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TRITERPENES FROM *MICONIA STENOSTACHYA*

WILFRED R. CHAN, VERONICA SHEPPARD, KATHLEEN A. MEDFORD,

Department of Chemistry, The University of the West Indies, St. Augustine, Trinidad and Tobago

WINSTON F. TINTO, WILLIAM F. REYNOLDS, and STEWART MCLEAN*

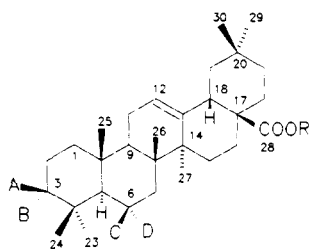
Department of Chemistry, University of Toronto, Toronto M5S 1A1, Canada

ABSTRACT.—Sumaresinolic acid [**1**] and 3-*epi*-sumaresinolic acid [**2**], a new natural product, have been isolated from *Miconia stenostachya* (Melastomataceae). The ^{13}C and ^1H chemical shifts of these compounds and a number of their derivatives have been assigned from 2D nmr spectra in which the FLOCK pulse sequence was used to establish 2- and 3-bond ^1H - ^{13}C connectivities.

Miconia stenostachya DC. (Melastomataceae) is a common shrub in Trinidad and belongs to a family that has species of medicinal value. Extraction of the leaves provided the known sumaresinolic acid [**1**] (**1**) and 3-*epi*-sumaresinolic acid [**2**], which has not previously been reported. Both compounds were converted to their methyl esters, **3** and **4**, respectively, by the action of CH_2N_2 in order to facilitate characterization. Selective acetylation of the 3-OH by treatment with cold Ac_2O in pyridine converted **3** to **5** and **4** to **6**. Pyridinium chlorochromate (PCC) oxidized the alcohols **5** and **6** to the ketones **7** and **8**. Oxidation of the diols **3** and **4** converted both to the same dione **9**. It follows that **1** and **2** dif-

fer in the configuration at C-3, and that **2** is 3-*epi*-sumaresinolic acid. In the derivatives **4**, **6**, and **8** of 3-*epi*-sumaresinolic acid, the nmr signal for H-3 appeared as a narrow unresolved multiplet with no large coupling constants, in accord with equatorial stereochemistry assigned to this hydrogen, while the corresponding signals in the derivatives of sumaresinolic acid were well resolved and clearly showed axial-axial (10 to 12 Hz) and axial-equatorial (4 to 6 Hz) couplings. The H-6 appeared as a narrow unresolved multiplet in both series, confirming the stereochemistry assigned at that center.

The derivatives **3**–**9** of sumaresinolic acid and its epimer were studied using 2D nmr spectroscopy: the standard HETCOR experiment showed all direct (one-bond) ^{13}C - ^1H connectivities, and two- and three-bond connectivities were established in experiments using our FLOCK pulse sequence (2), which has been shown to be particularly useful for structural investigations of natural products (3). The ^{13}C and ^1H chemical shift assignments made from these investigations are listed in Tables 1 and 2, respectively.



	A	B	C	D	R
1	HO	H	HO	H	H
2	H	HO	HO	H	H
3	HO	H	HO	H	Me
4	H	HO	HO	H	Me
5	AcO	H	HO	H	Me
6	H	AcO	HO	H	Me
7	AcO	H	-O-		Me
8	H	AcO	-O-		Me
9	-O-		-O-		Me

EXPERIMENTAL

PLANT MATERIAL.—*M. stenostachya* was collected in August 1986, at Santa Rosa Heights, Arima, Trinidad. It was identified at the National Herbarium, Department of Chemistry, University of the West Indies, St. Augustine, where a voucher specimen is lodged.

