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Chemical constituents from the stem of *Brosimum potabile* (Moraceae)

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ABSTRACT

Three coumarins, 5-methoxypsoralene, xanthyletin, and (–)-marmesin, have been isolated from the ethanolic extract of the stem of the Amazonian plant *Brosimum potabile*. The structures were determined on the basis of NMR analyses and by comparison with spectroscopic data in the literature. The analysis of the hexane fractions by GC-MS in EIMS mode suggested the presence of (1-methylpentyl)-benzene; *α*,*α*-dimethyl-4-(1-methylethyl)-benzenemethanol; 1-methyl-3,5-bis(1-methylethyl)-benzene; urs-12-ene; chola-5,22-dien-3*β*-ol; cholesta-4,6-dien-3*β*-ol; sitosteryl 9(*Z*)-octadecenoate; cholesta-5,22-dien-3*β*-ol; cholesta-4,6,22-trien-3-one; and cholesta-4,22-dien-3-one. NMR data of other hexane fractions indicated the presence of 3*β*-acetoxy-lup-12,20(29)-diene; 3*β*-acetoxy-olean-12-ene; 3*β*-acetoxy-urs-12-ene; and adian-5-ene. All these compounds are first described in *B. potabile.*

KEYWORDS: *Brosimum potabile,* coumarins, pentacyclic triterpenes, structural characterization by NMR and GC/MS.

Constituintes químicos do cerne de *Brosimum potabile* (Moraceae)

RESUMO

Três cumarinas, 5-metoxipsoraleno, xantiletina e (–)-marmesina, foram isoladas no extrato etanólico do cerne da planta amazônica *Brosimum potabile*. Suas estruturas foram determinadas a partir das análises por RMN e por comparação com dados espectroscópicos da literatura. As análises das frações hexânicas por CG/EM sugeriram a presença de (1-metilpentil)-benzeno; *α*,*α*-dimetil-4-(1-metiletil)-benzenometanol; 1-metil-3,5-bis(1-metiletil)-benzeno; urs-12-eno; cola-5,22-dien-3*β*-ol; colesta-4,6-dien-3*β*-ol; (9*Z*)-octadecenoato de sitosterila; colesta-5,22-dien-3*β*-ol; colesta-4,6,22-trien-3-ona e colesta-4,22-dien-3-ona. Dados de RMN de outras frações hexânicas indicaram a presença de 3*β*-acetóxi-lup-12,20(29)-dieno; 3*β*-acetóxi-olean-12-eno; 3*β*-acetóxi-urs-12-eno e adian-5-eno. Todos esses compostos foram identificados pela primeira vez em *B. potabile.*

PALAVRAS-CHAVE: *Brosimum potabile,* cumarinas, triterpenos pentacíclicos, caracterização estrutural por RMN e CG/EM.

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INTRODUCTION

Plants of the *Brosimum* (Moraceae) (Oliveira and Amaral 2004) genus are largely found in firm land regions of the Amazon forest (Correia 1978). Extracts from stem bark of *Brosimum* species, which are used as a nervous system stimulant in folk medicine, have also shown anti-syphilic, anti-inflammatory, and antirheumatic activities (Garret and Grishan 1988, Shultes and Foreword 1992). Several chemical compound classes have been isolated from *Brosimum* species: flavans (Torres *et al*. 1997; Teixeira *et al.* 2000), steroids, coumarins (Okahara 1936, Gottlieb *et al*. 1972), terpenes, benzophenone, xantones, tannins, saponines, alkaloids, and polyphenols (Filho *et al*. 1972). *Brosimum potabile* is popularly known as "amapá-doce" and largely used in Amazon region as medicinal extract (Berg 1972, Barroso 1978). But only few studies have been described about this species. We have previously investigated extract of its stem and 1-diaril-heptanoid (centrolobin), sitosterol, and stigmasterol were isolated (Alcântara *et al*. 2000).

In the present work we described a more exhaustive phytochemical investigation of the stem of *Brosimum potabile*. As consequence 17 compounds were characterized by IV, NMR (1D and 2D), and GC/MS analyses which were firstly described in this species.

