

ISOLATION AND CHARACTERIZATION OF A NEW  
GLABRETAL TRITERPENE FROM  
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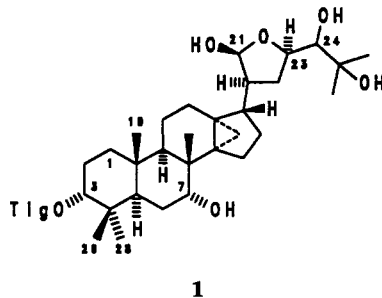
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ABSTRACT.—A new glabretal-type triterpene [**1**], was isolated from the roots of *Quassia multiflora*. Its structure was established by a combination of 2D nmr experiments.

*Quassia multiflora* (A. Juss.) Nootboom (= *Simaba multiflora*) is a member of the Simaroubaceae and has been widely investigated due mainly to its content of biologically active quassinoids (1–9). We have previously reported the isolation of quassinoids and squalene triterpenes from this plant (5,10). We have investigated further extracts of *Q. multiflora*, and report here the isolation and characterization of a new glabretal-type triterpene whose structure has been established as **1**. Glabretal triterpenes usually occur as epimeric mixtures at C-21 because most of them possess a hemiacetal in that position (11). However, since one epimer was present in a much higher concentration than the other, the characterization of **1** focused on the major component.

Compound **1**, C<sub>35</sub>H<sub>56</sub>O<sub>7</sub>, isolated as a colorless gum, had ir absorptions characteristic of hydroxyl (3500 cm<sup>-1</sup>) and unsaturated ester (1703 cm<sup>-1</sup>) functionalities. The <sup>13</sup>C-nmr spectrum displayed resonances for all 35 carbons of the major epimer. These included signals



due to one hemiacetal at  $\delta$  97.53 and five other sp<sup>3</sup> carbons bearing oxygen at  $\delta$  78.72, 78.14, 74.99, 74.22, and 73.50. The hemiacetal carbon at  $\delta$  97.53 was directly attached to a proton at  $\delta$  5.44 (d,  $J=3.5$  Hz) as determined by an HMQC experiment. In the <sup>1</sup>H-nmr spectrum, the protons of four oxymethines had signals at  $\delta$  4.68 ( $W_{1/2}=7.5$  Hz),  $\delta$  4.48 (dd,  $J=8.5$  and 7.5 Hz),  $\delta$  3.76 ( $W_{1/2}=8.0$  Hz), and  $\delta$  3.15 (d,  $J=7.1$  Hz). Further, there were six tertiary methyls, in addition to a cyclopropyl methylene group with signals at  $\delta$  0.68 and  $\delta$  0.48 (2H, ABq,  $J=4.3$  Hz). The presence of a tiglate group was evident from proton resonances at  $\delta$  6.86,  $\delta$  1.86, and  $\delta$  1.80. The foregoing evidence suggested that compound **1** was a glabretal-type triterpene containing a tiglate ester.

A series of 2D nmr experiments, which included DQF-COSY, HMQC, and HMBC sequences, led to the assign-

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ment of all resonances for **1**. In the HMBC experiment, methyl groups with resonances at  $\delta$  27.96 (C-28) and  $\delta$  21.82 (C-29) showed long-range correlations with each other, establishing their geminal disposition and that they were attached to C-4. In addition, these methyls showed long-range correlations to the oxymethine proton at  $\delta$  4.68. Also, the tiglate carbonyl at  $\delta$  167.66 displayed three-bond correlations with the same oxymethine at  $\delta$  4.68. These results indicated that the tiglate was attached to the oxygen at C-3. The oxymethine signal at  $\delta$  3.76 was located at C-7 on the basis of the DQF-COSY and the HMBC experiments. These

experiments, along with the HMQC sequence, also revealed that the oxymethine carbon at  $\delta$  74.99 was directly bonded to the proton at  $\delta$  3.15 and that it was located at C-24. The stereochemistry at all relevant positions except C-24 was determined on the basis of analysis of a NOESY experiment, the hydroxyl group at C-21 for the major epimer being  $\beta$ -oriented. These experiments led to the establishment of structure **1** for this new triterpenoid and the  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr assignments for this compound are reported in Table 1.

Compound **1** is closely related to a glabretal triterpene that was recently iso-

TABLE 1. Nmr Characteristics of Compound **1** in  $\text{CDCl}_3$  at 500 MHz.