TABLE 1. Assigned ^{13}C Chemical Shifts for Compounds 3-9.^a

Carbon	Compound						
	3	5	7	9	4	6	8
C-1	40.55	40.23	38.60	40.27	35.21	36.50	33.91
C-2	27.36	23.71	23.29	33.62	25.13	22.60	22.41
C-3	79.09	80.83	79.99	214.46	77.36	79.57	78.33
C-4	39.53	38.38	36.53	46.93	38.09	37.27	35.78
C-5	55.64	55.64	64.97	65.16	49.07	50.49	60.75
C-6	68.67	68.53	211.43	211.14	68.93	68.58	212.90
C-7	40.72	40.78	50.49	50.31	40.53	40.67	50.64
C-8	38.62	38.56	46.13	46.07	38.45	38.50	46.32
C-9	47.90	47.83	47.78	47.52	47.52	47.64	47.90
C-10	36.49	36.46	42.87	42.74	36.57	35.95	43.03
C-11	23.28	23.28	23.78	23.80	23.11	23.16	24.02
C-12	122.68	122.61	121.92	121.64	122.68	122.68	122.30
C-13	142.88	142.88	143.30	143.43	142.77	142.85	143.53
C-14	42.22	42.20	41.89	41.93	42.16	42.22	42.21
C-15	27.65	27.63	27.57	27.59	27.52	27.65	27.86
C-16	23.03	23.01	22.83	22.78	22.96	23.05	23.13
C-17	46.73	46.73	46.61	46.56	46.71	46.71	46.88
C-18	41.33	41.33	41.19	41.16	41.20	41.31	41.48
C-19	45.84	45.79	45.62	45.62	45.76	45.90	45.99
C-20	30.71	30.71	30.71	30.68	30.65	30.69	30.95
C-21	33.86	33.86	33.79	33.74	33.80	33.86	34.06
C-22	32.37	32.36	32.18	32.12	32.34	32.36	32.44
C-23	27.88	25.90	27.48	24.22	28.34	27.98	26.90
C-24	17.02	18.28	16.38	21.79	24.38	24.04	22.14
C-25	16.82	16.87	16.41	15.71	16.53	16.54	16.46
C-26	18.21	18.21	17.21	17.32	18.08	18.16	17.60
C-27	25.96	25.85	26.34	26.31	26.08	26.08	26.72
C-28	178.21	178.22	177.95	177.88	178.26	178.29	178.16
C-29	33.11	33.10	33.09	33.06	33.08	33.10	33.34
C-30	23.61	23.62	23.63	23.60	23.59	23.60	23.87
OCH ₃	51.58	51.57	51.62	51.63	51.54	51.57	51.86
CH ₃ CO	—	21.34	21.22	—	—	21.36	21.51
MeCO	—	171.02	170.97	—	—	170.75	170.60

^aSpectra were obtained at 100.6 MHz with solutions in CDCl_3 . All assignments are based on one-bond ^1H - ^{13}C shift-correlated 2D spectra (HETCOR) to establish direct connectivities and 2- and 3-bond shift-correlated spectra (FLOCK) to determine indirect connectivities. Listings of connectivity data are available from authors at the Toronto address.

EXTRACTION AND ISOLATION.—Dried leaves (1.5 kg) were ground and exhaustively extracted with 95% EtOH, and evaporation of the solvent provided a dark gum (39 g), which was re-dissolved in 90% MeOH. The solution was extracted with petroleum ether and then with EtOAc, and the EtOAc extract gave a residue (19.6 g). A fraction obtained on cc [Si gel, CHCl_3 -MeOH (13:1 to 4:1 gradient)] was separated by preparative tlc [petroleum ether-Me₂CO (3:1)] into sumaresinolic acid [**1**] (88 mg) and 3-*epi*-sumaresinolic acid [**2**] (310 mg). Each compound was treated with CH_2N_2 in Et_2O and converted to its methyl ester.

Methyl sumaresinolate [**3**].—Mp 223–224° [lit.

(4) 222–223.5°]; [α]_D +67.8° (c = 0.2, CHCl_3); ir 3444, 1722; eims 486 (6), 468 (5), 302 (6), 262 (62), 233 (8), 203 (100), 189 (33), 133 (23); hreims 486.3698, calcd for $\text{C}_{31}\text{H}_{50}\text{O}_4$, 486.3709. Treatment with Ac_2O /pyridine at room temperature gave 3-monoacetate **5**: mp 224–226° [lit. (4) 222–225°]; [α]_D +45.1° (c = 0.16, CHCl_3); ir 3452, 1722, 1717; eims 528 (2), 468 (6), 450 (7), 302 (5), 262 (63), 233 (6), 203 (100), 133 (35); hreims 528.3810, calcd for $\text{C}_{33}\text{H}_{52}\text{O}_5$, 528.3815.

*Methyl 3-*epi*-sumaresinolate* [**4**].—Mp 223–224°, [α]_D +29.8° (c = 0.7, CHCl_3); ir 3465, 1722; eims 486 (3), 468 (3), 302 (4), 262 (74),

