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GERMITOROSONE AND METHYLGERMITOROSONE, TWO HYDROANTHRACENE DERIVATIVES FROM SEEDLINGS OF *CASSIA TOROSA**

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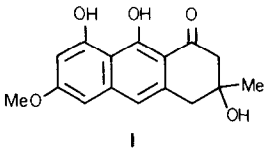
Key Word Index—*Cassia torosa*; Leguminosae; seedling; germitorosone; methylgermitorosone; hydroanthracene.

Abstract—Two new yellow pigments, germitosone and methylgermitorosone, were isolated from the seedling of *Cassia torosa*. The structures of these substances were established as 3,7 - dimethyl - 6 - methoxy - 1 - oxo - 2,3,8,9 - tetrahydroxy - 1,2,3,4 - tetrahydroanthracene and 6,9 - dimethoxy - 3,7 - dimethyl - 1 - oxo - 2,3,8 - trihydroxy - 1,2,3,4 - tetrahydroanthracene respectively.

INTRODUCTION

Previously we reported the isolation of several anthraquinones and a tetrahydroanthracene, torosachrysone (**1**), from the seeds of *Cassia torosa* Cavanilles [1]. Recently, another hydroanthracene, germichrysone, and two pairs of atropisomeric dimers, phlegmacin A_2 and B_2 and anhydrophlegmacin A_2 and B_2, were isolated from fresh seedlings of the same plant [2, 3]. This paper describes the isolation and identification of new two tetrahydroanthracene derivatives, germitorosone (**2**) and methylgermitorosone (**3**), two compounds which are found only in the radicle of young seedlings.



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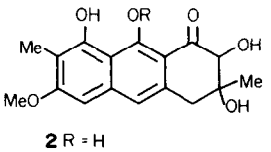
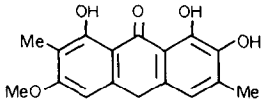


2 R = H
3 R = Me



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RESULTS AND DISCUSSION

The C_6H_6 extracts of the seedlings were chromatographed on silicic acid. Germitorosone (**2**) and methylgermitorosone (**3**) were obtained by rechromatography and prep. TLC.

Germitorosone (**2**) was obtained as yellow needles, mp 211–212°. High resolution MS gave the molecular formula as $C_{17}H_{18}O_6$, and major fragment ions were observed at *m/z* 300 $[M-H_2O]^+$ and 272 $[M-H_2O-CO]^+$. The similarity in the chromophore of germitorosone (**2**) to that of torosachrysone (**1**) was established on comparison of their UV and IR spectra. An intense band at 1640 cm^{-1} revealed the presence of a chelated carbonyl group, while the UV maxima at 302 and 313 nm showed that germitorosone (**2**) possessed a naphthalene nucleus. The ^1H NMR spectrum of germitorosone (**2**) showed the presence of two Me groups (aromatic and aliphatic), an aromatic OCH_3 group, two aromatic protons, and four hydroxy groups, two of which were chelated (Table 1). The above data indicated that germitorosone (**2**) had one secondary hydroxyl group and one aromatic methyl group more than torosachrysone (**1**) and one aromatic proton and one $-CH_2-$ group less. Germitorosone (**2**) was converted to a yellow substance (**4**), mp 241–243°, by sublimation. The UV maxima at 270, 280 and 332 nm suggested the compound might have an anthrone skeleton and the ^1H NMR spectrum showed the presence of two methyl groups, a methoxyl group, a $-CH_2-$ group, two aromatic protons and three hydroxyl groups. The MS gave the molecular formula as $C_{17}H_{16}O_5$, and the structure was established as 2,6 - dimethyl - 3 - methoxy - 1,7,8 - trihydroxy - anthrone by NOE. Finally, the structure of germitorosone (**2**) was determined from the NOE observed on the signals for H-5 (δ 6.53, 21%) on irradiation of the methoxy protons at δ 3.90, for H-10 (δ 6.87, 8%) on irradiation of H-5 and for H-10 (10%) on irradiation of $-CH_2-$ protons. The results indicated that the one methyl group of germitorosone was at C-7 and that one secondary hydroxyl group was at C-2. Therefore, the structure of germitorosone (**2**) was established as 3,7 - dimethyl - 6 - methoxy - 1 - oxo - 2,3,8,9 - tetrahydroxy - 1,2,3,4 - tetrahydroanthracene.

