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TRITERPENOIDS OF *JATROPHA GOSSYPIIFOLIA*

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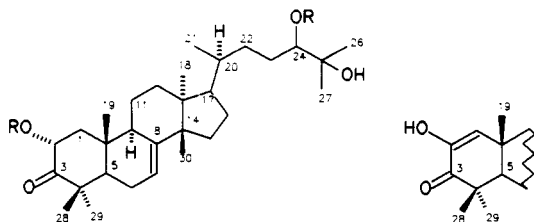
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ABSTRACT.—Two new triterpenes, the trihydroxy ketone **1** and the corresponding diosphenol **2** have been isolated from the leaves of *Jatropha gossypifolia* (Euphorbiaceae). Structures have been assigned by 2D nmr spectroscopy; the value of the FLOCK pulse sequence is illustrated.

Jatropha gossypifolia L. (Euphorbiaceae) is a common tropical shrub that has excited a considerable amount of interest because it contains metabolites that have cytotoxic and tumor-inhibitory activity; structurally novel diterpenes have been shown to be responsible for most of this activity (1,2). No investigation of the triterpenes of this plant has been reported previously. We describe here the isolation from the leaves of *J. gossypifolia* collected in Guyana of two new triterpenes and the elucidation of their structures.

Structure elucidation depended heavily on the determination of molecular connectivities by 2D nmr spectroscopy. Direct or one-bond ^{13}C - ^1H connectivities were established in a standard HETCOR experiment, and our FLOCK pulse sequence was used to establish 2- and 3-bond connectivities (3). Observed connectivities were more than sufficient to determine structures unequivocally; Table 1 lists the chemical shift assignments made from these experiments.

The major triterpene, **1**, was obtained as a glass, $\text{C}_{30}\text{H}_{50}\text{O}_4$ (hreims), $[\alpha]_{\text{D}} - 13^\circ$, which showed OH (3466 cm^{-1}) and C=O (1704 cm^{-1}) peaks in its ir spectrum. The minor triterpene, **2**, was obtained as a glass, $\text{C}_{30}\text{H}_{48}\text{O}_4$ (hreims), $[\alpha]_{\text{D}} + 12^\circ$, which showed absorption at 3450 , 1708 (weak), 1674 , and 1652 cm^{-1} in its ir spectrum, and at 270 nm ($\epsilon\ 5700$) in its uv spectrum. Although the ir peak at 1708 cm^{-1} (thin film) suggests that some diketonic tautomer is present, all of the peaks in the ^{13}C - and ^1H -nmr spectra could be assigned to the diosphenol tautomer, showing that **2** is mainly or entirely in this form in CDCl_3 solution. Ac_2O in pyridine converted **1** to its 2,24-diacetate **3**, which was also characterized by the 2D nmr methods above. When **3** was heated in methanolic KOH, diosphenol **2** was isolated, the product not only of saponification but also of oxidation. Similar aerial oxidations in alkaline media have been used synthetically (4) but normally under significantly more vigorous conditions.



1 R=H
3 R=Ac

2

TABLE 1. ^{13}C and ^1H Chemical Shifts of Compounds 1-3.^a

Position	Compound					
	1		2		3 ^b	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	48.22	2.38, 1.26	124.55	6.23	44.12	2.21, 1.55
2	69.24	4.60	143.68	—	71.83	5.62
3	216.44	—	200.99	—	209.13	—
4	47.28	—	43.71	—	48.26	—
5	53.07	1.72	48.64	2.10	52.61	1.73
6	24.20	<2.10>	23.45	<2.09>	24.14	<2.10>
7	117.48	5.31	118.50	5.37	117.76	5.32
8	145.82	—	145.97	—	145.57	—
9	48.60	2.29	46.44	2.53	48.60	2.33
10	35.56	—	36.64	—	35.93	—
11	18.37	<1.57>	18.45	1.75, 1.60	18.41	<1.58>
12	33.66	1.85, 1.68	33.83	1.88, 1.69	33.36	1.80, 1.64
13	43.47	—	43.39	—	43.39	—
14	51.28	—	51.64	—	51.24	—
15	33.92	<1.47>	34.15	<1.47>	33.88	<1.48>
16	28.45	1.95, 1.29	28.48	1.93, 1.31	28.35	1.96, 1.27
17	53.50	1.50	53.52	1.49	53.19	1.48
18	22.15	0.80	22.34	0.84	22.12	0.78
19	13.77	1.08	14.57	1.03	13.74	1.12
20	35.59	1.43	35.61	1.42	35.45	1.44
21	18.49	0.84	18.49	0.85	18.37	0.84
22	31.77	1.67, 1.18	31.84	1.64, 1.20	31.19	1.55, 0.99
23	28.63	<1.38>	28.69	<1.37>	26.26	1.66, 1.51
24	78.38	3.34	78.46	3.34	79.87	4.80
25	73.17	—	73.19	—	72.39	—
26	26.58	1.20	26.63	1.22	26.70	1.20
27	23.22	1.15	23.30	1.17	24.97	1.19
28	21.48	1.16	21.84	1.14	20.92	1.22
29	24.32	1.12	24.64	1.20	24.32	1.08
30	27.43	1.01	27.94	1.04	27.43	1.01

