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DITERPENES AND RELATED CYCLOADDUCTS FROM *TAIWANIA CRYPTOMERIOIDES*

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Key Word Index—*Taiwania cryptomerioides*; Taxodiaceae; leaves; diterpenes.

Abstract—Seven new compounds were isolated from the leaves of *Taiwania crypomerioides*. Taiwaniaquinone D and taiwaniaquinone E are diterpenes having a six-five-six fused ring skeleton. Taiwaniadduct A is a [4 + 2] cycloaddition product of β-myrcene and taiwaniaquinone A. Taiwaniadduct B and taiwaniadduct C are isomers derived from [4 + 2] cycloadditions of *trans*-ozic acid and taiwaniaquinone A. Taiwaniadduct D is formally an ene reaction product of taiwaniadduct B. Taiwaniadduct E is a [5 + 2] cycloaddition product of taiwaniaquinone A and *trans*-ozic acid. The structure determination of these new compounds was based on spectral analyses and chemical transformation. A crystalline compound, prepared by bismethylation of taiwaniadduct D, was analysed by X-ray diffraction to establish the stereochemistry.

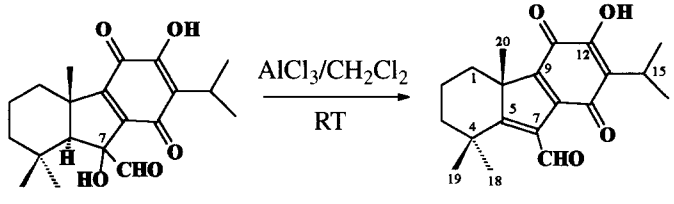
INTRODUCTION

Taiwania cryptomerioides Hayata is an endemic evergreen species with thick linear-triangular leaves and elongate ovoid cones. The chemical constituents of this plant have been investigated extensively [1–3]. Various sesquiterpenes, lignans and bisflavones have been found in the leaves and wood. Four diterpenes (taiwaniaquinones A–C and taiwaniaquinol A) and one norditerpene (taiwaniaquinol B) having the unusual 6-5-6 fused ring skeleton were recently isolated [4]. We now report on a further two diterpenes, **1** and **2**, of this type and five related terpenes (**3**–**7**) derived from the combination of taiwaniaquinone A with a monoterpene, β-myrcene, or a diterpene, *trans*-ozic acid.

RESULTS AND DISCUSSION

The acetone extract of the leaves of *T. cryptomerioides* was concentrated and taken up in chloroform. The soluble part was concentrated and subjected to chromatography to give compounds **1**–**7**.

Compound **1** gave rise to a molecular ion $[M]^+$ at *m/z* 328.168 consistent with a molecular formula $C_{20}H_{24}O_4$. The ^1H and ^{13}C NMR spectra (Table 1) indicated an aldehyde group [δ_H 10.38 (*s*) and δ_C 194.1 (*d*)] and two ketone groups [δ_C 185.1 (*s*) and 177.2 (*s*)]. The carbonyl groups were conjugated with olefinic double bonds as inferred from the IR absorptions at 1691 and 1630 cm^{-1} as well as the presence of six olefinic carbon signals at δ_C 176.6 (*s*), 152.2 (*s*), 147.7 (*s*), 147.1 (*s*), 134.4 (*s*) and 123.2 (*s*). Proton resonances for three methyl groups occurred at δ 1.14 (*s*), 1.28 (*s*) and 1.44 (*s*), whereas those for an isopropyl group occurred at δ 1.18 (*d*), 1.19 (*d*) and 3.15 (*sept*). Compound **1** was given the trivial name taiwaniaquinone D, and its structure was finally elucidated by means of HMBC and HMQC. Treatment of taiwaniaquinone B (or taiwaniaquinone C) with $AlCl_3$ in CH_2Cl_2 yielded a dehydration product which was identified as taiwaniaquinione D (Scheme 1).



Taiwaniaquinone B, 7β-OH
Taiwaniaquinone C, 7α-OH

1 (Taiwaniaquinone D)

Scheme 1. Chemical synthesis of taiwaniaquinone D.

