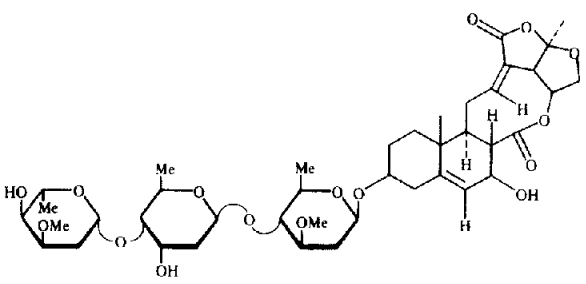

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Neocynapanoside A. Amorphous white powder (mp 105–108°), $[\alpha]_D$ −57.3° ($CHCl_3$; *c* 1.54). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1750 (C=O of five-membered lactone), 1715 (C=O, nine-membered lactone), 1660 (C=C of α,β-unsaturated five-membered lactone). UV λ_{max}^{EtOH} nm (ε): 209 (4800), 230 (5,500). FD MS *m/z*: 847[M+K]$^+$, 831[M+Na]$^+$, 808[M]$^+$, 663[M−144−H]$^+$, 533 [663−130]$^+$, 389 [533−144]$^+$. ^1H and ^{13}C NMR are shown in Tables 1 and 2.

Acknowledgements We acknowledge Drs Hong-Yen Hsu and Yuh-Pan Chen (Brion Research Institute of Taiwan) for identifying and supplying the plant material. We thank Professor emeritus Mitsuhashi (Hokkaido University) for providing the opportunity for this investigation.

reversed phase. TLC was carried out on precoated plates of Kieselgel $60F_{254}$ (Merck). Abreviations are used for sugars in this section as follows: cym, cymarose; dgt, digitoxose; ole, oleandrose.

Plant material. Xu-Chang-Qing used in this research was obtained in a Formosan market and identified by Dr. Hong-Yen Hsu (Brion Research Institute of Taiwan).

Isolation of neocynapanoside A (**1**). The extraction and isolation processes were the same as those described in the previous report [3]. The CC fr which gave cynapanoside B (**3**, 26.8 mg) afforded 19.7 mg of neocynapanoside A (**1**) by further prep. HPLC separation (Waters 45 type pump; column, Toyo Soda TSK gel ODS-80TM 4.6 mm i.d. × 25 cm, 5μ).

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A SUBSTITUTED CINNAMOYL ESTER FROM *CLEISTOPHOLIS STAUDTII*

PIERRE TANE, J. FOYERE AYAFOR* and B. LUC SONDENGAM

Department of Organic Chemistry, University of Yaoundé, Box. 812, Yaoundé, Cameroon

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Key Word Index—*Cleistopholis staudtii*; Annonaceae; Cleistophostaudin; 3-hydroxy-1,7,7-trimethylbicyclo [2.2.1]heptanyl-(*trans*)-4-hydroxy-3-methoxy cinnamate; methyl-(*trans*)-(*trans*)-10,11-dihydroxyfarnesoate.

Abstract—Cleistophostaudin, the novel ester, 3-hydroxy-1,7,7-trimethyl bicyclo[2.2.1]heptanyl-(*trans*)-4-hydroxy-3-methoxycinnamate was isolated from the stem bark of *Cleistopholis staudtii*, and its structure determined by spectroscopic data and degradative studies. The previously known methyl-(*trans*)-(*trans*)-10,11-dihydroxyfarnesoate was also isolated from the same source.

INTRODUCTION

The genus *Cleistopholis* (Engl. & Pierre) is widely known in the tropical forest zone of west and central Africa [1] for its folkloric application against a number of ailments such as tuberculosis, bronchitis, dysentery, whitlow and oedema [2]. Previous studies on the genus report [3–5] the isolation of alkaloids, sesquiterpenes and phenylpropenes. As part of our contribution to the study of the genus, we report herein the isolation and characterization of a novel substituted cinnamic acid ester (**1**) along with an acyclic farnesoic acid methyl ester (**2**) from *C. staudtii*

(Engl. & Pierre). The spectral characteristics of **2** were consistent with those previously reported [4].

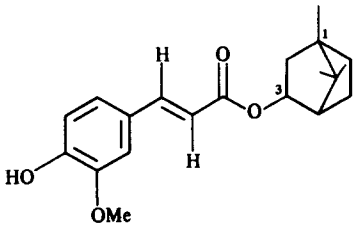
RESULTS AND DISCUSSION

The hexane extract of the powdered stem bark of *C. staudtii* was fractionated on silica gel (hexane–chloroform). Futher preparative TLC afforded two compounds, **1** and **2**, obtained in yields of 0.004 and 0.46%, respectively.

