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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 ¹³C NMR spectra (Table 1) indicated an aldehyde group [δ_H 10.38 (s) and δ_C 194.1 (d)] and two ketone groups $[\delta_C 185.1 (s)]$ 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 $\delta_{\rm C}$ 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). was given the Compound 1 trivial taiwaniaquinone D, and its structure was finally elucidated by means of HMBC and HMQC. Treatment of taiwaniaquinone B (or taiwaniaquinone C) with AlCl₃ in CH₂Cl₂ 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. 'C and	'H NMR spectral	data of compounds	1 and 2 (CDCl ₃ , δ in ppm)
	1		2

		1		2
	δ_{c}	$\delta_{\scriptscriptstyle ext{H}}$	$\delta_{_{ m C}}$	$\delta_{\scriptscriptstyleH}$
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)
2 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 ₂ CH ₃			52.3	3.73 (s)

^{*}The signal of the other proton was too weak to be assigned.

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%

Scheme 2. Chemical synthesis of compound 3.

[†]Coupling constants (J in Hz) in parentheses.

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, because 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** (CH₂N₂, Et₂O) were purified by HPLC and their structures were determined by spectroscopic methods (IR, MS, HRMS, and ¹H, ¹³C, HMBC and HMQC NMR). Compounds **4m** and **5m** were isomers giving rise to molecular ions [M] ⁺ at 660.439 attributable to the molecular formula C₄₂H₆₀O₆. The ¹H and ¹³C NMR spectra of **4m** showed the characteristic resonances (Table 2) of an

aldehyde group [$\delta_{\rm H}$ 9.60 (d) and $\delta_{\rm C}$ 205.4 (d)], a methyl ester [$\delta_{\rm H}$ 3.56 (s), $\delta_{\rm C}$ 51.8 (q) and 178.9 (s)], conjugated ketones [$\delta_{\rm C}$ 198.6 (s) and 201.3 (s)], a methoxy group [$\delta_{\rm H}$ 3.91 (s)], a terminal double bond [$\delta_{\rm C}$ 108.7 (t) and 146.8 (s)], a trisubstituted double bond [$\delta_{\rm C}$ 120.4 (d) and 144.2 (s)], as well as for a tetrasubstituted double bond [$\delta_{\rm C}$ 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, transozic 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.

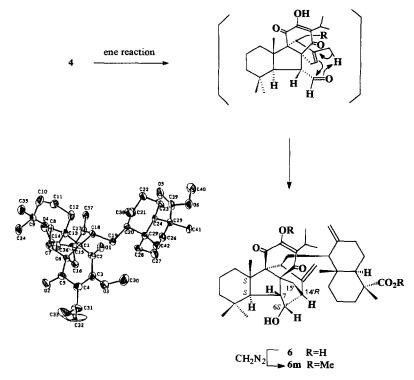
Scheme 3. Formation of compounds 4 and 5.

Table 2. ¹³C and ¹H NMR data of compounds 3 and 4m-7m (CDCl₃, 8 in ppm)

			Table 2.	Cand I NMR UA	ta or compa	Table 2. C and I living data of compounds 3 and 4111-1111 (CDCL ₃ , 9 in ppin)	DCI3: 0 III	/mdd		
		3		4m		Sm		bm b		7m
	δ.	δη	δ.	δ _H	Ø,	δ _H	δ.	δн	ğ	δн
-	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), 2.30n(m)
7	18.7	1.56 (m)*	18.3	*	18.0	*	18.3	1.46 (m)*	18.3	1.48 (m)*
٣.	41.5	1.15 (m)	41.5 (m)	().96 (m),	4.14	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)	9.95	2.08 (m)
9	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 (1, 9.0)	52.5	3.31 (dd, 13.4, 5.5)
œ	6.09		8.09		7.4		65.7		68.1	
6	63.4		65.9		60.2		0.99		143.7	
10	49.4		51.4		51.5		53.3		47.3	
Ξ	198.5		9.861		199.3		198.0		142.9	
1.2	155.4		159.0		160.1		159.6		193.9	
13	131.4		141.3		144.0		140.9		66.2	
4	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)
<u>8</u> 1	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	(x) 66.0

