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A TETRACYCLIC TRITERPENOID FROM *MUSA PARADISIACA*

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Key Word Index—*Musa paradisiaca*; Musaceae; flowers; tetracyclic triterpenoid; (24*R*)-4α,14α,24-trimethyl-5α-cholesta-8,25(27)-dien-3β-ol.

Abstract—The structure of a new tetracyclic triterpene isolated from the flowers of *Musa paradisiaca* was determined as (24*R*)-4α,14α,24-trimethyl-5α-cholesta-8,25(27)-dien-3β-ol.

INTRODUCTION

The plant *Musa paradisiaca* is well known for its various medicinal uses [1]. Previous investigators have revealed the presence of a number of 9,19-cyclotetracyclic triterpenes in the stalks, rhizomes, leaves and pulp of the plant [2–4]. We report herein the structure elucidation of a new tetracyclic triterpene (**1a**) isolated from the flowers of the plant.

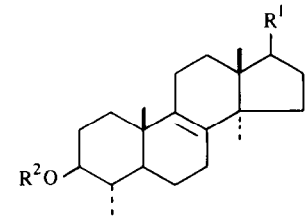
RESULTS AND DISCUSSION

The chloroform extract of the flowers of *M. paradisiaca* yielded after concentration and chromatography some known sterols and triterpenes [5] and the new compound **1a**, $C_{30}H_{50}O$ (M^+ at *m/z* 426). The IR spectrum of **1a** showed a band at 3500 cm^{-1} (–OH), besides those at 1640 and 890 cm^{-1} (>C=CH_2). It formed an acetate (**1b**), $C_{32}H_{52}O_2$ (M^+ at *m/z* 468) and a ketone, $C_{30}H_{48}O$ (M^+ at *m/z* 424).

The mass spectral fragmentation pattern of the acetate (**1b**) was typical of a tetracyclic triterpene [6]. The ion peak at *m/z* 341 $[M-\text{side chain}-2H]^+$ indicated that one double bond was located in the C_9-side chain [7]. On the other hand, the fragments at *m/z* 287 $[M-\text{side chain}-C_3H_7-CH_2]^+$ and 227 $[m/z\ 287-HOAc]^+$ suggested a 14α-methyl group in the ring system [8, 9] thus indicating the lanostane nucleus for the new compound.

The ^1H NMR spectrum of the acetate (**1b**) showed three tertiary methyl singlets and one methyl doublet, the chemical shifts of which agreed well with those of C_{18}, C_{19}, C_{30} and C_{32} of obtusifoliol acetate (**1c**) [10]. This established the ring system **1** in the compound. Further, the methyl singlet at δ 1.64 along with a broad two-proton singlet at δ 4.65 could be attributed to an isopropylidene group, while the equatorial orientation of the acetoxy group at C-3 was deduced from the one-proton double triplet at δ 4.36.

The ^{13}C NMR spectrum of **1b** was fully in conformity with the above structure. The chemical shifts of the ring carbons (C-1 to C-19, C-30 and C-32) were almost identical with those of obtusifoliol acetate (**1c**) and 24β-ethyl-31-norlanosta-8,25(27)-dien-3β-ol [11], while those of the side chain carbons (C-20 to C-23) could be compared with values reported for similar compounds [12]. The presence of an isopropylidene group was supported by signals at δ 109.3 and 150.0 assigned to C-27 and C-25, respectively.



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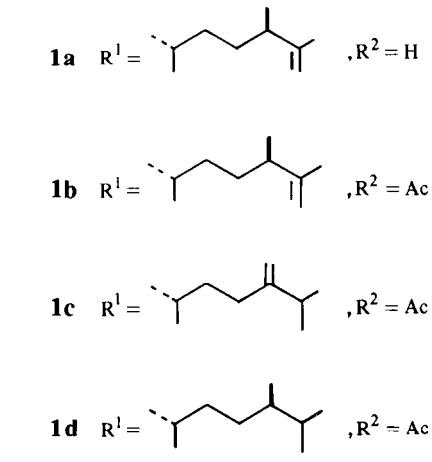

Finally, the stereochemistry at C-24 could be deduced via hydrogenation of **1b**, which afforded a dihydro derivative (**1d**). The physical constants and IR spectrum of **1d** agreed quite well with those of dihydroobtusifoliol acetate [13]. Since **1d** was more dextrorotatory (ΔM_D = +67°) than the corresponding 24-H compound [13], the 24*R*-Me configuration [14, 15] is established for **1a**.

