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A MINOR DITERPENE FROM *AMARACUS AKHDARENSIS*

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Key Word Index—*Amaracus akhdarensis*, Labiatae, diterpenoid, new isopimarane derivative, isoakhdartriol

Abstract—A new isopimarane diterpenoid, isoakhdartriol, was isolated in very small amount from the aerial part of *Amaracus akhdarensis* Its structure, isopimar-15-en-3β,8β,19-triol, was established by spectroscopic means

INTRODUCTION

We have recently reported [1] on the structure of three isopimarane diterpenoids isolated from *Amaracus akhdarensis* (Ietswaart et Boulos) Brullo et Furnari [2] (syn *Origanum akhdarensis*), Labiatae The products were akhdarenol (isopimara-7,15-dien-19-ol), akhdardiol (isopimara-15-en-8β,19-diol, **1**) and akhdartriol (isopimar-15-en-8β,11α,19-triol) From the acetone extract of this species a fourth product, isoakhdartriol, has been isolated now in very small amount its structure is here elucidated as isopimar-15-en-3β,8β,19-triol (**2**)

RESULTS AND DISCUSSION

Isoakhdartriol has formula $C_{20}H_{34}O_3$ The ^1H NMR data indicate the occurrence of three *tert* methyls, one vinyl group, one primary and one secondary hydroxy function The spectrum is very similar to that of akhdardiol, thus suggesting the same isopimarane skeleton, with three main differences First, a proton at δ3 42 (not present in **1**) appears as a double doublet with J_{ax-ax} 8 Hz and J_{ax-eq} 4 Hz, indicating a C–C$\underline{H}$OH–CH$_2$– group with the hydroxy function in the equatorial position Second, the separation of the two doublets of the C$\underline{H}_2$OH protons is greater than in akhdardiol and akhdartriol indeed, the doublets are centred at δ3 37 and δ4 23, whereas they fall at δ3 48 and δ3 78 in **1** respectively δ3 55 and δ3 90 in akhdartriol, such chemical shifts are observed [3] for 4β-CH$_2$OH isopimaranes having a 3β-OH substituent Third, the singlet attributed to 4α-Me is shifted from δ0 96 (akhdardiol) to δ1 21 (isoakhdartriol) These data strongly suggest the occurrence of a 3β-OH group in isoakhdartriol

The ^{13}C NMR data of isoakhdartriol **2**, compared with those of akhdardiol (**1**) (see Table 1), clearly confirm the occurrence of the secondary hydroxy group on C-3 Significant β-effects (downfield shifts) are observed for C-2 and C-4, while γ-effects (upfield shifts) occur for C-1 and C-18, and to a lesser extent for C-5 and C-19

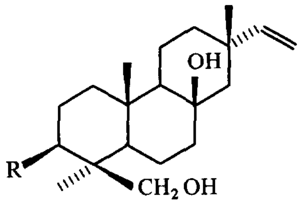
Hence isoakhdartriol has to be represented by the structure **2**

EXPERIMENTAL

Plant material was collected by Prof F Furnari (Institute of Botany, University of Catania) in Northern Cyrenaica (Libya), on the Gebel El Akhdar, in May 1981 Specimens are deposited in the Herbarium of the above Institute

Extraction and chromatography of the diterpene fraction were described in a previous note [1] Some fractions eluted with pet ether–AcOEt (60 40) and containing mainly akhdartriol revealed the co-occurrence of a product having close polarity Semipreparative HPLC (Waters instrument, μ-Porasil column 7 8 mm × 30 cm, eluant cyclohexane–EtOAc, 1 1, 2 ml/min) permitted the separation of akhdartriol (peak after 11′30″) from isoakhdartriol (peak after 15′) The product which was isolated (6 mg, oily, homogeneous on HPLC) could not be crystallized

High resolution MS found 322 257, $C_{20}H_{34}O_3$ requires 322 250 MS *m*/*z* 322, 307, 304, 289, 286, 273, 271, 223, 205 ^1H NMR (CDCl$_3$, 300 MHz) δ0 94 (*s*, 3H, 10β-Me), 1 21 (*s*, 3H,



