SWARTZIARBOREOLS A-E, FIVE NEW CASSANE DITERPENOIDS FROM *SWARTZIA ARBORESCENS* (AUBL.) PITTIER

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Abstract - Five new cassane diterpenoids, swartziarboreols A-E (**1**-**5**), have been isolated from *Swartzia arborescens* (Aubl.) Pittier. Their structures have been elucidated on the basis of spectroscopic data.

The genus *Swartzia* Schreb. includes some 135 tropical trees belonging to the family *Fabaceae*, tribe *Swartzieae*.[1] This tribe has been long recognized as transitional between the *Caesalpinoideae* and the *Papilionoideae* sub-families and its position within the family appears to be still discussed.[2-4] In a continuation of our chemical studies on plants of French Guyana,[5] we report here the structural elucidation of five diterpenoids named swartziarboreols A-E, isolated from the roots of *Swartzia arborescens* (Aubl.) Pittier, a tree widely distributed in the Amazonian district.[6-9]

Swartziarboreol A (1) was found to have the empirical formula $C_{21}H_{26}O_5$ determined by high resolution mass spectrometry and elemental analysis. The uv spectrum was modified in alkaline medium and indicated the presence of a phenolic group on a benzoic acid derivated chromophore. A fragment ion observed at m/z 259 (M-99) in EI-ms, together with a series of ^{13}C nmr signals (Table I) accounting for 3 CH_3 (δ 19.4, 20.2, 28.3), 4 CH_2 (δ 19.9, 31.3, 34.1, 35.3), 1 CH (δ 51.1) and three quaternary carbons (δ 38.5, 46.9, and 218.8) were typical for a 3-keto-4,4,10-trimethyldecalin-8-ene system such as that encountered in the *trans*-fused AB cycles of various triterpenes related to bryononic acid.[10-12] In addition, the ^1H (Table II) and ^{13}C (Table I) nmr spectra revealed the presence of an aromatic methoxyl group (δ_H 3.77, δ_C 61.5) and of the Ar-CH_2-CH_2-O-CO-Ar system of a dihydroisocoumarin skeleton (δ_H 2.99, 2.99, 4.27, 4.42 ; δ_C 23.3, 65.8, 164.2).[13, 14] The locations of the phenolic group, of the methoxyl group and of the fusion of the dihydropyran on the aromatic ring were deduced from the ^1H-^{13}C correlations observed on the 2D COLOC[15, 16] spectrum as described in Figure 1. The structure of swartziarboreol A was therefore characterized as 1.

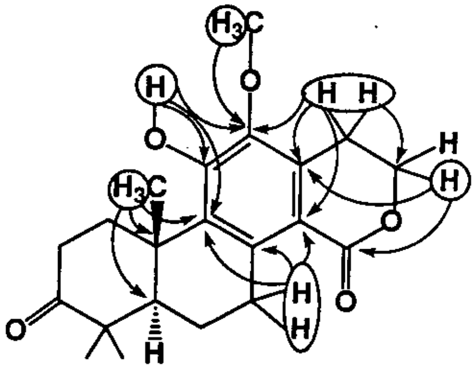
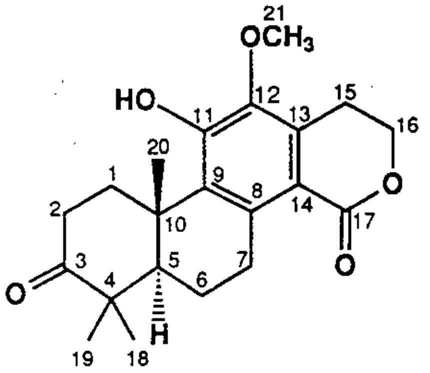


Figure 1 : Long range correlations observed in the 2D COLOC spectrum of 1.