2.05 (m) 2.34 (br d. 13.5)	37.3 1.63 (m)* 37	37.3 *		37.7	1.42 (<i>m</i>)*	
* 0.61	19	19.3 *		19.4	*	
36.7 1.41*		_	[.44 (m), 1.50 (m)	36.7	1.48 (m)*	36.7 1.46 (m)*
47.5	47			47.6		
50.0 1.75 (m)			1.85 (m)	50.1	1.80 (m)	_
			(<i>m</i>)	8.97	1.14 (m), 1.36 (m)	
37.6 2.25 (m)*			1.90 (m)	37.8	1.86 (m)	37.3 1.86 (m), 2.22 (m)
		2.25	2.25 (br d. 12.6		2.25 (br d. 12.0)	
146.8	147			146.6		
53.8 *	55		1.62 (m)	53.0	1.96 (m)	56.6 1.66 (m)
38.7	40	40.3		38.6		38.7
\$ *	26		1.28 (m)*	28.0	1.10 (m), 1.64 (m)	22.6 2.12 (m), 1.94 (m)
40.3 3.10 (m)		49.5 2.20	2.20 (dd, 10.6, 3.9)	39.7	3.10 (m)	
144.2	137	7.6		147.0		132.4
	5.47 (br d, 6.3) 124		5.55 (br s)	46.5	2.60 (br s)	
	1.98 (m), 2.29 (m) 27		2.38 (br d. 18.0)	33.9	2.10 (br d, 12.0)	30.4 1.36 (m), 2.08 (m)
		2.84	2.84 (dd, 18.0, 6.8)		2.16 (br d. 12.0)	
24.4 1.73 (s)			1.61 (s)	113.9	4.66 (s), 4.90 (s)	14.5 1.55 (s)
	4.58 (s), 4.87 (s) 107	107.0 4.62	4.62 (br s), 4.30 (br s)	8.801	4.78 (s), 4.90 (s)	107.8 4.73 (s), 4.36 (s)
				179.0		178.8
16.3 1.02 (s)			L.04 (s)	16.4	1.03 (s)	
			0.48 (s)	15.7	0.57 (s)	14.5 0.65 (s)
		51.9 3.61	3.61 (s)	51.8	3.57 (s)	51.7 3.57 (s)
59.8 3.91 (s)			3.90 (s)	59.4	3.85 (s)	

*The signal of one or both protons was too weak to be assigned. +Coupling constants (*I* 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 (allylcarbonyl 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,N, to give the corresponding methyl ester. 7m, having a molecular ion $[M]^+$ at m/z 646.423 attributable to the molecular formula C₄₁H₅₈O₆. The structure of 7m was determined by detailed analysis of the IR, MS, and ¹H, ¹³C, 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 $(\delta 2.08)$, H-7 $(\delta 3.31)$ to H-20 $(\delta 0.99)$, and H-12' $(\delta 5.19)$ to H-14' $(\delta 2.88)$ 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

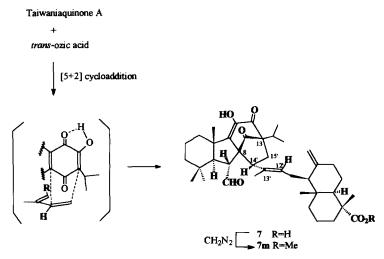
addition to the previously reported analogs from this plant source. Compounds 3-7 were derived from taiwaniaquinone A, β -myrcene and *trans*-ozic acid via [4+2] cycloaddition, [5+2] cycloaddition or an ene reaction. Since the enzymes for these reactions are not known in biological systems [10], compounds 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 μ m, 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 Me₂CO (71 × 3). The combined extracts were concd to ca 0.81, and taken up with CHCl₃ (0.81×3). The CHCl₃-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-CH₂Cl₂ (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. $[\alpha]_D^{22} = 4.9^\circ$ (CHCl₃; c 2.1). TLC (5% EtOAc in hexane) R_f 0.34.



