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AN ANTIFUNGAL TRITERPENOID FROM *MOLLUGO PENTAPHYLLA*

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Key Word Index—*Mollugo pentaphylla*, Molluginaceae; hopane, mollugogenol A; mollugogenol B, antifungal.

Abstract—An antifungal compound was isolated from the aerial parts of *Mollugo pentaphylla* and identified as mollugogenol A, along with the inactive major triterpenoid mollugogenol B. The structures were established by spectroscopic methods (UV, DCIMS, EIMS, ^{1}H and ^{13}C NMR) and comparison with authentic samples.

INTRODUCTION

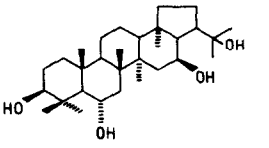
Continuing our search for biologically active compounds from traditional medicinal plants, we have undertaken an investigation of *Mollugo pentaphylla* L. (Syn. *M. stricta* L.) (Molluginaceae). This annual herb is eaten in India as a pot herb and reportedly contains carotenes, vitamin C, and a saponin [1, 2]. In the course of earlier phytochemical investigations of *M. pentaphylla*, the three novel flavone C-glycosides mollupentin, mollupentin 6-C-xyloside and isomollupentin 8-C-xyloside have been characterized [3, 4].

RESULTS AND DISCUSSION

The ethyl acetate soluble part of an aqueous ethanolic extract of *M. pentaphylla* contained an antifungal compound, evidenced by a bioassay on TLC using the plant pathogenic fungus *Cladosporium cucumerinum* [5]. Successive fractionation of the extract on silica gel and Sephadex LH 20 yielded the antifungal compound **1**, along with the inactive triterpene **2**.

The molecular formula of **1**, $C_{30}H_{52}O_4$, was derived from the DCIMS and the ^{13}C NMR spectra. The presence of three secondary and one tertiary hydroxyl groups was indicated by the successive elimination of four molecules of water observed in the DCI mass spectrum and the resonances of four oxygen bearing sp^3 carbons at δ78.17 (*d*), 67.79 (*d*), 67.29 (*d*) and 70.92 (*s*), respectively. Confirming evidence was obtained from the ^{1}H NMR spectrum, which showed signals of three secondary alcohols at δ4.1 (H-6$_{ax}$), 3.78 (H-16$_{ax}$) and 3.22 (H-3$_{ax}$) The multiplicities as determined by the DEPT spectra suggested a hopane or lupane-type skeleton. Compound **1** was finally identified as mollugogenol A by comparison with reported ^{13}C NMR data [6] and co-TLC with an authentic sample, previously isolated from *M. disticha* [7].

Compound **2**, $C_{30}H_{48}O_2$, exhibited a UV spectrum indicative of a heteroannular diene chromophore similar to hop-15,17(21)dienes [8]. The hopane skeleton and the positions of the functional groups were established by ^{13}C NMR and extensive ^{1}H NMR studies (COSY and NOE difference spectroscopy). Carbon resonances were assigned with the aid of DEPT spectra and data reported for related triterpenoids [9]. Compound **2** was found to be identical with mollugogenol B.



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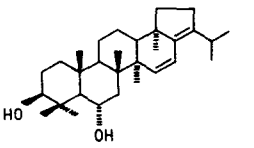

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Compounds **1** and **2** are both known compounds, which have been previously isolated from *M. hirta* [10–12] and *M. disticha* [7] However, no detailed NMR data of mollugogenol B (**2**) and no biological activity of the isolates have been reported.

Mollugogenol A(**1**) inhibited growth of the plant pathogenic fungus *Cladosporium cucumerinum* at 1.5 μg in a direct bioautographic assay on TLC [5], whereas diene **2** was inactive at 50 μg. Mollugogenol A is therefore about equally active in this test system as the well-known antifungal flavone tangeretin (2 μg) [13] No molluscicidal activity against *Biomphalaria glabrata* [14] was observed for either compound when tested at 50 ppm.

EXPERIMENTAL

General. DCIMS and EIMS were measured on a Ribermag-R10-1013 quadrupole instrument DCIMS spectra were recorded in the positive ion mode with NH_3 as reactant gas ^1H and ^{13}C NMR spectra were measured at 200 and 50 1 MHz, respectively TMS was used as an int standard. NOE difference spectra were measured with a presaturation delay of 3 sec A 1-2 Hz line broadening function was applied to the difference FID prior to Fourier transformation.

Plant material A voucher specimen of *Mollugo pentaphylla* L syn *M stricta* L has been deposited at the Jawaharlal Institute, Pondicherry (Voucher specimen No 10/76)

Extraction and isolation The air-dried plant material was extracted with aq. EtOH. The EtOAc-soluble portion of the extract (3 8 g) was submitted to CC over silica gel with $CHCl_3$–MeOH (100 0→4 1) as eluent Five fractions were collected Fraction 4 (55 mg), upon chromatography over Sephadex LH 20 ($CHCl_3$–C_6H_{12}–MeOH, 20 20 1), yielded antifungal compound 1 Mollugogenol B(**2**) (150 mg) was obtained from fraction 2 (660 mg) after CC on silica gel ($CHCl_3$) and Sephadex LH 20 ($CHCl_3$–C_6H_{12}–MeOH, 20·20 1)