Cleistophostaudin (**1**) was obtained as an amorphous colourless solid. It was shown to have the molecular formula $C_{20}H_{26}O_4$ by elemental analysis and high resolution EIMS which gave the molecular ion at *m/z* 330. Compound **1** gave positive phenol test and its IR spectrum showed adsorptions at 3350 (OH), 1680 (C=O); 1660 (C=C), 1620 and 1580 (aromatic), 1260 and 1160 (C–O). The UV spectrum λ_{max} (nm) 237 (ε 9700) and 328 (ε 17 200) was very similar to that reported by Fomum *et al.* [6] for *n*-octacosanyl-3-hydroxy-4-methoxycinnamate. The ^{1}H NMR spectrum suggested the presence of a substituted cinnamoyl moiety by the presence of doublets at δ6.30 and 7.60 (J = 16 Hz), 7.05 and 6.80 (J = 7.5 Hz) and a singlet at 7.01. This was supported by the mass spectrum which gave the base peak at *m/z* 177. The large coupling constant (J = 16 Hz) suggested a *trans*-configuration for the olefinic bond.

The second fragment of the molecule was characterized by the ^{13}C NMR spectrum which showed two fully substituted carbons at δ47.9 and 49.0; two methines at 45.0 and 79.9; three methylenes at 27.3, 28.1 and 36.9 and three methyls at 13.6, 18.9 and 19.7. These ^{13}C NMR results suggested a bicyclic monoterpene structure for this fragment. The ^{1}H NMR spectrum supported this suggestion by showing three methyl groups at δ0.88 (6H) and 0.91 (3H), seven-protons multiplet at 1.10–2.20 and a base proton of the oxygenated carbon at 5.01 (*ddd*, J = 9.5, 2.7, 2.7 Hz). The multiplicity of this proton at δ5.01 confirmed it to be at C-3.

Hydrolysis of **1** gave ferulic acid (**3**) [7], mp 171–172° and 3-hydroxy-1,7,7-trimethybicyclo[2.2.1]heptane or *epi*-borneol (**4**) [8], mp 179–180°. Cleistophostaudin (**1**) is therefore the novel ester, 3-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptanyl-(*trans*)-4-hydroxy-3-methoxycinnamate.



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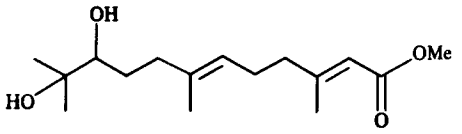

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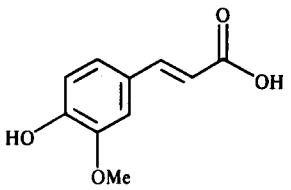

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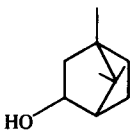

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EXPERIMENTAL

Mps: uncorr. IR spectra determined in KBr pellets and UV in EtOH. NMR spectra were run in $CDCl_3$ with TMS as internal standard. EIMS analyses were performed at 70 eV using a direct inlet system.

Plant material. Stem bark of *C. staudtii* was collected near Edea, Cameroon. Herbarium specimens documenting the collection are deposited at the National Herbarium, Yaoundé, Cameroon.

Extractions and isolations of compounds. The dried and powdered stem bark (4 kg) of *C. staudtii* was extracted with hexane to yield to gum (105 g) which was chromatographed on silica gel (700 g). Elution with hexane–$CHCl_3$ (9:1) gave crude **1** (150 mg) followed by a mixture of sterols (73 mg). Hexane–$CHCl_3$ (17:3) eluted a mixture with **2** as the major compound (16 g). Compounds **1** and **2** were purified using prep. TLC.

Cleistophostaudin (**1**). Amorphous solid, UV λ_{max}^{EtOH} nm (ε): see text; IR ν_{max} cm^{-1}: see text; ^{1}H NMR (60 MHz, $CDCl_3$): δ7.60 (1H, *d*, J = 16 Hz), 7.05 (1H, *d*, J = 7.5 Hz), 7.01 (1H, *s*), 6.90 (1H, *d*, J = 7.5 Hz), 6.30 (1H, *d*, J = 16 Hz), 5.01 (1H, *ddd*, J = 9.5, 2.7, 2.7 Hz) 3.90 (3H, *s*), 2.20–1.10 (7H, *m*), 0.91 (3H, *s*), 0.88 (6H, *s*); ^{13}C NMR ($CDCl_3$): δ167.7 (*s*), 148.0 (*s*), 146.9 (*s*), 144.9 (*d*), 127.1 (*s*), 123.0 (*d*), 115.0 (*d*), 114.8 (*d*), 109.5 (*d*), 79.9 (*d*), 50.8 (*q*), 49.0 (*s*), 47.9 (*s*), 45.0 (*d*), 36.9 (*t*), 28.1 (*t*), 27.3 (*t*), 19.7 (*q*), 18.9 (*q*), 13.6 (*q*). (Found: C, 72.81; H, 7.82. $C_{20}H_{26}O_4$ requires: C, 72.70; H, 7.93%) EIMS *m/z* (rel. int.): 330 $[M]^+$ (11.7), 194 (3.6), 177 (100), 153 (0.7).

Hydrolysis of **1**. A soln of **1** (70 mg) in(MeOH–KOH (9:1) was refluxed for 24 hr. Work-up gave **3** (30 mg), mp 171–172° (lit. [7] 171°) and **4** (10 mg), mp 179–180° (lit. [8] 181–182°).

