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FOUR FLAVONOIDS FROM *AGERATUM STRICTUM**

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Key Word Index—*Ageratum strictum*; Asteraceae; Eupatorieae; flavanones; chalcone.

Abstract—Four new flavonoids, three flavanones and one chalcone, were isolated from aerial parts of *Ageratum strictum*. Their structures were estabilised as 3'6'-dihydroxy-2', 4'-dimethoxy-3, 4-methylenedioxychalcone, 6-hydroxy-5,7-dimethoxy-3',4'-methylenedioxyflavanone, 6-hydroxy-5,7,3',4'-tetramethoxyflavanone and 6,4'-dihydroxy-5,7,3'-trimethoxyflavanone on the basis of spectral data and chemical degradation.

INTRODUCTION

As part of a continuing study on the chemistry of plants of the tribe Eupatorieae (Asteraceae), we have previously published on several flavonoids from *Ageratum corymbosum* Zucc. [1]. Now we have undertaken a study of *Ageratum strictum* Hemsl. and isolated the lignan sesamin [8], coumarin, taraxasterol, sitosterol and stigmasterol as well as four new flavonoids, whose structures were established by spectroscopic and chemical evidence.

RESULTS AND DISCUSSION

From the aerial parts of *Ageratum strictum* four new flavonoids, which we have named agestricin A, B, C and D were isolated. For the sake of convenience, we discuss first the structure of agestricin B (**2a**), $C_{18}H_{16}O_7$, mp 136–137°, $[\alpha]_D + 23.6°$. Both the UV (278, 342 nm) and the IR (1670, 1610 cm^{-1}) absorptions were typical of flavanones [3]. The ^1H NMR showed an ABX system with signals centered at δ 5.25, 2.97 and 2.65 due to H-2 and H-3 protons, which confirmed the flavanone nucleus. Two sharp singlets at δ 3.87 (3H) and 3.90 (3H) indicated the presence of two methoxy groups. Two further singlets at 6.30 (1H) and 5.93 (2H) could be assigned either to H-6 or H-8 and the 3', 4'-methylenedioxy protons, respectively. The remaining three protons of the B-ring were observed as a non-first order pattern at 6.7–7.0. The ^1H NMR reveals the presence of one hydroxyl group (IR band at 3410 cm^{-1}) non-hydrogen bonded at 5.52, which was confirmed by acetylation of **2a** affording the monoacetate **2b**, mp 215–216°, (δ 2.25, *s*, 3H).

The MS of agestricin B (**2a**) was in agreement with the proposed structure, the molecular ion peak was observed at *m/z* 344 ($C_{18}H_{16}O_7$) and other significant fragments were at *m/z* 196 $[C_9H_8O_5]^+$ 100.0%), 181 $[C_9H_8O_5\text{–Me}]^+$ and 153 $[C_9H_8O_5\text{–Me–CO}]^+$ due to the A-ring and at *m/z* 148 ($C_9H_8O_2$) due to the B-ring. The low intensity of the peak at *m/z* 181 suggested the absence of a methoxy group at C-6 and C-8 [2]. Therefore the hydroxyl group could be placed at one of these positions.

Methylation with dimethyl sulfate of agestricin B (**2a**) afforded the trimethyl ether **2c**. The MS of **2c** (M^+ 358), suggested the presence of a new methoxy group either at C-6 or C-8, since it showed a prominent peak at *m/z* 195 (93.91) due to the $[A_1 - Me]^+$ fragment [2]. The ethyl ether (**2d**) showed the same fragmentation peak at *m/z* 195 (100.0%) due to $[A_1 - Et]^+$. Alkaline degradation of **2c** with 50% potassium hydroxide gave 6-hydroxy-2, 3, 4-trimethoxyacetophenone (**4a**) [1] and piperonyl alcohol (**5a**) as major products. Piperonylic aldehyde (**5b**) was also identified as a secondary product as well as the corresponding 6'-hydroxy-2',3',4'-trimethoxy-3,4-methylenedioxychalcone (**1c**), which was also obtained as a major product when **2c** was treated with 50% potassium hydroxide at room temperature. Degradation products of **2c** established the substitution pattern of agestricin B (**2a**). Hence **2a** is the most likely structure for agestricin B.