*Part 11 in the series "Studies of the Constituents of Purgative Crude Drugs". For Part 10, see Kitanaka, S. and Takido, M. (1981) *Phytochemistry* **20**, 1951.

Table 1. ^{1}H NMR spectral data of compounds **1–4** (100 Mz, $CDCl_3$, TMS as int. standard)

	1	2	3		4	
H-2	2.83*s*(*br*)	4.28*d* (*J* = 1.5 Hz)	4.45*s*(*br*)	OH-1	12.61s	
				Me-2	2.11*s*	
OH-2		3.84*d* (*J* = 1.5 Hz)		OMe-3	3.91*s*	37%
Me-3	1.45*s*	1.53*s*	1.55*s*	H-4	6.43*s*	24%
OH-3	1.68*s*(*br*)	2.15*s*(*br*)	1.93*s*(*br*)	H-10	4.19*s*	23%
H-4	3.04*s*(*br*)	3.11*s*(*br*)	3.27*s*(*br*)	H-5	6.66*s*	
		10%				
H-10	6.86*s*(*br*)	6.87*t* (*J* = 1.0 Hz)	7.26*t* (*J* = 1.0 Hz)	Me-6	2.33*s*	
				OH-7	5.63*s*	
		8%				
H-5	6.54*d* (*J* = 2.4 Hz)	6.53*s*	6.58*s*	H-8	12.46*s*	
		21%				
OMe-6	3.88*s*	3.90*s*	3.92*s*			
H-7	6.48 *d* (*J* = 2.4 Hz)					
Me-7		2.17*s*	2.20*s*			
OH-8	9.79*s*	9.58*s*	10.05*s*			
OH-9	16.10 *s*	14.61*s*				
OMe-9			4.05*s*			

Arrows and figures in % indicate enhancement in NOE experiment.

Methylgermitorosone (**3**) was obtained as very pale yellow needles, mp 214°, $C_{18}H_{20}O_6$ (MS). Its UV spectrum was similar to that of germitorosone (**2**) and it was obtained from germitorosone by methylation with CH_2N_2. The ^{1}H NMR data indicated that the structure of methylgermitorosone (**3**) had one more methoxyl group (δ 4.05) and one less chelated hydroxyl group (δ 14.61, C-9) than germitorosone (**2**) (Table 1). Therefore, the structure of methylgermitorosone (**3**) was established as 6,9 - dimethoxy - 3,7 - dimethyl - 1 - oxo - 2,3,8 - trihydroxy - 1,2,3,4 - tetrahydroanthracene.

It is an interesting fact that these two new compounds are found only in the radicle.

EXPERIMENTAL

Plant material was obtained from the Drug Plant Garden, College of Science and Technology, Nihon University. CC: silicic acid (Mallinckrodt); Prep. TLC: oxalic acid (0.5 N)–Si gel (0.5 mm) developed with C_6H_6–EtOAc (7:3).

Extraction and isolation. Seeds (5.0 kg) were sterilized with 5% NaOCl soln and germinated in the dark at 29° on a wet cotton-wool bed. After 1 week, the yellow seedlings (2–3 cm high) were harvested and extracted with cold C_6H_6 for 3 days. The brown C_6H_6 extract (70 g) was chromatographed over silicic acid with C_6H_6–EtOAc (9:1) to afford a mixture of germitorosone (**2**) and methylgermitorosone (**3**). Prep. TLC of the mixture gave pure **2** (45 mg) and **3** (14 mg).

