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A LINEAR DITERPENE DIOL FROM *LEMNA MINOR*

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Key Word Index—*Lemna minor*, Lemnaceae, isoprenoids, 4-hydroxyisophytol

Abstract—Four known isoprenoids were isolated from *Lemna minor* besides a novel diterpene which was attributed the structure (4*R*)-4-hydroxyisophytol by spectroscopic studies and chemical correlation

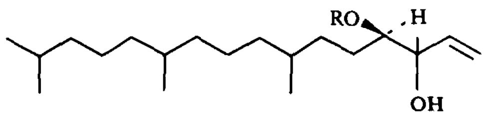
INTRODUCTION

In the course of our investigations of the constituents of the aquatic plant *Lemna minor*, we have determined the composition of the free and esterified fatty acids [1] In the present paper, we describe the isolation and structural elucidation of some isoprenoids from the same source

RESULTS AND DISCUSSION

Column chromatography followed by preparative TLC of the unsaponifiable lipid fraction of an ether extract of *Lemna minor* gave the hydrocarbons *trans*-1,3-phytadiene [2] and lycopersene [3] (identified on the basis of their spectroscopic properties), the monohydric alcohols sitosterol [4] and phytol [5] (identified by comparison with authentic samples) and a new diol, $[\alpha]_D + 1\ 5°$, which was attributed the structure of (4*R*)-4-hydroxyisophytol (**1a**) on the basis of the following spectral and chemical evidence

The mass spectrum showed $[M]^+$ at *m*/*z* 312 which corresponded to $C_{20}H_{40}O_2$ and the IR spectrum showed significative absorption bands at 3565, 1065 (hydroxyl groups) and 1635, 990 (C=C) cm^{-1} The ^1H NMR spectrum showed the same pattern of signals for four secondary methyl groups (δ 0 849, 0 857 and 0 871) as those of phytadiene and phytol, a methyl group at δ 1 261, a signal at δ 3 390 attributable to a proton geminal with a hydroxyl group and signals at δ 5 183, 5 352 and 5 930 characteristic of a terminal double bond Acetylation with acetic anhydride in dry pyridine gave the monoacetyl derivative **1b**, thus confirming the presence of a secondary and a tertiary hydroxyl group The relatively high shieldings of the hydroxyl-bearing carbons in the ^{13}C NMR of **1a** as well as biogenetic considerations suggested the presence of a vicinal diol proof of such a system was provided by the formation of the corresponding acetonide Definite confirmation of the structure was provided by the conversion of **1a** into isophytol [6], $[\alpha]_D + 9\ 5°$, by tosylation and subsequent lithium aluminium hydride treatment of the tosyl derivative Finally, the stereochemistry *R* at the chiral centre C-4 was assigned through the GLC modification of Horeau's method according to Brooks and Gilbert [7]



1a R = H

1b R = Ac

EXPERIMENTAL

Isolation of the isoprenoid-containing fraction Air-dried plants of *L minor* were continuosly extracted with cold Et_2O to give an extract (3 3 g) which was refluxed in MeOH–H_2O (3 2, 100 ml with NaOH (5%) The neutral fraction (300 mg) was extracted with Et_2O, then directly absorbed on a silica gel column which was eluted with petrol containing increasing percentages of Et_2O Petrol (140 ml) eluted a mixture (90 mg) of phytadiene and lycopersene which was separated by prep TLC (petrol–Et_2O, 19 1) Petrol–Et_2O (4 1, 200 ml) gave phytol (45 mg) and sitosterol (108 mg) Petrol–Et_2O (3 2, 80 ml) gave the diol **1a** (32 mg) $[\alpha]_D + 1\ 5°$ (*c* 1 0), MS *m*/*z* 312 $[M]^+$, 294 $[M - H_2O]^+$, 279, 276, 239, 220, 205, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3565, 1635, 1065, 990, ^1H NMR (270 MHz, $CDCl_3$, TMS int standard) δ 0 849 (*d*, 3H, *J* = 5 Hz), 0 857 (*d*, 3H, *J* = 5 Hz), 0 871 (*d*, 6H, *J* = 6 5 Hz), 1 251 (*s*, 3H), 3 390 (*t*, 1H, *J* = 7 Hz), 5 183 (*d*, 1H, *J* = 10 5 Hz), 5 352 (*d*, 1H, *J* = 17 2 Hz), 5 930 (*dd*, 1H, *J* = 10 5 and 17 2 Hz), ^{13}C NMR (67 88 MHz, $CDCl_3$, TMS as int standard) δ 19 46 (*q*), 19 72 (*q*), 21 47 (*q*), 22 66 (*q*), 24 43 (*t*), 24 75 (*t*), 27 95 (*d*) 28 20 (*t*), 29 17 (*d*), 29 65 (*t*), 32 75 (*d*), 32 91 (*d*), 37 10 (*t*), 37 25 (*t*), 37 38 (*d*), 39 33 (*t*), 75 64 (*d*), 80 45 (*s*), 114 32 (*t*), 142 71 (*d*)