Position	$\delta_{\text{C}}$	$\delta_{\text{H}}$ ( $J_{\text{HH}}$ )	HMBC
1	34.17	1.38, 1.15	4.68, 0.90
2	26.28	1.92, 1.62	
3	78.14	4.68 ( $W_{1,2}$ 7.5)	0.90, 0.86
4	36.55	—	4.68, 2.05, 0.90, 0.86
5	41.26	2.05	4.68, 3.76, 0.90, 0.86
6	24.21	1.62, 1.58	3.76, 2.05
7	74.22	3.76 ( $W_{1,2}$ 8.0)	2.05, 1.62, 1.04
8	37.06	—	3.76 (w), 1.62, 1.04
9	44.20	1.30	3.76, 2.05, 1.04, 0.90
10	37.25	—	2.05, 1.62, 0.90
11	16.13	1.29, 1.29	
12	22.72	1.91, 1.55	1.29
13	28.91	—	2.17, 1.68, 1.55, 0.48
14	38.91	—	1.04
15	25.71	2.08, 1.72	2.17, 0.68, 0.48
16	27.47	1.68, 1.68	2.17
17	44.96	2.17	1.97, 1.55, 0.48
18	13.74	0.68, 0.48 (ABq, 4.3)	2.17, 1.91, 1.55
19	15.73	0.90	2.05, 1.30, 1.15
20	48.76	1.85	5.34, 4.48, 2.17, 1.97, 1.84
21	97.53	5.34 (3.5)	4.48, 2.17, 1.85
22	29.48	1.97, 1.84	5.34, 4.48, 3.15, 1.85
23	78.72	4.48 (8.5, 7.5)	5.34, 3.15, 1.97
24	74.99	3.15 (7.1)	4.48, 1.97, 1.28, 1.26
25	73.50	—	1.28, 1.26
26	26.74	1.26	3.15, 1.28
27	26.73	1.28	3.15, 1.26
28	27.86	0.86	4.68, 0.90
29	21.82	0.90	4.68, 2.05, 0.86
30	19.56	1.04	3.76, 1.30
1'	167.66	—	6.86, 4.68, 1.86, 1.80
2'	129.26	—	6.86, 1.86, 1.80
3'	136.62	6.86 (7.0, 1.5)	1.86, 1.80
4'	12.20	1.86 (<1.0)	6.86
5'	14.42	1.80 (7.0, <1.0)	6.86

lated from *Aglaia ferruginaea* (Meliaceae) by Mulholland and Monkhe (11). The biosynthesis of glabretal triterpenes should involve a tirucallane precursor since all known examples to date have been isolated from plant families of the order Rurales (11–14), of which the tirucallanes are characteristic (15).

### EXPERIMENTAL

**GENERAL EXPERIMENTAL PROCEDURES.**—Ir spectra were obtained on a Nicolet 3DX Ft-ir spectrometer. A Perkin-Elmer 243B polarimeter was used to obtain  $[\alpha]_D$  values. Nmr spectra were recorded on a Varian Unity 500 spectrometer with TMS as internal standard. A VG-70-250S mass spectrometer was used to obtain ms data.

**PLANT MATERIAL.**—The plant material was collected at the Goethe Creek, Essequibo, Guyana, in November 1987. Voucher specimens (CAP 334) were deposited at the Jenman's Herbarium, University of Guyana.

**EXTRACTION AND ISOLATION.**—The dried, ground roots (6.54 kg) were extracted with 95% EtOH (93.5 liters). The extract was concentrated to a small volume (500 ml), defatted with hexane (5×200 ml), and subsequently extracted with CH<sub>2</sub>Cl<sub>2</sub> to yield a brown viscous syrup (167 g) on removal of the solvent. This material, in portions, was chromatographed on Si gel using CH<sub>2</sub>Cl<sub>2</sub> with increasing amounts of MeOH as the solvent system to yield eight major fractions. Fraction 4 was rechromatographed on Si gel using hexane-Me<sub>2</sub>CO (3:1) as mobile phase to give **1** (32 mg).

**Compound 1.**—Colorless gum;  $[\alpha]_D -17.3^\circ$  ( $c=0.3$ , CHCl<sub>3</sub>); ir  $\nu$  max 3500, 1703 cm<sup>-1</sup>; eims  $m/z$  570 (M<sup>+</sup>-H<sub>2</sub>O, 5), 552 (3), 470 (12), 452 (11), 412 (23), 381 (18), 312 (28), 295 (25), 187 (58), 107 (44), 83 (100); hreims  $m/z$  570.3926 calcd for C<sub>35</sub>H<sub>56</sub>O<sub>7</sub> (M<sup>+</sup>-H<sub>2</sub>O) 570.3920; <sup>1</sup>H- and <sup>13</sup>C-nmr data, see Table I.

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