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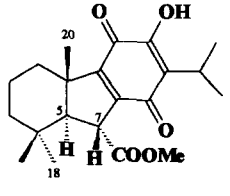
Table 1. ^{13}C and ^{1}H NMR spectral data of compounds **1** and **2** ($CDCl_3$, δ in ppm)

	1		**2**	
	δ_C	δ_H	δ_C	δ_H
1	35.2	2.40 (*br d*, 13.0)*†	34.3	2.22 (*br d*, 12.0), 1.58 (*m*)
2	18.3	1.68 (*m*), 1.94 (*m*)	19.2	1.75 (*m*), 1.62 (*m*)
3	43.3	1.72 (*m*), 1.26 (*m*)	41.2	1.45 (*m*), 1.22 (*m*)
4	38.0		33.7	
5	176.6		62.4	2.13 (*d*, 11.6)
6	194.1	10.38 (*s*)	174.2	
7	134.4		47.0	3.61 (*d*, 11.6)
8	147.1		148.5	
9	147.7		151.6	
10	55.9		48.0	
11	177.2		181.2	
12	152.2		151.1	
13	123.2		124.7	
14	185.1		185.2	
15	24.0	3.15 (*sept*, 7.1)	24.0	3.10 (*sept*, 7.0)
16	19.9	1.19 (*d*, 7.1)	19.8	1.14 (*d*, 7.0)
17	19.9	1.18 (*d*, 7.1)	19.7	1.17 (*d*, 7.0)
18	33.7	1.14 (*s*)	32.0	0.82 (*s*)
19	25.6	1.28 (*s*)	21.4	1.03 (*s*)
20	21.3	1.44 (*s*)	19.9	1.10 (*s*)
CO_2CH_3			52.3	3.73 (*s*)

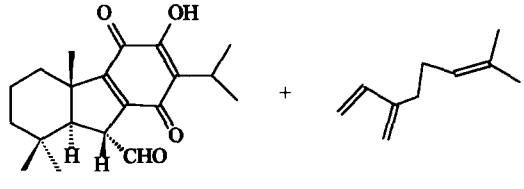
*The signal of the other proton was too weak to be assigned.
†Coupling constants (J in Hz) in parentheses.

Compound **2** ($C_{21}H_{28}O_5$) exhibited characteristic spectroscopic properties of a *p*-quinone moiety, i.e. UV absorption at 431 nm, IR absorption at 1635 cm^{-1} and NMR at δ 185.2 (*s*), 181.2 (*s*), 151.6 (*s*), 151.1 (*s*), 148.5 (*s*) and 124.7 (*s*). A methyl ester group was inferred from the IR absorption at 1735 cm^{-1}, the proton resonance at δ 3.73 (*s*), and the carbon signals at δ 174.2 (*s*) and 52.3 (*q*). Compound **2** is named taiwaniaquinone E, and its structure is similar to that of taiwaniaquinone A, except for the aldehyde group in the latter structure being replaced with a methoxycarbonyl group. The proton and carbon resonances were assigned according to the HMBC and HMQC spectra. The stereochemistry was established from NOE studies. Thus, irradiation of H-18 (δ 0.82) caused an 11% enhancement of H-5 (δ 2.13) and irradiation of H-20 (δ 1.10) caused a 15% enhancement of H-7 (δ 3.61).

Compound **3** was given the trivial name taiwaniadduct A, and its structure was determined by chemical and spectral methods. The exact mass of the molecular ion $[M]^+$ (*m/z* 466.309) indicated a molecular formula $C_{30}H_{42}O_4$. The proton and carbon signals (Table 2) were assigned according to the HMBC and HMQC spectra. Triterpene **3** was presumably derived from the [4 + 2] cycloaddition of the monoterpene, β-myrcene, and the diterpene, taiwaniaquinone A (Scheme 2). The stereochemistry was deduced from NOE studies. For example, irradiation of H-6 (δ 9.94) caused an 8%