^aChemical shifts are for solutions in CDCl_3 , δ_{C} at 100.6 MHz, δ_{H} at 400 MHz. The δ_{H} for each identifiable proton (or methyl) is listed; the <mean δ_{H} > is reported for incompletely resolved CH_2 multiplets. One-bond connectivities were determined from a standard HETCOR experiment; 2- and 3-bond connectivities were determined from a FLOCK experiment. Listings of connectivity data are available from authors at the Toronto address.

^bAdditional signals: 2-OAc δ_{C} 20.76, 170.26, δ_{H} 2.17; 24-OAc δ_{C} 21.11, 171.10, δ_{H} 2.10.

The structures of **1** and **2** are unequivocally established from the 2D nmr data just described, but the connectivity data provide no explicit information on stereochemical questions. However, evidence from ^1H - ^1H nOe difference measurements carried out on **1** indicated the tirucallos/euphol stereochemistry for the ring system: enhancements were observed at H-9 when the C-18 protons were irradiated, and at H-2 when the C-19 protons were irradiated.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were determined on a micro hot stage. Selected ir absorptions (Ft-ir) are reported (in cm^{-1}). Uv spectra were obtained for MeOH solutions; λ max (ϵ) values are reported (in nm). Nmr spectra were obtained on a Varian XL-400 spectrometer operating at 400 MHz for ^1H and at 100.6 MHz for ^{13}C and equipped with a 5-mm computer-switchable ^1H /multinuclear probe; CDCl_3 solutions were used. A VG 70-250S mass spectrometer, operating at 70 eV, was used to obtain mass spectra; m/z values (with intensity at % of base peak) are reported for significant peaks.

PLANT MATERIAL.—Plants were collected in January 1990, at Rosignol, Guyana. Voucher specimens are deposited at the Herbarium of the University of Guyana.

EXTRACTION.—Dried leaves (500 g) were ground and extracted with EtOH. Evaporation of the EtOH left a dark residue (23.9 g), which was dissolved in MeOH-H₂O (9:1) and extracted with hexane. The MeOH/H₂O layer was diluted to 40% H₂O and thoroughly extracted with CHCl₃. The CHCl₃ solution afforded a residue (9.5 g) that was subjected to chromatography on SiO₂ with CH₂Cl₂ as eluent. The second (of four) fractions was separated by preparative tlc [SiO₂ with hexane-Me₂CO (4:1)] into **1** (203 mg) and **2** (26 mg).

Compound 1.—Isolated as a glass: $[\alpha]_D - 13^\circ$ ($c = 0.28$, CHCl₃); ir 3466, 1704; eims 474 (8), 456 (8), 441 (63), 423 (33), 329 (14), 273 (24), 127 (34), 59 (100); hreims 474.3682, calcd for C₃₀H₅₀O₄, 474.3709. With Ac₂O/pyridine, it forms 2,24-diacetate **3**: mp 118–120°, $[\alpha]_D + 4^\circ$ ($c = 0.3$, CHCl₃); ir 3487, 1740, 1724; eims 558 (2), 540 (38), 525 (40), 483 (31), 465 (32), 423 (50), 405 (32), 383 (32), 59 (100); hreims 558.3899, calcd for C₃₄H₅₄O₆, 558.3920.

Compound 2.—Isolated as a glass: $[\alpha]_D + 12^\circ$ ($c = 0.4$, CHCl₃); ir 3450, 1708, 1674, 1652; uv 270 (5700); eims 472 (9), 455 (16), 437 (16), 320 (25), 287 (19), 201 (23), 175 (48), 59 (100);

hreims 472.3526, calcd for C₃₀H₄₈O₄, 472.3553. A solution of compound **3** (92 mg) in 10% methanolic KOH was heated to reflux for 1 h. Neutralization and workup provided **2** (80 mg), identical with that just described.

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