PHYTOCHEMICAL PROCEDURE

General methods

Uncorrected melting points were determined using METTLER equipment, model FP82. FTIR spectra were determined in KBr disk on a FTIR Perkin Elmer Spectrum 200 spectrometer. GC/MS spectra were obtained on a Perkin Elmer - Auto System chromatographer coupled to a Perkin Elmer - Q-Mass 910 mass spectrometer (70 eV, 30 m/0.2 nm methyl silicone fused silica column, helium gas, draw speed: 1.5 mL/min). The sample components were identified based on software comparison of mass spectra fragmentation patterns with those of the Wiley Library Database Version 2005 (New York, USA). Retention time (RT) is given in minutes. Chromatographic purification was carried out on silica gel (70-230 Mesh), alumina, and Sephadex LH-20. A mixture of silica gels $60F_{254}$ and 60G (1:3) was used in thin layer chromatographic analysis.

^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX 400 – AVANCE spectrometer, with inverse probes and field gradient operating at 400.129 and 100.613 MHz, respectively. The samples were dissolved in 0.75 mL $CDCl_3$ and transferred to a 5-mm NMR tube; TMS was used as an internal reference (δ = 0.00). Chemical shifts are given in the δ-scale (ppm) and coupling constants, *J,* in Hz. Experiments were carried out using pulse sequences and programs provided by the manufacturer. One-dimensional (1D) ^{1}H and ^{13}C NMR spectra were acquired under standard conditions by using a direct detection 5-mm $^{1}H/^{13}C$ dual probe. Standard pulse sequences were used for two-dimensional (2D) homonuclear and heteronuclear shift correlation spectra by using a multinuclear, inverse detection, 5-mm probe with field gradient at z axis.

Plant material

A *Brosimum potabile* sample was collected in November 1999 at the Adolpho Ducke Reserve, Manaus, Brazil. A voucher specimen of *Brosimum potabile* has been deposited at the herbarium of the Instituto Nacional de Pesquisas da Amazônia (INPA-Manaus), under the code 105.994. The plant was identified by S. S. da Silva (Departamento de Botânica, Universidade Federal do Amazonas) and later confirmed by Dr. J. E. L. da Silva and C. A. C. Ferreira (Departamento de Botânica, Herbário do INPA).

Extraction and isolation

The collected plant was dried at room temperature and triturated. The powered material (2.4 kg) was submitted to extraction in hexane and EtOH at room temperature, furnishing hexanic (EH; 100.5 g) and ethanolic (EE; 430.0 g) extracts, respectively. EH was submitted to column chromatography (CC) using silica gel as the stationary phase (CCS) and eluted with hexane, CH_2Cl_2, EtOAc, EtOH, and MeOH mixtures in increasing polarity order. The chromatographic fractionation of EH was followed by thin layer chromatography (TLC) and similar fractions were grouped. Group 3 (eluted with hexane) was obtained as a colorless liquid (6 mg) and identified as mixture of 1 to 3. Group 7 (eluted with hexane and dichloromethane 9:1) was submitted to CCS fractionation eluted with hexane/CH_2Cl_2 in gradient. The fraction eluted with hexane/CH_2Cl_2 (8:2) was recrystallized in EtOH, afforded a white solid (compound 4, 3 mg). Group 8 (eluted with hexane/CH_2Cl_2 6:4) was rechromatographed in silica gel with a gradient hexane/CH_2Cl_2. The fractions obtained with hexane/CH_2Cl_2 7:3 were recrystallized in EtOH yielded a white solid (21 mg) identified as a mixture of compounds **5** to **8**.

Group 11 (eluted hexane/CH_2Cl_2) was submitted to CCS fractionation eluted with hexane/CH_2Cl_2 in gradient. The fractions eluted with CH_2Cl_2 were recrystallized in EtOH, providing a white solid (7 mg) identified as a mixture of compounds **9** to **13**. Group 13 (eluted with CH_2Cl_2/EtOAc 9.5:0.5) was submitted to CCS fractionation eluted with hexane/CH_2Cl_2 in gradient. The fractions obtained with CH_2Cl_2 were purified by recrystallization in EtOH, afforded a white solid (3 mg) identified as compound **14**. EE was submitted to CCS fractionation eluted with hexane, CH_2Cl_2, EtOAc, EtOH, and MeOH mixtures in increasing polarity.

