Five Novel Taccalonolides from the Roots of the Vietnamese Plant *Tacca paxiana*

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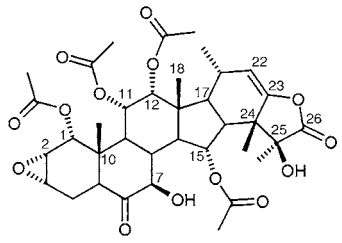
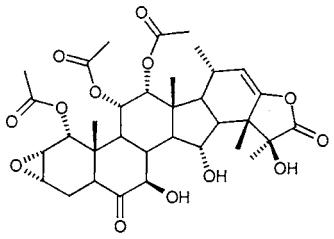
Chemical investigation of the roots of the Vietnamese plant *Tacca paxiana* resulted in the isolation of five new steroidal compounds, taccalonolide R (**6**), S (**7**), T (**8**), U (**9**), and V (**10**). Their structures were established on the basis of NMR and mass-spectral data. In addition, the five known taccalonolides A (**1**), B (**2**), E (**3**), K (**4**), and N (**5**) were also isolated and identified.

Introduction. – The genus *Tacca* (Taccaceae) includes some 50 species distributed predominately in tropic zones, especially in asiatic countries like China and Vietnam [1]. In folk medicine, *Tacca* species are used against slugs and snails, as an agent for controlling roundworms [2], for treatment of gastric ulcer, toothache, and stomachache [3]. Some *Tacca* species have been investigated chemically, and amino acids [4], anthocyanins [5], steroidal saponins, and sapogenins [6–8] have been isolated. From *Tacca plantaginea*, the thirteen taccalonolides A–M [9–13], from a *Tacca* spec. taccalonolide N [14], and from *Tacca subflaellata* taccalonolides O–Q [15] have been isolated so far. Taccalonolide A (**1**) is claimed to be important for initiation of paclitaxel-like microtubule bundling; therefore, taccalonolide A is the first microtuble-stabilizing agent isolated from a plant since identification of the mechanism of action of paclitaxel, and it is the first natural-product steroid identified to have these cellular effects [16]. In the present paper, we report the isolation and structure elucidation of five novel taccalonolides, taccalonolide R (**6**), S (**7**), T (**8**), U (**9**), and V (**10**), which were isolated as minor components besides the known-taccalonolides A (**1**), B (**2**), E (**3**), K (**4**), and N (**5**) from the roots of *Tacca paxiana* collected in Vietnam.

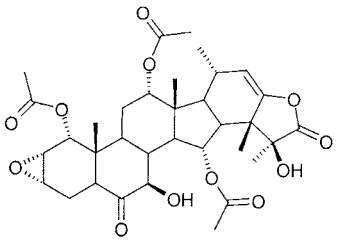
Results and Discussion. – About 1000 kg of wet *Tacca paxiana* roots were collected in Thai Nguyen province in northern Vietnam and subsequently extracted with 3000 l of MeOH to afford 43 kg of crude extract. After liquid-liquid partition of the extract, taccalonolides were enriched in the *t*-BuOMe fraction. Isolation of taccalonolides was



