

STRUCTURE OF TRIGONOSTEMONE, A NEW PHENANTHRENONE
FROM THE THAI PLANT *TRIGONOSTEMON REIDIOIDES*UDOM KOKPOL,* SUPA THEBPATIPHAT, SUPRARB BOONYARATAVEJ, VIPA CHEDCHUSKULCAI,
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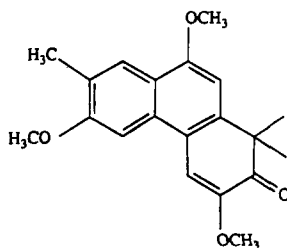
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*Department of Chemistry, University of Central Florida, Orlando, Florida 32816***ABSTRACT.**—Trigonostemone [**1**] has been isolated from *Trigonostemon reidioides*. Its structure has been established spectroscopically and confirmed by X-ray crystallography.

Trigonostemon reidioides Craib (Euphorbiaceae) is found predominantly in northeastern Thailand (1). Extracts of the roots are used in traditional medicine as an expectorant and a laxative and in treatment of skin diseases (2). There are no reports involving chemical investigations of this species; however, there is a verbal report (the reference cannot be confirmed) of an investigation in a Thai government research report. The limited investigation of the chemistry of this plant prompted an examination of the constituents of the roots. In this paper, we report the isolation and structure elucidation of the compound 1,1,7-trimethyl-3,6,9-trimethoxy-2-phenanthrenone [**1**] from *T. reidioides*. This compound was assigned the name trigonostemone.

Pure trigonostemone [**1**] was crystallized from a hexane/CHCl₃ eluent of a Si gel column as green needles, mp 184–185°. A molecular formula of C₂₀H₂₂O₄ was established by eims ([M]⁺ *m/z* 326) and elemental analysis. This formula provided ten degrees of unsaturation. The presence of aromaticity in the molecule was suggested by ir (KBr) bands at 1630 and 1460 cm⁻¹ and by the uv absorption at 256 nm (log ε = 4.57) and 403 (log ε = 4.09).

The presence of an α,β-unsaturated ketone (3) was indicated by the uv absorption at 213 nm (log ε = 4.74) and 234 nm (log ε = 4.47) and by an ir (KBr) band at 1670 cm⁻¹. This compound gave a positive test to KMnO₄, Br₂ in CCl₄, and 2,4-dinitrophenylhydrazine, which confirmed the presence of a double bond and a carbonyl

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group. The aromatic nature of trigonostemone [1] was confirmed by the ^1H -nmr (CDCl_3) spectrum, which gave resonances at δ 7.28 (1H, s, H-5), 7.32 (1H, s, H-10), and 8.04 (1H, s, H-8) for three isolated protons on an aromatic ring.

A further study of the ^1H -nmr spectrum of 1 provided evidence of three methoxy groups at δ 3.96 (3H, s, H-13) and 4.02 (6H, s, H-14 and H-16). The ^1H -nmr spectrum also gave signals for a *gem*-dimethyl group at 1.56 (6H, s, H-11 and H-12), a methyl group at 2.36 (3H, s, H-15), and a vinylic proton at 6.74 (1H, s, H-4). The ^{13}C -nmr spectrum showed nineteen resonances, which indicated a structure with a pair of equivalent carbons. Off-resonance decoupling showed singlets at δ 49.52 (C-1), 199.32 (C-2), 147.42 (C-3), 130.74 (C-4a), 157.80 (C-6), 127.15 (C-7), 114.32 (C-9a), 154.93 (C-9), and 119.20 (C-10a), doublets at δ 99.01 (C-4), 110.20 (C-5), 123.37 (C-8), and 100.65 (C-10), quartets for two methyl groups at δ 16.65 (C-11 and C-12) and δ 28.33 (C-15), and three quartets for three methoxy groups at δ 55.90 (C-14), 55.36 (C-16), and 55.47 (C-13). The singlet at δ 199.32 (C-2) was attributed to a carbonyl, and the singlet at δ 49.52 (C-1) assigned as the quaternary carbon of a *gem*-dimethyl group.

Consideration of the ^{13}C chemical shifts for the carbons of naphthalene, together with the well-established standard chemical shift values (4,5) for the various substituents (-Me, -OMe), permitted assignment of the chemical shift values for 7-methyl-1,6-dimethoxy naphthalene. These values closely relate to those obtained for the naphthalenic portion of 1 except for C-3 and C-4 (Table 1). These two carbons are not expected to be in agreement because they were extension points to the other parts of the structure.


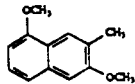
The structure of compound 1 was confirmed by X-ray crystallography. A computer-generated perspective drawing is shown in Figure 1.

EXPERIMENTAL

PLANT COLLECTION.—*T. reidioides* was collected from Karasin in Thailand. A voucher specimen (No. 37033) is deposited at the Forest Herbarium (BKF), Royal Forest Department, Flora of Thailand, Bangkok, Thailand.

ISOLATION OF TRIGONOSTEMONE [1].—The dried, ground roots (16.3 kg) of *T. reidioides* were extracted in a Soxhlet extractor with hexane. The hexane solution was evaporated in vacuo. The hexane fraction was chromatographed on an open column with Si gel as an absorbent. The column was eluted with

TABLE 1. Chemical Shifts of 1 and 7-Methyl-1,6-dimethoxynaphthalene.

