Peritassines A and B, New Sesquiterpene Alkaloïds from Peritassa compta

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PERITASSINES A AND B, NEW SESQUITERPENE ALKALOIDS FROM *PERITASSA COMPTA*

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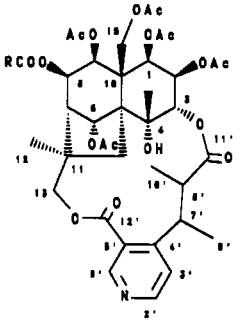
ABSTRACT.—Two new sesquiterpene alkaloids, peritassines A [**1**] and B [**2**], and the known compounds euonine [**3**], ebenifoline W-I [**4**], euojaponine F [**5**], and wilforine [**6**], were isolated from the stems and bark of *Peritassa compta*. The structures of **1** and **2** were elucidated by high resolution nmr spectroscopy.

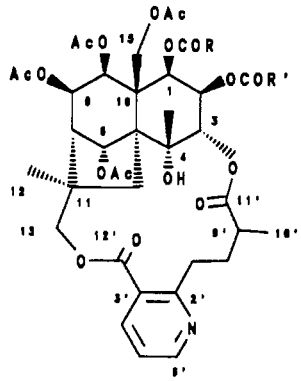
Plants belonging to the family Celastraceae are a rich source of polyester-type sesquiterpene alkaloids. These alkaloids have attracted much attention mainly due to their potent insecticidal and antitumor activities (1,2). In the course of an investigation of the medicinal plants of Guyana, we have examined extracts of the stems and bark of the vine *Peritassa compta* Miers (Celastraceae), from which we have isolated six alkaloids. This plant appears not to have been previously investigated.

Peritassines A [**1**] and B [**2**] appear to be completely new compounds, while euonine [**3**], ebenifoline W-I [**4**], euojaponine F [**5**], and wilforine [**6**] have been described previously (1–4). Compounds **3–6** had spectroscopic data in agreement with literature data (1–4).

Peritassine A [**1**], $C_{38}H_{47}NO_{18}$, was isolated as colorless crystals, mp 116–117°. The ir spectrum showed absorptions due to OH (3459 cm^{-1}) and ester (1743 cm^{-1}) groups. The ^{1}H-nmr spectrum had six acetyl singlets at δ 1.84, 2.00, 2.16, 2.17, 2.21, and 2.32. Oxymethine protons at δ 5.51, 5.20, and 4.70 were assigned to H-1, H-2, and H-3, while signals at δ 7.04, 2.33, 5.49, and 5.34 were assigned to H-6, H-7, H-8, and H-9, on the basis of a ^{1}H-^{1}H COSY experiment. Resonances at δ 9.02 (s), 8.71 (d, J=5.7 Hz), and 7.50 (d, J=5.7 Hz), along with two methyl doublets at δ 1.07 (7.1 Hz) and 1.38 (6.8 Hz), led to a



1 R=Me
2 R=Ph



3 R=Me, R′=Me
4 R=Ph, R′=Ph
5 R=Ph, R′=Me
6 R=Me, R′=Ph

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structure for the dibasic acid moiety that was isomeric with evoninic acid. The assignment of this acid moiety was achieved by an analysis of the HMQC and HMBC spectra of the more abundant peritassine B [**2**]. On the basis of the foregoing evidence, structure **1** is proposed for peritassine A.

Peritassine B [**2**], $C_{43}H_{49}NO_{18}$, was isolated as an amorphous powder, mp 148–150°. The ir spectrum was similar to that of **1** and had absorptions at 3459, 1748, and 1726 cm^{-1}. The ^1H-nmr spectrum had five acetyl resonances at δ 1.82, 1.98, 2.06, 2.13, and 2.17. The presence of a benzoyl group was evident from resonances at δ 8.11 (ortho), 7.48 (meta), and 7.60 (para). Resonances at δ 9.01 (s), 8.72 (d, J=5.0 Hz), and 7.37 (d, J=5.0 Hz) indicated that the pyridine ring of the dibasic acid was 4′,5′-disubstituted instead of the usual 2′,3′ as in evoninic acid. However, because of the small amounts of alkaloids isolated, the structure of the dibasic acid was not determined by methanolysis. The substitution pattern in the pyridine ring, as well as in the substituents, was determined

TABLE 1. Nmr Spectral Data for Peritassines A [**1**] and B [**2**] in $CDCl_3$ solution (values in parentheses refer to coupling constants in Hertz).