The empirical formula of swartziarboreol B (2) was established as $C_{21}H_{24}O_5$. The uv spectrum contrasted with that of 1 and characterized an isocoumarin chromophore.[17] In good agreement with this statement, a typical band was observed at ν^{KBr}_{max} 1730 cm^{-1} on the ir spectrum.[17] The ^{13}C nmr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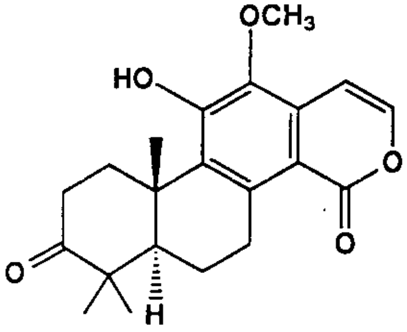
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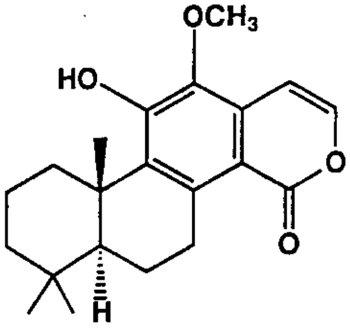
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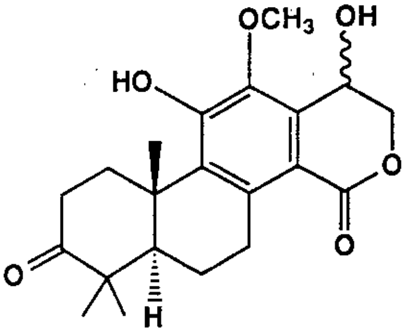
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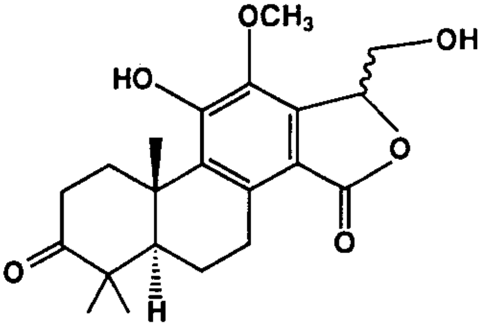
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Table I : ^{13}C Nmr chemical shifts (δppm)
of swartziarboreols A-E (**1-5**)*
(75 MHz, $CDCl_3$/TMS)

Carbons	1	2	3	4	5
1	35.3	35.2	36.2	35.1	35.0
2	34.1	34.1	19.3	34.1	34.1
3	218.8	218.4	41.2	218.9	218.4
4	46.9	46.9	33.4	47.0	47.2
5	51.1	50.8	52.0	51.2	51.5
6	19.9	19.9	18.6	20.0	19.2
7	31.3	32.1	33.6	31.9	27.5
8	139.4	140.7	137.9	139.9	136.0**
9	133.4	135.1	138.2	135.6	135.6
10	38.5	38.9	40.3	38.8	38.7
11	151.1	156.2	152.6	152.4	152.5
12	141.1	138.4	141.8	141.7	138.9
13	131.6	129.9	129.4	131.8	135.1**
14	115.6	112.4	112.4	114.6	115.3
15	23.3	100.4	100.5	60.3	78.5
16	65.8	145.1	144.7	71.8	63.3
17	164.2	160.8	160.9	163.7	169.7
18	28.3	28.3	33.4	28.4	28.3
19	20.2	20.3	22.1	20.3	20.4
20	19.4	19.4	19.3	19.3	19.4
21	61.5	62.2	62.1	63.6	61.0

* The attributions of the signals have been unambiguously determinated by HETCORR and COLOC experiments for the five compounds.

** Assignments may be reversed.

Table II : ^{1}H Nmr spectra of swartziarboreols A-E (1-5) (300 MHz, $CDCl_3$/TMS, δ ppm, J in Hz)

Protons	1	2	3	4	5
1 ax.	1.90 ddd J=14, 9, 5	1.90 m	1.15 m	1.92 ddd J=14, 9, 5	1.95 ddd J=14, 8, 6
eq.	3.07 ddd J=14, 7, 5	3.11 ddd J=15, 8, 6	3.17 m	3.10 ddd J=14, 7, 6	3.14 ddd J=14, 8, 6
2 ax.	2.43 ddd J=15, 9, 5	2.48 ddd J=15, 9, 6	1.60 m	2.45 ddd J=15, 9, 5	2.51 ddd J=15, 8, 6
eq.	2.68 ddd J=15, 7, 5	2.72 ddd J=15, 8, 6	1.75 m	2.70 ddd J=15, 7, 6	2.70 ddd J=15, 8, 6
3			1.30 m 1.42 m		
5	2.03 dd J=13, 2	2.05 dd J=13, 2	1.25 m	2.03 dd J=13, 1.5	2.04 dd J=13, 2
6 ax.	1.48 qd J=13, 5	1.57 qd J=13, 5	1.46 m	1.48 dtd J=15, 13, 5	1.60 qd J=13, 5
eq.	1.82 ddt J=13, 6, 2	1.90 m	1.96 ddt J=13, 7, 2	1.84 dddd J=15, 6, 3, 1.5	1.88 ddt J=13, 6, 2
7 ax.	3.16 ddd J=18, 13, 6	3.20 ddd J=19, 13, 6	3.28 ddd J=19, 13, 7	3.18 m	2.88 ddd J=19, 13, 6
eq.	3.34 ddd J=18, 5, 2	3.68 ddd J=19, 5, 2	3.48 ddd J=19, 5, 1	3.18 m	3.70 ddd J=19, 5, 2
11 (OH)	6.93 s (D_2O exch.)	6.75 s (D_2O exch.)	6.66 s (D_2O exch.)	6.94 s (D_2O exch.)	6.62 s (D_2O exch.)
15	2.99 m 2.99 m	6.58 d J=6	6.55 d J=6	5.03 t J=1.5	5.57 d J=6, 3.5
16	4.27 td J=10, 5 4.42 dt J=10, 5	7.25 d J=6	7.22 d J=6	4.38 dd J=12, 1.5 4.58 dd J=12, 1.5	3.87 ddd J=13, 8, 3.5 4.20 ddd J=13, 7, 6
18	1.16 s	1.20 s	0.99 s	1.17 s	1.21 s
19	1.11 s	1.18 s	0.97 s	1.11 s	1.17 s
20	1.30 s	1.39 s	1.40 s	1.29 s	1.33 s
21	3.77 s	3.85 s	3.84 s	3.97 s	3.91 s
OH				1.22 br.s (D_2O exch.)	2.13 dd J=8, 7 (D_2O exch.)

