Phytochemistry, Vol. 28, No. 7, pp. 1980–1981, 1989.
Printed in Great Britain.

0031–9422/89 \$3.00 + 0.00

AN ACYCLIC TRITERPENE FROM *PHYLLANTHUS NIRURI**

BIKRAM SINGH, PAWAN K. AGRAWAL and RAGHUNATH S. THAKUR

Central Institute of Medicinal and Aromatic Plants, Lucknow 226016, India

(*Received* 29 *September* 1988)

Key Word Index—*Phyllanthus niruri*; Euphorbiaceae; triterpene; 3,7,11,15,19,23-hexamethyl-2*Z*,6*Z*,10*Z*,14*E*,18*E*,22*E*-tetracoshexen-1-ol.

Abstract—An acyclic triterpene isolated from the *Phyllanthus niruri* was shown to be 3,7,11,15,19,23-hexamethyl-2*Z*,6*Z*,10*Z*,14*E*,18*E*,22*E*-tetracoshexen-1-ol by spectral and chemical methods.

INTRODUCTION

In continuation of our chemical investigation studies on the hexane extract of the *Phyllanthus niruri* [1–3], we now report the isolation and structure determination of an acyclic triterpene (**1**).

RESULTS AND DISCUSSION

The compound (**1**) had the molecular formula $C_{30}H_{50}O$. Its IR spectrum indicated the presence of a hydroxyl group (3340 cm^{-1}) and isolated double bonds (1658 cm^{-1}). Its ^1H NMR displayed seven methyl signals as singlets at $\delta 1.59$ (3 × Me), 1.66 (3 × Me) and 1.73 (Me), 10 methylenes between $\delta 2.02$ and 2.05, a hydroxymethylene at $\delta 4.06$ as a doublet ($J = 6$ Hz), five olefinic protons at $\delta 5.07$ and an olefinic proton as a triplet ($J = 6$ Hz) at $\delta 5.40$ (Table 1). The mass spectrum showed, beside the molecular peak at m/z 426, fragments at m/z 411 $[M-Me]^+$, 408 $[M-H_2O]^+$, 397 $[M-(Me+H_2O)]^+$, and a series of fragments due to allylic cleavages in the side chain [4] at m/z 357 $[M-C_5H_9]^+$, 289 $[M-C_{10}H_{17}]^+$, 221 $[M-C_{15}H_{25}]^+$, 137 $[C_{10}H_{17}]^+$ and 69 $[C_5H_9]^+$. The ^{13}C NMR contained signals due to six olefinic quaternary olefinic carbons and six olefinic methines in the region $\delta 134.33$–138.59 and $\delta 123.90$–124.76 respectively, a hydroxymethylene signal at $\delta 58.44$ and the remaining methylene and methyl signals between $\delta 15.56$ and 33.44 (Table 1). All of these spectral features suggested an acyclic triterpene of the squalene type [5].

Compound **1** formed a monoacetyl derivative (**2**) which lacked a hydroxyl absorption band in its IR spectrum; instead there was an acetyl carbonyl absorption band at 1730 cm^{-1}. Its ^1H NMR displayed a singlet at $\delta 2.02$ for acetoxymethyl and acetoxymethylene at $\delta 4.50$ as a doublet ($J = 6$ Hz) and an olefinic proton at $\delta 5.30$ as triplet. On going from **1** to **2**, carbon signals due to C-1–C-3 were displaced by +2.57, 5.40 and +3.80 ppm respectively while other carbon signals remained almost unaffected. These acetylation shifts were consistent with those observed for allylic alcohols [6] and similar compounds [7, 8].

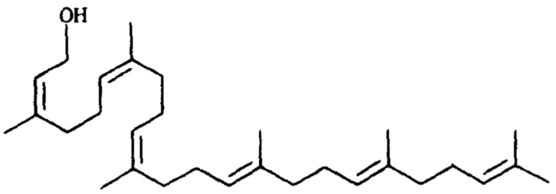
Critical analysis of the ^1H and ^{13}C NMR shielding data suggested the existence of *E*,*E*,*E*-farnesene and *Z*,*Z*,*Z*-farnesol units as methyl resonances were observed at $\delta 1.57$, 1.66 and 1.73 in a ratio of 3:3:1 and could be assigned to 3 × *cis*-Me, 3 × *trans*-Me and Me in an α-*Z*-terminal unit [7, 8]. In the ^{13}C NMR spectrum methylene resonances adjacent to quarternary olefinic carbon appeared at $\delta 39.44$ and 31.67, each corresponding to three carbon resonances, thus revealing three olefinic bonds with *E*-geometry and three olefinic bonds with *Z*-geometry [9]. The appearance of the methyl carbon resonances at $\delta 22.89$ (3 × Me) and 15.56 (2 × Me) further supported the *Z*-olefinic configuration in the farnesol unit and the *E*-olefinic configuration in the farnesene unit [9, 10]. The methyl signals at $\delta 17.30$ and 25.52 were assigned to the methyls of the isopropylidene group [10, 11]. Hence, on the basis of above evidence, the structure of compound **1** was elucidated as 3,7,11,15,19,23-hexamethyl-2*Z*,6*Z*,10*Z*,14*E*,18*E*,22*E*-tetracoshexen-1-ol or (2*Z*,6*Z*,10*Z*,14*E*,18*E*)-farnesyl farnesol.