Position	Compound			
	1[a]		**2**[b]	
	δ_C	δ_H	δ_C	δ_H
1	73.33	5.51 (3.9)	73.49	5.58 (3.8)
2	68.66	5.20 (3.9, 2.6)	68.70	5.24 (3.8, 2.6)
3	75.86	4.70 (2.6)	75.89	4.74 (2.6)
4	70.41	4.64 (<1) (OH)	70.75	4.88 (1.0) (OH)
5	94.28	—	94.15	—
6	73.68	7.04	73.90	7.19
7	50.57	2.33 (4.2)	50.94	2.57 (3.9)
8	68.92	5.49 (6.1, 4.2)	70.01	5.68 (6.0, 3.9)
9	70.54	5.34 (6.1)	70.75	5.48 (6.0)
10	52.09	—	51.98	—
11	84.30	—	84.27	—
12	18.48	1.68	18.57	1.76
13	70.29	6.03 (11.8), 3.71 (11.8)	70.20	6.07 (11.8), 3.74 (11.8)
14	22.78	1.53 (<1)	22.60	1.53 (1.0)
15	59.94	5.10 (13.6), 4.45 (13.6)	60.37	5.27 (13.6), 4.38 (13.6)
2′	152.91	8.71 (5.71)	152.92	8.72 (5.0)
3′	121.49	7.50 (5.7)	121.49	7.37 (5.0)
4′	156.42	—	156.41	—
5′	125.20	—	125.22	—
6′	150.91	9.02	150.91	9.01
7′	33.39	4.74 (6.8)	33.33	4.73 (7.0)
8′	45.64	2.42 (7.1)	45.64	2.47 (7.3)
9′	11.33	1.38 (6.8)	11.34	1.38 (7.0)
10′	10.01	1.07 (7.1)	10.02	1.09 (7.3)
11	173.58	—	173.52	—
12′	167.96	—	168.00	—

[a]δ_C at 100.6 MHz, δ_H at 400 MHz. Acetates: C=O δ 168–171, CH_3CO δ 21.64, 21.32, 21.02, 21.02, 20.48, 20.39.

[b]δ_C at 125.8 MHz, δ_H at 500 MHz. Bz C=O δ_C (δ_H) 166.21, ipso 129.58, ortho 129.94 (8.11), meta 128.58 (7.48), para 133.69 (7.60). Acetates: C-1 δ 169.10, 20.59, (1.98), C-2 168.69, 21.64 (2.13), C-6 169.88, 20.99 (2.17), C-9 169.10, 20.42 (1.82), C-15 170.82, 21.29 (2.06).

from correlations observed in the COSY, HMQC, and HMBC spectra (Table 1). In the HMBC spectrum, the C-4′ resonance at δ 156.41 showed correlations with H-7′ (δ 4.74) and H_3-9 (δ 1.38). The 2D experiments also led to the placement of the benzoyl group at C-8 and assignment of the acetates. Recently, a sesquiterpene alkaloid containing an isowilfordic acid moiety was isolated from *Tripterygium wilfordii* (5).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were determined on a Kofler hot stage. Ir spectra were obtained on a Nicolet 5DX Ft-ir spectrometer with samples dissolved in $CHCl_3$. Uv spectra were obtained on a Cary 14UV spectrophotometer with solutions in MeOH. Nmr spectra were obtained on a Varian XL-400 spectrometer at 400 MHz for ^1H and 100.6 MHz for ^{13}C or on a Varian Unity 500 MHz spectrometer at 500 MHz for ^1H and 125.8 MHz for ^{13}C. A VG 70-250S mass spectrometer (70 eV) was used to obtain the ms.

PLANT MATERIAL.—Plant material was collected at Mabura Hills, Linden, Guyana, in March 1990. Voucher specimens have been deposited in the Herbarium of the University of Guyana.

EXTRACTION AND ISOLATION.—Dried stems and bark (3.3 kg) were ground and extracted with EtOAc, and evaporation at reduced pressure gave a light brown residue (22.7 g), which was separated into five major fractions by chromatography on Si gel with hexane/EtOAc elution. The most polar fraction was rechromatographed on the same system, and the most polar fraction obtained from this separation was subjected to hplc (C_{18} column) with MeOH-H_2O (3:1). Euonine [**3**] (1.5 mg), peritassine A [**1**] (1.0 mg), ebenifoline W-I [**4**] (13 mg), euojaponine F [**5**] (7.5 mg), wilforine [**6**] (6 mg), and peritassine B [**2**] (8.5 mg), were eluted in order. Compounds **3–6** had physical and spectroscopic data identical (mp, ir, nmr, ms) with literature values (1–4).

Peritassinie A [**1**].—Colorless crystals, mp 116–117°; $[\alpha]_D$ +24.6° (c=0.07, $CHCl_3$); ir 3459, 1743, 1586, 1525 cm^{-1}; uv 230 nm (ε 5500), 267 nm (ε 1300); eims $[M]^+$ 805 (25%), 791 (17), 762 (8), 746 (31), 688 (13), 206 (51), 178 (53), 107 (100); exact mass 805.2850 (calcd for $C_{38}H_{47}NO_{18}$, 805.2793); ^1H and ^{13}C nmr see Table 1.

Peritassine B [**2**].—Mp 148–150°; $[\alpha]_D$ −39.2° (c=0.13, $CHCl_3$); ir 3459, 1748, 1726, 1604, 1590, 1552, 1235 cm^{-1}; uv 231 nm (ε 7400), 268 nm (ε 1800); eims $[M]^+$ 867 (27%), 852 (29), 824 (7), 808 (24), 794 (27), 206 (32), 178 (39), 105 (100); exact mass 867.3010 (calcd for $C_{43}H_{49}NO_{18}$, 867.2950); ^1H and ^{13}C nmr see Table 1.

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