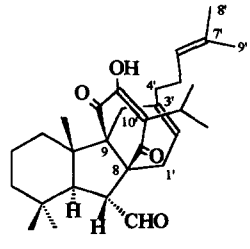


2



Taiwaniaquinone A β-Myrcene

cat. $Eu(fod)_3$
CH_2Cl_2
RT



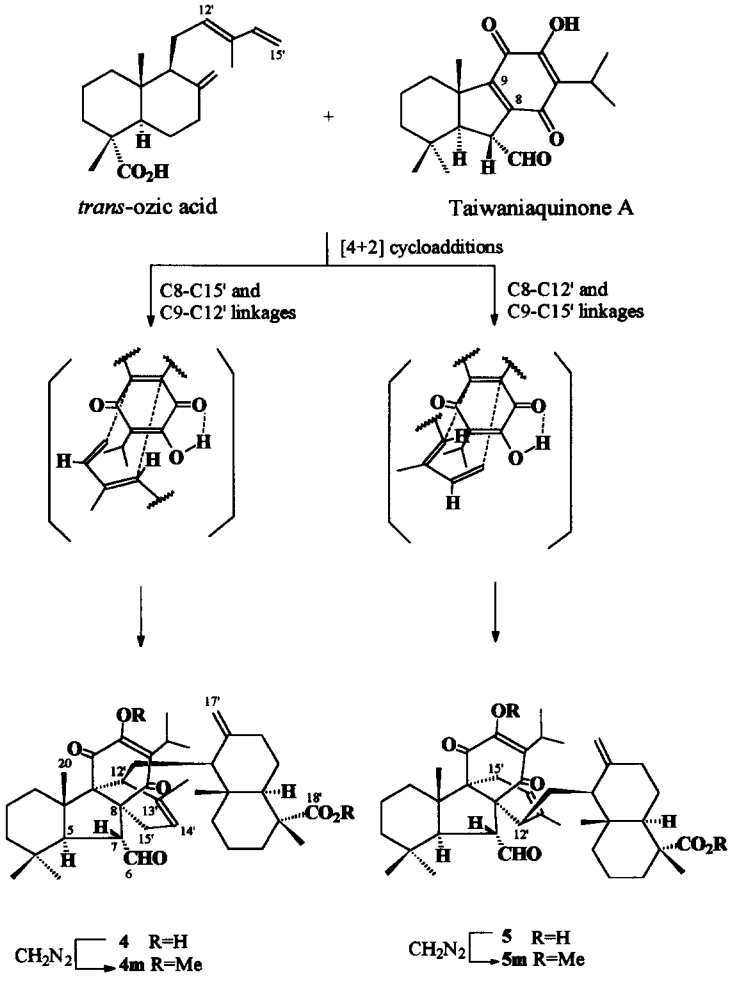
3

Scheme 2. Chemical synthesis of compound **3**.

enhancement of H-1′ (δ 2.34), indicating that the monoterpene moiety and the aldehydr group were on the same face. The Diels–Alder reaction [5, 6] between taiwaniaquinone A and β-myrcene was promoted by a Lewis acid Eu(fod)$_3$ to give a single product identical to **3**. The reaction occurred in a regio- and stereospecific manner, i.e. β-myrcene attacked the less hindered α-face of taiwaniaquinone A to form C8-C1′ and C9-C10′ bonds. The 10-methyl group of taiwaniaquinone A presumably hindered a β-face approach by β-myrcene. The regio-isomer with C8-C10′ and C9-C1′ bonds was not formed, becuase it would exert severe repulsion between the 13-isopropyl and 3′-alkyl groups.