Agestricin A (**1a**), $C_{18}H_{16}O_7$, mp 190–192° was the less polar flavonoid isolated as a dark-red crystalline compound. This colour indicated that it could be a chalcone. The UV spectrum confirmed this assumption since it showed a strong band at 364 nm typical of a chalcone [3]. IR absorption bands at 3400 and 1625 cm^{-1} indicated the presence of a hydrogen bonded (–O–H . . . O=C–) system.

The ^1H NMR confirmed the presence of the hydroxyl group strongly hydrogen bonded at δ 13.12, which must be placed at C-6'. Two sharp three proton singlets at 3.85 and 3.92 revealed the presence of two methoxy groups. Three further singlets at 6.0 (2H),

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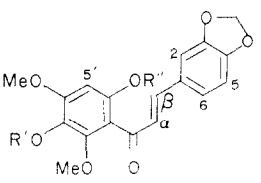
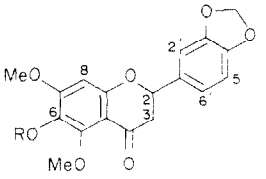
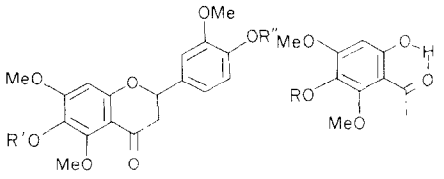


1a R′=R″=H
1b R′=R″=Me
1c R′=Me, R″=H

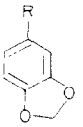


2a R=H
2b R=Ac
2c R=Me
2d R=Et



3a R′=H, R″=Me
3b R′=Ac, R″=Me
3c R′=R″=H
3d R′=R″=Ac

4a R=Me
4b R=H



5a R=CH₂OH
5b R=CH=O
5c R=COOH

6.29 (1H) and 7.75 (2H) were assigned to the methylenedioxy group, H-5′ and to the α- and β-protons respectively. The remaining three protons were observed as two doublets at 6.8 ($J = 8.5$ Hz), 7.12 ($J = 2$ Hz) and a doublet of doublets at 7.07 ($J = 8.5$ and 2 Hz), which could be assigned to H-5, H-2 and H-6 respectively; hence the methylenedioxy group can be placed at C-3 or C-4. Since chalcones sometimes occur together with flavanones of the corresponding substitution pattern [4], we can represent agestricin A, as 6′, 3′-dihydroxy-2′, 4′-dimethoxy-3, 4-methylenedioxychalcone (**1a**). This assumption was confirmed by treatment of agestricin A with dimethyl sulfate to give the methyl derivative **1b**, which was identical with the methylation product obtained from the chalcone **1c** previously obtained from agestricin B.

The MS of agestricin A (**1a**) was in accord with the proposed structure. It showed a molecular ion peak at *m/z* 344 [$C_{18}H_{16}O_7$] and the same fragmentation peaks as agestricin B (**2a**) at *m/z* 196, 181, 153 and 148, indicating a major contribution of the isomeric flavanone [3]. Final confirmation of the structures **1a** and **2a** for agestricin A and B was achieved by alkaline degradation of agestricin B (**2a**) which yielded 3, 6-dihydroxy-2, 4-dimethoxyacetophenone (**4b**) which was identical in all aspects with a synthetic sample obtained by Dr. Shin [5]. Piperonylalcohol (**5a**), piperonylic acid (**5c**) and tiny amounts of piperonylic aldehyde (**5b**) were also identified, as well as a chalcone which was identical with agestricin A (**1a**).

