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ENT-ATISANE-3β,16α,17-TRIOL, A DITERPENE FROM *EUPHORBIA ACAULIS*

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Key Word Index—*Euphorbia acaulis*, Euphorbiaceae, *ent*-atisane-3β,16α,17-triol, ^{13}C NMR

Abstract—A new *ent*-atis-16-ene diterpene was isolated from the rhizomes of *Euphorbia acaulis*. On the basis of chemical and spectral evidence and its partial synthesis by the sodium borohydride reduction of 3-oxoatisane-16α,17-diol, its structure was established as *ent*-atisane-3β,16α,17-triol

INTRODUCTION

The paste of rhizomes of *Euphorbia acaulis* has been used by the Tharu tribes of Kheri district of central India as a cure for inflammatory disorders A study of the constituents of the rhizomes has been conducted in an attempt to isolate the physiologically active compounds In previous communications [1, 2] we reported spectral and X-ray data of caudicifolin and a new *ent*-atis-16-ene diterpene, 3-oxoatisane-16α,17-diol (**1**) This paper describes the isolation and characterisation of another new *ent*-atis-16-ene diterpene, *ent*-atisane-3β,16α,17-triol (**2**), from this plant material

RESULTS AND DISCUSSION

The methanol extract of the rhizomes of *Euphorbia acaulis* was fractioned by the usual procedure as described in the Experimental to give compound **2** (0 0015%) The molecular formula of **2** was determined to be $C_{20}H_{34}O_3$ on the basis of mass spectral and elemental analysis. The ^{1}H NMR spectrum of **2** showed signals for three tertiary methyl groups at δ0 95, 0 98 and 1 15 The signals at δ3 35 and 3 78 which shifted to δ4.48 and 4 00, respectively, on acetylation were assigned to the geminal protons of the secondary and primary hydroxyl groups The ^{13}C NMR spectrum revealed the presence of 20 carbon atoms in the molecule The resonance frequencies (Table 1) indicated that all the carbon atoms in **2** are in a state of sp^3 hybridization The signals for the oxygenated carbon atoms in the spectrum were recorded at δ69 5 (triplet), 78 0 (doublet) and 74 0 (singlet) The molecular composition and the absence of any sp^2 hybridized carbon atom in the molecule indicated **2** to be tetracyclic.

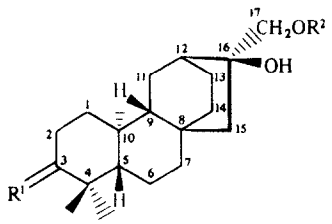
A comparative study of the ^{13}C NMR values of **1** and **2** (Table 1) indicated that the two compounds differ appreciably in ring A Since compound **2** was determined to be a triol and devoid of any carbonyl function, it was considered that compound **2** could be a reduction product of **1** and this was also supported by the difference of 2H atoms in their molecular composition The higher polarity of compound **2** in comparison to **1** (as indicated by the solubility and R_f value comparison on TLC) also supported this assumption

Compound **1**, when subjected to sodium borohydride reduction in methanol gave a product which was found to be identical to **2** in all respects (mmp, superimposable IR and mmp of their acetates). Further proof to the structure of **2** was obtained by Jone's oxidation of the acetonide of **2** and then its comparison with the acetonide of **1** by mmp and co-TLC

EXPERIMENTAL

General Mps uncorr

Plant material Rhizomes of *E acaulis* Roxh were collected in the vicinity of Dudhwa National Park, Madhya Pradesh (India) and adjoining the territory of Nepal in the state of Uttar Pradesh between 27 41′ and 28° 42′ N, and 80° 20′ and 81 19′ E A herbarium specimen has been deposited at the National Botanical Research Institute Lucknow, India



	R^1	R^2
1	O	H
2	H, OH	H
3	H, OAc	Ac

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Table 1 ^{13}C NMR values of compounds **2** (C_5D_5N) and **1** ($CDCl_3$)*