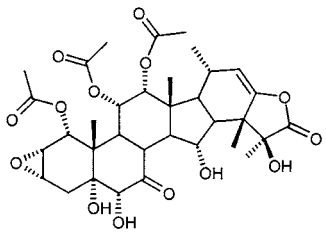
1 taccalonolide A



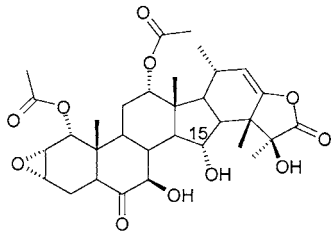
2 taccalonolide B



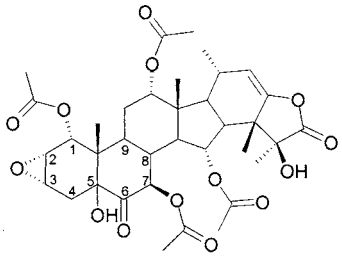
3 taccalonolide E



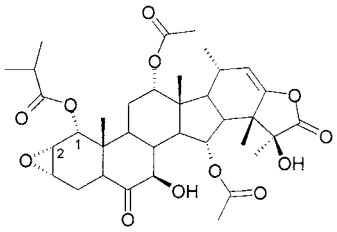
4 taccalonolide K



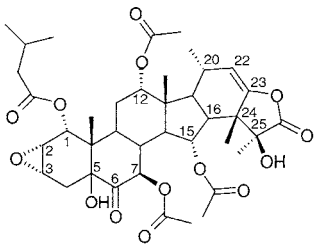
5 taccalonolide N



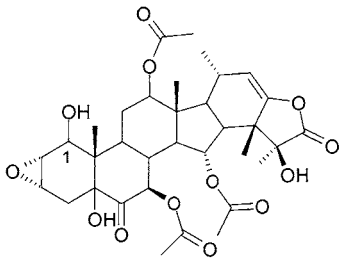
6 taccalonolide R



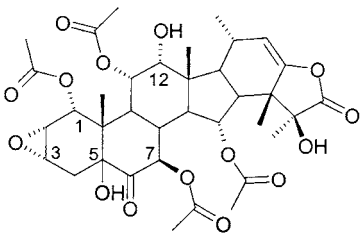
7 taccalonolide S



8 taccalonolide T



9 taccalonolide U



10 taccalonolide V

then performed on reversed-phase materials (*C18*) with H_2O/NH_4HCOO/MeOH gradients or on silicagel with CH_2Cl_2/MeOH gradients. In total, the ten taccalonolides A, B, E, K, N, R, S, T, U, and V (**1**–**10**, resp.) were isolated and their structures elucidated.

Whereas the known taccalonolides A (**1**), B (**2**), E (**3**), K (**4**), and N (**5**) were identified in the first instance by comparison of spectral data with those previously described [17][10][12], the complex structures of the five novel as well as the known metabolites were elucidated by a combination of ESI-HPLC-MS and 1D and 2D NMR spectroscopy. All one-bond $^1H,^{13}C$ connectivities were established by a heteronuclear multiple-quantum-coherence (HMQC) experiment, $^1H,^1H$ connectivities by correlation spectroscopy (COSY), and two- or three-bond $^1H,^{13}C$ connectivities by heteronuclear multiple-bond connectivity (HMBC) experiments. Ionization of taccalonolides was in most cases only observed in the negative mode of the ESI-LC-MS. Adducts with formate (HCOO) or acetate (ACO), were formed depending on the chromatographic gradient system.

For taccalonolide A (**1**), the ESI-HR-MS displayed a peak at *m/z* 747 corresponding to $C_{37}H_{47}O_{16}$ ($[M+HCOO]^-$), for taccalonolide B (**2**) at *m/z* 659 corresponding to $C_{34}H_{43}O_{13}$ ($[M-H]^-$), for taccalonolide E (**3**) at *m/z* 689 corresponding to $C_{35}H_{45}O_{14}$ ($[M+HCOO]^-$), and for taccalonolide K (**4**) at *m/z* 675 corresponding to $C_{34}H_{43}O_{14}$ ($[M-H]^-$). The ^1H- and ^{13}C-NMR shifts of **1**–**4** (*Tables 1* and *2*) were identical to those described in the literature. The structures were confirmed by analyzing their 2D spectra.

Taccalonolide N (**5**) displayed a molecular-ion peak at *m/z* 601 ($[M-H]^-$) in the negative and *m/z* 603 ($[M+H]^+$) in the positive mode of ESI-LC-MS. The ^1H-NMR (*Table 1*) was similar to that of taccalonolide E (**3**) but correlated also with the mass difference of 42.

The H–C(15) signal at δ 5.50 (*dd*) in **3** was shifted to δ 4.41 (*dd*) in **5** showing the loss of an Ac group. Besides, only two Ac signals could be observed for **5** at δ 2.11 (*s*) and 2.12 (*s*) whereas, for **3**, three signals corresponding to the Ac groups at δ 1.99 (*s*) and 2.10 (2*s*) were detected.

In addition to the five known taccalonolides, the five novel taccalonolides R, S, T, U, and V (**6**–**10**, resp.) were identified.

The ESI-LC-MS of taccalonolide R (**6**) exhibited $[M+AcO]^-$ at *m/z* 761 and $[M-H]^-$ at *m/z* 701 showing the same MS but a different ^1H-NMR spectrum (*Table 3*) as taccalonolide A (**1**). Further comparison of the spectroscopic data with those of **3** and taccalonolide 6 [12] established the structure of **6**.

