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IDENTIFICATION OF 24-METHYLENELOPHENOL FROM HEARTWOOD OF *AZADIRACHTA INDICA*

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Key Word Index—*Azadirachta indica*; Meliaceae; neem; wood; 24-methylenelophenol; sterol.

Abstract—24-Methylenelophenol was identified from the heartwood of the neem tree, *Azadirachta indica*.

INTRODUCTION

In a previous communication, we reported the identification by GC-MS data [1] of a sterol isolated from the heartwood of *Azadirachta indica* A. Juss. The antifeedant property of the ethanolic extract of the heartwood against *Diacrisia obliqua* Walker, has prompted us to reinvestigate this material. Chromatography of the petroleum ether fraction of the ethanolic extract over silica gel resulted in the isolation of the sterol [1] in pure crystalline form. Based on spectroscopic data and chemical transformtations, its structure is elucidated now as 4α-methyl-5α-ergosta-7, 24(28)-dien-3β-ol (24-methylene lophenol).

RESULTS AND DISCUSSION

Compound **1**, $C_{29}H_{48}O$ ($[M]^+$ at *m/z* 412) showed IR absorptions assignable to hydroxyl and $C{=}CH_2$ functions. On acetylation it yielded a monoacetate (**1a**), $C_{31}H_{50}O_2$ ($[M]^+$ at *m/z* 454), and on oxidation it gave a keto derivative (**1b**), $C_{29}H_{46}O$ ($[M]^+$ at *m/z* 410), confirming the presence of a free hydroxyl group.

The ^1H NMR spectrum of **1** was similar to the reported values [2]. The chemical shifts in the ^{13}C NMR spectra of **1**, **1a** and **1b** are recorded in Table 1. The signals arising from the ring system carbons were assigned by comparison with the literature data for 5α-cholest-7-en-3β-ol [3–5] and side chain signals by comparison and correlation with the data for cycloeucalenol [6]. Moreover these assignments were supported by the observed multiplicities in the single-frequency off-resonance decoupled (SFORD) and noise off-resonance decoupled (NORD) spectra. The chemical shifts at δ117.49 (C-7) and 139.04 (C-8) for **1** fully supported the presence of a double bond at C-7/C-8 and not at C-8/C-9 as reported earlier [1].

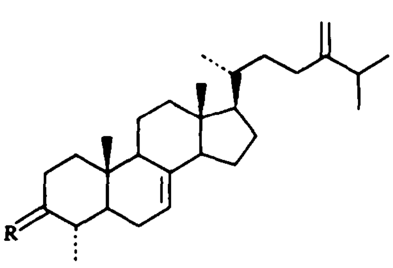
It is pertinent to note that 24-methylenelophenol (4α-methyl-5α-ergosta-7,24(28)-dien-3β-ol) has also been reported from a marine source [2] as well as the plants *Solanum tuberosum* [7], *Saccharum officinarum* [8] and *Lophocereus schottii* [9]. However, this is the first report of it as a constituent of heartwood from the Meliaceae.

EXPERIMENTAL

Mps (open capillary): uncorr.; IR: KBr; ^1H NMR: 90 MHz, $CDCl_3$, TMS as int. reference; ^{13}C NMR: CFT-20, $CDCl_3$, shifts reported in ppm with respect to TMS. TLC: Silica gel G, spray 10% H_2SO_4 (w/v).

Powdered, air-dried heartwood (10 kg) of *A. indica* collected locally (voucher specimen has been deposited at the institute) were extracted exhaustively with 90% EtOH at room temp. The solvent was removed *in vacuo* and the residue (98.5 g) chromatographed on a Si gel column using increasing concns of C_6H_6 in petrol as the eluant yielding **1** (1.5 g, 0.015% yield) mp 164–165° (EtOH); $[\alpha]_D^{25}$ +4.7° (*c* 0.08 in $CHCl_3$): IR ν_{max}^{KBr} cm^{-1}: 882, 1640 ($>C{=}CH_2$), MS *m/z* (rel. int.): 412 $[M^+]$ (8) ($C_{29}H_{48}O$), 397 (7) $[M-Me]^+$, 379 (8) $[M-(Me+H_2O)]^+$, 328 (16) $[M-84]^+$, 313 (5) $[M-(Me+84)]^+$, 285 (100) $[M-(\text{side chain}+2H)]^+$, 267 (66) $[M-(\text{side chain}+2H+H_2O)]^+$, 245 (7) $[M-(\text{side chain}+42)]^+$, 227 (13) $[M-(\text{side chain}+H_2O+42)]^+$. ^1H NMR: δ0.80 (6H, *s*) 0.92 (3H, *s*), 0.98 (3H, *s*), 1.02 (3H, *s*), 1.20 (3H, *s*), 3.08 (1H, *m*, $W_{1/2}$ = 5 Hz), 4.56, 4.64 (1H each, both *s*, H-28), 5.18 (1H, *m*, $W_{1/2}$ = 10 Hz, H-7); ^{13}C NMR: see Table 1.