A third pale-yellow compound, agestricin C (**3a**) ($C_{19}H_{20}O_7$) was isolated after rechromatography of later fractions, mp 159–160° $[\alpha]_D + 2.8°$. The UV spectrum showed absorption bands at 277, 340 nm and IR absorption bands at 1667, 1608 cm^{-1} typical of flavanones [3]. The IR spectrum also indicated the presence of hydroxyl group(s) (band at 3400 cm^{-1}) which was confirmed by obtaining the monoacetate **3b**, mp 182–183°, (IR, 1762 cm^{-1}; δ 2.3, *s*, 3H). The ^{1}H NMR spectrum of **3a** (Table 1) was very similar to that of agestricin B (**2a**), but lacked the two-proton methylenedioxy singlet, and showed two extra methoxy group signals which could be placed at C-3′ and C-4′ instead of the methylenedioxy group. The MS of **3a** supported this assumption since it showed a molecular ion peak at *m/z* 360 [$C_{19}H_{20}O_7$]$^+$ and diagnostic peaks at *m/z* 196 (100.0%) 181, 153 which indicated the same A-ring substitution as agestricin B (**2b**) and at *m/z* 164 [$C_{10}H_{12}O_2$]$^+$ due to the B-ring fragment which must bear the two extra methoxy groups. Therefore the structure of agestricin C should be represented by 6-hydroxy-5,7,3′,4′-tetramethoxyflavanone (**3a**).

A third flavanone which we name agestricin D (**3c**), was obtained by prep. TLC, and crystallized from $CHCl_3$–Et_2O, mp 180–182°, $[\alpha]_D + 12°$. The UV and IR spectra were very similar to those of **2a** and **3a**. The ^{1}H NMR spectrum (Table 1) was almost identical to that of **3a**, but lacked one methoxy group signal and showed an extra hydroxyl singlet at 5.67 (interchangeable with D_2O). Acetylation of **3c** gave the diacetate **3d**, mp 178–180°, confirming the presence of two hydroxyl groups, one of them on the A-ring. Since the mass spectral fragments at *m/z* 196 [A_1]$^+$, 181 [A_1 – Me]$^+$, 153 [A_1 – Me – CO]$^+$ indicate the same substitution on the A-ring as in **2a** and **3a**, the second hydroxyl group must be on the B-ring, as indicated by the peak at *m/z* 150 due to the B-ring fragment bearing one methoxyl and one hydroxyl group. Alkaline degradation of agestricin D afforded the same acetophenone, **4b**, obtained from **2a** and 3-methoxy-4-hydroxybenzaldehyde (vainillin). Hence the structure of agestricin D corresponds to 6, 4′-dihydroxy-5, 7, 3′-trimethoxyflavanone (**3c**).

Table 1. ^{1}H NMR spectral data of agestricin A (**1a**), B (**2a**), C (**3a**), D (**3c**) and derivatives*

	1a	**1b**	**1c**		**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**3d**
H-β	7.75	7.34 *d*	7.78	H-2	5.25 *dd*	5.32 *dd*	5.35 *dd*	5.30 *dd*	5.33 *dd*	5.28 *dd*	5.38 *dd*
H-α	7.75	6.81 *d*	7.78	H-3	2.65 *dd*	2.65 *dd*	2.68 *dd*	2.70 *dd*	2.70 *dd*	2.70 *dd*	2.73 *dd*
					2.97 *dd*	2.97 *dd*	3.03 *dd*	3.03 *dd*	3.03 *dd*	3.02 *dd*	3.00 *dd*
H-5′	6.29	6.34	6.30	H-8	6.32	6.36	6.37	6.35	6.35	6.34	6.35
H-2	7.12 *d*	7.10 *d*	7.18 *d*	H-2′	—	—	—	—	—	—	—
H-5	6.80 *d*	6.79 *d*	6.83 *d*	H-5′	6.7–7.0†	6.7–7.0†	6.9–7.1†	6.7–7.0†	6.7–7.0†	6.9† *br s*	7.0 *br s*
H-6	7.07 *dd*	7.03 *dd*	7.10 *dd*	H-6′	—	—	—	—	—	—	—
OCH_2O	6.0	6.02	6.01		5.95	5.96	6.0	—	—	—	—
OMe	3.85	3.78	3.84		3.87	3.77(6H)	3.82	3.87	3.80	3.88	3.81
	3.92	3.85	3.90		3.90		3.88	3.89(6H)	3.84	3.90	3.85(6H)
		3.88	3.93				3.95	3.92	3.87	3.93	
		3.94							3.89		
OH	5.15	—	—		5.52	—	—	—	—	5.40	—
	13.12									5.67	
OAc	—	—	—		—	2.25	—	—	2.3	—	2.3
											2.32

