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FRIEDELANE TRITERPENOIDS FROM *PERITASSA COMPTA*: COMPLETE ^1H AND ^{13}C ASSIGNMENTS BY 2D NMR SPECTROSCOPYJOY KLASS, WINSTON F. TINTO,*¹

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ABSTRACT.—An investigation of the stems and bark of *Peritassa compta* has led to the isolation of three new natural products, friedelane-3,15-dione [**3**], 15 α -hydroxyfriedelin [**4**], and 15 α -hydroxyfriedelane-1,3-dione [**5**], along with friedelin [**1**] and friedelane-1,3-dione [**2**]. Complete ^1H and ^{13}C assignments for all compounds were achieved by 2D nmr spectroscopy.

Peritassa compta Miers (Celastraceae) is a vine that is endemic to Guyana and appears not to have received previous phytochemical investigation. In a continuing investigation of Guyanese medicinal plants we describe herein the isolation of five friedelane (1–5) triterpenes of *P. compta*.

The ^1H -nmr spectra of all five compounds had signals due to one secondary and seven quaternary methyls, suggesting that they all had the friedelane skeleton. A standard HETCOR experiment was used to establish connectivity between carbons and their directly attached protons, while two- and three-bond correlations were determined using the FLOCK pulse sequence (6). Complete ^1H and ^{13}C assignments are shown in Tables 1 and 2, respectively.

Compounds **1** and **2** were identified as friedelin and friedelane-1,3-dione, respectively (1,7). Compound **3**, mp 269–271 $^\circ$, was isomeric with friedelane-1,3-dione [**2**] (7). In the FLOCK experiment, a carbonyl resonance at δ 213.06 showed correlation with the secondary methyl at δ 0.89 ($J = 6.5$ Hz), while the second carbonyl, at δ 214.14, showed correlations with the C-26 methyl singlet at δ 1.22. These results indicated that compound **3** was friedelane-3,15-dione; **3** was previously obtained as an ozonolysis product of friedelin (8).

Compound **4**, $\text{C}_{30}\text{H}_{50}\text{O}_2$, mp 275–276 $^\circ$, had ir absorptions at 3459 cm^{-1} (OH) and 1704 cm^{-1} (CO). The ^1H -nmr spectrum had a resonance due to an oxymethine proton at δ 3.73 ($J = 8.5, 2.5$ Hz), which was assigned to C-15 on the basis of the



- 1** $\text{R}^1 = \text{R}^2 = \text{H}_2$
2 $\text{R}^1 = \text{O}, \text{R}^2 = \text{H}_2$
3 $\text{R}^1 = \text{H}_2, \text{R}^2 = \text{O}$
4 $\text{R}^1 = \text{H}_2, \text{R}^2 = \text{H}, \alpha\text{-OH}$
5 $\text{R}^1 = \text{O}, \text{R}^2 = \text{H}, \alpha\text{-OH}$

- 6** $\text{R} = \text{H}$
7 $\text{R} = \text{OH}$

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TABLE 1. ^1H -nmr Assignments for Compounds 1–5 in CDCl_3 Solutions.^a

Proton	Compound				
	1	2	3	4	5
H-1	1.96, 1.68	—	1.95, 1.68	1.94, 1.68	—
H-2	2.39, 2.28	3.46, 3.24	2.40, 2.28	2.40, 2.28	3.46, 3.25
H-4	2.25	2.58	2.30	2.24	2.58
H-6	1.75, 1.28	1.90, 1.39	1.70, 1.54	1.78, 1.31	1.92, 1.42
H-7	1.49, 1.37	1.54, 1.43	1.80, 1.33	1.82, 1.53	1.92, 1.61
H-8	1.39	1.25	1.85	1.49	1.35
H-10	1.53	2.38	1.60	1.51	2.38
H-11	1.46, 1.26	2.15, 1.14	1.46, 1.18	1.50, 1.24	2.19, 1.11
H-12	1.34, 1.34	1.41, 1.41	1.51, 1.51	1.50, 1.24	1.55, 1.29
H-15	1.46, 1.27	1.52, 1.27	—	3.73	3.70
H-16	1.57, 1.36	1.56, 1.35	2.52, 2.19	2.16, 1.25	2.16, 1.25
H-18	1.56	1.57	1.86	1.59	1.60
H-19	1.38, 1.20	1.36, 1.41	1.49, 1.41	1.31, 1.14	1.29, 1.15
H-21	1.51, 1.30	1.46, 1.27	1.50, 1.28	1.46, 1.28	1.45, 1.28
H-22	1.50, 0.94	1.49, 0.94	1.73, 1.10	1.37, 0.97	1.38, 0.97
H-23	0.87	1.05	0.89	0.87	1.05
H-24	0.71	0.69	0.73	0.72	0.69
H-25	0.86	1.20	0.90	0.88	1.22
H-26	1.00	1.03	1.22	1.06	1.09
H-27	1.05	1.02	0.92	0.99	0.96
H-28	1.17	1.18	1.33	1.29	1.29
H-29	1.00	1.00	1.01	1.01	1.02
H-30	0.95	0.94	0.96	0.94	0.94