Terpenes **4** (taiwaniadduct B) and **5** (taiwaniadduct C) were not readily purified. Compounds **4m** and **5m** obtained by bismethylation of **4** and **5** (CH_2N_2, Et_2O) were purified by HPLC and their structures were determined by spectroscopic methods (IR, MS, HRMS, and ^1H, ^{13}C, HMBC and HMQC NMR). Compounds **4m** and **5m** were isomers giving rise to molecular ions $[M]^+$ at 660.439 attributable to the molecular formula $C_{42}H_{60}O_6$. The ^1H and ^{13}C NMR spectra of **4m** showed the characteristic resonances (Table 2) of an aldehyde group [δ_H 9.60 (*d*) and δ_C 205.4 (*d*)], a methyl ester [δ_H 3.56 (*s*), δ_C 51.8 (*q*) and 178.9 (*s*)], conjugated ketones [δ_C 198.6 (*s*) and 201.3 (*s*)], a methoxy group [δ_H 3.91 (*s*)], a terminal double bond [δ_C 108.7 (*t*) and 146.8 (*s*)], a trisubstituted double bond [δ_C 120.4 (*d*) and 144.2 (*s*)], as well as for a tetrasubstituted double bond [δ_C 141.3 (*s*) and 159.0 (*s*)]. The regio- and stereochemistry of **4m** was supported by the NOESY spectrum. H-5 (δ 1.57) had NOE correlations with H-6 (δ 9.60) and H-12′ (δ 3.10), whereas H-7 (δ 3.10) had a correlation to H-20 (δ 0.63), whereas the NOESY spectrum of **5m** showed the correlations of H-6 (δ 9.50) to H-12′ (δ 2.20), H-5 (δ 1.79) to H-14′ (δ 5.55) and H-7 (δ 3.14) to H-20 (δ 0.73).

Compounds **4** and **5** were presumably derived from [4 + 2] cycloadditions of the labdane diterpene, *trans*-ozic acid, and taiwaniaquinone A (Scheme 3). Compound **4** had the linkages at C8-C15′ and C9-C12′, whereas compound **5** had the alternative linkages at C8-C12′ and C9-C15′. The stereochemistry shown in **4** and **5** is consistent with cycloadditions of two components occurring at the less hindered faces and following the endo-selectivity of conventional Diels–Alder reactions.



Scheme 3. Formation of compounds **4** and **5**.

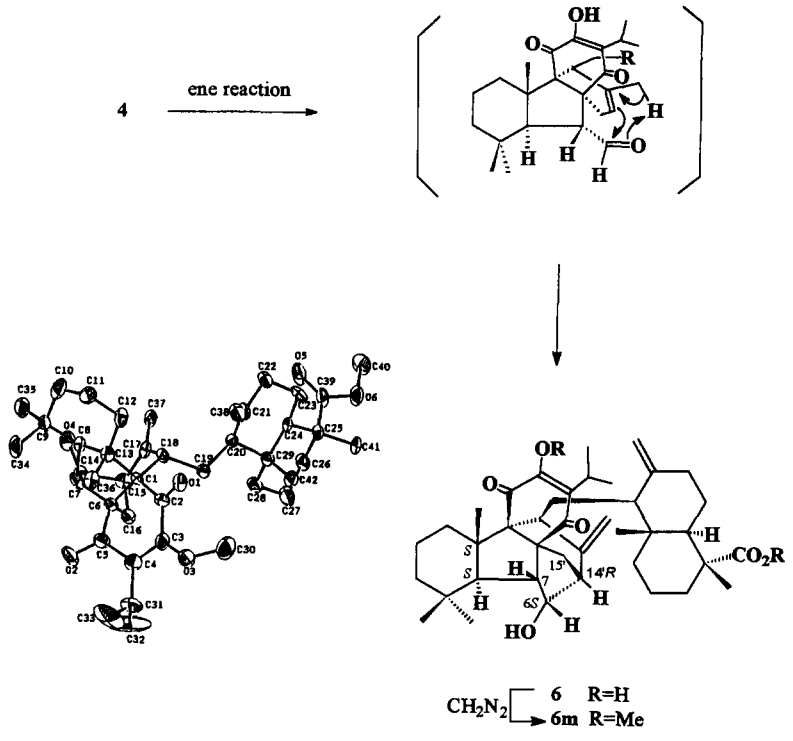
Table 2. ^{13}C and ^{1}H NMR data of compounds **3** and **4m–7m** ($CDCl_3$, δ in ppm)