Acetylation of **1a** **1a** (10 mg) was dissolved in dry pyridine (0 5 ml) and treated overnight with Ac_2O (excess) Usual work-up gave the monoacetate **1b** IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600, 1735, 1235, ^1H NMR (270 MHz, $CDCl_3$, TMS int standard) δ 1 230 (*s*, 3H), 1 985 (*s*, 3H), 4 558 (*t*, 1H), 5 180 (*d*, 1H), 5 347 (*d*, 1H), 5 930 (*dd*, 1H)

Isophytol **1a** was treated with tosyl chloride in dry pyridine overnight to give the crude tosylate of **1a** $LiAlH_4$ treatment of the tosylate in Et_2O gave isophytol which after purification by prep TLC had $[\alpha]_D + 10°$ (*c* 0 8), MS *m*/*z* 296 $[M]^+$, 278 $[M - H_2O]^+$

Acetonide of **1a** **1a** (10 mg) was treated with Me_2CO and a drop of 70% $HClO_4$ to give, after usual work-up, the acetonide (11 mg) ^1H NMR δ 1 248 (*s*, 6H), 1 442 (*s*, 3H), 4 562 (*t*, 1H)

Configuration of C-4 **1a** (20 μmol) in dry pyridine (14 μl), was treated with (±)-α-phenylbutyric anhydride (freshly crystallized, excess) at 40° for 1 5 hr (*R*)-α-Phenylethylamine (12 μl) was added and after 15 min the mixture was diluted with dry EtOAc (800 μl) and checked by GLC on a 25 m glass capillary column coated with OV-101 at 210°, following the procedure described in ref [7] A peak decrement of 4 for the (*R*)-acid indicated the *R*-configuration at C-4

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A DITERPENOID OF THE ATIS-16-ENE CLASS FROM *ELAEOSELINUM FOETIDUM*

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Key Word Index—*Elaeoselinum foetidum*, Umbelliferae, diterpenoid, *ent*-atis-16-ene derivative

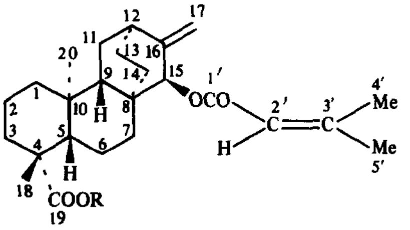
Abstract—A new diterpenoid has been isolated from the root of *Elaeoselinum foetidum* Its structure was established as *ent*-15α-senecioxy-atis-16-en-19-oic acid mainly by ^{1}H NMR and ^{13}C NMR spectroscopic studies of its methyl ester derivative

INTRODUCTION

In a previous communication [1], we reported *ent*-kaur-16-en-19-oic acid and the new methyl *ent*-8,9-seco-9,16-diketo-17-nor-kaur-8(15)-en-19-oate (foetidin) as the major diterpenic constituents of the aerial parts of *Elaeoselinum foetidum* (L) Boiss, an umbelliferous plant endemic at the Iberian Peninsula A study of the root of this plant, has now allowed the isolation of large amounts of the previously known *ent*-kaur-16-en-19-oic acid [2] together with a minor new diterpenic acid (**1**), which was purified as the methyl ester derivative (**2**), and whose structure was established by spectroscopic means

RESULTS AND DISCUSSION

The methyl ester (**2**) of the new diterpenoid had a molecular formula $C_{26}H_{38}O_4$ and its IR spectrum showed strong and broad ester (1718 cm^{-1}) and exocyclic methylene (3080, 1653 and 910 cm^{-1}) absorptions and no hydroxyl bands The ^{1}H NMR spectrum of **2** showed characteristic signals for a senecic ester [δ5 79 (1H, *qq*, J_{allylic} = 1 17 Hz, $J_{\text{allylic}'}$ = 0 95 Hz), 2 22 (3H, *d*, $J_{\text{allylic}'}$ = 0 95 Hz) and 1 94 (3H, *d*, J_{allylic} = 1 17 Hz)] attached to a carbocyclic secondary carbon atom This carbon is between an sp^3 tetrasubstituted carbon atom and an exocyclic methylene group, as the signal of its geminal proton showed a triplet at δ5 12 (J_{allylic} = 2 0 Hz) and the signals assigned to the exocyclic methylene group appeared as two triplets (J_{gem} = J_{allylic} = 2 0 Hz) at δ4 97 and 4 88 Double resonance experiments confirmed all the above assignments, because on irradiation at δ5 79 (olefinic proton of the senecic ester group) the signals at δ2 22



	R
1	H
2	Me