1 R = H
2 R = OH

Table 1 ^{13}C NMR chemical shifts of compounds **1** and **2**

C	**1**	**2**	C	**1**	**2**
1	39 59 *t*	37 75 *t*	11	17 18 *t*	17 50 *t*
2	18 07 *t*	27 73 *t*	12	38 13 *t*	38 18 *t*
3	35 74 *t*	80 94 *d*	13	37 20 *s*	36 91 *s*
4	38 68 *s*	43 07 *s*	14	51 57 *t*	51 70 *t*
5	57 21 *d*	56 33 *d*	15	151 59 *d*	151 53 *d*
6	18 35 *t*	17 81 *t*	16	108 57 *t*	108 72 *t*
7	43 99 *t*	43 99 *t*	17	24 28 *q*	24 39 *q*
8	72 49 *s*	72 28 *s*	18	27 08 *q*	22 69 *q*
9	58 21 *d*	56 97 *d*	19	65 25 *t*	64 42 *t*
10	36 43 *s*	35 65 *s*	20	16 21 *q*	16 26 *q*

4α-Me), 1 23 (*s*, 3H, 13β-Me), 3 42 (*dd*, 1H, J = 8 Hz and 4 Hz, H-3), 3 37 and 4 23 (doublets, J = 10 75 Hz, 4β-C$\underline{H}_2$OH), 4 81 and 4 86 (six lines pattern, 2H, J = 10 5 Hz, 17 5 Hz, 1 5 Hz, –CH=C$\underline{H}_2$), 5 71 (*dd*, 1H, J = 10 5 Hz and 17 5 Hz, –C$\underline{H}$=CH$_2$) ^{13}C NMR (CDCl$_3$, 75 45 MHz) see Table 1

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A DITERPENE WITH A NEW CARBON SKELETON FROM *SOLIDAGO ALTISSIMA*

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Key Word Index—*Solidago altissima*, Compositae, diterpenes, new carbon skeleton

Abstract—An Indian sample of *Solidago altissima* afforded in addition to several clerodanes already isolated from other *Solidago* species, a diterpene with a new carbon skeleton Furthermore a ketone and a new anethole derivative were present

Solidago altissima has been studied previously In addition to widespread compounds, several clerodanes were isolated [1] We now have studied a sample collected at Jaipur, India The aerial parts gave 1β-hydroxygermacra-4(15),5,10(14)-triene [2], the known *cis*-clerodane lactones solidago lactone II [1], III [1], V [1] and VII [1] as well as the corresponding tiglate [3]

The roots also contain solidago lactone II, III, V, VII and the corresponding tiglate as well as the precursors of the latter two, where the epoxide was replaced by a 3,4-double bond [5] and 2-oxo-kolavenic acid lactone, already prepared from the corresponding alcohol [4] Furthermore the angelate **2**, the *trans*-clerodanes kolavenic acid [5], 7α-acetoxykolavenic acid [6], and 2-oxo-kolavenic acid [7] were present together with the aldehyde **1** The structure of the anethole derivative **2** clearly followed from the spectral data (see Experimental)

The acid **1** was transformed to the methyl ester **1a** The molecular formula was $C_{21}H_{32}O_3$ and the ^{1}H NMR spectral data (see Experimental) indicated the presence of an aldehyde by the singlet at δ9 96 The similarity of several signals with those of methyl kolavenoate showed that most likely these two diterpenes were closely related The presence of a homoallylic coupling between H-18 and H-1 required a five membered ring, especially as by careful spin decoupling all signals and, accordingly, all sequences could be established Therefore kolavenic acid is the precursor of **1**, which may be formed via oxidative cleavage followed by aldol condensation Alternatively a rearrangement of 2-hydroxy-3,4-epoxy kolavenic acid can be considered Compound **1** we have named solidagonal acid

The co-occurrence of *cis*- and *trans*-clerodanes in this species is remarkable In all cases, where a 6-oxygen function is present, the configuration is 9β-methyl and 10αH, while in all other cases *trans*-clerodanes with 10βH and 9α methyl were observed

EXPERIMENTAL

The air dried aerial parts (200 g) and the roots (70 g), collected in the campus of Rajasthan University, Jaipur, India, voucher deposited in RUBL-Herbarium, were extracted with Et$_2$O–petrol, 1 2, and worked-up in the usual fashion [8] CC fractions of the aerial parts (A) and the roots (R) were as follows 1 (petrol), 2 (Et$_2$O–petrol, 1 4), 3 (Et$_2$O–petrol, 1 1) and 4 (Et$_2$O) Fraction 2A (aerial parts) gave 15 mg 1β-hydroxygermacra-4(15),5,10(14)-triene TLC of 3A (CH$_2$Cl$_2$–C$_6$H$_6$–Et$_2$O, 4 4 1) gave 40 mg solidago lactone VII (R_f 0 5), 50 mg of the corresponding tiglate (R_f 0 4) and 10 mg solidago lactone V (R_f 0 7)