The ^1H-NMR and $^1H,^1H$ 2D COSY data of **6** revealed also four Ac groups but differences in shifts of H–C(1), H–C(2), H–C(3), CH_2(4), H–C(7), H–C(8), and H–C(9) in comparison to **1**. The signal of H–C(5) was missing in comparison to **3**. Comparing the spectroscopic data of **6** to those of taccalonolide G [12], it was deduced that H–C(5) of **3** was replaced by an OH group. Therefore, H–C(1) of **3** was shifted from δ 4.61 (*d*, $J=5.4$ Hz) to 4.85 (*d*, $J=4.9$ Hz) in **6**, H–C(2) from δ 3.51 (*dd*, $J=3.7$ Hz) to 3.72 (*m*), H–C(3) from δ 3.39 (*m*) to 3.60 (br. *s*), and CH_2(4) from δ 2.21 (*m*) to 2.55 and 2.25 (2*m*). Besides, C(5) was shifted from δ 43.72 in **3** to 79.36 in **6** and C(6) from δ *ca.* 210 to 201 supporting that one OH group was attached to position C(5) (*Table 2*). The strong low-field shift of H–C(7) at δ 3.89 (*d*, $J=9.8$ Hz) in **3** to 5.61 (*d*, $J=10.7$ Hz) in **6** suggested that the fourth AcO group was located at C(7), which was also supported by shift differences of H–C(8) and H–C(9).

Table 1. *^{1}H-NMR Data* (500 MHz) *of* **1**–**5**. δ in ppm, J in Hz.

	1[a])	**2**[b])	**3**[a])	**4**[a])	**5**[a])
H–C(1)	4.73 (d, J = 5.4)	4.60 (d, J = 4.6)	4.61 (d, J = 5.4)	4.88 (d, J = 5.35)	4.65 (d, J = 5.12)
H–C(2)	3.49 (dd, J = 5.1, 3.9)	3.34 (m)	3.51 (dd, J = 3.7)	3.69 (dd, J = 4.4, 4.5)	3.55 (dd, J = 4.0)
H–C(3)	3.39 (m)	2.10 (m)	3.39 (m)	3.54 (m)	3.43 (m)
CH_2(4)	2.23, 2.20 (2m)	1.96, 2.05 (2m)	2.21 (m)	2.55, 2.17 (2m)	2.18, 2.29 (2m)
H–C(5)	2.77 (m)	2.68 (m)	2.68 (dd, J = 7.3)	–	2.74 (dd, J = 4.55, 11.4)
H–C(6)	–	–	–	4.31 (s)	–
H–C(7)	4.00 (d, J = 10.2)	4.20 (d, J = 10.8)	3.89 (d, J = 9.8)	–	4.03 (d, J = 10.3)
H–C(8)	1.71 (m)	1.80 (m)	1.71 (m)	3.06 (m)	1.74 (m)
H–C(9)	2.72 (m)	2.62 (m)	2.13 (m)	3.08 (m)	2.13 (m)
H–C(11) or CH_2(11)	5.32 (dd, J = 11.7, 2.5)	5.13 (dd, J = 14.7, 2.2)	1.70 (m)	5.42 (m)	1.71 (m)
H–C(12)	5.27 (d, J = 2.5)	5.04 (d, J = 2.2)	5.01 (br. s)	5.23 (m)	5.01 (m)
H–C(14)	2.45 (dd, J = 9.9)	2.00 (m)	2.40 (m)	2.33 (m)	2.10 (m)
H–C(15)	5.54 (dd, J = 9.7, 9.7)	4.27 (dd, J = 9.0, 9.4)	5.49 (dd, J = 9.3, 9.3)	4.24 (dd, J = 8.5, 9.1)	4.41 (dd, J = 9.6, 9.6)
H–C(16)	2.42 (dd, J = 9.0, 9.0)	2.40 (dd, J = 10.0, 13.0)	2.40 (m)	2.47 (m)	2.42 (m)
H–C(17)	1.78 (m)	1.68 (m)	1.70 (m)	1.88 (s)	2.03 (m)
Me(18)	0.99 (s)	0.84 (s)	0.86 (s)	1.00 (s)	0.86 (s)
Me(19)	0.78 (s)	0.67 (s)	0.71 (s)	1.23 (s)	0.78 (s)
H–C(20)	2.21 (m)	2.13 (m)	2.20 (m)	2.24 (m)	2.23 (m)
Me(21)	0.92 (d, J = 7.1)	0.75 (d)	0.97 (d, J = 6.8)	0.87 (d, J = 7.0)	0.98 (d, J = 6.7)
H–C(22)	5.08 (br. s)	4.96 (br. s)	5.10 (d, J = 1.2)	5.00 (m)	5.05 (br. s)
Me(27)	1.64 (s)	1.51 (s)	1.65 (s)	1.63 (s)	1.70 (s)
Me(28)	1.35 (s)	1.16 (s)	1.36 (s)	1.27 (s)	1.40 (s)
AcO–C(1)	2.18 (s)	1.80 (s)	2.10 (s)	2.06 (s)	2.11 (s)
AcO–C(7)	–	–	–	–	–
AcO–C(11)	1.99 (s)	2.05 (s)	–	1.89 (s)	–
AcO–C(12)	2.13 (s)	2.05 (s)	2.10 (s)	2.06 (s)	2.12 (s)
AcO–C(15)	2.00 (s)	–	1.99 (s)	–	–