	3		**4m**		**5m**		**6m**		**7m**	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	32.7	1.55 (*m*), 1.68 (*m*)	34.8	1.88 (*m*)*	32.0	*	31.3	1.42 (*m*), 1.58 (*m*)	35.1	1.54 (*m*), 2.30*n*(*m*)
2	18.7	1.56 (*m*)*	18.3	*	18.0	*	18.3	1.46 (*m*)*	18.3	1.48 (*m*)*
3	41.5	1.15 (*m*)	41.5 (*m*)	0.96 (*m*),	41.4	1.38 (*m*), 1.10 (*m*)	41.7	0.86 (*m*), 1.32 (*m*)	41.0	1.08 (*m*), 1.38 (*m*)
		1.44 (*m*)		1.30 (*m*)						
4	33.9		33.7		33.8		34.2		33.6	
5	52.9	2.08 (*d*, 12.9)†	54.2	1.57 (*d*, 13.1)	54.5	1.79 (*d*, 12.7)	52.5	1.44 (*m*)	56.6	2.08 (*m*)
6	204.3	9.94 (*d*, 4.1)	205.4	9.60 (*d*, 4.6)	204.9	9.50 (*d*, 4.2)	72.7	3.99 (*m*)	204.4	9.87 (*d*, 5.5)
7	56.4	3.44 (*dd*, 12.9, 4.1)	56.2	3.10 (*m*)	58.7	3.14 (*dd*, 12.7, 4.2)	41.6	2.99 (*t*, 9.0)	52.5	3.31 (*dd*, 13.4, 5.5)
8	60.9		60.8		64.7		65.7		68.1	
9	63.4		65.9		60.2		66.0		143.7	
10	49.4		51.4		51.5		53.3		47.3	
11	198.5		198.6		199.3		198.0		142.9	
12	155.4		159.0		160.1		159.6		193.9	
13	131.4		141.3		144.0		140.9		66.2	
14	201.3		201.3		202.3		201.2		198.8	
15	25.4	3.17 (*sept*, 7.0)	26.4	3.10 (*m*)	25.3	3.30 (*sept*, 7.0)	25.7	3.10 (*m*)	27.1	2.16 (*m*)
16	18.8	1.14 (*d*, 7.0)	20.6	1.16 (*d*, 7.0)	20.1	1.22 (*d*, 7.0)	19.2	1.08 (*d*, 7.0)	17.9	0.96 (*d*, 7.0)
17	19.6	1.16 (*d*, 7.0)	19.3	1.07 (*d*, 7.0)	20.2	1.16 (*d*, 7.0)	20.4	1.15 (*d*, 7.0)	17.9	1.00 (*d*, 7.0)
18	35.6	0.77 (*s*)	35.7	0.69 (*s*)	35.3	0.75 (*s*)	37.0	0.84 (*s*)	34.5	0.78 (*s*)
19	21.9	0.85 (*s*)	21.9	0.75 (*s*)	21.9	0.78 (*s*)	22.8	0.75 (*s*)	21.7	0.85 (*s*)
20	19.6	0.73 (*s*)	20.1	0.63 (*s*)	22.3	0.73 (*s*)	20.2	0.60 (*s*)	19.6	0.99 (*s*)

