

PROPENYLBENZENES FROM *GUATTERIA GAUMERI*

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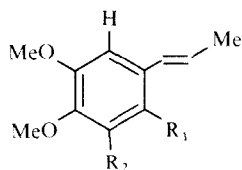
Key Word Index — *Guatteria gaumeri*; Annonaceae; Yumel, Elemuy; hypocholesteremia; propenylbenzenes.

Abstract—Because of the hypocholesteremic properties attributed to extracts of *Guatteria gaumeri* in folk medicine, the non-polar fraction was examined and three propenylbenzenes and asaraldehyde were isolated. Asarone, the major component appears to be of great importance in the pharmacological properties exhibited by this plant. Although closely related, β -asarone was not detected. The remaining propenylbenzenes were the minor components and their structures were determined by spectroscopic methods.

INTRODUCTION

The use of *Guatteria gaumeri* in folk medicine is widespread in the south-east part of Mexico for the treatment of gallstones. It has been claimed in recent work that the EtOH extract of this plant is effective in reducing the human serum cholesterol level [1]. In other pharmacological experiments, asarone (**1**), obtained from the hexane extract of *G. gaumeri* was reported to produce a substantial reduction of the cholesterol levels in the rat and dog (Mandoki, J. J., unpublished results).

The genus *Guatteria* has been examined for its alkaloidal content [2,3] although no report about **1** or related compounds is available. This work describes the isolation and characterization of **1**, asaraldehyde (**2**), and two propenylbenzenes identified as *trans*-isoelemicin (**3**) and *trans*-isomysticin (**4**).



	R ₁	R ₂
1	Me	H
3	H	MeO
4	MeO	MeO

From the known effects of asarone and its *Z* isomer [4,9] it is likely that other members of this family of compounds may have an important potential use as well as a significant biological role in the plant. Compounds **3** and **4** deserve some attention in regard to the hypocholesteremia observed experimentally with **1** and with the complete non-polar extract.

RESULTS AND DISCUSSION

Dried ground bark[‡] (1.25 kg) was allowed to stand at room temperature for 24 hr with 4 × 1.5 l. portions of hexane. The combined extracts were evaporated *in vacuo* to yield a total residue of 12.3 g. From the concentrated extract, a solid (mp 58–59°) could be separated. Recrystallization from hexane–Me₂CO afforded three crops of crystals for a total 5.2 g (42.2% from the crude extract) of a white powder which was identified as **1**.

The mother liquors were submitted to column chromatography over Kieselgel (70–230 mesh) eluting first with hexane and then with increasing proportions of EtOAc, up to a ratio of 4:1. In this manner, an additional amount of **1** was recovered but this was contaminated with at least two other substances, as detected by TLC. These were purified by PLC run twice using a mixture of hexane–EtOAc (17:3) which afforded substances **3** and **4**. From the most polar fractions of the column, a white solid (mp 113–114°) was obtained and identified as **2**. Order of increasing polarity: **4**, **3**, **1**, **2**.

1,2,4-Trimethoxy-5-(1-propenyl)benzene; asarone 1. The IR and ¹H NMR spectra were identical to those reported earlier [10,11]. Mmp showed no depression upon admixture with the authentic sample. MS 70 eV, ion source 200°; *m/e* 208 (M⁺, 100), 193 (M⁺ – Me; 22.4), 165 (M⁺ – Me + CO; 15.5), 162 (M⁺ – Me + OMe; 8.2).

2,4,5-Trimethoxybenzaldehyde; asaraldehyde 2. The IR [10, 12] and ¹H NMR [13] spectra were identical to those previously reported. Mmp showed no depression with the authentic sample. MS: *m/e* 196 (M⁺, 100), 181 (M⁺ – Me, 61), 165 (M⁺ – 71, 37.3), 150 (M⁺ – Me + OMe, 28.8).

[‡] The plant material was collected at Mérida, Yucatán and is popularly known as Yumel or Elemuy. The identification was carried out by Q. Oscar Sánchez López from Propulsora Homeopática, Mirto No. 26, México 4, D.F.

1,2,3-Trimethoxy-5-(1-propenyl) benzene; *trans-isoelemicin* **3**. The IR spectra were superimposable with that reported in ref. [10]. Additional spectroscopic data were obtained from the 80 MHz FT-¹H NMR spectra (CDCl₃) which showed: δ 6.52 (2 H, s); ABX₃ system 6.31 (1 H, d, br), 6.1 (1 H, dq, J_{AB} = 16 Hz), 1.87 (d, br, J_{BX} = 6 Hz), 3.87 (6 H, s), 3.82 (3 H, s). MS: m/e 208 (M⁺, 100), 193 (M⁺ - Me, 85.5), 177 (M⁺ - Me, 5.8), 165 (M⁺ - C₂H₃O, 12.3).

1,2,3,4-Tetramethoxy-5-(1-propenyl) benzene; (*trans-isomyristicin*) **4**. The 90 MHz ¹H NMR spectrum (CDCl₃) shows: δ 6.81 (1 H, s), ABX₃ system 6.49 (1 H, d, br), 6.23 (1 H, dq, J_{AB} = 16.5 Hz), 1.90 (d, br, J_{BX} = 6 Hz); 3.96 (3 H, s), 3.93 (3 H, s), 3.90 (3 H, s) and 3.83 (3 H, s). MS: m/e 238 (M⁺, 100), 223 (M⁺ - Me, 22), 195 (M⁺ - Me + CO, 17.2), 192 (M⁺ - Me + OMe, 63.4).

The chemical shifts of the aromatic protons of **3** and **4** correlated with the corresponding values of the tri- and tetra-methoxybenzenes reported in the literature [14]. In the case of **3**, the chemical shifts of δ 6.44 and 5.91 respectively were used for comparison with the experimental value of 6.52 found with the propenyl derivative. Considering that the type of double bond involved will generally cause a downfield effect on the protons in the *ortho* position, **3** can be directly correlated with a 1,2,3-methoxyl substitution. In a similar manner, those chemical shifts in the two 1,2,3,4- and 1,2,3,5-tetramethoxybenzenes (δ 6.42 and 5.95, respectively) excluded the latter when these were compared to the experimental value of 6.81 found for **4**.

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PRENYLATED BENZOPHENONES FROM *VISMIA DECIPiens*

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INTRODUCTION

During the systematic study [1–5] of the components of the South American species of *Vismia* (Guttiferae), we isolated from the fruits the known harunganin [6] and nine new prenylated anthranoids (i.e. vismione A and B, deacetylvismione A, ferruginin A and B, vismin, ferruanthrone, γ -hydroxyferruginin A and γ,γ' -dihydroxyferruginin A). In the fruits of *V. decipiens*, collected in Brazil,

besides ferruginin A, γ -hydroxy- and γ,γ' -dihydroxyferruginin A, three other less polar pigments are present [5]. This paper deals with the structural determination of these pigments, which were named vismiaphenone A and B and iso-vismiaaphenone B.

RESULTS AND DISCUSSION

Vismiaaphenone A, C₂₄H₂₈O₄ (M⁺ 380), showed IR (ν_{CO} at 1600 cm⁻¹), UV (Table 1) and MS (ion at m/e 105) suggesting the structure of a benzophenone with one unsubstituted ring. The bathochromic shifts of the UV maxima (Table 1) after addition of AlCl₃ (+34 nm) and of

* Part VI in the series "Chemistry of the *Vismia* Genus". For Part V see ref. [5].

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