The chromatographic fractionation of EE was followed by TLC and similar fractions were grouped. Group 2 was eluted in CH_2Cl_2, providing a white solid. This solid was submitted to CCS and eluted with gradient of hexane/CH_2Cl_2. Fractions obtained with hexane/CH_2Cl_2 3:7 were grouped and recrystallized in hexane, yielded a white solid (18 mg) identified as compound **15**. Group 5 (eluted with CH_2Cl_2) afforded a light yellow solid after washing with MeOH (compound **16**, 45.7 mg). Group 8 (eluted with CH_2Cl_2/EtOAc 1:1) was submitted to CC using Sephadex LH-20 as a stationary phase and MeOH as eluent. Fractions 8 and 9 were grouped and submitted to CC using neutral alumina as the stationary phase and eluted with CH_2Cl_2 afforded a white solid (Compound **17**, 5.7 mg).

Mixture of compounds **1** to **3**: (1-methylpentyl)-benzene, *α*,*α*-dimethyl-4-(1-methylethyl)-benzenemethanol, and 1-methyl-3,5-bis(1-methylethyl)-benzene, respectively. GC/MS (EI, 70 eV) RT= 3.42 min, *m/z* 162 [M$^+$], 105 (base peak), 91, 77, 41, and 29; RT= 5.45 min, *m/z* 178 [M$^+$], 163, 145, 121, 105, and 43 (base peak); RT= 9.16 min, *m/z* 161, 147, 133, 119, 105, 91, 77, and 43 (base peak).

Compound **4**: urs-12-ene. GC/MS (EI, 70 eV) RT = 20.81 min, *m/z* 498, 406, 392, 296, 218, 203, 191, 179, 165, 151 (base peak), 133, 115, 84, and 58.

Mixture of compounds **5** to **8**: 3*β*-acetoxy-lup-12,20(29)-diene, 3*β*-acetoxy-olean-12-ene, 3*β*-acetoxy-urs-12-ene, and adian-5-ene, respectively. See Table 1 for NMR data.

Mixture of compounds **9** to **13**: chola-5,22-dien-3*β*-ol, cholesta-4,6-dien-3*β*-ol, sitosteryl 9(*Z*)-octadecenoate, cholesta-5,22-dien-3*β*-ol, and cholesta-4,6,22-trien-3-one, respectively. GC/MS (EI; 70 eV) RT = 24.40 min, *m/z* 255, 207, 189, 159 (base peak), 145, 131, 122, 119, 109, and 105; RT = 25.81 min, *m/z* 394, 275, 211, 191, 177, 157, 143 (base peak), 135, 129, 119, and 105; RT = 26.02 min, *m/z* 396, 288, 275, 255, 213, 195, 177, 159, 147, 140 (base peak), 128, 119, and 105; RT = 28.20 min, *m/z* 413, 394, 369, 351, 314, 300, 283, 271, 255, 213, 189, 173, 159, 147, 133, 119, 105 (base peak), 95, 81, 69, 55, and 41; RT = 29.05 min, *m/z* 414, 396, 381, 329, 303, 273, 255, 213, 159, 145, 133, 121, 107, 95, 81, 69, 55, and 43 (base peak); RT= 30.49 min, *m/z* 270, 255, 227, 207, 175, 159, 147, 133, 119, 105, 95, 81, 69 (base peak), and 55.

Compound **14**: cholesta-4,22-dien-3-one. GC/MS (EI; 70 eV) RT = 3.62 min, *m/z* 423, 411, 395, 367, 312, 298, 269, 245, 218, 175, 161, 147, 135, 123, 107 (base peak), 95, 81, 69, and 55.

Compound **15**: 5-methoxypsoralen. M.p.: 142.0-145.0 °C. IR (KBr, cm^{-1}) ν_{max} 3220, 3163, 3151, 3077, 2955, 1765, 1593, 1494, 1366, 1180, 1058, 939, and 809. ^{1}H NMR (400 MHz; $CDCl_3$; ppm) δ_H 8.16 (d, *J*= 8.9 Hz; H-4), 7.60 (d, *J*= 2.4 Hz; H-2'), 7.13 (s; H-8), 7.02 (d, *J*= 2.4 Hz; H-3'), 6.28 (d, *J*= 8.9 Hz; H-3), 4.30 (s; H-2"). ^{13}C NMR (100 MHz; $CDCl_3$; ppm) δ_C 161.2 (C-2), 158.4 (C-7), 152.5 (C-9), 149.6 (C-5), 144.8 (C-2'), 139.2 (C-4), 113.1 (C-6), 112.5 (C-3), 106.4 (C-10), 105.0 (C-3'), 93.8 (C-8), and 60.1 (C-2").