[a]) In $CDCl_3$. [b]) In (D_6)DMSO.

Taccalonolide S (**7**) displayed molecular-ion peaks at *m/z* 731 ($[M + AcO]^-$) and *m/z* 671 ($[M - H]^-$) consistent with the proposed structure.

The ^{1}H-NMR of **7** (*Table 3*) was very similar to that of **3** but showed a *d* for two Me groups at δ 1.01 (d, J = 4.5 Hz) and an additional CH group at δ 2.22 (m). Only two Ac groups at δ 2.11 (s) and 2.00 (s) were observed. Therefore, it was deduced that one Ac group of **3** was replaced by a Me_2CHCO group in **7**. This was confirmed by ^{1}H,^{13}C long-range correlation from H–C(1) at δ 4.58 and the CH of Me_2CH at δ 2.22 to the C=O of COO at 171.60. H–C(1) correlated with H–C(2) at δ 3.52 (m) in the ^{1}H,^{1}H 2D COSY experiment.

The ESI-LC-MS of taccalonolide T (**8**) exhibited $[M + AcO]^-$ at *m/z* 803 and $[M - H]^-$ at *m/z* 745. The ^{1}H-NMR spectrum (*Table 3*) was very similar to that of **6** but indicated the presence of a 3-methylbutanoyl instead of an Ac group.

Table 2. *^{13}C-NMR Data of* **1**–**4** *and* **6**–**9**. δ in ppm.

	1[a])	**2**[b])	**3**[a])	**4**[a])	**6**[a])	**7**[a])	**8**[a])	**9**[a])
C(1)	73.18	72.50	71.37	73.80	72.34	70.69	72.16	69.98
C(2)	49.59	51.66	50.08	50.04	50.64	49.64	50.55	52.93
C(3)	52.12	52.99	53.32	53.55	54.59	52.88	54.66	54.34
C(4)	21.05	21.08	21.39	28.52	26.86	21.07	26.82	26.97
C(5)	41.97	41.65	43.72	80.63	79.36	43.24	79.27	79.87
C(6)	209	208	210.54	77.11	201.18	210.24	201.06	201.46
C(7)	75.01	75.90	77.18	212.47	76.06	76.80	76.07	75.75
C(8)	43.03	41.36	43.44	44.70	39.80	43.16	39.73	40.04
C(9)	40.03	39.55	37.38	41.50	33.97	36.84	33.88	33.60
C(10)	42.87	42.59	41.16	42.32	44.16	40.93	43.98	44.43
C(11)	70.89	70.62	25.50	70.37	26.17	25.12	26.81	26.22
C(12)	73.76	73.44	74.34	73.18	74.25	73.87	73.98	73.41
C(13)	43.32	43.37	43.52	44.04	44.03	43.25	39.28	43.80
C(14)	54.28	57.13	54.88	52.19	54.30	54.29	54.11	54.64
C(15)	71.37	75.90	72.29	70.12	71.89	71.85	71.90	71.60
C(16)	51.04	40.08	54.99	50.11	51.54	50.97	51.47	51.07
C(17)	48.62	47.50	48.44	47.58	48.25	48.43	48.14	47.93
C(18)	13.29	12.82	13.67	11.69	13.61	13.19	13.56	13.31
C(19)	12.97	12.48	13.52	14.20	14.86	13.12	14.75	14.07
C(20)	30.63	30.34	30.86	30.06	30.91	30.70	30.80	30.51
C(21)	20.07	19.69	20.27	18.66	20.04	19.75	19.91	19.55
C(22)	111.21	110.55	111.84	110.02	111.61	112.45	111.53	111.38
C(23)	154.46	154.10	154.83	154.08	154.24	154.55	154.37	154.08
C(24)	49.73	49.92	50.36	50.26	50.24	50.07	50.24	49.84
C(25)	79.28	78.71	79.56	78.82	79.09	78.88	78.52	79.01
C(26)	178.20	175.16	178.57	175.45	177.90	178.23	177.99	177.85
C(27)	20.57	21.73	20.90	20.35	20.61	20.39	20.52	20.27
C(28)	25.20	24.76	25.69	23.20	25.34	25.12	25.32	24.99
*Me*COO–C(1)	20.79	20.48	21.28	18.98	21.29			
*Me*COO–C(7)	–	–	–		20.50		21.26	20.89
*Me*COO–C(11)	21.06	20.50		19.53				
*Me*COO–C(12)	20.79	20.50	21.28	18.98	21.07	21.03	21.44	20.93
*Me*COO–C(15)	22.57		22.89		22.92	22.44	22.94	22.58
Me*C*OO–C(1)	169.44	170.04	169.73	169.48	169.37			
Me*C*OO–C(7)					170.87		171.05	169.89
Me*C*OO–C(11)	170.56	169.63		170.51				
Me*C*OO–C(12)	169.27	169.63	169.32	169.56	169.49	169.24	169.26	170.78
Me*C*OO–C(15)	172.17		172.37		172.05	172.29	172.59	171.81
Me_2*C*H···C(1)						30.73	31.31	
Me$_2$CH···C(1)						22.37	22.43	
*C*OO–C(1)						171.60	171.88	