^aAssignments based on HETCOR and FLOCK experiments for all compounds except **2**, for which only a HETCOR experiment was done.

FLOCK experiment. Oxidation of compound **4** gave a product that was identical to **3** in all respects (mp, ir, nmr).

Compound **5**, $\text{C}_{30}\text{H}_{48}\text{O}_3$, mp 245–248°, had absorptions due to hydroxyl (3416 cm^{-1}) and carbonyl (1730 and 1704 cm^{-1}) groups in its ir spectrum. A uv absorption at 255 nm along with an AB quartet centered at δ 3.36 ($J = 18.0\text{ Hz}$) indicated that **5** was a 1,3-diketone. An oxymethine resonance at δ 3.70 ($J = 8.0, 1.5\text{ Hz}$) was assigned to C-15 by analogy with compound **4**. This assignment was confirmed by HETCOR and FLOCK experiments.

Methyl ethers **6** and **7** were prepared by treatment of compounds **2** and **5**, respectively, with CH_2N_2 . Compound **6** was determined to be 3-methoxyfriedel-2-en-1-one (**7**) on the basis of 2D nmr spectroscopy. Compound **7**, mp 291–294°, had spectroscopic data similar to **6** except for the resonance due to the secondary hydroxyl group. Complete ^1H and ^{13}C assignments for compounds **6** and **7** are shown in Table 3.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were taken on a Kofler hot stage apparatus and are uncorrected. Ir spectra were done on a Nicolet 3DX FTIR spectrometer in CHCl_3 solutions. The nmr spectra were recorded on a Varian XL-400 spectrometer in CDCl_3 solutions with TMS as an internal standard. A VG 70-250S mass spectrometer operating at 70 eV was used to obtain mass spectra.

PLANT MATERIAL.—*P. compta* 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 to give a light brown residue (22.7 g) on evaporation of the solvent. Cc of the extract on Si gel with hexane/EtOAc elution gave compounds 1–5 in that order.

TABLE 2. ^{13}C -nmr Assignments for Compounds 1-5.^a

Carbon	Compound				
	1	2	3	4	5
C-1	22.27	202.82	22.25	22.35	202.73
C-2	41.51	60.65	41.40	41.50	60.71
C-3	213.17	204.17	213.06	213.07	204.07
C-4	58.19	59.08	58.20	58.18	59.06
C-5	42.13	37.85	42.04	42.03	37.74
C-6	41.27	40.65	40.45	41.29	40.67
C-7	18.23	18.06	21.26	19.99	19.68
C-8	53.08	52.17	45.28	53.46	52.56
C-9	37.42	37.24	37.20	37.81	37.58
C-10	59.45	71.93	59.25	59.40	71.85
C-11	35.61	34.60	34.37	35.76	34.65
C-12	30.50	30.17	29.40	31.19	30.81
C-13	39.68	39.52	42.36	40.58	40.64
C-14	38.28	38.25	54.20	44.10	44.01
C-15	32.76	32.44	214.14	74.60	74.69
C-16	36.00	35.92	53.99	48.38	48.61
C-17	29.98	30.00	33.48	30.22	30.22
C-18	42.77	42.72	43.98	41.60	41.55
C-19	35.32	35.31	34.92	35.59	35.52
C-20	28.16	28.18	27.89	28.16	28.15
C-21	32.40	32.78	33.75	31.91	31.93
C-22	39.24	39.28	38.62	38.85	38.88
C-23	6.83	7.31	6.83	6.82	7.30
C-24	14.65	15.98	14.97	14.50	15.82
C-25	17.94	18.02	17.35	17.99	18.05
C-26	20.26	20.34	14.69	14.06	14.07
C-27	18.67	18.75	18.94	18.75	18.85
C-28	32.09	32.05	32.16	32.61	32.68
C-29	31.79	31.78	33.26	30.92	30.97
C-30	35.03	35.02	33.37	35.67	35.62

^aAssignments based on HETCOR and FLOCK experiments for all compounds except **2**, for which only a HETCOR experiment was done.