*Run at 80 MHz in $CDCl_3$ with TMS as int. standard. Values are in δ values $J_{2,6} = 2$ Hz, $J_{5,6} = 8.5$ Hz, $J_{\alpha,\beta} = 16$ Hz, $J_{2,3ax} = 12$ Hz, $J_{2,3ec} = 4$ Hz, $J_{2ax,2ec} = 16$ Hz.

†Non-first order pattern.

EXPERIMENTAL

Ageratum strictum Hemsl. was collected in August 1981, in Mexico: Morelos, highway to Cuernavaca, *ca* 60 km south of Mexico City. A voucher, Calderon 60, is on deposit at the Herbarium of Instituto de Biología (UNAM), Mexico.

Dried leaves and flowers (800 g) were extracted with $CHCl_3$ at room temp. The crude syrup obtained (23 g) after elimination of the solvent, was percolated on a column packed with 200 g Tonsil Optimum Extra (suppled by Tonsil Mexicana) and eluted with petrol, and mixtures of petrol–EtOAc. 200 ml fractions were taken and all monitored by TLC. From the less polar fractions eluted with petrol–EtOAc (8:2), sesamin [8], coumarin, taraxasterol and a mixture of sitosterol and stigmasterol were identified.

Agestricin A (**1a**). Fraction 4, eluted with petrol–EtOAc (1.5 g) was chromatographed on Si gel (50 g). Chromatography of fractions eluted with petrol–EtOAc (95:5), afforded **1a** (125 mg) as dark-red crystals from Me_2CO–Et_2O, mp 190–192°. UV λ_{max}^{MeOH} nm (ϵ): 364 (25 262), 310 sh (13 437); IR ν_{max}^{KBr} cm^{-1}: 3400, 1600, 1623, 1500, 1440. EIMS (probe) 70 eV *m/z* (rel. int.): 344 $[M]^+$ (38.1), 196 $[C_9H_8O_5]^+$ (100), 181 $[C_9H_8O_5 - Me]^+$ (13.4), 153 $[C_9H_8O_5 - Me - CO]^+$ (31.0), 148 $[C_9H_8O_2]^+$ (12.1).

Agestricin B (**2a**). Fraction 5 eluted with petrol–EtOAc (4:6) afforded after crystallization 3.5 g **2a** as needles from $CHCl_3$–Et_2O, mp 136–137°. $[\alpha]_D$ + 23.6° ($CHCl_3$; *c* 0.186). UV λ_{max}^{MeOH} nm (ϵ): 237 (19 275), 278 (14 827), 342 (4151). IR ν_{max}^{film} cm^{-1}: 3400, 1670, 1610, 1440, 1490. EIMS (probe) 70 eV *m/z* (rel. int.): 344 $[M]^+$ (49.0), 196 $[C_9H_8O_5]^+$ (100), 181 $[C_9H_8O_5 - Me]^+$ (13.4), 153 $[C_9H_8O_5 - Me - CO]^+$ (47.2), 148 $[C_9H_8O_2]^+$ (21.9). (Found: C, 62.69; H, 4.73; O, 32.2. $C_{18}H_{16}O_7$ requires: C, 62.79; H, 4.68; O, 32.53.)

