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TRANS-TRIACONTYL-4-HYDROXY-3-METHOXYCINNAMATE, A NEW COMPOUND FROM THE THAI PLANT *BRIDELIA OVATA*

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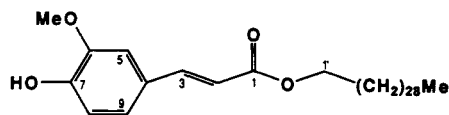
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ABSTRACT.—24-Methylstanosta-9(11)-25-dien-3-one, 24,24-dimethylstanosta-9(11)-25-dien-3-one, friedelin, friedelan-3 β -ol, β -sitosterol, stigmasterol, campesterol, and *trans*-triacontyl-4-hydroxy-3-methoxycinnamate [**1**] were isolated from the Thai plant *Bridelia ovata* (Euphorbiaceae). The structures were elucidated by chemical and spectroscopic evidence. Compound **1** has not previously been reported in the literature and is a novel natural product.

Bridelia ovata Dcne., a small tree in the Euphorbiaceae family, is a traditional medicinal plant in Thailand and is known locally as Ma-Ga. In Thai traditional medicine, a decoction of the dried leaves is used as an expectorant and laxative. The bark is used as a medicinal astringent (1). The appearance of *B. ovata* is similar to that of *Bridelia tomentosa* (local name is Knon), so both plants are used for the same purposes in Thai traditional medicine. No chemical studies have been reported on *B. ovata*, but friedelin, friedelan-3 β -ol, glutin-5-en-3 β -ol (D: B-friedoolean-5-en-3 β -ol), stigmasterol, β -sitosterol, 24-methylstanosta-9(11),25-dien-3-one, and 24,25-dimethylstanosta-9(11),25-dien-3-one have been found in other *Bridelia* species (2). In this paper, we report the isolation of 24-methylstanosta-9(11)-25-dien-3-one, 24,24-dimethylstanosta-9(11)-25-dien-3-one, friedelin, friedelan-3 β -ol, β -sitosterol, stigmasterol, campesterol, and the novel compound *trans*-triacontyl-4-hydroxy-3-methoxycinnamate [**1**] from the dried branches of *B. ovata*.



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Compound **1**, mp 73–74°, was obtained as a colorless, crystalline solid by cc of the CHCl₃ extract over Si gel. Compound **1** gave a molecular formula of C₄₀H₇₀O₄ based upon elemental analysis and a molecular ion of 614 *m/z* in the ms. The uv spectrum of **1** showed absorption maxima at 320, 296, and 242 nm. Ir data indicated the presence of a conjugated ester (1725 cm⁻¹), double bond (1640 cm⁻¹), phenyl group (1600 and 1520 cm⁻¹), and a phenol group (3500 and 1170 cm⁻¹). The ¹H-nmr spectrum confirmed the presence of an OH group (δ 5.84, s), an MeO group (δ 3.93, 3H, s), and aromatic protons (δ 7.15, 1H, d and δ 6.94, 1H, s). The ¹H nmr also contained signals for *trans* olefinic hydrogens (δ 6.23 and 7.61, d, *J* = 15.8 Hz) and a series of methylene groups that can be assigned to a long chain hydrocarbon (δ 1.26 and 0.89). Two strongly deshielded protons at δ 4.12 could be assigned to a C-1' methylene group which is attached to oxygen (3). The ¹³C-nmr spectrum of **1** showed a carbonyl carbon at δ 167.39, eight olefinic and aromatic carbons, and one MeO group (3,4). A series of signals at δ 14.12–29.68 indicated the presence of a long chain hydrocarbon.

Hydrolysis of **1** in 5% NaOH yielded triacontanol and ferulic acid, whose

structures were confirmed by mixed mp, co-tlc, ir, ms, and gc comparison with authentic samples. Therefore, the chemical and spectroscopic evidence was consistent with the assignment of the structure of **1** as *trans*-triacontyl-4-hydroxy-3-methoxycinnamate.

The structures of 24-methylstanosta-9(11)-25-dien-3-one, 24,24-dimethylstanosta-9(11)-25-dien-3-one, friedelin, friedelan-3 β -ol, β -sitosterol, stigmasterol, and campesterol were identical upon comparison by mixed mp, co-tlc, ir, nmr, ms, and gc with authentic samples.

In summary, this is the first report of the presence of these eight compounds in the Thai plant *B. ovata* and the first report of the novel compound *trans*-triacontyl-4-hydroxy-3-methoxycinnamate [**1**].