1′	33.1	2.05 (*m*) 2.34 (*br d*, 13.5)	37.3	1.63 (*m*)*	37.3	*	37.7	1.42 (*m*)*	38.0	1.04 (*m*), 1.66 (*m*)
2′	120.6	5.39 (*br d*)	19.0	*	19.3	*	19.4	*	19.3	1.66 (*m*)*
3′	140.6		36.7	1.41*	36.9	1.44 (*m*), 1.50 (*m*)	36.7	1.48 (*m*)*	36.7	1.46 (*m*)*
4′	36.5	1.92 (*m*)	47.5		47.7		47.6		47.5	
5′	25.4	1.98 (*m*)	50.0	1.75 (*m*)	50.1	1.85 (*m*)	50.1	1.80 (*m*)	49.5	1.86 (*m*)
6′	123.5	4.95 (*br s*)	26.0	*	25.9	1.12 (*m*)*	26.8	1.14 (*m*), 1.36 (*m*)	26.4	1.07 (*m*), 1.32 (*m*)
7′	131.8		37.6	2.25 (*m*)*	37.8	1.90 (*m*) 2.25 (*br d*, 12.6	37.8	1.86 (*m*) 2.25 (*br d*, 12.0)	37.3	1.86 (*m*), 2.22 (*m*)
8′	25.5	1.63 (*s*)	146.8		147.9		146.6		148.0	
9′	17.6	1.56 (*s*)	53.8	*	55.6	1.62 (*m*)	53.0	1.96 (*m*)	56.6	1.66 (*m*)
10′	34.7	2.23 (*d*, 14.2) 2.67 (*d*, 14.2)	38.7		40.3		38.6		38.7	
11′			26.7	*	26.6	1.28 (*m*)*	28.0	1.10 (*m*), 1.64 (*m*)	22.6	2.12 (*m*), 1.94 (*m*)
12′			40.3	3.10 (*m*)	49.5	2.20 (*dd*, 10.6, 3.9)	39.7	3.10 (*m*)	133.3	5.19 (*br s*)
13′			144.2		137.6		147.0		132.4	
14′			120.4	5.47 (*br d*, 6.3)	124.9	5.55 (*br s*)	46.5	2.60 (*br s*)	47.5	2.88 (*t*, 9.0)
15′			31.7	1.98 (*m*), 2.29 (*m*)	27.1	2.38 (*br d*, 18.0) 2.84 (*dd*, 18.0, 6.8)	33.9	2.10 (*br d*, 12.0) 2.16 (*br d*, 12.0)	30.4	1.36 (*m*), 2.08 (*m*)
16′			24.4	1.73 (*s*)	24.0	1.61 (*s*)	113.9	4.66 (*s*), 4.90 (*s*)	14.5	1.55 (*s*)
17′			108.7	4.58 (*s*), 4.87 (*s*)	107.0	4.62 (*br s*), 4.30 (*br s*)	108.8	4.78 (*s*), 4.90 (*s*)	107.8	4.73 (*s*), 4.36 (*s*)
18′			178.9		179.0		179.0		178.8	
19′			16.3	1.02 (*s*)	16.5	1.04 (*s*)	16.4	1.03 (*s*)	16.4	1.05 (*s*)
20′			15.0	0.52 (*s*)	14.4	0.48 (*s*)	15.7	0.57 (*s*)	14.5	0.65 (*s*)
CO_2CH_3			51.8	3.56 (*s*)	51.9	3.61 (*s*)	51.8	3.57 (*s*)	51.7	3.57 (*s*)
OCH_3			59.8	3.91 (*s*)	60.2	3.90 (*s*)	59.4	3.85 (*s*)		

*The signal of one or both protons was too weak to be assigned.

†Coupling constants (J in Hz) in parentheses.



Scheme 4. Formation of compound **6** and ORTEP drawing of compound **6m**.

Terpene **6** was treated with CH_2N_2 to give a crystalline bismethylated compound, **6m** ($C_{42}H_{60}O_6$), the structure of which was determined by an X-ray diffraction study along with other spectroscopic methods (IR, MS, and ^1H, ^{13}C, HMBC and HMQC NMR). The NOESY spectrum also supported the assigned stereochemistry. Compound **6**, namely taiwaniadduct D, was presumably derived from the ene reaction (allyl-carbonyl coupling, for reviews see refs 7 and 8) of **4** (Scheme 4). The newly formed chiral centres had the (6*S*,14′*R*)-configuration.

Terpene **7** was treated with CH_2N_2 to give the corresponding methyl ester, **7m**, having a molecular ion $[M]^+$ at *m/z* 646.423 attributable to the molecular formula $C_{41}H_{58}O_6$. The structure of **7m** was determined by detailed analysis of the IR, MS, and ^1H, ^{13}C, HMBC and HMQC NMR spectra. H-14′ was in the proximity of the aldehyde group as indicated by the NOESY spectrum. The stereochemistry was similarly assigned: NOE correlations of H-6 (δ 9.87) to H-5 (δ 2.08), H-7 (δ 3.31) to H-20 (δ 0.99), and H-12′ (δ 5.19) to H-14′(δ 2.88) were observed. Compound **7**, namely taiwaniadduct E, appeared to be derived from the [5 + 2] cycloaddition [9] between taiwaniaquinone A and *trans*-ozic acid with the formation of linkages at C8-C14′ and C13-C15′ (Scheme 5). The alternative [5 + 2] cycloaddition with the linkages at C8-C15′ and C13-C14′ was unfavourable presumably due to the severe repulsion between the isopropyl group at C-13 and the methyl group at C-13′.

