Cassane-Type Diterpenes from the Seeds of *Caesalpinia crista*

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A new dimer **1** and two new cassane-type diterpenes **2** and **3**, designated taepeenin J–L, were isolated from the seeds of *Caesalpinia crista* L. Compound **1** possesses a dimeric vouacapane skeleton. Their structures were elucidated on the basis of spectroscopic analysis.

Introduction. – *Caesalpinia crista* L., known locally as 'Taepee' in Thai, is a climber distributed from India and Ceylon through most of Southeast Asia to the Ryu-Kyu Islands, Queensland, and Caledonia [1]. In the preceding paper, we isolated taepeenin A–I and nortaepeenin A and B from the stems and roots of *C. crista* [2]. As a continuation of our study on this plant, we now report the isolation of a new dimer **1** and of two new cassane-type diterpenes **2** and **3** along with three known compounds, (5α,8β)-vouacapane (**4**) [3], (5α,6β,8β)-vouacapan-6-ol (**5**) [4], and (5α)-vouacapa-8(14),9(11)-diene (**6**) [5] from the seeds of *C. crista*[1]).

Results and Discussion. – The optically active taepeenin J (**1**) was obtained as a viscous oil and has the molecular formula $C_{40}H_{54}O_2$ based on HR-EI-MS (M^+ at *m/z* 566.4109). The UV spectrum (λ_{max} 217, 255, 283, and 293 nm) suggested the presence of a benzofuran chromophore [6]. The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), HMBC, and NOESY data established the dimeric structure of taepeenin J, which was confirmed by comparison of the NMR data with those of **4** [3] and **6** [5].

The ^{13}C-NMR and DEPT data of **1** showed 40 C-atoms. Twelve of these were sp^2 C-atoms, attributable to 4 CH and 8 quaternary C-atoms. The ^{1}H-NMR data displayed two fragments, **1a** and **1b**, both being a cassane-type diterpene. Fragment **1a** displayed the presence of three tertiary Me groups at δ(H) 1.24 (*s*, Me(20)), 0.95 (*s*, Me(18)), and 0.94 (*s*, Me(19)), one aromatic Me group at δ(H) 2.28 (*s*, Me(17)), a CH at δ(H) 1.35 (*dd*, *J*=12.6, 2.1 Hz, H–C(5)), and two aromatic protons at δ(H) 7.26 (*s*, H–C(11)), and 6.08 (*s*, H–C(15)). These data indicated that fragment **1a** and **6** [5] were closely related, except for the disappearance of the aromatic proton signal at δ(H) 7.51 (H–C(16)) in fragment **1a**. The ^{1}H-NMR data of fragment **1b** showed the presence of four tertiary Me groups at δ(H) 1.64 (*s*, Me(17′)), 0.90 (*s*, Me(20′)), 0.82 (*s*, Me(19′)), and 0.75 (*s*, Me(18′)), and three aliphatic CH signals at δ(H) 1.65–1.75 (*m*, H–C(9′)), 1.64–1.70 (*m*, H–C(8′)), and 0.73 (*dd*, *J*=10.8, 2.1 Hz, H–C(5′)). Resonances at δ(H) 7.22

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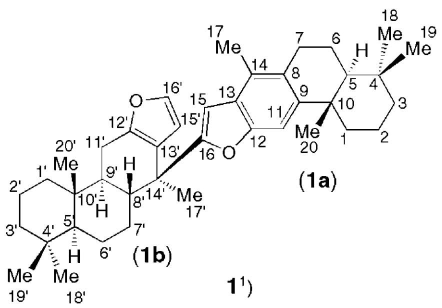
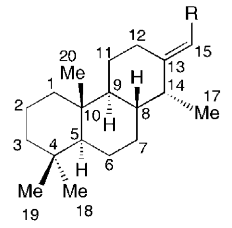
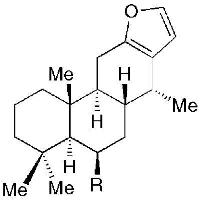
[1]) Arbitrary numbering; for systematic names, see the *Exper. Part*.