Atom	^{13}C Standard Chemical Shifts (ppm)			Chemical Shift (ppm)		
	1-OMe	2-OMe	2-Me			1
C-1	+27.6	-22.0	-1.0	127.7	154.6	154.93
C-2	-22.0	+31.9	+9.6	125.6	101.5	100.55
C-3	+0.1	-6.9	+2.3	125.6	125.6	119.20
C-4	-7.6	+1.6	-0.1	127.7	118.9	130.74
C-5	-0.4	-0.1	-0.2	127.7	105.2	110.20
C-6	+0.6	-2.2	-0.8	125.6	160.4	157.80
C-7	-0.6	+0.7	+0.1	125.6	127.7	127.15
C-8	-5.8	-1.0	-0.6	127.7	122.5	123.37
C-4a	+1.0	-4.4	-1.8	133.4	133.8	130.77
C-8a	-7.9	+1.2	+0.2	133.4	121.3	114.32

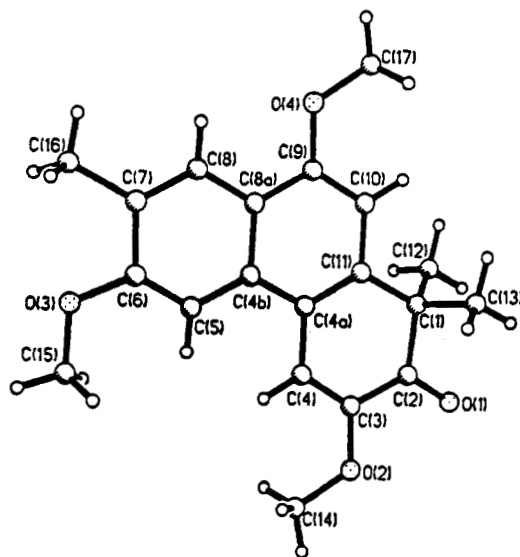


FIGURE 1. X-ray model of Compound 1.

hexane/CH₂Cl₂/MeOH. The 50% CH₂Cl₂/hexane fractions were combined. Recrystallization using a mixture of hexane/CHCl₃ yielded **1** (620 mg) as green needles: mp 184–185°; ir (KBr) γ max 1670, 1630, 1595, 1510, 1390, 1375, 1240, 1170, 1095 cm⁻¹, uv λ max 213 nm (log ϵ = 4.74), 234 nm (log ϵ = 4.47), 256 nm (log ϵ = 4.57), 403 nm (log ϵ = 4.09). *Anal.* calcd for C₂₀H₂₂O₄, C 73.62, H 6.75, mol wt 326.39, found C 73.465, H 6.79, mol wt (ms) 326.16. ¹H nmr (CDCl₃) δ 1.56 (6H, s, H-11 and H-12), 2.36 (3H, s, H-15), 3.96 (3H, s, H-13), 4.02 (6H, s, H-14 and H-16), 6.74 (1H, s, H-4), 7.28 (1H, s, H-5), 7.32 (1H, s, H-10), 8.04 (1H, s, H-8); ¹³C nmr 199.32 (C-2), 157.80 (C-6), 154.93 (C-9), 147.42 (C-3), 130.77 (C-5a), 130.74 (C-4a), 127.15 (C-7), 123.37 (C-8), 119.20 (C-10a), 114.32 (C-9a), 110.20 (C-5), 100.65 (C-10), 99.01 (C-4), 55.90 (C-14), 55.47 (C-13), 55.36 (C-16), 49.52 (C-1), 28.33 (C-15), 16.65 (C-11 and C-12) ppm; eims *m/z* (rel. int. %) 326 (100), 311 (14), 283 (80), 268 (11).

X-RAY DATA FOR 1.—C₂₀H₂₂O₄, orthorhombic, $a = 19.463$ (3), $b = 12.223$ (2), $c = 7.1131$ (4) Å; $V = 1692.3$ (8) Å³ (by least-squares techniques involving diffractometer-measured 2θ -values for fifteen centered reflections, $\lambda = 1.54178$ Å), space group $Pna2_1$, $Z = 4$, $D_{\text{calc}} = 1.281$ g/cm³. Colorless needles, mounted on glass fiber with epoxy. Crystal dimensions 0.2 × 0.2 × 0.2 mm, μ (Cu-K α) 0.678 mm⁻¹.

Data for unit cell determination and also for the structural studies were collected utilizing a Syntex P2₁ diffractometer. A total of 1254 reflections were measured at room temperature with graphite-monochromated CuK α radiation up to $\theta = 57^\circ$, using an ω -scan speed of 1.50°/min. After data reduction, 675 reflections with $F \geq 3\sigma(F)$ were taken as observed.

The structure was solved by direct methods; hydrogen atoms were obtained from a difference Fourier map. Full-matrix least-squares refinements with anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for riding hydrogen atoms led to $R = 0.069$ and $R_w = 0.073$ for 217 variables { weighting scheme: $w^{-1} = [\sigma^2(F) + 0.001(F^2)]$ }. The final difference Fourier synthesis showed no significant features [0.29 eÅ⁻³]. The final calculations were performed using the SHELXTL PLUS system of programs on a Micro VAX II computer.²

ACKNOWLEDGMENTS

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²Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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