Friedelin [1].—Friedelin [1] was recrystallized from $\text{CHCl}_3/\text{MeOH}$ (20 mg) and had mp 260–263°; $[\alpha]_{\text{D}} -22.5^\circ$ ($c = 1.0$, CHCl_3); ir 1702 cm^{-1} (CO); eims m/z $[\text{M}]^+$ 426 (36%), 411 (32), 341 (16), 302 (36), 273 (72), 254 (40), 205 (80), 69 (100). Found $[\text{M}]^+$ 426.3839; $\text{C}_{30}\text{H}_{50}\text{O}$ requires $[\text{M}]^+$ 426.3862.

Friedelane-1,3-dione [2].—Compound **2** (160 mg): mp 270–272°; $[\alpha]_{\text{D}} +2.2^\circ$ ($c = 0.14$, CHCl_3); λ_{max} (MeOH) 218 nm (6100), 260 nm (5000); ir 1730, 1704 cm^{-1} ; eims m/z $[\text{M}]^+$ 440 (38%), 316 (71), 287 (57), 261 (20), 246 (25), 205 (33), 123 (49), 69 (100). Found $[\text{M}]^+$ 440.3636; $\text{C}_{30}\text{H}_{48}\text{O}_2$ requires $[\text{M}]^+$ 440.3654.

Friedelane-3,15-dione [3].—Compound **3** (35 mg): mp 269–271°; $[\alpha]_{\text{D}} -0.6^\circ$ ($c = 0.8$, CHCl_3); ir 1703, 1700 cm^{-1} ; eims m/z $[\text{M}]^+$ 440 (59%), 425 (67), 407 (40), 355 (64), 221 (66), 194 (95), 109 (87), 69 (100). Found $[\text{M}]^+$ 440.3637; $\text{C}_{30}\text{H}_{48}\text{O}_2$ requires $[\text{M}]^+$ 440.3654.

15 α -Hydroxyfriedelan-3-one [4].—Compound **4** (96 mg): mp 275–276°; $[\alpha]_{\text{D}} -32.1^\circ$ ($c = 0.4$, CHCl_3); ir 3450, 1704 cm^{-1} ; eims m/z $[\text{M}]^+$ 442 (22%), 425 (72), 409 (52), 355 (51), 247 (87), 229 (90), 177 (89), 109 (100). Found $[\text{M}]^+$ 442.3793; $\text{C}_{30}\text{H}_{50}\text{O}_2$ requires $[\text{M}]^+$ 442.3811.

OXIDATION OF 15 α -HYDROXYFRIEDELAN-3-ONE [4].—Compound **4** (25 mg) was dissolved in CH_2Cl_2 (2 ml) and added to a suspension of PCC (50 mg) in CH_2Cl_2 (2 ml). After stirring for 30 min, Et_2O (15 ml) was added and the material filtered through Florisil to give compound **3** (18 mg) on evaporation of the solvent; **3** was identical to an authentic sample (ir, ms, nmr).

TABLE 3. ^{13}C - and ^1H -nmr Assignments for Compounds **6** and **7**.^a

Position	(6) ^b		(7)	
	δC	δH	δC	δH
1	200.27	—	200.06	—
2	102.54	5.22	102.56	5.19
3	175.56	—	175.56	—
4	49.86	2.54	49.82	2.52
5	41.59	—	41.50	—
6	41.06	1.91, 1.30	41.07	1.92, 1.33
7	17.62	1.46, 1.46	19.29	1.82, 1.55
8	52.24	1.24	52.63	1.32
9	37.09	—	36.01	—
10	68.69	2.05	68.63	2.02
11	35.05	2.52, 1.15	35.16	2.57, 1.11
12	30.38	1.40, 1.25	31.09	1.52, 1.26
13	39.35	—	39.33	—
14	38.31	—	42.69	—
15	32.49	1.50, 1.25	74.73	3.69
16	35.99	1.58, 1.34	48.42	2.14, 1.23
17	29.93	—	30.40	—
18	42.66	1.57	41.53	1.58
19	35.29	1.32, 1.29	35.53	1.28, 1.14
20	28.16	—	28.15	—
21	32.77	1.46, 1.26	32.59	1.45, 1.27
22	39.32	1.50, 0.92	38.89	1.36, 0.95
23	8.55	1.04	8.56	1.02
24	15.14	0.89	14.98	0.87
25	18.16	1.17	18.24	1.17
26	20.38	1.03	14.12	1.08
27	18.74	1.01	18.86	0.94
28	32.01	1.19	32.09	1.29
29	31.71	1.02	30.91	1.01
30	35.05	0.96	35.67	0.93
OMe	55.64	3.63	55.65	3.61

^aAssignments based on HETCOR and FLOCK experiments.