[a]) In $CDCl_3$. [b]) In (D_6)DMSO.

Two additional ^{1}H-NMR signals for two Me groups at δ 1.01 (d, $J = 5.5$ Hz) and 1.02 (d, $J = 5.5$ Hz), one CH_2 group at δ 2.20 (d), and one CH group at δ 2.20 (m) were compatible with a 3-methylbutanoyl group in **8**. Because of a ^{1}H,^{13}C long-range correlation from the CH_2 group, at δ 2.20 and the H–C(1) at δ 4.81 to the C=O at δ 171.88, it was assumed that the AcO group at C(1) was replaced by Me_2CHCH_2COO, in accordance with the MS data.

Table 3. *^{1}H-NMR Data* ($CDCl_3$) *of* **6**–**10**. δ in ppm, J in Hz.

	6	**7**	**8**	**9**	**10**
H–C(1)	4.85 ($d, J = 4.9$)	4.58 ($d, J = 5.2$)	4.81 ($d, J = 5.1$)	3.86 ($d, J = 4.9$)	4.85 ($d, J = 5.4$)
H–C(2)	3.72 (m)	3.52 (m)	3.73 ($dd, J = 4.2$)	3.54 (m)	3.72 (m)
H–C(3)	3.60 (br. s)	3.37 (m)	3.58 (m)	3.62 (m)	3.61 (m)
CH_2(4)	2.55, 2.25 ($2m$)	2.18 (m)	2.53, 2.22 ($2m$)	2.58, 2.14 ($2m$)	2.12, 2.66 ($2m$)
H–C(5)	–	2.65 (m)	–	–	–
H–C(7)	5.61 ($d, J = 10.7$)	3.87 ($d, J = 9.8$)	5.59 ($d, J = 10.1$)	5.61 ($d, J = 10.4$)	4.71 ($d, J = 10.3$)
H–C(8)	2.01 (m)	1.72 (m)	1.99 (m)	1.99 (m)	1.76 (m)
H–C(9)	2.87 (m)	2.12 (m)	2.85 ($td, J = 12.4, 4.0$)	2.93 ($dd, J = 9.7, 12.2$)	3.19 (m)
CH_2(11) or H–C(11)	1.72 (m)	1.70 (m)	1.70 (m)	2.11, 1.64 ($2m$)	5.23 (m)
H–C(12)	5.01 (br. s)	5.00 (m)	5.00 (m)	5.05 (m)	5.07 ($d, J = 13.4$)
H–C(14)	2.58 (m)	2.35 (m)	2.56 (m)	2.58 (m)	2.52 (m)
H–C(15)	5.55 ($dd, J = 9.1$)	5.48 ($dd, J = 9.5$)	5.52 ($dd, J = 9.1$)	5.52 ($dd, J = 9.3, 9.1$)	5.55 ($dd, J = 9.8$)
H–C(16)	2.41 (m)	2.39 (m)	2.38 ($dd, J = 13.4, 9.6$)	2.40 (m)	2.49 (m)
H–C(17)	2.02 (m)	1.95 (m)	1.99 (m)	2.04 (m)	1.88 (m)
Me(18)	0.92 (s)	0.85 (s)	0.89 (s)	0.91 (s)	1.05 (s)