Scheme 5. Formation of compound 7.

IR $\nu_{\rm max}^{\rm KBr}$ cm⁻¹: 3361, 1691, 1630; UV $\lambda_{\rm max}^{\rm MeOH}$ nm (ε): 477 (756), 340 (6410), 226 (12655); 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°, $[\alpha]_{12}^{22} - 204°$ (CHCl₃; c 1.3). TLC (5% EtOAc in hexane) R_f 0.25. IR $\nu_{\rm max}^{\rm KBr}$ cm $^{-1}$: 3383, 1735, 1635; UV $\lambda_{\rm max}^{\rm MeOH}$ 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 C₂₁H₂₈O₅ requires: 360.1937. Found: 360.1940.

Taiwaniadduct A (3). Solid, mp: 128–129°, $[\alpha]_{\rm D}^{20}$ –106.3° (CHCl₃; c 12.8). TLC (5% EtOAc in hexane) R_f 0.27. IR $\nu_{\rm max}^{\rm KBr}$ cm⁻¹: 3347, 1711, 1640; UV $\lambda_{\rm max}^{\rm MeOH}$ 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 C₃₀H₄₂O₄ requires: 466.3085. Found: 466.3094.

Taiwaniadduct *B* (**4**). Compound **4** (298 mg) was treated with CH₂N₂ in Et₂O to give the bismethylated compound **4m** (282 mg). Solid, mp: 158–160°, $[\alpha]_D^{25}$ –15.6° (CHCl₃; *c* 14.1). TLC (5% EtOAc in hexane R_f 0.1. IR ν_{\max}^{KBr} cm⁻¹: 1713, 1657; UV $\lambda_{\max}^{\text{MeOH}}$ nm (ε): 304 (2309), 288 (2614), 204 (14 630); EIMS (70 eV) m/z (rel. int.): 661 [M + 1]⁻¹ (7), 660 [M]⁺ (1.5), 601 (1.5), 494 (40), 412 (7), 259 (15), 246 (100). HR-MS for C₄₂H₆₀O₆ requires: 660.4392. Found: 660.4391.

Taiwaniadduct C (5). Compound 5 (45 mg) was treated with CH₂N₂ in Et₂O to give the bismethylated compound 5m (40 mg). Solid, mp: 156–157°, $[\alpha]_D^{28}$ -82.3° (CHCl₃; c 2.0). TLC (5% EtOAc in hexane) R_f 0.1. IR $\nu_{\rm max}^{\rm KBr}$ cm⁻¹: 1715, 1658; UV $\lambda_{\rm max}^{\rm MeOH}$ 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 C₄₂H₆₀O₆ 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-

CH₂Cl₂ (1:9), mp: 210.5–212.0°, $[\alpha]_{0}^{25}$ –60.1° (CHCl₃; c 14.4). TLC (5% EtOAc in hexane) R_f 0.1. IR $\nu_{\text{max}}^{\text{KBr}}$ cm $^{-1}$: 3512, 1710, 1658; UV $\lambda_{\text{max}}^{\text{MeoH}}$ 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 CH₂N₂ in Et₂O to give the monomethylated compound 7m (222 mg). Solid, mp: 114–116°, $[\alpha]_{\rm D}^{2.5}$ +25.3° (CHCl₃; c 11.1). TLC (5% EtOAc in hexane) R_f 0.1. IR $\nu_{\rm max}^{\rm KBr}$ cm⁻¹: 3418, 1753, 1721, 1668, 1627; UV $\lambda_{\rm max}^{\rm MeOH}$ nm (ε): 286 (7661), 202 (27 140). FAB (+) 647.3 [M+1]⁺. HR-MS for C_{4.1}H_{5.8}O₆ requires: 646.4235. Found: 646.4225.

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