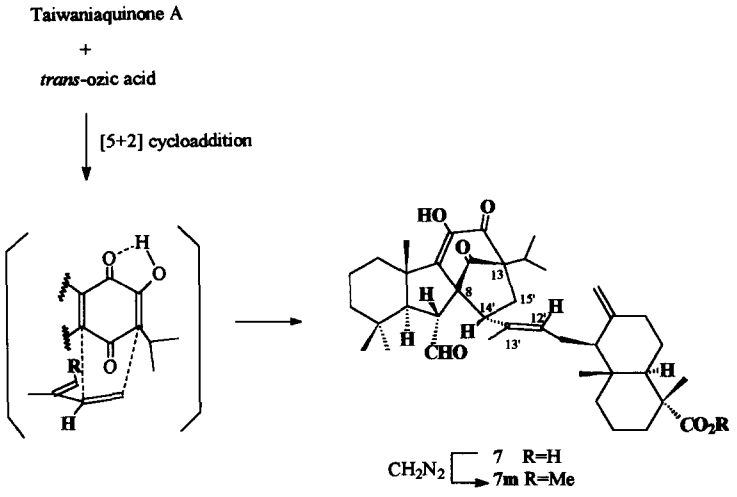
In summary, diterpenes **1** and **2** having a 6-5-6 fused ring skeleton were found in *T. cryptomerioides*, in addition to the previously reported analogs from this plant source. Compounds **3–7** were derived from taiwaniaquinone A, β-myrcene and *trans*-ozic acid via [4 + 2] cycloaddition, [5 + 2] cycloaddition or an ene reaction. Since the enzymes for these reactions are not known in biological systems [10], compounds **3-7** are probably artefacts. It is, however, rather uncommon that combinations of taiwaniaquinone A with β-myrcene or *trans*-ozic acid occurred during the separation procedure.

EXPERIMENTAL

General. HPLC: Hibar Lichrosorb Si 60 column (10 μm, 25 cm × 1 cm i.d.); TLC: Merck silica gel 60F sheets.

Plant material. The dried leaves (1.75 kg) of *T. cryptomerioides* were exhaustively extracted with Me_2CO (71 × 3). The combined extracts were concd to *ca* 0.8 l, and taken up with $CHCl_3$ (0.8 l × 3). The $CHCl_3$-soluble portion was concd (55 g) and subjected to silica-gel CC. The portion obtained from elution of EtOAc–hexane (5–40%) was further subjected to flash chromatography and HPLC with elution of EtOAc–hexane (5–30%) or EtOAc–CH_2Cl_2 (10%) to give compounds **1** (42 mg), **2** (26 mg), **3** (256 mg), **4** (298 mg), **5** (45 mg), **6** (311 mg) and **7** (256 mg). Acids **4–7** were further transformed into their corresponding methyl ester derivatives **4m–7m**, which were purified by HPLC.

Taiwaniaquinone D (**1**). Red gum, $[\alpha]_D^{22}$ − 4.9° ($CHCl_3$; *c* 2.1). TLC (5% EtOAc in hexane) R_f 0.34.



Scheme 5. Formation of compound **7**.

IR ν_{max}^{KBr} cm^{-1}: 3361, 1691, 1630; UV λ_{max}^{MeOH} nm (ε): 477 (756), 340 (6410), 226 (12 655); EIMS (70 eV) *m/z* (rel. int.): 328 $[M]^+$ (36), 300 (20), 285 (58), 259 (100), 231 (14), 215 (8), 173 (6). HR-MS for $C_{20}H_{24}O_4$ requires: 328.1675. Found: 328.1678.

Taiwaniaquinone E (**2**). Yellow solid, mp: 79–81°, $[\alpha]_D^{22}$ −204° ($CHCl_3$; *c* 1.3). TLC (5% EtOAc in hexane) R_f 0.25. IR ν_{max}^{KBr} cm^{-1}: 3383, 1735, 1635; UV λ_{max}^{MeOH} nm (ε): 431 (542), 341 (7911), 228 (15 488); EIMS (70 eV) *m/z* (rel. int.): 360 $[M]^+$ (30), 300 (100), 285 (30), 244 (10), 231 (22), 217 (18), 189 (12). HR-MS for $C_{21}H_{28}O_5$ requires: 360.1937. Found: 360.1940.