TABLE 2. Assigned ^1H Chemical Shifts for Compound 3-9.^a

Proton	Compound						
	3	5	7	9	4	6	8
H-1	1.58 0.98	1.59 1.04	1.72 1.32	2.04 1.57	<1.31>	1.35 1.17	<1.44>
H-2	<1.64> ^b	1.72 1.61	<1.64>	2.78 2.19	2.02 1.52	1.97 1.58	1.89 1.63
H-3	3.17	4.44	4.41	—	3.37	4.61	4.52
H-5	0.74	0.84	2.22	2.45	1.33	1.26	2.55
H-6	4.56	4.54	—	—	4.43	4.47	—
H-7	1.59 1.49	1.72 1.61	2.46 1.86	2.47 1.91	1.75 1.45	1.77 1.46	2.51 1.87
H-9	1.58	1.60	2.11	2.15	1.71	1.69	2.21
H-11	<1.96>	2.03 1.89	<1.98>	<2.03>	<1.97>	<1.97>	<1.97>
H-12	5.34	5.34	5.34	5.35	5.34	5.34	5.36
H-15	1.66 1.06	1.64 1.04	1.57 0.96	1.58 0.95	1.65 1.04	1.65 1.05	1.59 0.96
H-16	1.96 1.62	1.96 1.61	1.98 1.63	1.98 1.64	1.96 1.61	1.96 1.61	1.99 1.64
H-18	2.89	2.88	2.90	2.90	2.88	2.89	2.90
H-19	1.64 1.16	1.63 1.16	1.62 1.18	1.61 1.16	1.63 1.16	1.65 1.15	1.64 1.17
H-21	1.33 1.19	1.33 1.18	1.34 1.20	1.34 1.19	1.33 1.18	1.33 1.18	1.35 1.20
H-22	1.69 1.52	1.69 1.51	1.69 1.53	1.69 1.53	1.69 1.51	1.69 1.51	1.69 1.53
H-23	1.07	1.09	0.94	1.09	1.03	0.93	0.90
H-24	1.18	1.24	1.29	1.49	1.22	1.28	1.31
H-25	1.30	1.32	0.95	1.20	1.30	1.32	0.94
H-26	1.03	1.02	0.77	0.82	1.01	1.03	0.78
H-27	1.11	0.94	1.25	1.24	1.11	1.16	1.31
H-29	0.90	0.89	0.91	0.90	0.90	0.89	0.91
H-30	0.94	0.92	0.93	0.93	0.92	0.93	0.93
OCH ₃	3.63	3.62	3.61	3.62	3.62	3.63	3.62
CH ₃ CO	—	2.06	2.05	—	—	2.06	2.07

^aSpectra were obtained at 400 MHz with solutions in CDCl₃.

^bThe δ_{H} for each identifiable proton (or methyl) is listed; the <mean δ_{H} > is reported for incompletely resolved CH₂ multiplets.

233 (5), 203 (100), 189 (50), 133 (28); hreims 486.3686, calcd for C₃₃H₅₀HO₄, 486.3709. On treatment with Ac₂O in pyridine at room temperature, 3-monoacetate **6** formed: mp 145–147°; $[\alpha]_{\text{D}} + 1.6^\circ$ ($c = 0.3$, CHCl₃); ir 3444, 1721, 1718; eims 528 (3), 468 (10), 450 (7), 302 (6), 262 (65), 233 (7), 203 (100), 133 (23); hreims 528.3797, calcd for C₃₃H₅₂O₅, 528.3815.

OXIDATIONS.—A solution of the monoacetate **5** (16 mg) in 1 ml of CH₂Cl₂ was added to a stirred suspension of PCC (20 mg) in 2 ml of CH₂Cl₂. After 1 h, 10 ml of Et₂O was added, and the mixture was filtered through Florisil. Chromatography [Si gel, hexane-Me₂CO (4:1)] of the product gave the monoketone **7** (13 mg): mp 286–288°; $[\alpha]_{\text{D}} + 51.4^\circ$ ($c = 0.06$, CHCl₃); ir

1722, 1714; eims 526 (5), 466 (15), 407 (18), 302 (5), 262 (48), 203 (100), 133 (29); hreims 526.3656, calcd for C₃₃H₅₀O₅, 526.3658.

Oxidation of the monoacetate **6** (65 mg) by the same procedure converted it to the monoketone **8** (58 mg), glass: $[\alpha]_{\text{D}} + 8.6^\circ$ ($c = 0.5$, CHCl₃); ir 1718; eims 526 (2), 466 (18), 407 (13), 302 (5), 262 (48), 203 (100), 133 (24); hreims 526.3685, calcd for C₃₃H₅₀O₅, 526.3658.

The same oxidation conditions converted the diols **3** (20 mg) and **4** (80 mg) to the same diketone **9** (17 mg and 76 mg, respectively): mp 188–190°, $[\alpha]_{\text{D}} + 27.1^\circ$ ($c = 0.3$, CHCl₃); ir 1722, 1709; ms 482 (20), 423 (27), 302 (5), 262 (36), 233 (11), 203 (100), 189 (42), 133 (26); hreims 482.3392, calcd for C₃₁H₄₆O₄, 482.3396.

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