spectrum was essentially similar to that of 1. Nevertheless, striking differences were observed for the signals of C-17, C-16 and C-15 which appeared at δ_C 160.8, 145.1 and 100.4 respectively, indicating a pyran D-ring instead of a dihydropyran one.[18, 19] This was further supported by one pair of typical doublets (J = 6 Hz) at 6.58 and 7.25 ppm in ^1H nmr, which were assigned to H-15 and H-16 on the isocoumarin moiety.[13, 19] A COLOC experiment indicated an aromatic substitution pattern identical with that of 1. The structure of swartziarboreol B was therefore established as 2.

The empirical formula of swartziarboreol C (3) was determinated as $C_{21}H_{26}O_4$. The uv spectrum was superimposable on that of 2 indicating the same chromophore and the same aromatic substitution pattern. The ^{13}C nmr spectrum was closely related to that of 2. Noticeable differences of chemical shift were only observed for the signals of the A-ring, where the main feature was the lack of carbonyl resonance. This evidence permitted us to depict the structure of swartziarboreol C as 3, in good agreement with ^{13}C nmr data previously published for various related di- and triterpenes bearing no carbonyl group on the A-ring.[12, 20-22]

Swartziarboreol D (4) and swartziarboreol E (5) both exhibited in EI-ms a molecular ion at m/z 374, corresponding to the empirical formula $C_{21}H_{26}O_6$. The uv spectrum of 4 was identical with that of 1. In contrast the uv spectrum of 5 differed from those of 1 and 4. The ^1H and ^{13}C nmr signals of both compounds were closely related to those of 1 and 2 for the A, B and C-ring resonances. The D-ring resonances of 4 were typical for a 5-hydroxy-5,6-dihydroxy-2-pyrone unit,[23] whereas those of 5 characterized a 5-hydroxymethyl-2(5*H*)-furanone unit.[23-25] The structures of swartziarboreols D and E are therefore established as 4 and 5, respectively.

The absolute configuration of the A-B ring system of swartziarboreols A-E were determined by comparison of their optical rotations with those of analogous compounds belonging to the abietane series [26, 27] and were in full agreement with the biogenesis of the cassane-vouacapane series of diterpenoids in the family *Fabaceae.*

Other diterpenoids of the cassane-vouacapane series have been previously isolated from both the *Cesalpinoideae* sub-family (i.e., *Erythrophleum* alkaloids,[28] *Vouacapoua* diterpenoids[29]) and the *Papilionoideae* sub-family (i.e., terpenoids from *Dipterix*[30] and *Pterodon*[31] species). The isolation of swartziarboreols from *Swartzia arborescens* emphasizes the transitional character of the tribe *Swartzieae* between the two sub-families.

EXPERIMENTAL

Melting points were determinated on a Köfler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Spectra were recorded on the following apparatus : ir, Perkin-Elmer 257 ; ms, Nermag R-10-10 C in electron impact (70 eV) (ei) or desorption-chemical ionization (reagent gas : NH_3) (dci) ; ^1H and ^{13}C nmr, Bruker AC 300 (300 MHz). Multi-impulsional DEPT, COSY, ^{13}C-^1H HETCORR and COLOC experiments were performed on Bruker AC 300, using the standard Bruker microprograms.