This compound is synthetically known [12] but to the best of our knowledge, this is the first report of its isolation from a plant source.

EXPERIMENTAL

IR: neat. ^1H NMR: 80 MHz ($CDCl_3$). ^{13}C NMR: 20 MHz ($CDCl_3$), TMS as int. standard; TLC: silica gel G, the spots were visualized by spraying with 50% H_2SO_4.

The plant material was collected from the Institute farm during August 1983 and identified by a member of the Botany Department of our Institute. A specimen No. 439 is held in the



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*CIMAP Publication No. 795.

Table 1. ^{13}C and ^1H NMR spectral data for compounds **1** and **2** in $CDCl_3$

	1		**2**	
C/H	^{13}C	^1H	^{13}C	^1H
1	58.44	4.06	61.01	4.50
2	124.76[a]	5.40	119.36	5.30
3	138.59		142.39	
4	31.67	2.02	31.95	2.02
5	26.10	2.05	26.08	2.05
6	124.65[a]	5.07	124.69[a]	5.06
7	134.85[b]		134.84[b]	
8	31.67	2.02	31.68	2.02
9	26.10	2.05	26.08	2.05
10	124.65[a]	5.07	124.69[a]	5.06
11	134.85[b]		134.84[b]	
12	31.67	2.02	31.68	2.02
13	26.10	2.05	26.08	2.05
14	124.33[a]	5.07	124.35[a]	5.06
15	134.64[b]		134.60[b]	
16	39.44	2.05	39.42	2.05
17	26.36	2.02	26.30	2.02
18	124.21	5.07	124.20[a]	5.06
19	134.39		134.40[b]	
20	39.44	2.05	39.42	2.05
21	26.49	2.02	26.38	2.02
22	124.19	5.07	124.15[a]	5.06
23	134.33		134.40[b]	
24	25.52	1.66	25.51	1.67
25	17.30	1.57	17.30	1.58
26	15.56	1.57	15.54	1.58
27	15.56	1.57	15.54	1.58
28	22.89	1.66	22.87	1.67
29	22.89	1.66	22.87	1.67
30	22.89	1.73	22.87	1.73
CO			170.02	
Me			20.57	2.02

[a, b] Assignments bearing the same superscript may be exchanged in a vertical column.

herbarium. Dried powdered aerial parts (1 kg) were mixed with $Ca(OH)_2$ in a ratio of 10:3 and extracted exhaustively with hexane. The total hexane extract was concd, the concentrate (30 g) dissolved in hot hexane (1 l) and MeOH (3 × 200 ml) added to obtain a ppt. (5 g). The filtrate was concd to yield a residue (25 g), a part (10 g) of which was chromatographed over silica gel (300 g) and eluted with hexane and hexane containing increasing amount of EtOAc. Fractions 16–27 eluted with hexane–EtOAc (19:1) showed the presence of one major compound which was further purified by prep. TLC (silica gel, hexane–EtOAc 9:1) to give compound **1** (R_f 0.30) as a colourless viscous mass (40 mg). IR ν_{max}^{neat} cm^{-1}: 3340, 2940, 2855, 1658, 1440, 1355, 1000, 835; ^1H and ^{13}C NMR: see Table 1; MS m/z (rel. int.): 426 $[M]^+$ (100), 411 $[M-Me]^+$ (20), 408 $[M-H_2O]^+$ (8), 397 $[M-(Me+H_2O)]^+$ (1), 357 $[M-C_5H_9]^+$ (1), 289 $[M-C_{10}H_{17}]^+$ (1.5), 274 $[M-(C_{10}H_{17}+Me)]^+$ (25), 271 $[M-(C_{10}H_{17}+H_{20})]^+$ (8), 257 (30), 221 $[M-C_{15}H_{25}]$ (4), 205 $[C_{15}H_{17}]^+$ (32), 190 (95), 175 (25), 161 (27), 147 (36), 137 $[C_{10}H_{17}]^+$ (40), 135 (62), 121 (76), 109 (63), 95 (87), 81 (96), 69 $[C_5H_9]^+$ (97), 55 (82), 43 (62).

Acetylation of compound **1**. Compound **1** was acetylated with Ac_2O–pyridine at room temp and, after usual work-up, gave a monoacetate **2**. IR ν_{max}^{neat} cm^{-1}: 2940, 2855, 1730, 1655, 1440, 1230, 835; ^1H and ^{13}C NMR: see Table 1; MS m/z (rel. int.): 468 (30), 426 (52), 411 (18), 408 (16), 399 (22), 397 (2), 357 (9), 331 (7), 289 (5), 271 (8), 221 (7), 205 (28), 190 (65), 137 (36), 69 (98), 60 (42), 59 (40), 55 (75), 43 (100).

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