Me(19)	0.73 (s)	0.70 (s)	0.72 (s)	0.60 (s)	0.78 (s)
H–C(20)	2.24 (m)	2.19 (m)	2.21 (m)	2.22 (m)	2.22 (m)
Me(21)	0.97 ($d, J = 6.9$)	0.96 ($d, J = 6.8$)	0.97 ($d, J = 6.9$)	1.01 ($d, J = 6.9$)	0.89 ($d, J = 7.1$)
H–C(22)	5.13 (s)	5.09 (m)	5.11 (br. s)	5.12 (br. s)	5.04 (br. s)
Me(27)	1.66 (s)	1.64 (s)	1.63 (s)	1.64 (s)	1.36 (s)
Me(28)	1.37 (s)	1.35 (s)	1.33 (s)	1.33 (s)	1.66 (s)
AcO–C(1)	2.17 (s)	–	–	–	2.13 (s)
AcO–C(7)	2.13 (s)	–	2.15 (s)	2.16 (s)	2.16 (s)
AcO–C(11)	–	–	–	–	2.00 (s)
AcO–C(12)	2.13 (s)	2.11 (s)	2.10 (s)	2.14 (s)	–
AcO–C(15)	1.99 (s)	2.00 (s)	1.97 (s)	1.96 (s)	1.98 (s)
$Me_2CH\cdots$C(1)	–	2.22 (m), 1.01 ($d, J = 4.5$)	2.20 (m), 1.02 ($d, J = 5.5$)	–	–

The ESI-LC-MS of taccalonolide U (**9**) exhibited $[M + AcO]^-$ at *m/z* 705 and $[M - H]^-$ at *m/z* 659, revealing that one Ac group was replaced by a H-atom in comparison to taccalonolide R (**6**). The ^{1}H-NMR spectrum of **9** (*Table 3*; H–C(1) at δ 3.86 ($d, J =$ 4.9 Hz)) indicated that an OH group was attached to C(1), rather than an AcO group like in **6**.

The ESI-LC-MS of taccalonolide V (**10**) exhibited $[M + AcO]^-$ at *m/z* 777 and $[M - H]^-$ at *m/z* 717. The ^{1}H-NMR spectrum (*Table 3*) suggested that the basic structure was similar to taccalonolide A (**1**) with the difference that an OH group was attached at C(5).

The OH–C(5) of **10** was supported by the low-field shifts of H–C(2), H–C(3), and CH_2(4) (*Table 3*; *cf.* data of taccalonolide R (**6**)). In contrast to taccalonolide A (**1**), the AcO group of **10** was attached to C(7) and not to C(12) as supported by the shift differences of H–C(12) and H–C(7).