Compound **16**: xanthyletin. M.p.: 162.0-164.0 °C. IR (KBr, cm^{-1}) ν_{max} 3000-2200, 2900-2800, 1695, 1610, 1550, 1440, 1360, 1270, 1130, 1010, 980, and 815. ^{1}H NMR (400 MHz; $CDCl_3$; ppm) δ_H 7.57 (d, *J*= 9.5 Hz; H-4), 7.04 (s; H-5), 6.72 (s; H-8), 6.34 (d, *J*= 9.9 Hz; H-4'), 6.21 (d, *J*=9.5 Hz; H-3), 5.68 (d, *J*= 9.9 Hz; H-3'), and 1.47 (s; H-1"). ^{13}C NMR (100 MHz; $CDCl_3$; ppm) δ_C 161.2 (C-2), 156.9 (C-7), 155.5 (C-9), 143.3 (C-4), 131.2 (C-3'), 124.8 (C-5), 120.8 (C-4'), 118.5 (C-6), 113.1 (C-3), 112.7 (C-10), 104.4 (C-8), 77.7 (C-2'), and 28.4 (C-1"/2").

Compound **17**: (–)-marmesin. M.p.: 123.4-127.0 °C. IR (KBr; cm^{-1}) ν_{max} 3400-2600, 1710, 1615, 1555, 1480, 1395, 1360, 1275, 1150, 1125, 920, 895, and 820. ^{1}H NMR (400 MHz; $CDCl_3$; ppm) δ_H 7.59 (d, *J*= 9.6 Hz; H-4), 7.22 (s; H-5), 6.74 (s; H-8), 6.21 (d, *J*= 9.6 Hz; H-3), 4.74 (t, *J*= 8.9 Hz; H-2'), 3.20 (m; H-3'), 1.67 (s; OH), 1.37 (s; H-2"a), and 1.24 (s; H-2"b). ^{13}C NMR (100 MHz; $CDCl_3$; ppm) δ_C 163.2 (C-7), 161.4 (C-2), 156.0 (C-9), 143.7 (C-4), 125.0 (C-6), 123.4 (C-5), 112.8 (C-10), 112.3 (C-3), 91.1 (C-2'), 71.7 (C-1"), 29.5 (C-3'), 26.1 (C-2"b), and 24.3 (C-2"a).

RESULTS AND DISCUSSION

The GC chromatogram of the Group 3 in hexane showed three peaks with RT = 3.42, 5.45, and 9.16 min. MS data bank suggested structures with the respective indices of similarity given in parenthesis (1-methylpentyl)-benzene (**1**) (90%), *α*,*α*-dimethyl-4-(1-methylethyl)-benzenemethanol (**2**) (69%), and 1-methyl-3,5-bis(1-methylethyl)-benzene, (**3**) (75%), respectively. The GC chromatogram of the Group 7 showed a peak with RT = 20.81 min. MS data bank suggested the triterpene pentacyclic urs-12-ene (**4**) (68%).

The ^{1}H NMR spectrum of the Group 8 in hexane showed several signals from δ_H 5.25 to 4.43, which were attributed to hydrogen atoms of alkenyl and carbinolic groups. The signals at δ_H 2.36 to 0.76 were attributed to aliphatic hydrogen atoms. The ^{13}C NMR spectra and DEPT 135° subspectra showed signals attributed to carbon atoms of alkenyl groups: non-hydrogenated (at δ_C 150.9, 145.6, 145.1, and 139.3), mono-hydrogenated (at δ_C 124.3, 121.8, and 117.6), and di-hydrogenated (at δ_C 109.3). The signals at δ_C 81.1, 80.9, and 77.6 were attributed to carbinolic carbon atoms. The intense signal at δ_C 170.9 indicated that the signals at δ_C 81.1, 80.9, and 77.6 could be better attributed to acetylated carbinolic carbon atoms (Olea and Roque 1990). All these signals are characteristic of pentacyclic triterpenes (Mahato and Kundu 1994). The carbon chemical shifts recorded on the ^{13}C NMR

spectrum (shown in Table 1) matched the values reported in the literature for triterpenes 3β-acetoxy-lup-12,20(29)-diene (**5**), 3β-acetoxy-olean-12-ene (6), 3β-acetoxy-urs-12-ene (**7**), and adian-5-ene (**8**).