EXPERIMENTAL

Mps are uncorr. IR spectra were determined in Nujol mull, rotations in $CHCl_3$ and MS at 70 eV. ^1H NMR (90 MHz) and ^{13}C NMR (25.05 MHz) spectra were measured in $CDCl_3$ solns

with TMS as int. standard, chemical shifts being expressed in δ units.

Isolation of **1a**. Dried, powdered flowers (5 kg) of *M. paradisiaca* (collected locally and identified by Botanical Survey of India, Calcutta) were extracted successively with petrol (60–80°) and $CHCl_3$. The $CHCl_3$ extract was concd and then chromatographed over silica gel. The petrol–C_6H_6 (1:3) eluate on purification by repeated CC followed by prep. TLC yielded **1a** besides cycloeucalenol, 24-methylenecycloartanol, 31-norcyclolaudenone, sitosterol and stigmasterol.

Compound **1a** crystallized from $CHCl_3$–MeOH as fine needles (0.2 g), mp 135°, $[\alpha]_D + 72°$. IR ν_{max} cm^{-1}: 3500 (OH), 1640 and 890 (>=CH_2); MS *m/z* (rel. int.): 426 $[M]^+$ (87), 411 (100), 408 (19), 393 (13), 301 (44), 300 (63), 285 (20), 283 (22), 245 (25). (Found: C, 84.26; H, 11.95; $C_{30}H_{50}O$ requires: C, 84.4; H, 11.8%.)

Acetylation of **1a**. Compound **1a** (0.1 g) was acetylated with Ac_2O (1 ml) and pyridine (0.2 ml) at room temp. overnight. Usual work-up, CC over silica gel and crystallization from MeOH afforded **1b** (90 mg), mp 110°, $[\alpha]_D + 34°$. IR ν_{max} cm^{-1}: 1725 (OAc), 1640 and 885 (>=CH_2); ^{1}H NMR: δ 0.70 (3H, *s*, H-18), 0.85 (3H, *d*, J = 7 Hz, H-30), 0.88 (3H, *s*, H-32), 0.98 (3H, *s*, H-19), 1.64 (3H, *s*, H-26), 2.03 (3H, *s*, 3β-OAc), 4.36 (1H, *dt*, *J* = 5, 11 Hz, H-3α) and 4.65 (2H, *s*, H-27); ^{13}C NMR: δ 15.1 (C-30), 15.7 (C-18), 18.1 (C-26), 18.7 and 18.8 (C-19, C-21), 20.2 (C-28), 20.8 (C-6), 21.3 (COC$\underline{H}_3$), 21.8 (C-11), 24.4 (C-30), 25.5 (C-12), 27.2 (C-2), 28.1 (C-7), 30.8 (C-16), 31.1 (C-15), 31.5 (C-23), 34.0 (C-22), 34.7 (C-1), 36.1 (C-4), 36.2 (C-10), 36.4 (C-20), 41.6 (C-24), 44.5 (C-13), 47.2 (C-5), 49.9 (C-14), 50.4 (C-17), 78.8 (C-3), 109.3 (C-27), 133.3 (C-8), 134.8 (C-9), 150.0 (C-25) and 170.8 (C=OMe); MS *m/z* (rel. int.): 468 $[M]^+$ (65), 453 (100), 408 (15), 393 (49), 369 (8), 341 (6), 323 (6), 309 (10), 301 (8), 287 (32), 269 (47), 241 (18), 227 (28).

Oxidation of **1a**. Compound **1a** (25 mg) was added to PCC (27 mg) in dry CH_2Cl_2 (5 ml) and the soln stirred at 20° for 3 hr. Usual work-up followed by CC over silica gel afforded the ketone (15 mg), mp 115–116°, $[\alpha]_D + 54°$. IR ν_{max} cm^{-1}: 1710 (C=O), 1640 and 880 (>=CH_2); MS *m/z* (rel. int.): 424 $[M]^+$ (85), 409 (100), 381 (5), 299 (32), 285 (40), 257 (22), 243 (55), 231 (45).

Hydrogenation of **1b**. Compound **1b** (20 mg) was hydrogenated with Adams catalyst in EtOH for 6 hr. Removal of catalyst and solvents followed by crystallization from MeOH yielded **1d** (15 mg), mp 128–130°, $[\alpha]_D + 72°$. IR ν_{max} cm^{-1}: 3500 (OH); ^{1}H NMR: δ 0.70 (3H, *s*, H-18), 0.79 (6H, *d*, *J* = 6 Hz, H-26 and 27), 0.85 (3H, *d*, *J* = 7 Hz, H-30), 0.90 (3H, *s*, H-32), 0.98 (3H, *s*, H-19), 2.05 (3H, *s*, 3β-OAc), 4.39 (1H, *m*, H-3α).

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