammatory activity from the stems of *Jasminum officinale*. Fitoterapia. 2019, 135, 22-26.
7. Yue, Z.G.; Qin, H.; Li, Y.H.; Sun, Y.; Wang, Z.P.; Yang, T.H.; Liu, L.; Wang, M.C.; Feng, F.; Mei, Q.B. Chemical Constituents of the Root of *Jasminum giraldii*. Molecules. 2013, 18, 4766-4775.
8. Sun, J.M.; Yang, J.S.; Zhang, H. Two New Flavanone Glycosides of *Jasminum lanceolarium* and Their Anti-oxidant Activities. Chem. Pharm. Bull. 2007, 55(3) 474-476.
9. Tomassinia, L.; Ventronea, A.; Frezzaa, C.; Serafinib, I.; Biancob A.; Cometa M.F. Lignans and secoiridoid glycosides from the stem barks of *Jasminum tortuosum*. Natural Product Research, 2018, 32(15) 1853–1857.
10. Olatunde, O.Z.; Yong, JP.; Lu, C.Z. Isolation, Structural Elucidation of a New Triterpenoid from the Roots of *Jasminum sambac* (L.) Ait. with Potent Cytotoxicity against MCF 7 Cell Lines. ACS Omega. 2023, 8(16), 14662−14664.
11. Olatunde, O.Z.; Yong, J.P.; Lu, C.Z. Chemical Constituents from the roots of *Jasminum sambac* (L.) Ait. and cytotoxicity to the cancer cell lines. Anticancer Agents in Medicinal Chemistry. DOI:10.2174/1871520623666230504102455