Plant material

The plant material was collected at Vidal (French Guyana) in October 1986. Herbarium samples (Kodjoed JFK 116) are held in the herbaria of the Centre ORSTOM de Cayenne and of the Muséum National d' Histoire Naturelle (Paris).

Extraction and isolation

The crushed dried roots of *Swartzia arborescens* (5 Kg) were lixiviated by CH_2Cl_2

chromatography on silica gel 60 Merck (particle size : 0.040-0.063 mm). Elution was with cyclohexane-EtOAc of increasing polarity (90 : 10 → 20 : 80) and yielded successively oleanyl acetate (500 mg), stigmasterol (150 mg), betulinic acid (35 mg), swartziarboreol B (75 mg), afrormosine (500 mg), swartziarboreol E (115 mg), swartziarboreol D (195 mg), swartziarboreol A (415 mg), and swartziarboreol C (125 mg). The known compounds were identified by comparison with authentic samples.

Swartziarboreol A (1) : white needles, mp 248 °C (MeOH) ; $[\alpha]^{25}_D$ + 270 ° (c = 0.21, MeOH) ; uv λ max nm (MeOH) (log ε) : 220 (4.33), 228 (sh.), 273 (4.04) nm, (MeOH+KOH) : 222, 247, 325 nm ; ir ν max (KBr) : 3260, 2940, 1710, 1680, 1580, 1175 cm^{-1} ; EI-ms (m/z) : 358, 343, 301, 259, 245, 233 ; ^1H nmr : see Table II ; ^{13}C nmr : see Table I. High resolution EI-ms : Calcd for $C_{21}H_{26}O_5$: 358.1780. Found : 358.1770. Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found : C, 70.25; H, 7.23.

Swartziarboreol B (2) : colorless needles, mp 226 °C (MeOH) ; $[\alpha]^{25}_D$ + 250 ° (c = 0.20, MeOH) ; uv λ max nm (MeOH) (log ε) : 241 (sh.), 249.5 (4.69), 263 (sh.), 278 (sh.), 292 (sh.), 326 (3.63) nm ; ir ν max (KBr) : 3300, 2930, 1730, 1690, 1250 cm^{-1} ; EI-ms (m/z) : 356, 341, 299, 257, 243, 231 ; ^1H nmr : see Table II ; ^{13}C nmr : see Table I. High resolution EI-ms : Calcd for $C_{21}H_{24}O_5$: 356.1624. Found : 356.1620. Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found : C, 70.54; H, 6.93.

Swartziarboreol C (3) : amorphous solid, $[\alpha]^{25}_D$ + 105 ° (c = 0.10, MeOH) ; uv λ max nm (MeOH) (log ε) : 241 (sh.), 249.5 (4.51), 263 (sh.), 278 (sh.), 292 (sh.), 326 (3.42) nm ; ir ν max (KBr) : 3280, 2930, 1730, 1250, 1170 cm^{-1} ; EI-ms (m/z) : 342, 327, 285, 271, 257, 245, 231 ; ^1H nmr : see Table II ; ^{13}C nmr : see Table I. High resolution EI-ms : Calcd for $C_{21}H_{26}O_4$: 342.1831. Found : 342.1830. Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found : C, 73.84; H, 7.63.

Swartziarboreol D (4) : colorless needles, mp 245 °C (MeOH) ; $[\alpha]^{25}_D$ + 255 ° (c = 0.22, MeOH) ; uv λ max nm (MeOH) (log ε) : 220 (4.38), 228 (sh.), 272 (3.97), 300 (sh.) ; ir ν max (KBr) : 3320, 2950, 1710, 1690, 1250, 1170 cm^{-1} ; EI-ms (m/z) : 374, 343, 317, 271, 245, 97 ; ^1H nmr : see Table II ; ^{13}C nmr : see Table I. High resolution EI-ms : Calcd for $C_{21}H_{26}O_6$: 374.1729. Found : 374.1730. Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found : C, 67.27; H, 7.12.

Swartziarboreol E (5) : colorless needles, mp 280 °C (MeOH) ; $[\alpha]^{25}_D$ + 263 ° (c = 0.11, MeOH) ; uv λ max nm (MeOH) (log ε) : 219 (4,52), 225 (sh.), 266 (4.08), 294 (sh.) ; ir ν max (KBr) : 3340, 2930, 1710, 1695, 1250, 1160 cm^{-1} ; EI-ms (m/z) : 374, 343, 317, 271, 245, 97 ; ^1H nmr : see Table II ; ^{13}C nmr : see Table I. High resolution EI-ms : Calcd for $C_{21}H_{26}O_6$: 374.1729. Found : 374.1730. Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found : C, 67.31; H, 6.93.

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