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's are uncorrected. Ir spectra were recorded on a Shimadzu 440 ir spectrophotometer. Gc was recorded by a Shimadzu GC-R1 gas chromatograph. Ms was obtained on a JEOL JMX-DX 300 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240 C elemental analyzer. Uv spectral data were measured with a Shimadzu 240 spectrophotometer.

PLANT MATERIAL.—The dried branches of *B. ovata* were collected from Kanchanaburi Province, Thailand, in June of 1985. A voucher specimen (No. 050203) of the plants was deposited at the herbarium of the faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok, Thailand.

EXTRACTION AND ISOLATION.—Dried and ground branches of *B. ovata* (40 kg) were macerated and extracted with CHCl_3 . Removal of the CHCl_3 in vacuo yielded 240 g of a crude extract that was chromatographed over Si gel (Merck 60–200 mesh) and eluted with hexane and increasing quantities of CHCl_3 (a total of eleven 1-liter fractions were collected) to give 24-methylstanosta-9(11)-25-dien-3-one, 24,24-dimethylstanosta-9(11)-25-dien-3-one, friedelin, and friedelan-3 β -ol from the CHCl_3 -hexane (1:9) fraction. β -Sitosterol, stigmasterol, campesterol and *trans*-triacontyl-4-hydroxy-3-methoxycinnamate [**1**] were obtained from the CHCl_3 -hexane (1:3) eluate.

trans-Triacontyl-4-hydroxy-3-methoxycinnamate

[**1**].—White crystals from hexane/ CHCl_3 [R_f 0.65 on Si gel, solvent MeOH- CHCl_3 (1:49)]: mp 73–74°; ir (KBr) ν max 3500 and 1170 (phenol), 1725 (C=O of conjugate ester), 1600, 1500, and 1440 (Ar), 1640, 980 (C=C, trans); ms m/z [M]⁺ 614, 914 (acid part), 85, 71, 57, 43; ¹H nmr (CDCl_3) δ 0.89 (3H, t, Me), 1.26 (27 \times CH_2), 3.93 (3H, s, OMe), 4.12 (2H, t, O- CH_2), 5.84 (1H, s, OH, exchangeable with D_2O), 6.23 (1H, d, d, $J = 15.8$ Hz), 6.94 (1H, s, Ar-H), 7.15 (2H, d, ArH), and (1H, dd, $J = 15.8$ Hz); ¹³C nmr (CDCl_3) 167.39 (C=O), 147.84 (C-6), 146.71 (C-3), 144.672 (C-7), 127.11 (C-4), 122.99 (C-8), 115.72 (C-9), 114.65 (C-2), 109.35 (C-5), 64.59 (C-1'), 55.94 (-OMe), 31.94 (C-2'), 29.68 (C-25), 25.98 (C-26'), 22.70 (C-27'), 14.12 (C-28'). Anal. calcd for $\text{C}_{40}\text{H}_{70}\text{O}_4$: C 78.12, H 11.47; found C 77.94, H 11.49.

HYDROLYSIS OF COMPOUND 1.—Compound **1** (0.1 g) was treated with 5% NaOH in 10 ml of EtOH. The mixture was refluxed for 10 h, and the EtOH was removed by evaporation. The residue was suspended in H_2O and extracted with Et_2O . The dried (Na_2SO_4) Et_2O was removed in vacuo to give a white solid which was recrystallized from hexane to yield 0.05 g of a pure compound: mp 83–84°; tlc R_f 0.48 (Si gel, solvent CHCl_3); ir (KBr, pellet) ν max cm^{-1} 3350 (OH), 1460 ($-\text{CH}_2$), ms m/z [M]⁺ 438. Gc-ms was performed using an OV-1 column with N_2 as the carrier gas and column and injector temperatures of 260° and 300°, respectively. This compound was identical upon comparison of mixed mp, co-tlc, ir, ms, and gc-ms with an authentic sample of triacontanol.

The H_2O fraction was neutralized with dilute HCl and then extracted with Et_2O . The dried (Na_2SO_4) Et_2O was evaporated, and the residue, from CHCl_3 /hexane, gave yellow needles (0.02 g); mp 169–171°, tlc R_f 0.45 [Si gel, solvent CHCl_3 -MeOH (1:4)]; ir (KBr, pellet) ν max cm^{-1} , 3500–2500 and 1680 (COOH), 1650 (C=C), 1600 (Ar); uv (CHCl_3) λ max nm 320 (log ϵ 4.70) 293 (log ϵ 4.70) 242 (log ϵ 4.58); ms m/z [M]⁺ 194 ($\text{C}_{10}\text{H}_{10}\text{O}_4$). This compound was identical upon mixed mp, co-tlc, ir, and ms with an authentic sample of ferulic acid.

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