Mollugogenol A (**1**). $C_{30}H_{52}O_4$ White crystals. DCIMS (positive ion mode, NH_3) *m/z* 477 $[M+H]^+$, 476 $[M]^+$, 459 $[(M+H)-18]^+$, 441 $[(M+H)-36]^+$, 423 $[(M+H)-54]^+$, 405 $[(M+H)-72]^+$, 207, 187, 180 EIMS *m/z* (rel int) 400 (2), 382 (1), 346 (2), 205 (23), 187 (100). ^1H NMR ($CDCl_3$ + 10% C_5D_5N) δ 4 1 (1H, *ddd*, H-6ax), 3 78 (1H, *ddd*, H-16ax), 3 22 (1H, *dd*, H-3ax), 1 44, 1 25, 1 22, 1 09, 1 05, 1 01, 0 90, 0 74, (3H each, 8 × Me) ^{13}C NMR ($CDCl_3$ + 10% C_5D_5N) δ 78 17 (*d*) (C-3), 70.92 (*s*) (C-22), 67 79[a] (*d*) (C-6), 67 29[a] (*d*) (C-16), 60 07 (*d*) (C-5), 57 34 (*d*) (C-17), 51 90 (*d*) (C-21), 49 12 (*d*) (C-9), 47 17 (*d*) (C-13), 46 47 (*s*) (C-18), 45 38 (*t*) (C-15), 43 42 (*s*) (C-14), 42 66 (*t*) (C-7), 42 56 (*s*) (C-8), 39 45 (*t*) (C-19), 39 04[b] (*s*) (C-4), 38 87[b] (*s*) (C-10), 38 47 (*t*) (C-1), 30 78 (*q*) (C-29), 29.99 (*q*) (C-23), 26 69 (*t*) (C-2), 25 85 (*t*) (C-20), 22 95 (*t*) (C-12), 22 59 (*q*) (C-30), 20 62 (*t*) (C-11), 17 92 (*q*) (C-28), 17 48 (*q*) (C-27), 16 66 (*q*) (C-26), 16 08 (*q*) (C-24), 15 29 (*q*) (C-25)
[a,b] Assignments interchangeable

Mollugogenol B (**2**) $C_{30}H_{48}O_2$, White crystals UV λ_{max}^{MeOH} nm (log ε) 261sh (3 98), 251 (4 16), 244 (4.13). DCIMS (positive ion mode, NH_3) *m/z* 458 $[M+NH_4]^+$, 441 $[M+H]^+$, 423 $[(M+H)-18]^+$, 405 $[(M+H)-36]^+$, 187 EIMS *m/z* (rel int.): 440 (4) $[M]^+$, 425 (2), 407 (4), 397 (0 3), 389 (2), 201 (7), 187 (100) ^1H NMR ($CDCl_3$) δ 6 20 (1H, *d*, *J* = 10 2 Hz, H-16), 5 57 (1H, *d*, *J* = 10 2 Hz, H-15), 4 06 (1H, *ddd*, *J* = 10.5/10 5/4.0 Hz, H-6*ax*), 3 18 (1H, *dd*, *J* = 11.1/5 0 Hz, H-3*ax*), 2 73 (1H, *sept*, *J* = 5 6 Hz, H-22), 2 31 (1H, *dd*, *J* = 16/6 2 Hz, H-20a), 2 15 (1H, *dd*, *J* = 16/8 3 Hz, H-20b), 1 80 (1H, *dd*, *J* = 12/4.1 Hz, H-7*eq*), 1 70 (H-2a, H-19a, H-9), 1 60 (H-2b), 1 55 (H-7*ax*), 1 32 (H-19b, H-23), 1 15 (H-27), 0 98 (*d*, *J* = 5 6 Hz, H-29 or H-30), 0 96 (H-24, H-25 or H-26), 0.94 (*d*, *J* = 5 6 Hz, H-30 or H-29), 0 90 (H-1), 0 85 (H-5*ax*), 0.84 (H-28, H-26 or H-25) ^{13}C NMR ($CDCl_3$) δ 140 77[a] (*s*) (C-21), 138 70[a] (*s*) (C-17), 134 47 (*d*) (C-16), 119 79 (*d*) (C-15), 78 66 (*d*) (C-3), 68 88 (*d*) (C-6), 60 77 (*d*) (C-5), 49 97 (*d*) (C-9), 47 90 (*s*) (C-18), 46 65 (*d*) (C-13), 45 95 (*s*) (C-14), 45 70 (*t*) (C-19), 42 51 (*s*) (C-8), 40 20 (*t*) (C-7), 39 43[b] (*s*) (C-4), 39 22[b] (*s*) (C-10), 38 50 (*t*) (C-1), 30 94 (*q*) (C-23), 28 16 (*t*) (C-20), 27.03 (*t*) (C-2), 26 48 (*d*) (C-22), 22 24[c] (*t*) (C-12), 21.64[c] (*t*) (C-11), 21 64[d] (*q*) (C-29), 21 26[d] (*q*) (C-30), 20 37[d] (*q*) (C-28), 18 77 (*q*) (C-26), 17 45 (*q*) (C-27), 16 69 (*q*) (C-24), 15 45 (*q*) (C-25) [a,b,c,d] Assignments interchangeable

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