The GC chromatogram of the Group 11 in hexane showed six peaks (RT = 24.40, 25.81, 26.02, 28.20, 29.05, and 30.49 min). The structure of chola-5,22-dien-3β-ol (**9**) (54%), cholesta-4,6-dien-3β-ol (**10**) (70%), sitosteryl 9(*Z*)-octadecenoate (**11**) (73%), cholesta-5,22-dien-3β-ol (**12**) (69%), and cholesta-4,6,22-trien-3-one (**13**) (63%), respectively, were suggested by EIMS fragmentation data matching with Wiley library databases with the respective indices of similarity given in parenthesis. Similarly, the structure of cholesta-4,22-dien-3-one (**14**) (69%) was suggested for the Group 13 in hexane (RT = 3.62 min).

Structural analysis of the Group 2 in ethanol was based on NMR data. The ^{1}H NMR spectrum showed two doublet signals at δ_H 6.28 (1H; J = 8.9 Hz) and 8.16 (1H; J = 8.9 Hz). These signals were attributed to hydrogen atoms of conjugated double linking with carbonyl group. Two doublet signals at d_H 7.60 (1H; J = 2.4 Hz) and 7.02 (1H; J = 2.4 Hz) were also attributed to aromatic hydrogen atoms in vicinal carbons atoms. The singlet signal at δ_H 7.13 (1H) was attributed to an aromatic hydrogen atom distant from the others. The singlet signal at δ_H 4.30 was attributed to the hydrogen atom of the methoxyl group. The ^{13}C NMR spectrum showed signals at δ_C 161.2, 158.4, 149.6, and 106.4, which corresponded to non-hydrogenated carbon atoms. The signals at δ_C 144.8, 139.2, 112.5, 105.0, and 93.8 corresponded to mono-hydrogenated carbon atoms. The signal at δ_C 60.1 was attributed to the carbon atom of the methoxyl group. The 1D NMR spectra are characteristic of furocoumarin structures (Steck and Zazurek 1972). The ^{1}H-^{1}H COSY contour map showed correlations between signals at δ_H 8.16 (H-4) and 6.28 (H-3), as well as between signals at δ_H 7.60 (H-2') and 7.02 (H-3'). The ^{1}H-^{13}C HMBC contour map showed correlations between the hydrogen signal at δ_H 8.16 (H-4) and the carbon signals at δ_C 161.2 (C-2) and 149.6 (C-5). The hydrogen signal at 7.60 (H-2') correlated with carbon signals at δ_C 158.4 (C-7) and 112.5 (C-6). The hydrogen signal at d_H 7.13 (H-8) correlated with carbon signals at δ_C 158.4 (C-7), 112.5 (C-6), and 106.4 (C-10). The hydrogen signal at δ_H 7.02 (H-3') correlated with carbon signals at δ_C 158.4 (C-7), 144.8 (C-2'), and 112.5 (C-6). The hydrogen signal at d_H 6.28 (H-3) correlated with carbon signals at δ_C 161.2 (C-2) and 106.4 (C-10). The hydrogen signal at d_H 4.30 (H-2") correlated with a carbon signal at δ_C 149.6 (C-5), indicating the localization of the methoxyl group in the coumarinic skeleton. These HMBC correlations agree with 5-methoxypsoralen (**15**), a coumarin previously isolated from *Brosimum acutifolium* (Xavier 2001) and *Brosimum gaudichaudii* (Okahara 1936).