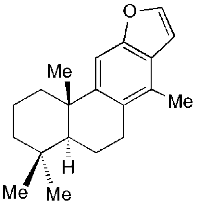
1^{1})



2^{1}) R = CHO
3^{1}) R = CH_2OH



4 R = H
5 R = OH



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and 6.08 (each *d*, $J = 1.8$ Hz) were typical of a 1,2-disubstituted furan. The ^{1}H-NMR data of fragment **1b** were almost identical to those of **4** [3], except for the splitting pattern of the Me signal (Me(17′)) in **1b** which was a *s* at δ(H) 1.64 but a *d* at δ(H) 0.94 in **4**. The connectivity of both fragments was confirmed by HMBC correlations (*Figure, a*). The Me protons at δ(H) 1.64 (Me(17′)) showed correlations with the C-atoms at δ(C) 162.3 (C(16)), 121.9 (C(13′)), 44.2 (C(8′)), and 40.3 (C(14′)), a CH proton at δ(H) 1.64–1.70 (H–C(8′)) with the C-atoms at δ(C) 162.3 (C(16)) and 40.3 (C(14′)), and an aromatic proton at δ(H) 6.08 (H–C(15)) with δ(C) 162.3 (C(16)), 153.3 (C(12)), 127.3 (C(14)), 126.4 (C(13)), and 40.3 (C(14′)), confirming that fragments **1a** and **1b** were connected at C(16) and C(14′), respectively. The relative configuration at C(14′) was determined on the basis of NOESY experiments (*Figure, b*). The cross-peaks H–C(5′)/H–C(9′) and H–C(9′)/Me(17′) suggested the α-axial orientation of H–C(5′), H–C(9′), and Me(17′).

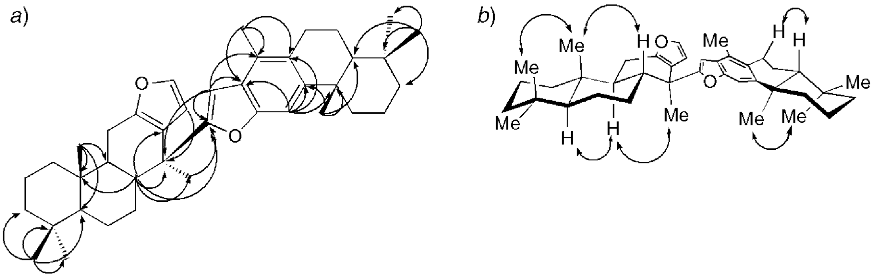

Figure. a) *Major HMBC correlations and* b) *important NOESY cross-peaks of dimer* **1**

Taepeenin K (**2**) has the molecular formula $C_{20}H_{32}O$ (M^+ at m/z 288.2466) as determined by HR-EI-MS. The IR (1682 cm^{-1}) and UV (λ_{max} 224 nm) absorption bands were characteristic of a conjugated carbonyl functionality. The structure of **2** was established

Table 1. *^{1}H-NMR Data* (300 MHz) *of* **1**–**3** *in CDCl$_3$.* δ(H) in ppm, *J* in Hz[a])

	1a	**1b**[b])	**2**	**3**
CH$_2$(1)	2.29–2.37 (*m*), 1.42–1.52 (*m*)	1.67–1.74 (*m*), 0.99–1.06 (*m*)	1.60–1.80 (*m*), 0.88–1.15 (*m*)	1.65–1.77 (*m*), 0.86–1.00 (*m*)
CH$_2$(2)	1.95–2.03 (*m*), 1.79–1.87 (*m*)	1.61–1.69 (*m*), 1.43–1.55 (*m*)	1.62–1.74 (*m*), 1.39–1.57 (*m*)	1.44–1.58 (*m*), 1.36–1.41 (*m*)
CH$_2$(3)	1.42–1.50 (*m*), 1.36–1.42 (*m*)	1.38–1.44 (*m*), 1.13–1.17 (*m*)	1.32–1.50 (*m*), 1.09–1.29 (*m*)	1.35–1.47 (*m*), 1.09–1.20 (*m*)
H–C(5)	1.35 (*dd*, *J* = 12.6, 2.1)	0.73 (*dd*, *J* = 10.8, 2.1)	0.89–0.93 (*m*)	0.78–0.88 (*m*)
CH$_2$(6)	1.58–1.67 (*m*), 1.45–1.51 (*m*)	1.51–1.57 (*m*), 1.19–1.23 (*m*)	0.95–1.05 (*m*)	1.58–1.67 (*m*), 1.20–1.35 (*m*)
CH$_2$(7)	2.90 (*dd*, *J* = 17.1, 3.3), 2.68–2.72 (*m*)	2.08–2.13 (*m*), 2.04–2.08 (*m*)	1.49–1.53 (*m*), 1.30–1.40 (*m*)	1.46–1.54 (*m*)
H–C(8)	–	1.64–1.70 (*m*)	1.43–1.53 (*m*)	1.50–1.57 (*m*)
H–C(9)	–	1.65–1.75 (*m*)	1.10–1.24 (*m*)	1.08–1.19 (*m*)
H–C(11) or CH$_2$(11)	7.26 (*s*)	2.76 (*dd*, *J* = 16.5, 6.0), 2.45 (*dd*, *J* = 16.5, 9.6)	1.80–2.00 (*m*), 1.19–1.28 (*m*)	1.71–1.82 (*m*), 0.90–1.01 (*m*)
CH$_2$(12)	–	–	3.18 (br. *dd*, *J* = 13.8, 3.0), 2.10–2.21 (*m*)	2.39–2.50 (*m*), 1.84–1.94 (*m*)
H–C(14)	–	–	2.30–2.40 (*m*)	2.17–2.24 (*m*)
H–C(15)	6.08 (*s*)	6.08 (*d*, *J* = 1.8)	5.83 (*dd*, *J* = 8.4, 0.9)	5.37 (*td*, *J* = 7.2, 1.5)
H–C(16) or CH$_2$(16)	–	7.22 (*d*, *J* = 1.8)	10.00 (*d*, *J* = 8.4)	4.12 (*d*, *J* = 7.2)
Me(17)	2.28 (*s*)	1.64 (*s*)	1.05 (*d*, *J* = 7.2)	0.95 (*d*, *J* = 7.2)
Me(18)	0.95 (*s*)	0.75 (*s*)	0.87 (*s*)	0.86 (*s*)
Me(19)	0.94 (*s*)	0.82 (*s*)	0.83 (*s*)	0.82 (*s*)
Me(20)	1.24 (*s*)	0.90 (*s*)	0.81 (*s*)	0.79 (*s*)