Methyl-(trans)-(trans)-10,11-*dihydroxyfarnesoate* (**2**). Colourless oil, UV and IR in agreement with lit. [4]; ^{1}H NMR (60 MHz, $CDCl_3$): δ5.67 (1H, *s*), 5.15 (1H, *m*), 3.30 (1H, *dd*, J = 9.3, 1.1 Hz), 3.00 (2H, *s*), 1.95–2.30 (9H, *m*), 1.60 (3H, *s*), 1.40 (2H, *m*), 1.20 (3H, *s*), 1.01 (3H, *s*); ^{13}C NMR ($CDCl_3$): δ167.3 (C-1), 115.3 (C-2), 160.0 (C-3), 40.8 (C-4), 25.8 (C-5), 123.3 (C-6), 136.0 (C-7), 36.6 (C-8), 29.8 (C-9), 77.9 (C-10), 73.0 (C-11), 23.1 (C-12), 26.3 (C-13), 15.9 (C-14), 18.8 (C-15), 50.8 (CH_2–O).

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ARYLALKANONES FROM *HORSFIELDIA GLABRA*

MADALENA M. M. PINTO, ANAKE KIJJOA*, BUMRUNG TANTISEWIE†, MASSAYOSHI YOSHIDA‡ and OTTO R. GOTTLIEB‡

Laboratorio de Química Organica, Faculdade de Farmácia do Porto, Universidade do Porto, 4000 Porto, Portugal; * Laboratório de Química, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, 4000 Porto, Portugal; † Department of Pharmacognosy, Faculty of Pharmacy, Chulalongkorn University, Bangkok, Thailand; ‡Instituto de Quimica, Universidade de São Paulo, 05508 São Paulo, Brazil

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Key Word Index—*Horsfieldia glabra*; Myristicaceae; arils; arylphenyl alkanones; arylalkenone; lignans.

Abstract—Besides the new compounds 1-(2,4,6-trihydroxyphenyl)-9-phenylnonan-1-one and 1-(2,6-dihydroxyphenyl)-4-methyl-4-tridecen-1-one, the known 1-(2,6-dihydroxyphenyl)-11-phenylundecan-1-one, (+)-asarinin, (−)-dihydrocubebin and trimyristin were isolated from the methanol extract of arils of *Horsfieldia glabra*.

INTRODUCTION

Horsfieldia glabra Warb. which is indigenous to Thailand, is a large tree. Its bark and leaves have been used as an aromatic to treat intestinal affections. The bark is also a remedy for sores and pimples [1]. Although the chemical constituents of *H. iryaghedhi* Warb. have been previously investigated [2–4], nothing has been published so far on the constituents of *H. glabra*. We report here the isolation of trimyristin [3], (+)-asarinin [3],(−)-dihydrocubebin [3] and of polyketides including the known **1a** [5] and the novel **1b** and **2a**.

RESULTS AND DISCUSSION

The molecular formula $C_{21}H_{26}O_4$ of compound **1b** was determined by low-resolution mass spectrometry and NMR H count. It was recognized as a diarylnonanone by the ^{1}H NMR signals for a phenyl group and a 2,4,6-trihydroxybenzoyl group, as well as for eight methylene units, two of which were vicinal to carbonyl or aryl moieties. An aluminium trichloride shift and a 1650 cm^{-1} band were both indicative of an *ortho*-hydroxycarbonyl substituted aryl. The mass spectrum was compatible with the structure showing the base peak at *m/z* 153 (trihydroxybenzoyl ion), a peak of high relative intensity at *m/z* 168 $[C_6H_3(OH)_3C(OH)=CH_2]^+$ and a peak of moderate intensity at *m/z* 91 (tropylium ion). Acetylation led to the diacetate **1c** (δ 2.36, 2.35, 2*s*, 2OAc) and the triacetate **1d** (δ 2.29, *s*, OAc and δ 2.25), *s*, 2OAc).

The structure of the diarylnonanoid **1b** belongs to the type previously detected in the fruits of *Myristica malabarica* Lam. [6]. The most significant difference between **1b** and the malabaricones is the phloroglucinol unit in the former is replaced by a resorcinol unit in the latter.

Compound **2a**, $C_{20}H_{30}O_3$, was characterized by ^{1}H NMR as a tridecenoylresorcinol comprising a 2,6-dihydroxybenzoyl group and a single olefinic proton (δ 5.34, *t*, $J=5.5$ Hz). The double bond must be separated by two CH_2 groups from the carbonyl since the ^{1}H NMR spectrum shows signals for two α-protons (δ 3.14, *t*, $J=7$ Hz) and for four allylic protons (δ 2.02, *br d* and δ 1.71, *t*, $J=7$ Hz). Double resonance at one of the allylic frequencies (δ 1.71) transforms the triplet (δ 3.14) due to both α-protons, to a singlet, but does not affect the triplet (δ 5.34) due to the olefinic proton. Double resonance at the other allylic methylene frequency (δ 2.02) transforms the triplet (δ 5.34), due to the olefinic proton, to a singlet. This evidence, together with a ^{1}H NMR multiplet (δ 1.32–1.25) for 15 protons (six methylene groups plus one methyl group) leads to the conclusion that the olefinic proton is on C-5 while a methyl group is on C-4.