Agestricin C (**3a**). Fraction 6 eluted with EtOAc (6.8 g) was chromatographed on Si gel (100 g). Chromatography fractions eluted with petrol–EtOAc (6:4) afforded 180 mg **3a**, mp 159–160° from $CHCl_3$–Et_2O. $[\alpha]_D$ + 2.9° (MeOH; *c* 0.104). UV λ_{max}^{MeOH} nm (ϵ): 235 (26 550), 277 (17 325), 340 (4950). IR ν_{max}^{film} cm^{-1}: 3400, 1667, 1608, 1450, 1490, 1512. EIMS (probe) 70 eV *m/z* (rel. int.): 360 $[M]^+$ (63.8), 196 $[C_9H_8O_5]^+$ (100), 181 $[C_9H_8O_5 - Me]^+$ (7.3), 153 $[C_9H_8O_5 - Me - CO]^+$ (18), 164 $[C_{10}H_{12}O_2]^+$ (36.3). (Found: C, 63.51; H, 5.68; O, 30.7. $C_{19}H_{20}O_7$ requires: C, 63.33; H, 5.59; O, 31.08.)

Agestricin D (**3c**). Fractions 12 and 13 eluted with petrol–EtOAc (6:4), after purification by prep. TLC afforded 130 mg **3a** and 40 mg **3c**. Agestricin D (**3c**) was crystallized from Me_2CO–Et_2O, mp 180–182°. $[\alpha]_D$ + 12° (MeOH; *c* 0.1). UV λ_{max}^{MeOH} nm (ϵ): 235 (14 338), 277 (10 100), 342 (2970). IR ν_{max}^{KBr} cm^{-1}: 3350, 1670, 1605, 1450, 1490. EIMS (probe) 70 eV *m/z* (rel. int.): 346 $[M]^+$ (79.7), 196 $[C_9H_8O_5]^+$ (100), 197 $[C_9H_9O_5]^+$ (65.5), 181 $[C_9H_8O_5 - Me]^+$ (14.1), 153 $[C_9H_8O_5 - Me - CO]^+$ (26.4), 150 $[C_9H_{10}O_2]^+$ (12.6).

Agestricin A dimethyl ether (**1b**). A 20 mg sample of **1a** with Me_2SO_4 (0.3 ml) in dry Me_2CO (20 ml) and dry K_2CO_3 (300 mg) was refluxed for 24 hr and worked-up as usual to give, after prep. TLC purification (petrol–Et_2O, 2:3, twice), the dimethyl ether **1b**, mp 108–110° (Et_2O). UV λ_{max} nm (ϵ): 298 sh (11 267), 342 (20 853). IR ν_{max}^{film} cm^{-1}: 1640, 1600, 1445, 1490. EIMS (probe) 70 eV *m/z* (rel. int.): 372 $[M]^+$ (100), 357 $[M - Me]^+$ (20.7), 341 $[M - OMe]^+$ (14.6), 310 $[M - 2 \times OMe]^+$ (15.8), 225 $[C_{11}H_{13}O_5]^+$ (19.5), 147 $[C_9H_7O_2]^+$ (6).

Agestricin B acetate (**2b**). Acetylation of 50 mg **2a**, with Ac_2O–C_5H_5N as usual, gave the monoacetate, **2b**, mp 215–216° (MeOH). $[\alpha]_D$ + 18.7° ($CHCl_3$; *c* 0.112). UV λ_{max}^{MeOH} nm (ϵ): 230 sh (25 733), 274 (18 906), 313 (5105). IR ν_{max}^{film} cm^{-1}: 1760, 1680, 1608, 1565, 1485, 1440. EIMS (probe) 70 eV *m/z* (rel. int.): 386 $[M]^+$ (10.9), 344 $[M - 42]^+$ (32.7), 196 $[C_9H_8O_5]^+$ (100), 181 $[C_9H_8O_5 - Me]^+$ (8.5), $[C_9H_8O_5 - Me - CO]^+$ (18.7), 148 $[C_9H_8O_2]^+$ (25.5), 147 $[C_9H_7O_2]^+$ (19.6), 43 $[Ac]^+$ (14.6).