Germitorosone (**2**). Yellow needles (Me_2CO) mp 211–212; high resolution MS: found; 318.1102, calcd for $C_{17}H_{16}O_6$; 318.1085; $[\alpha]_D^{22}$ – 20° (dioxane, *c* 0.40); UV $\lambda_{max}^{dioxane}$ nm (log ϵ): 260 (sh, 4.75), 274 (4.81), 302 (sh, 3.86), 313 (4.06), 326 (4.00), 398 (4.09); IR ν_{max}^{KBr} cm^{-1}: 3200–3550, 2950, 1640, 16220, 1580, 1510, 1460, 1410, 1390, 1350, 1300, 1280, 1250, 1230, 1200, 1170, 1150, 1130, 1110, 1090, 1080, 1040, 990, 960, 950, 850, 840, 820, 750, 730, 640, 625, 620: MS 70 eV *m/z* (rel. int.): 318 $[M]^+$ (100), 300 $[M-H_2O]^+$ (28), 287 $[M-OMe]^+$ (21), 285 $[M-H_2O-Me]^+$ (12), 282 $[M-2H_2O]^+$ (7), 272 $[M-H_2O-CO]^+$ (39), 271 $[M-H_2O-CHO]^+$ (53), 260 $[M-COCHOH]^+$ (8), 258 $[M-2H_2O-CO]^+$ (10), 257 $[M-H_2O-Me-CO]^+$ (29), 254 $[M-2H_2O-CO]^+$ (10), 244 $[M-CHOHCMeOH]^+$ (6), 230 $[M^+-OMe-CO-CHO]^+$ (11).

Methylgermitorosone (**3**). Pale yellow prisms (C_6H_6) mp 214°; high resolution MS: found; 332.1238, calcd for $C_{18}H_{20}O_6$; 332.1258; UV $\lambda_{max}^{dioxane}$ nm (log ϵ): 222 (4.30), 275 (4.86), 308 (sh, 3.70), 318 (3.83), 333 (3.74), 378 (3.79); IR ν_{max}^{KBr} cm^{-1}: 3200–3550, 2950, 1680, 1630, 1600, 1570, 1500, 1460, 1450, 1440, 1410, 1380, 1340, 1290, 1260, 1230, 1200, 1150, 1110, 1070, 1040, 980, 960, 950, 920, 890, 860, 820, 810, 750, 730, 650, 630, 620; MS 70 eV *m/z* (rel. int.): 332 $[M]^+$ (100), 286 $[M-CO-H_2O]^+$ (9), 285 $[M-CHO-H_2O]^+$ (27), 274 $[M-COCHOH]^+$ (8), 271 $[M-CO-H_2O-Me]^+$ (58), 258 $[M-CHOHCMeOH]^+$ (7), 244 $[M-CHOHCMeOHCH_2]^+$ (7).

Conversion of **2** *to* 2,6 - *dimethyl* - 3 - *methoxy* - 1,7,8 - *trihydroxyanthrone* (**4**). **2** (20 mg) was sublimed *in vacuo* at 200°. The sublimed substance was chromatographed on silicic acid with C_6H_6–EtOAc (9:1) to give **4** (4 mg).

2,6 - *Dimethyl* - 3 - *methoxy* - 1,7,8 - *trihydroxyanthrone* (**4**). Yellow needles, mp 243–244°; high resolution MS: found; 300.0973, calcd for $C_{17}H_{16}O_5$: 300.0996; UV $\lambda_{max}^{dioxane}$ nm (log ϵ): 231 (4.08), 261 (3.52), 270 (3.56), 279 (3.66), 330 (3.96); IR ν_{max}^{KBr} cm^{-1}: 3300–3600, 2950, 1620, 1595, 1560, 1470, 1410, 1340, 1320, 1280, 1260, 1240, 1230, 1150, 1120, 1060, 1020, 935, 920, 840, 790, 765, 745, 700, 660, 620; MS 70 eV *m/z* (rel. int.): 300 $[M]^+$ (100), 299 $[M-H]^+$ (7), 285 $[M-OMe]^+$ (9), 257 $[M-Me-CO]^+$ (10).

Synthesis of germitorosone (**2**) *to methylgermitorosone* (**3**). A soln of **2** (5 mg) dissolved in $CHCl_3$ (10 ml) was methylated with CH_2N_2 at room temp. for 1 hr. The soln was evaporated to give a yellow residue, on crystallization from C_6H_6, mp 213° (3 mg) which was identified as **3** by comparison of IR and mmp.

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