Experimental Part

General. Chemicals of anal. grade were obtained from *Merck* (Darmstadt, Germany) or *Sigma Aldrich* (Deisenhofen, Germany). Anal. HPLC: *HP-1100* unit (*Hewlett-Packard*, Waldbronn, Germany) with automated sample injector and diode-array detector; *LiChroSpher-C-18* column (125 × 2 mm; 5 μm; *Macherey & Nagel*); eluent: *A* = 25 mmol NH_4OAc in H_2O, *B* = 25 mmol NH_4OAc in MeOH; start 20% *B*, 30 min 60% *B*, 31 min 100% *B* 40 min 100% *B*; flow 0.4 ml/min; detection at 210 nm and with ELSD; t_R in min. NMR Spectra: *Bruker Avance-500* spectrometer, at 500.13 MHz (^1H) with the solvent peak as internal reference ($CDCl_3$: δ(H) 7.24, δ(C) 77.0; (D_6)DMSO: δ(H) 2.49, δ(C) 39.5). ESI-HPLC-MS and ESI-HR-MS: instrument 1: *HP-1100* coupled to a *Micromass-LCT* mass spectrometer (*Micromass*, Manchester, UK), *Waters* symmetry column as stationary phase (50 × 2.1 mm; 3 μM); eluent: *A* = 0.1% HCOOH in H_2O, *B* = 0.1% HCOOH in MeCN, start 100% *A*, 1 min 100% *A*, 5 min 10% *A*, 6 min 10% *A*, 7 min 100% *B*; instrument 2: *HP-1100* coupled to *TSQ700* (*Finnigan*), *Inertsil-ODS3* column (250 × 2.1 mm; 5 μM); eluent: *A* = 25 mM NH_4OAc in H_2O, *B* = 25 mmol NH_4OAc in MeOH, start 50% *B*, 10 min 60% *B*, 30 min 100% *B*, 40 min 100% *B*; flow 0.2 ml/min; temp. 10°; in *m*/*z*.

Plant Material. The plant material of *Tacca paxiana* was collected in Thai Nguyen province in northern Vietnam in 1999.

Extraction and Isolation. The *Tacca paxiana* roots (1000 kg) were extracted with MeOH (3000 l) to afford dry crude extract (43 kg). The extract was dissolved in H_2O/MeOH 95 : 5 (80 l) and extracted five times with heptane (30 l) and *t*-BuOMe (30 l). The *t*-BuOMe fraction was mixed with silica gel (3 kg) and evaporated and the residue put in a fritted-glass funnel and eluted with CH_2Cl_2 (60 l): 315 g of material. Thereof, 50-g portions were chromatographed (*Biotage* silica-gel columns (*KP-SIL* 32–63 μM; 350 × 75 mm; eluent: *A* = CH_2Cl_2, *B* = MeOH; start 100% *A*, 121 min 95% *A*, 131 min 95% *A*, 141 min 90% *A*, 151 min 80% *A*, 191 min 80% *A*; flow 98 ml/min).

Taccalonolides A (**1**; 2 g), E (**3**; 1.5 g), N (**5**; 1 mg), S (**7**; 13 mg), T (**8**; 28 mg), and U (**9**; 4 mg) were obtained in pure form from fractions that eluted between 80 and 100 min by repeated prep. HPLC: *Gilson Abimed* HPLC (UV detector, binary pump system); software Unipoint 1.71 (*Gilson*); 1. *Nucleosil C18* (7 μm; 250 × 20 mm; *Macherey & Nagel*); flow 25 ml/min; eluent: *A* = 0.1% CF_3COOH in H_2O, phase *B* = 0.1% CF_3COOH in MeCN, start 85% *A*, 1 min 85% *A*, 30 min 25% *A*, 35 min 25% *A*; 2. *Nucleosil C18* (7 μm; 250 × 20 mm; *Macherey & Nagel*); flow 25 ml/min; eluent: *A* = 0.1% CF_3COOH in H_2O; *B* 0.1% CF_3COOH in MeCN, start 70% *A*, 1 min 70% *A*, 30 min 25% *A*, 35 min 25% *A*; 3. *Nucleosil C18* (7 μm; 250 × 10 mm; *Macherey & Nagel*); flow rate 12.5 ml/min; eluent: *A* = H_2O + 2 g of NH_4HCOO/l *B* = MeCN + 2 g of NH_4HCOO/l, start 80% *A*, 40 min 40% *A*, 41 min 0% *A*.

Taccalonolides B (**2**; 2 mg), K (**4**; 0.3 mg), R (**6**; 2.2 mg), and V (**10**; 0.4 mg) were obtained in pure form from fractions that eluted between 60 and 80 min by repeated prep. HPLC methods described above.

Taccalonolide A (**1**): Amorphous solid. t_R 23.36; log *P* = 2.37 (pH 2.3), log *P* = 2.35 (pH 7.5). ^1H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 2): 761 ($[M + AcO]^-$), 701 ($[M - H]^-$). ESI-HR-MS: 747.2866 ($[M + HCOO]^-$, $C_{37}H_{47}O_{16}^-$; calc. 747.28641).

Taccalonolide B (**2**): Amorphous solid. t_R 24.51; log *P* = 2.58 (pH 2.3), log *P* = 2.56 (pH 7.5). ^1H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 1): 659 $[M - H]^-$). ESI-HR-MS: 659.27045 ($C_{34}H_{43}O_{13}^-$; calc. 659.27037).