C	1	2	C	1	2
1	43.0 *t*	37 0 *t*	11	23 3 *t*†	23 2 *t*
2	33 9 *t*	29 0 *t*	12	32 0 *d*	32 0 *d*
3	217 5 *s*	78.0 *d*	13	23 5 *t*†	24 2 *t*
4	47 5 *s*	39 0 *s*	14	26 0 *t*	28.0 *t*
5	55 5 *d*	55 5 *s*	15	52 0 *t*	53 0 *t*
6	19 5 *t*	19 5 *t*	16	73.5 *s*	74.0 *s*
7	43.5 *t*	40.3 *t*	17	68.5 *t*	69.5 *t*
8	40.0 *s*	38 0 *s*	18	27 0 *q*	27 5 *q*
9	51 5 *d*	52 0 *d*	19	21 0 *q*	16 0 *q*
10	33 0 *s*	32 5 *s*	20	13.5 *q*	14 0 *q*

*Assignments have been made on the basis of proton noise decoupled spectra, SFORD spectra and comparison with reported data for similar compounds [3–5]

†Assignments are interchangeable

Extraction, fractionation and isolation The rhizomes of *E acaulis* were extracted with MeOH and the MeOH extract residue was partitioned in CH_2Cl_2 and EtOAc The residue from the EtOAc fraction was charged over a column of silica gel and eluted with $CHCl_3$–MeOH (19.1) mixture to afford **2** in a fairly high state of purity. The final purification by crystallization from EtOAc yielded colourless crystals. Compound **2**, mp 226°, CD(MeOH) $[\theta]$ $-7\,2\times10^{-2}$, IR ν_{max}^{KBr} cm^{-1} 3300–3400 (O–H stretching), 1440, 1385, 1130, 1050 (C–O stretching), ^{1}H NMR (60 MHz, C_5D_5N) δ0 95, 0.98 and 1 15 (three tertiary methyl groups) 3.35 (1H, *t*, $J=7$ Hz, –CHOH), 3 78 (2H, *s*, $-CH_2OH$); ^{13}C NMR (22 5 MHz, C_5D_5N). (Table 1) EIMS (probe) 70 eV, *m/z* (rel. int.) 322 $[M]^+$ (0 5), 291 $[M-CH_2OH]^+$ (100), 273 $[M-CH_2OH-H_2O]^+$ (77 7)

Acetylation of compound **2** A sample of **2** (20 mg) was treated with Ac_2O–pyridine at room temp overnight The work-up in the usual way afforded a diacetate derivative (22 mg) compound **3**, as a colourless solid, recrystallized from petrol–EtOAc mp 154°, ^{1}H NMR (60 MHz $CDCl_3$) δ0.80, 0.85 and 1 00 (three tertiary methyl groups) 2 02 and 2.08 (2*s*, 2 × OAc), 4.00 (ABq, $J=12$ Hz, $-CH_2OAc$) 4 48 (*t*, 1H, $J=7$ Hz, $-CHOAc$)

Acetonide of compound **2**. A sample of compound **2** (15 mg) was dissolved in dry Me_2CO and 2 drops of HCl were added The reaction mixture was kept at room temp overnight. The careful removal of Me_2CO afforded a colourless solid, recrystallized from petrol–EtOAc (12 mg), mp 129°

Jone's oxidation of the acetonide of compound **2** A sample of the acetonide (10 mg) dissolved in Me_2CO was treated with Jone's reagent and the reaction mixture was stirred for 2 hr. The work-up in the usual way afforded a colourless solid (5 mg), recrystallized from petrol–EtOAc mp 172°, mmp with the acetonide of **1** was 171°

$NaBH_4$ *reduction of compound* **1** A sample of compound **1** (30 mg) was dissolved in MeOH and chilled in an ice bath $NaBH_4$ (10 mg) was added to this and the reaction mixture stirred for 2 hr. The MeOH was removed under red. pres The residue was acidified with 10% HCl and filtered. Solid (28 mg) was washed with H_2O (2 × 20 ml) and recrystallized from EtOAc, mp 226°, mmp with **2** was 226°.

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