Agestricin B methyl ether (**2c**). Methylation of 250 mg **2a** with Me_2SO_4 afforded 230 mg of the methyl ether, **2c**, after crystallization from MeOH, mp 181–182°. $[\alpha]_D$ – 2.0° ($CHCl_3$; *c* 0.2). UV λ_{max}^{MeOH} nm (ϵ): 233 (22 822), 278 (17 363), 320 (4430). IR ν_{max}^{film} cm^{-1}: 1670, 1600, 1565, 1500, 1450. EIMS (probe) 70 eV *m/z* (rel. int.): 358 $[M]^+$ (43.9), 210 $[C_{10}H_{10}O_5]^+$ (100), 195 $[C_{10}H_{10}O_5 - Me]^+$ (93.9), 167 $[C_{10}H_{10}O_5 - Me - CO]^+$ (84.8), 148 $[C_9H_8O_2]^+$ (25.6), 147 $[C_9H_7O_2]^+$ (23.9).

Agestricin B ethyl ether (**2d**). Ethylation of 100 mg of **2a** with EtI in dry Me_2CO and dry K_2CO_3 gave the ethyl ether, **2d**, mp 161–162°. $[\alpha]_D$ – 5.8° ($CHCl_3$; *c* 0.172). UV λ_{max}^{MeOH} nm (ϵ): 233 (21 220), 277 (15 979), 320 (4142). IR ν_{max}^{film} cm^{-1}: 1670, 1600, 1565, 1450. EIMS (probe) 70 eV *m/z* (rel. int.): 372 $[M]^+$ (38.2), 343 $[M - Et]^+$ (10.2), 224 $[C_{11}H_{12}O_5]^+$ (35.3), 195 $[C_{11}H_{12}O_5 - Et]^+$ (100), 167 $[C_{11}H_{12}O_5 - Et - CO]^+$ (50.4), 148 $[C_9H_8O_2]^+$ (14.1), 147 $[C_9H_7O_2]^+$ (18.2).

Agestricin A monomethyl ether (**1c**). A 100 mg sample of **2c** was dissolved in the minimum quantity of 50% KOH in EtOH. After 5 min the reaction mixture was acidified with cold dil. HCl and extracted with EtOAc. After elimination of the solvent the residue was crystallized from $CHCl_3$–Et_2O to give the chalcone, **1c**, mp 129–130°. UV λ_{max}^{MeOH} nm (ϵ): 310 sh (2692), 371 (27 338). IR ν_{max}^{film} cm^{-1}: 1620, 1610, 1550, 1485, 1440. EIMS (probe) 70 eV *m/z* (rel. int.): 358 $[M]^+$ (62.9), 210 $[C_{10}H_{11}O_5]^+$ (78), 195 $[C_{10}H_{11}O_5 - Me]^+$ (100), 167 $[C_{10}H_{11}O_5 - Me - CO]^+$ (46.2), 148 $[C_9H_8O_2]^+$ (10.9).

Alkaline degradation of **1c**. Compound **1c** (100 mg) was refluxed with 50% KOH (20 ml) in EtOH (10 ml) under N_2 for 24 hr. The reaction mixture was cooled, acidified with dil. HCl and extracted with EtOAc. The EtOAc extract washed with H_2O, dried (Na_2SO_4), distilled *in vacuo* and purified by prep. TLC ($CHCl_3$–Me_2CO, 95:5). The less polar degradation product was identified as 6-hydroxy-2, 3, 4-trimethoxyacetophenone (**4a**), previously obtained from agecorynin A [1]. The more polar product was piperonyl alcohol (**5a**) [7]. **1c** and small amounts of piperonylic aldehyde (**5b**) [7] were also identified.