Taccalonolide E (**3**): Amorphous solid. t_R 22.96; log *P* = 2.36 (pH 2.3), log *P* = 2.34 (pH 7.5). ^1H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 2): 703 ($[M + AcO]^-$), 643 ($[M - H]^-$). ESI-HR-MS: 689.2813 ($[M + HCOO]^-$, $C_{34}H_{45}O_{12}^-$; calc. 689.28093).

Taccalonolide K (**4**): Amorphous solid. t_R 20.10; log *P* = 2.58 (pH 2.25). ^1H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 1): 675 ($[M - H]^-$).

Taccalonolide N (**5**): Amorphous solid. t_R 25.81; log *P* = 2.61 (pH 2.3), log *P* = 2.60 (pH 7.5). ^1H-NMR: *Table 1*. ESI-MS (instrument 1): 601 ($[M - H]^-$).

Taccalonolide R (= *(1α,2α,3α,7β,12α,15α,16β,24β,25S)-1,7,12,15-Tetrakis(acetyloxy)-2,3-epoxy-5,23,25-trihydroxy-6-oxo-16,24-cycloergost-22-en-26-oic Acid γ-Lactone*; **6**): Amorphous solid. t_R 27.00; log *P* = 2.75 (pH 2.3), log *P* = 2.73 (pH 7.5). ^1H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 2): 761 ($[M + AcO]^-$), 701 ($[M - H]^-$). ESI-HR-MS: 747.2864 ($[M + HCOO]^-$, $C_{37}H_{47}O_{16}^-$; calc. 747.2864).

Taccalonolide S (= *(1α,2α,3α,7β,12α,15α,16β,24β,25S)-12,15-Bis(acetyloxy)-2,3-epoxy-7,23,25-trihydroxy-1-(2-methyl-1-oxopropoxy)-6-oxo-16,24-cycloergost-22-en-26-oic Acid γ-Lactone*; **7**): Amorphous solid. t_R 26.45; log *P* = 1.93 (pH 2.3), log *P* = 1.91 (pH 7.5). ^1H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 2): 731 ($[M + AcO]^-$), 671 ($[M - H]^-$).

Taccalonolide T (=*(1α,2α,3α,7β,12α,15α,16β,24β,25S)-7,12,15-Tris(acetyloxy)-2,3-epoxy-5,23,25-trihydroxy-1-(3-methyl-1-oxobutoxy)-6-oxo-16,24-cycloergost-22-en-26-oic Acid γ-Lactone*; **8**): Amorphous solid. t_R 25.53; log P = 3.58 (pH 2.3), log P = 3.57 (pH 7.5). ^{1}H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 2): 803 ($[M+AcO]^-$), 745 ($[M-H]^-$). ESI-HR-MS: 789.33347 ($[M+HCOO]^-$, $C_{40}H_{53}O_{16}^-$; calc. 789.33347).

Taccalonolide U (=*(1ξ,2α,3α,7β,12ξ,15α,16β,24β,25S)-7,12,15-Tris(acetyloxy)-2,3-epoxy-1,5,23,25-tetrahydroxy-6-oxo-16,24-cycloergost-22-en-26-oic Acid γ-Lactone*; **9**): Amorphous solid. t_R 26.22; log P = 2.45 (pH 2.3), log P = 2.43 (pH 7.5). ^{1}H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 1): 705 ($[M+HCOO]^-$), 659 ($[M-H]^-$). ESI-HR-MS: 705.27528 ($[M+HCOO]^-$, $C_{35}H_{45}O_{15}^-$; calc. 705.27585).

Taccalonolide V (=*(1α,2α,3α,7β,11α,12α,15α,16β,24β,25S)-1,7,11,15-Tetrakis(acetyloxy)-2,3-epoxy-5,12,23,25-tetrahydroxy-6-oxo-16,24-cycloergost-22-en-16-oic Acid γ-Lactone*; **10**): Amorphous solid. t_R 21.52; log P = 2.35 (pH 2.3). ^{1}H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. ESI-MS (instrument 2): 777 ($[M+AcO]^-$, 717 ($[M-H]^-$). ESI-HR-MS: 763.28102 ($[M+HCOO]^-$], $C_{37}H_{47}O_{17}^-$; calc. 763.28102).

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