^bCompound **6** was dissolved in CDCl_3 (ca. 0.7 ml) containing one drop of $\text{DMSO}-d_6$.

15 α -Hydroxyfriedelane-1,3-dione [**5**].—Compound **5** (36 mg): mp 245–248°; $[\alpha]_{\text{D}} -19.8^\circ$ ($c = 0.16$, CHCl_3); λ_{max} (MeOH) 218 nm (7600), 260 nm (5500); ir 3416, 1730, 1704 cm^{-1} ; eims m/z $[\text{M}]^+$ 456 (7%), 438 (23), 426 (32), 316 (22), 261 (58), 163 (54), 95 (68), 69 (100). Found $[\text{M}]^+$ 456.3558; $\text{C}_{30}\text{H}_{48}\text{O}_3$ requires $[\text{M}]^+$ 456.3603.

3-Methoxyfriedel-2-en-1-one [**6**].—A solution of **2** (50 mg) in $\text{MeOH}-\text{CH}_2\text{Cl}_2$ (1:1) (10 ml) was treated with excess ethereal CH_2N_2 and left to stand at room temperature for 4 h. The crude product was purified by preparative tlc [hexane-EtOAc (5:1)] to yield methyl ether **6** (21 mg): mp 325–326°; $[\alpha]_{\text{D}} -28.1^\circ$ ($c = 0.16$, CHCl_3); λ_{max} (MeOH) 228 nm (16300), 255 nm (5700); ir 1650, 1614 cm^{-1} ; eims m/z $[\text{M}]^+$ 454 (33%), 439 (76), 423 (20), 369 (12), 301 (30), 205 (33), 153 (100), 95 (68). Found $[\text{M}]^+$ 454.3806; $\text{C}_{31}\text{H}_{50}\text{O}_2$ requires $[\text{M}]^+$ 454.3811.

3-Methoxy-15 α -hydroxyfriedel-2-en-1-one [**7**].—Compound **5** (25 mg) was methylated under the same conditions as for compound **2** to give the methyl ether **7** (13 mg): mp 291–294°; $[\alpha]_{\text{D}} -6.3^\circ$ ($c = 0.14$, CHCl_3); λ_{max} (MeOH) 228 nm (18200), 255 nm (7400); ir 3444, 1644, 1612 cm^{-1} ; eims m/z $[\text{M}]^+$ 470 (39%), 455 (62), 452 (14), 439 (36), 303 (30), 275 (43), 221 (14), 153 (100). Found $[\text{M}]^+$ 470.3728; $\text{C}_{31}\text{H}_{50}\text{O}_3$ requires $[\text{M}]^+$ 470.3760.

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LITERATURE CITED

1. H.E. Gottlieb, P.A. Ramaiah, and D. Lavie, *Magn. Reson. Chem.*, **23**, 616 (1985).
2. A.A.L. Gunatilaka, N.P.D. Nanayakkara, M.U.S. Sultanbawa, and M.I.M. Wazeer, *Org. Magn. Reson.*, **14**, 415 (1980).
3. A. Patra, A.K. Mukhopadhyay, and A.K. Mitra, *Org. Magn. Reson.*, **17**, 166 (1981).
4. A.A.L. Gunatilaka, N.P.D. Nanayakkara, and M.I.M. Wazeer, *Phytochemistry*, **22**, 991 (1983).
5. A. Patra and S.K. Chaudhuri, *Magn. Reson. Chem.*, **25**, 95 (1987).
6. W.F. Reynolds, S. McLean, M. Perpick-Dumont, and R.G. Enriquez, *Magn. Reson. Chem.*, **27**, 162 (1989).
7. N.C. Tewari, K.N.N. Ayenger, and S. Rangaswami, *J. Chem. Soc., Perkin Trans. 1*, 146 (1974).
8. E. Akiyama, M. Tada, T. Tsuyuki, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **52**, 164 (1979).

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