Structural analysis of the Group 5 in ethanol was based on NMR data. The ^{1}H NMR spectrum showed two doublet signals at δ_H 7.57 (1H; J = 9.5 Hz) and 6.21 (1H; J = 9.5 Hz). These signals were attributed to hydrogen atoms of conjugated double bond with carbonyl group. Two doublet signals at δ_H 6.34 (1H; J = 9.9 Hz) and 5.68 (1H; J = 9.9 Hz) were also attributed to alkenyl hydrogen atoms on vicinal carbon atoms. The singlet signals at δ_H 7.04 (1H) and 6.72 were attributed to aromatic hydrogen atoms distant from others. The singlet signal at δ_H 1.47 (6H) was attributed to hydrogen atoms of two methyl groups. ^{13}C NMR spectrum showed signals at δ_C 161.2, 156.9, 155.5, 118.5, 112.7, and 77.7 which corresponded to non-hydrogenated carbon atoms. The signals at δ_C 143.3, 131.2, 124.8, 120.8, 113.1, and 104.4 corresponded to mono-hydrogenated carbon atoms. The signal at δ_C 28.4 was attributed to two carbon atoms of the methyl groups. The 1D NMR spectra are characteristic of pyrancoumarin structures (Steck and Mazurek 1972). The ^{1}H-^{1}H COSY contour map showed correlations between signals at δ_H 7.57 (H-4) and 6.21 (H-3) as well as between signals at δ_H 6.34 (H-4') and 5.68 (H-3'). The ^{1}H-^{13}C HMBC contour map showed correlations between the hydrogen signal at δ_H 7.57 (H-4) and the carbon signals at δ_C 161.2 (C-2), 155.5 (C-9), and 124.8 (C-5). The hydrogen signal at 7.04 (H-5) correlated with the carbon signals at δ_C 156.9 (C-7), 155.5 (C-9), 143.3 (C-4), and 120.8 (C-6). The hydrogen signal at δ_H 6.72 (H-8) correlated with the carbon signals at δ_C 156.9 (C-7), 155.5 (C-9), and 118.5 (C-6). The hydrogen signal at δ_H 6.34 (H-4') correlated with carbon signals at δ_C 156.9 (C-7), 124.8 (C-5), and 77.7 (C-2'). The hydrogen signal at δ_H 6.21 (H-3) correlated with the carbon signals at δ_C 161.2 (C-2) and 112.7 (C-10). The hydrogen signal at δ_H 5.68 (H-3´) correlated with the carbon signals at δ_C 118.5 (C-6), 77.7 (C-2'), and 28.4 (C-1"/2"). The hydrogen signal at δ_H 1.47 (H-1"/2") correlated with the carbon signals at δ_C 131.2 (C-3') and 77.7 (C-2'). All these HMBC correlations match xanthyletin (**16**) (Lee *et al*. 2006), a coumarin previously isolated from *Brosimum gaudichaudii* (Okahara 1936).

Structural analysis of the Group 8 in ethanol was also based on NMR data. The ^{1}H NMR spectrum showed two doublet signals at δ_H 7.60 (1H; J = 9.6 Hz) and 6.19 (1H; J = 9.60 Hz). These signals were attributed to hydrogen atoms of conjugated double bond with carbonyl group. The triplet signal at δ_H 4.72 (1H; J = 8.9 Hz) and the multiplet signal at δ_H 3.19 (2H) were attributed to hydrogen atoms on vicinal carbon atoms. The other hydrogen signals, δ_H 7.19 (H-5) and δ_H 6.74 (H-8), were singlet. The ^{13}C NMR spectrum showed signals at δ_C 163.2, 161.4, 156.2, 125.0, 112.8, and 71.7 corresponding to non-hydrogenated carbon atoms. The signals at δ_C 143.7, 123.4, 112.3, 98.0, and 91.1 corresponded to mono-hydrogenated carbon atoms. The signal at δ_C 29.5 corresponded to methylene group. The signals at δ_C 26.1