[a]) Assignments were made using HMQC and HMBC data. [b]) The atom labelling is H–C(1′), H–C(2′), H–C(3′), *etc.*

by its ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), HMBC, and NOESY data and comparison with those of **4** [3].

The ^{13}C-NMR and DEPT spectrum of **2** exhibited a total of 20 C-atoms, with one C=O at δ(C) 191.0 and two sp^2 C-atoms at δ(C) 172.0 and 123.9. The ^{1}H-NMR data showed the presence of an aldehyde proton at δ(H) 10.00 (*d*, *J* = 8.4 Hz, H–C(16)) which coupled with an olefinic proton at δ(H) 5.83 (*dd*, *J* = 8.4, 0.9 Hz, H–C(15)). This indicated that the conjugated carbonyl group was at an exocyclic C=C bond. Signals of three tertiary Me groups at δ(H) 0.87 (Me(18)), 0.83 (Me(19)), and 0.81 (Me(20)), and a Me *d* at δ(H) 1.05 (*d*, *J* = 7.2 Hz, Me(17)) were displayed similarly to those of **4** [3]. The observed HMBC correlations between the Me protons at δ(H) 1.05 (Me(17)) with C-atoms at δ(C) 172.0 (C(13)), 45.2 (C(14)), and 40.8 (C(8)), and an olefinic proton at δ(H) 5.83 (H–C(15)) with C-atoms at δ(C) 45.2 (C(14)) and 24.5 (C(12)) confirmed that the C=C bond was attached at C(13). The relative configuration of **2** was determined on the basis of coupling constants and NOESY experiments. The (*E*)-configuration was determined by a NOESY cross-peak between the olefinic proton at δ(H) 5.83 (H–C(15)) and a CH proton at δ(H) 2.35 (H–C(14)).

Table 2. *^{13}C-NMR Data* (75 MHz) *of* **1**–**3** *in CDCl$_3$*. δ(C) in ppm.

	1a	**1b**[a])	**2**	**3**
C(1)	39.9	39.4	39.6	39.7
C(2)	19.2	18.8	18.8	18.9
C(3)	41.7	41.8	42.1	42.2
C(4)	33.5	33.1	33.2	33.2
C(5)	49.9	54.2	55.2	55.8
C(6)	19.5	21.4	21.6	21.7
C(7)	28.0	28.6	31.3	31.7
C(8)	127.3	44.2	40.8	40.7
C(9)	146.8	47.5	48.0	48.4
C(10)	38.4	37.6	37.1	37.0
C(11)	104.3	22.1	27.0	26.6
C(12)	153.3	150.6	24.5	23.7
C(13)	126.4	121.9	172.0	151.0
C(14)	127.3	40.3	45.2	44.3
C(15)	102.6	108.5	123.9	118.7
C(16)	162.3	140.6	191.0	58.7
C(17)	15.9	24.6	14.1	14.4
C(18)	33.3	33.4	33.7	33.7
C(19)	21.7	22.1	22.0	22.1
C(20)	25.3	14.3	14.0	14.2

[a]) The atom labelling is C(1′), C(2′), C(3′), *etc.*

Taepeenin L (**3**) showed the molecular ion M^+ at m/z 290.2603 in the HR-EI-MS in agreement with the formula $C_{20}H_{34}O$. The presence of an OH functionality was evident from the IR absorption at 3409 cm^{-1}. The ^{1}H- and ^{13}C-NMR data of **3** (*Tables 1* and *2*) showed characteristics similar to those of **2** except that a CH_2O signal (δ(H) 4.12 (*d*, $J = 7.2$ Hz)) replaced the aldehyde-proton signal (δ(H) 10.00). This finding was supported by the HMBC spectrum of **3** (correlation CH_2(16)/C(13) and C(15)). Therefore, taepeenin L was determined to be **3**.