Alkaline degradation of agestricin B (**2a**). Degradation of 200 mg **2a** under the same conditions as above afforded after prep. TLC ($CHCl_3$–Me_2CO, 9:1, ×2) an acetophenone which was identified as 3, 6-dihydroxy-2, 4-dimethoxyacetophenone (**4b**), by comparison with a synthetic sample [5], mp 158–159° (lit. 162° [6]). UV λ_{max} nm (ϵ): 212 (9769), 239 (7897), 282 (8939), 350 (3286). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550, 1626, 1610, 1485, 1440. ^1H NMR (80 MHz, $CDCl_3$): δ 2.67 (3H, *s*, COMe), 3.87 (3H, *s*, OMe), 3.92 (3H, *s*, OMe), 5.07 (1H, *s*, 3-OH), 6.21 (1H, *s*, H-5), 13.05 (1H, *s*, 6-OH). EIMS (probe) 70 eV *m/z* (rel. int.): 212 $[M]^+$ (100), 197 $[M - Me]^+$ (90.2), 182 $[M - OCH_2]^+$ (24.8), 151 $[M - OCH_2 - OMe]^+$ (20.7). From the less polar fraction after further prep. TLC (petrol–Et_2O, 2:3, ×3) agestricin A (**1a**) was also isolated as well as tiny amounts of piperonylic aldehyde (**5b**) [7]. From the more polar fractions, piperonyl alcohol (**5a**) [7] and piperonylic acid (**5c**) [7] were identified.

Agestricin C acetate (**3b**). A 30 mg sample of agestricin C (**3a**) acetylated with Ac_2O–C_5H_5N as usual gave the monoacetate **3b** (25 mg), mp 182–183°. $[\alpha]_D$ + 22.6° ($CHCl_3$; *c* 0.084). UV λ_{max}^{MeOH} nm (ϵ): 230 (21 607), 273 (12 562), 314 (3266). IR ν_{max}^{film} cm^{-1}: 1760, 1675, 1605, 1565, 1515. EIMS (probe) 70 eV *m/z* (rel. int.): 402 $[M]^+$ (10.9), 360 $[M - C_2H_2O]^+$ (30.1), 196 $[C_9H_8O_5]^+$ (100), 181 $[C_9H_8O_5 - Me]^+$ (6.09), 153 $[C_9H_8O_5 - Me - CO]$ (17.07), 164 $[C_{10}H_{12}O_2]$ (36.5), 43 $[C_2H_3O]^+$ (17.07).

Agestricin D diacetate (**3d**). Acetylation of 10 mg **3c** gave the diacetate, **3d**, mp 180–182°. $[\alpha]_D$ + 7.9° ($CHCl_3$; *c* 0.063).

UV λ_{max}^{MeOH} nm (ϵ): 218 (23 381), 273 (13 437), 314 (3661). IR ν_{max}^{film} cm^{-1}: 1760, 1675, 1605, 1565. EIMS (probe) 70 eV *m/z* (rel. int.): 430 $[M]^+$ (2.6), 388 $[M - C_2H_2O]^+$ (34.9), 346 $[M - 2 \times C_2H_2O]^+$ (12.1), 196 $[C_9H_8O_5]^+$ (100), 181 $[C_9H_8O_5 - Me]^+$ (7.8), 153 $[C_9H_8O_5 - Me - CO]^+$ (17.07), 150 $[C_9H_{10}O_2]^+$ (12.1), 43 $[C_2H_3O]^+$ (15.8).

Alkaline degradation of agestricin D (**3c**). A 30 mg sample of agestricin D (**3c**) treated under the same conditions as described before, afforded the same acetophenone, **4b**, and 4-hydroxy-3-methoxy benzaldehyde (vainillin) which was identified by comparison with an authentic sample.

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