Taiwaniadduct A (**3**). Solid, mp: 128–129°, $[\alpha]_D^{20}$ −106.3° ($CHCl_3$; *c* 12.8). TLC (5% EtOAc in hexane) R_f 0.27. IR ν_{max}^{KBr} cm^{-1}: 3347, 1711, 1640; UV λ_{max}^{MeOH} nm (ε): 345 (4091), 290 (7017); EIMS (70 eV) *m/z* (rel. int.): 466 $[M]^+$ (12), 449 (4), 384 (2), 300 (100), 257 (5), 231 (20), 217 (4). HR-MS for $C_{30}H_{42}O_4$ requires: 466.3085. Found: 466.3094.

Taiwaniadduct B (**4**). Compound **4** (298 mg) was treated with CH_2N_2 in Et_2O to give the bismethylated compound **4m** (282 mg). Solid, mp: 158–160°, $[\alpha]_D^{25}$ −15.6° ($CHCl_3$; *c* 14.1). TLC (5% EtOAc in hexane) R_f 0.1. IR ν_{max}^{KBr} cm^{-1}: 1713, 1657; UV λ_{max}^{MeOH} nm (ε): 304 (2309), 288 (2614), 204 (14 630); EIMS (70 eV) *m/z* (rel. int.): 661 $[M+1]^+$ (7), 660 $[M]^+$ (1.5), 601 (1.5), 494 (40), 412 (7), 259 (15), 246 (100). HR-MS for $C_{42}H_{60}O_6$ requires: 660.4392. Found: 660.4391.

Taiwaniadduct C (**5**). Compound **5** (45 mg) was treated with CH_2N_2 in Et_2O to give the bismethylated compound **5m** (40 mg). Solid, mp: 156–157°, $[\alpha]_D^{28}$ −82.3° ($CHCl_3$; *c* 2.0). TLC (5% EtOAc in hexane) R_f 0.1. IR ν_{max}^{KBr} cm^{-1}: 1715, 1658; UV λ_{max}^{MeOH} nm (ε): 282 (5053), 202 (13 800); EIMS (70 eV) *m/z* (rel. int.): 660 $[M]^+$ (10), 600 (5), 494 (18), 410 (25), 316 (85), 247 (50), 121 (100). HR-MS for $C_{42}H_{60}O_6$ requires: 660.4392. Found: 660.4390.

Taiwaniadduct D (**6**). Compound **6** (311 mg) was treated with CH_2N_2 in Et_2O to give the bismethylated compound **6m** (288 mg). Crystals from MeOH–CH_2Cl_2 (1:9), mp: 210.5–212.0°, $[\alpha]_D^{25}$ −60.1° ($CHCl_3$; *c* 14.4). TLC (5% EtOAc in hexane) R_f 0.1. IR ν_{max}^{KBr} cm^{-1}: 3512, 1710, 1658; UV λ_{max}^{MeOH} nm (ε): 279 (8858), 202 (20 431). FAB (+) 661.7 $[M+1]^+$. HR-MS for $C_{42}H_{60}O_6$ requires: 660.4392. Found: 660.4343.

Taiwaniadduct E (**7**). Compound **7** (256 mg) was treated with CH_2N_2 in Et_2O to give the monomethylated compound **7m** (222 mg). Solid, mp: 114–116°, $[\alpha]_D^{25}$ +25.3° ($CHCl_3$; *c* 11.1). TLC (5% EtOAc in hexane) R_f 0.1. IR ν_{max}^{KBr} cm^{-1}: 3418, 1753, 1721, 1668, 1627; UV λ_{max}^{MeOH} nm (ε): 286 (7661), 202 (27 140). FAB (+) 647.3 $[M+1]^+$. HR-MS for $C_{41}H_{58}O_6$ requires: 646.4235. Found: 646.4225.

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