Conclusions. – Several cassane-type diterpenoids have already been isolated from plants of the genus *Caesalpinia*, *e.g.*, from *C. bonducella* [6][7], *C. minax* [8]–[10], and *C. pulcherrima* [11]. We now reported the isolation of a new dimer and two new cassane-type diterpenes from *C. crista* with 5-deoxycassane skeletons. The isolated dimer **1** was structurally derived from compounds **4** and **6** which are linked in **1** at C(14) and C(16), respectively.

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Experimental Part

General. Quick column chromatography (QCC) and column chromatography (CC): silica gel *60* F_{254} (*Merck*) and silica gel *100* (*Merck*), respectively. Anal. TLC: precoated plates of silica gel *60* F_{254}. M.p.: *Fisher-John* melting point apparatus. $[\alpha]_D$: *Autopol*^{R} *II* automatic polarimeter. UV Spectra: *Specord S 100* (*Analytikjena*); λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer FTS* FT-IR spectrophotometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: 500-MHz *Varian Unity-Inova* and 300-MHz *Bruker FT NMR-Ultra-Shield*^{TM} spectrometers; $CDCl_3$ solns.; δ in ppm rel. to $SiMe_4$, as an internal reference, *J* in Hz. EI-MS: *MAT-95-XL* mass spectrometer; in *m*/*z*.

Plant Material. The seeds of *C. crista* L. were collected from Trang province, Thailand, in May 2004. Identification was made by Prof. *Puangpen Sirirugsa*, Department of Biology, Faculty of Science, Prince of Songkla University, and a specimen (No. SC03) deposited at the Prince of Songkla University Herbarium.

Extraction and Isolation. The seeds (110.7 g) of *C. crista* were extracted with acetone at r.t. for 5 days. The extract was evaporated and the residue (16.3 g) separated by QCC (hexane/AcOEt mixtures): *Fractions S1–S5*. *Fr. S2* (677.9 mg) was purified by CC (CH_2Cl_2/hexane 1:19): taepeenin J (**1**; 17.3 mg) and ($5\alpha,8\beta$)-vouacapane (**4**; 11.8 mg). *Fr. S3* (150.0 mg) was separated by CC (AcOEt/hexane 1:19): (5α)-vouacapa-8(14),9(11)-diene (**6**; 4.8 mg) and ($5\alpha,6\beta,8\beta$)-vouacapan-6-ol (**5**; 6.9 mg). *Fr. S4* (118.5 mg) was purified by CC (AcOEt/hexane 1:9) followed by prep. TLC (AcOEt/hexane 1:9): taepeenin K (**2**; 7.3 mg) and L (**3**; 12.4 mg).

Taepeenin J (*=1,1′,2,2′,3,3′,4,4′,4a,4′a,5,5′,6,6′,6a,7,11,11a,11b,11′b-Eicosahydro-4,4,4′,4′,7,7′,11b,11′b-Octamethyl-7,9′-biphenanthro[3,2-*b*]furan*; **1**): Viscous oil. $[\alpha]_D^{27}=+36.6$ ($c=0.27$, $CHCl_3$). UV ($CHCl_3$): 217 (4.12), 255 (4.00), 283 (3.67), 293 (3.66). IR (neat): 1652. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-EI-MS: 566.4109 (M^+, $C_{40}H_{54}O_2^+$; calc. 566.4124).

Taepeenin K (*=[Dodecahydro-1,4b,8,8-tetramethylphenanthren-2(1*H*)-ylidene]acetaldehyde*; **2**): Amorphous solid. M.p. 189–190°. $[\alpha]_D^{27}=+28.3$ ($c=0.07$, $CHCl_3$). UV ($CHCl_3$): 224 (3.24). IR (neat): 1682. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-EI-MSI: 288.2466 (M^+, $C_{20}H_{32}O^+$; calc. 288.2453).

Taepeenin L (*=2-[Dodecahydro-1,4b,8,8-tetramethylphenanthren-2(1*H*)-ylidene]ethanol*; **3**): Viscous oil. $[\alpha]_D^{27}=+23.0$ ($c=0.06$, $CHCl_3$). UV ($CHCl_3$): 222 (3.40). IR (neat): 3409. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-EI-MS: 290.2603 (M^+, $C_{20}H_{34}O^+$; calc. 290.2610).

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