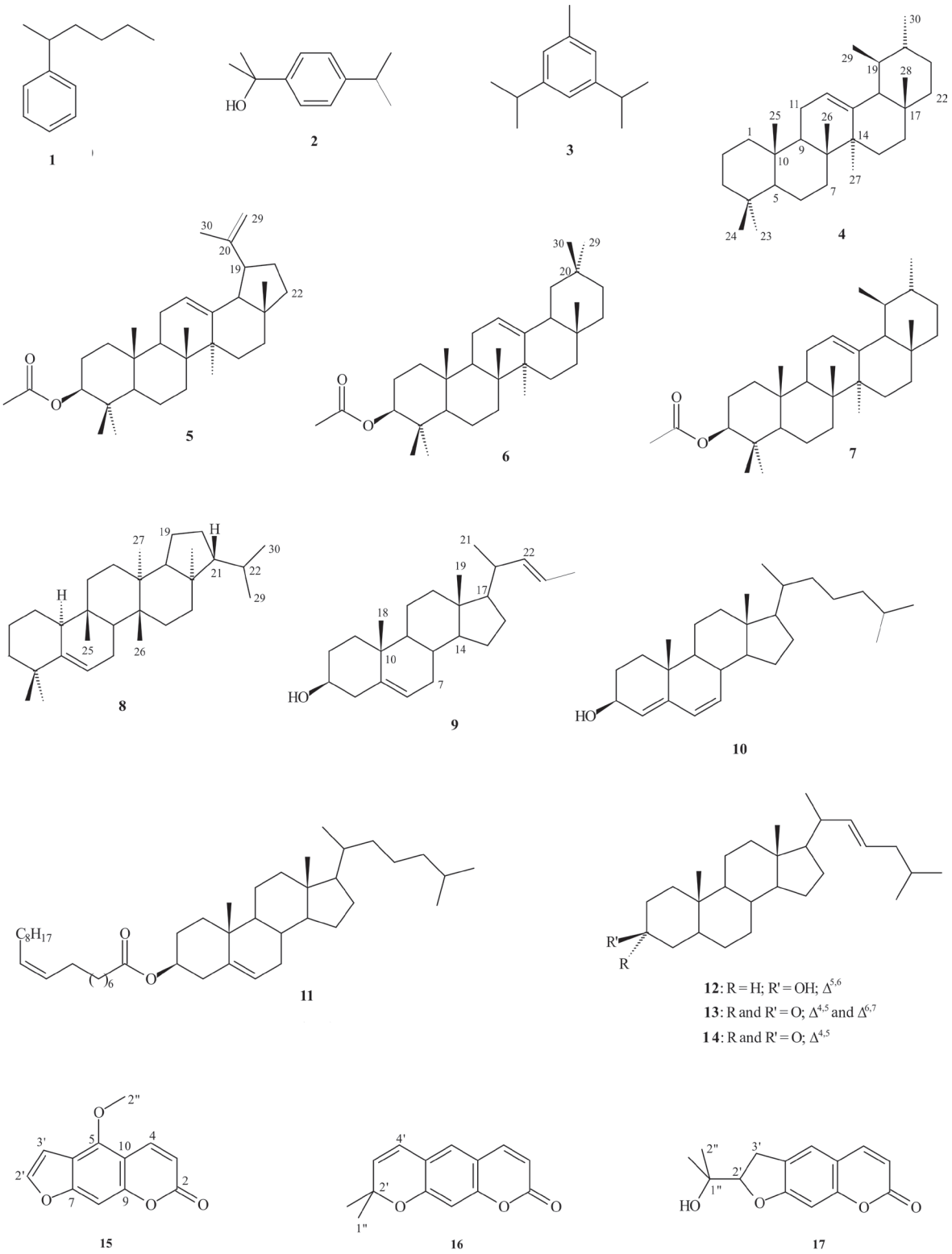

Figure 1 - Chemical structures isolated from stem of *Brosimum potabile*.

and 24.3 corresponded to two methyl groups. The 1D NMR spectra are also characteristic of prenylated coumarin structures (Steck and Mazurek 1972). The ^{1}H-^{1}H COSY contour map showed correlations between δ_H 7.60 (H-4) and 6.19 (H-3), as well as between δ_H 4.72 (H-2') and 3.19 (H-3'). The HMBC contour map showed correlations between the hydrogen signal at δ_H 7.60 (H-4) and carbon signals at δ_C 161.4 (C-2), 156.2 (C-9), 123.4 (C-5), and 112.8 (C-10). The hydrogen signal at δ_H7.19 (H-5) correlated with carbon signals at δ_C 163.2 (C-7), 156.2 (C-9), 143.7 (C-4), 112.8 (C-10), and 29.5 (C-3'). The hydrogen signal at δ_H 6.74 (H-8) correlated with carbon signals at δ_C 163.2 (C-7), 156.2 (C-9), 125.0 (C-6), and 112.8 (C-10). The hydrogen signal at δ_H 6.19 (H-3) correlated with carbon signals at δ_C 161.4 (C-2) and 112.80 (C-10). The hydrogen signal at δ_H 4.72 (H-2') correlated with carbon signals at δ_C 26.1 (C-2"a) and 24.3 (C-2"b). The hydrogen signal at δ_H 3.19 (H-3') correlated with carbon signals at δ_C 163.2 (C-7), 125.0 (C-6), 123.4 (C-5), 91.1 (C-2'), and 71.7 (C-1"). The hydrogen signals at δ_H 1.36 (H-2"b) and 1.22 (H-2"a) correlated with carbon signals at δ_C 91.1 (C-2'), 71.7 (C-1"), 26.1 (C-2"a), and 24.3 (C-2"b). All these HMBC correlations agree with (–)-marmesin (**17**) (Liu *et al*. 2005), a prenylated coumarin previously isolated from *Brosimum gaudichaudii* (Okahara 1936).