Monoacetate **1a** (90 mg) was obtained from **1** (100 mg) by treatment with Ac_2O–pyridine, mp 137–138° (EtOH); $[\alpha]_D^{25}$



1 R = α-H, β-OH
1a R = α-H, β-OCOMe
1b R = O

+25.9° (c 0.57 in $CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 1724, 1250, (OCOMe), 1638, 885 (>C=CH_2); MS m/z (rel. int.): 445 $[M]^+$ (5) ($C_{31}H_{50}O_2$), 439 (4) $[M-Me]^+$, 379 (2) $[M-(Me+60)]^+$, 370 (8) $[M-84]^+$, 355 (5) $[M-(Me+84)]^+$, 327 (100) $[M-(\text{side chain}+2H)]^+$, 267 (12) $[M-(\text{side chain}+2H+60)]^+$, 287 (3) $[M-(\text{side chain}+42)]^+$, 227 (8) $[M-(\text{side chain}+42+60)]^+$. ^1H NMR: 0.80 (6H, s), 0.84 (3H, s), 0.94 (3H, s), 1.01 (3H, s), 1.21 (3H, s), 4.30 (1H, m, $W_{1/2}$ = 5 Hz), 4.59, 4.65 (1H each, both s, H-28), 5.15 (1H, m, $W_{1/2}$ = 10 Hz, H-7), ^{13}C NMR see Table 1.

Oxidation of **1** *to* **1b**. To a soln of **1** (100 mg) in Me_2CO (10 ml) was added Jone's reagent (20 ml) when **1b** (55 mg) was obtained, mp 125–127°, $[\alpha]_D^{25}$ +20.7° (c 0.02 in $CHCl_3$); IR ν_{max}^{Kbr}cm^{-1}: 1715 (C=O), 1642, 890 (C=CH_2); MS m/z (rel. int.); 410 $[M]^+$ (8) ($C_{29}H_{46}O$), 395 (6) $[M-Me]^+$, 326 (8) $[M-84]^+$, 311 (5) $[M-(Me+84)]^+$, 283 (100) $[M-(\text{side chain}+2H)]^+$, 243 (5) $[M-(\text{side chain}+42)]^+$. ^1H NMR: 0.88 (3H, s), 0.96 (6H, s), 1.04 (3H, s), 1.08 (3H, s), 1.36 (3H, s), 4.65 (2H, br s, H-28), 5.15 (1H, m, $W_{1/2}$ = 5 Hz, H-7); ^{13}C NMR: see Table 1.

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Table 1. ^{13}C NMR chemical shifts for compounds **1**, **1a** and **1b**

Carbon atom	Chemical shifts ppm **1**	**1a**	**1b**
1	37.05	36.54	39.42
2	30.99	27.00	38.05
3	76.21	78.28	213.30
4	40.21	36.93	45.64
5	46.62	46.63	50.20
6	26.62	26.53	27.62
7	117.49	117.11	117.15
8	139.04	138.84	139.20
9	49.65	49.40	49.23
10	34.65	34.60	35.12
11	21.41	21.44	21.51
12	39.58	39.43	39.67
13	43.38	43.22	43.32
14	54.94	54.78	54.76
15	22.89	22.74	23.05
16	27.94	28.49	28.09
17	55.98	55.99	56.03
18	11.83	11.66	12.02
19	14.15	13.77	13.71
20	36.20	36.39	36.07
21	18.87	18.68	18.38
22	34.86	35.98	35.02
23	29.72	31.01	31.30
24	156.79	156.41	156.25
25	33.81	33.69	33.70
26	21.90*	21.69*	21.67*
27	22.04*	21.80*	21.82*
28	106.00	105.92	105.68
29	15.21	14.92	11.54
OCOMe	—	170.38	—
OCOMe	—	21.26	—

*Assignment may be interchanged.