Table 1 - Carbon chemical shifts registered on the ^{13}C NMR spectra of **8**, **9**, **10**, and **11** and corresponding values (in parenthesis) registered in the literature (Mahato and Kundu 1994)

Carbon	Pentacyclic triterpene			
	8	9	10	11
C-1	38.3 (38.7)	38.3 (38.7)	38.3 (38.7)	23.6 (23.8)
C-2	27.5 (27.4)	27.4 (27.3)	27.2 (27.2)	22.0 (21.9)
C-3	80.9 (78.9)	81.1 (79.0)	80.6 (78.3)	40.8 (40.9)
C-4	39.5 (38.8)	38.5 (38.8)	38.2 (38.7)	34.7 (34.8)
C-5	55.3 (55.3)	55.3 (55.3)	55.2 (55.2)	145.9 (145.6)
C-6	18.1 (18.3)	18.3 (18.5)	18.1 (18.3)	117.5 (117.6)
C-7	34.1 (34.2)	32.8 (32.8)	32.8 (32.9)	34.1 (34.3)
C-8	40.8 (40.8)	38.2 (38.8)	39.9 (40.0)	51.5 (51.8)
C-9	50.3 (50.4)	47.6 (47.7)	47.5 (47.7)	35.5 (35.7)
C-10	37.0 (37.1)	37.7 (37.6)	36.9 (36.9)	43,4 (44.3)
C-11	20.9 (20.9)	23.5 (23.6)	23.3 (23.3)	25.9 (25.9)
C-12	25.0 (25.1)	121.6 (121.8)	124.2 (124.3)	29.2 (29.2)
C-13	38.0 (38.0)	145.1 (145.1)	139.5 (139.3)	38.5 (38.7)
C-14	42.7 (42.8)	41.6 (41.8)	42.0 (42.0)	39.5 (39.4)
C-15	27.5 (27.4)	26.1 (26.2)	28.7 (28.7)	29.7 (29.2)
C-16	35.5 (35.5)	27.0 (27.0)	26.5 (26.6)	35.5 (35.5)
C-17	42.9 (43.0)	32.4 (32.5)	33.7 (33.7)	42,3 (42.9)
C-18	48.2 (48.2)	47.2 (47.4)	59.0 (58.9)	52.9 (52.9)
C-19	47.9 (47.9)	46.8 (46.9)	39.7 (39.6)	20.9 (20.8)
C-20	150.7 (150.9)	31.0 (31.1)	39.7 (39.6)	28.3 (28.4)
C-21	29.6 (29.8)	34.7 (34.8)	30.9 (31.2)	59.8 (60.1)
C-22	39.9 (40.0)	37.6 (37.2)	41.5 (41.5)	30.9 (30.8)
C-23	28.0 (28.0)	28.1 (28.2)	28.1 (28.1)	29.8 (30.0)
C-24	15.5 (15.4)	15.7 (15.5)	15.8 (15.6)	29.8 (29.8)
C-25	16.1 (16.1)	15.8 (15.6)	15.7 (15.6)	16.4 (16.1)
C-26	15.9 (15.9)	16.7 (16.9)	16.8 (16.8)	17.6 (17.9)
C-27	14.4 (14.5)	25.7 (26.0)	23.2 (23.3)	15.4 (15.1)
C-28	17.9 (18.0)	28.3 (28.4)	27.9 (28.1)	15.8 (15.8)
C-29	109.3 (109.3)	33.5 (33.3)	17.4 (17.4)	21.8 (22.0)
C-30	19.2 (19.3)	23.9 (23.7)	21.3 (21.3)	22.6 (22.9)

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