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A NEW SESQUITERPENE ALCOHOL FROM *PTEROCARPUS MARSUPIUM*

DAMA ADINARAYANA and KODAKANDLA VENKATA SYAMASUNDAR*

Department of Chemistry, S.V. University Post Graduate Extension Centre, Kurnool 518001, India; *Department of Chemistry, S.V. University College, Tirupati 517502, India

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Key Word Index—*Pterocarpus marsupium*; Leguminosae; sesquiterpene alcohol; eudesmane alcohol; selin-4(15)-en-1β,11-diol.

Abstract—The petrol extract of *Pterocarpus marsupium* afforded a new sesquiterpene alcohol of the eudesmane type, selin-4(15)-en-1β,11-diol, besides β-eudesmol, erythrodiol-3-monoacetate and pterostilbene.

INTRODUCTION

Pterocarpus marsupium Roxb. commonly known as vengisa or bijasal, is well known for its medicinal properties in Ayurvedic and Unani systems for the treatment of diabetes [1]. The water extract of the heartwood and root shows good curative properties in the treatment of diabetes which may be due to the presence of pterostilbene [2]. Earlier work [3, 4] on this plant has shown the presence of two phytosterols (pterocarpol A and pterocarpol B), pterostilbene, liquiritigenin and isoliquiritigenin in heartwood; pterostilbene together with small quantities of isoliquiritigenin in sapwood; 1-*epi*-catechin and pterostilbene in kinobark. This report describes the structure determination of a new sesquiterpene alcohol and other terpenes from root extracts of this plant.

RESULTS AND DISCUSSION

The petrol soluble part of an acetone extract of the root wood of *P. marsupium* on CC over Si gel yielded pterostilbene, β-eudesmol, erythrodiol-3-monoacetate and the new sesquiterpene alcohol (**1**).

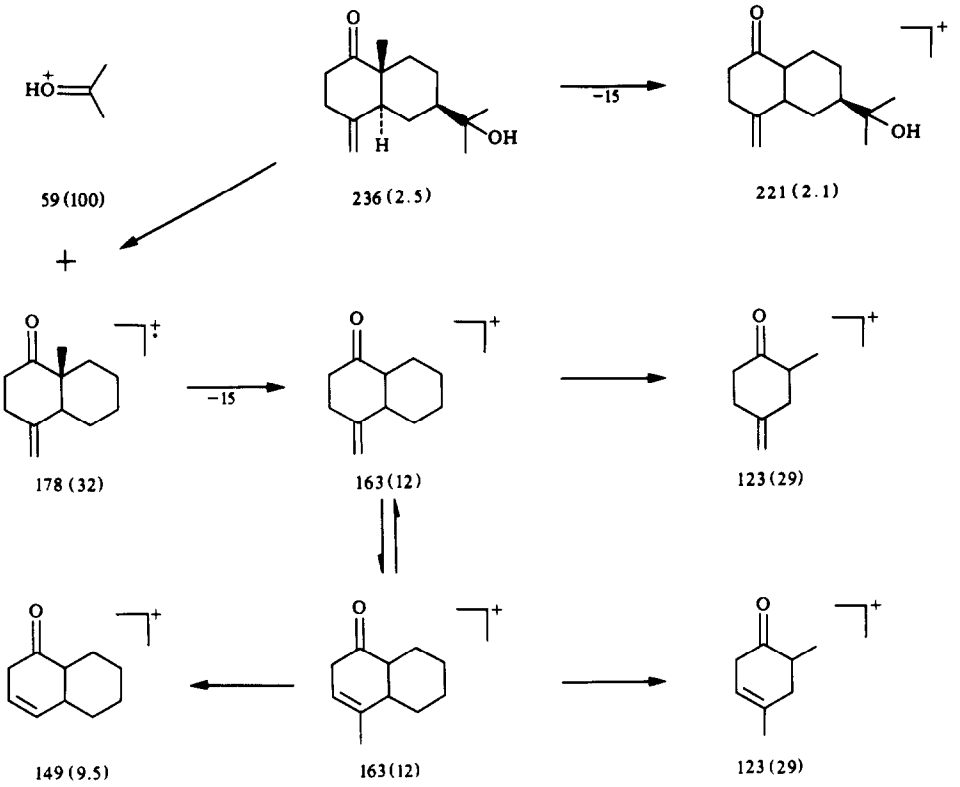
The new alcohol (**1**), $C_{15}H_{26}O_2$ had one double bond (IR, 1650 and 885 cm^{-1}) which was easily hydrogenated (Pd–C/H_2) to yield a dihydro-compound, $C_{15}H_{28}O_2$, showing that **1** was bicyclic. The co-occurrence of **1** with β-eudesmol was indicative that it also possessed the eudesmane carbon skeleton and this was established by NMR studies. In the ^1H NMR spectrum of the compound the signal at δ 0.68 for the angular methyl group at C-10 was characteristic of *trans*-fused eudesmanes [5]. The formation of a monoacetate (mp 79–80°) at room temperature and of a liquid diacetate at reflux temperature revealed that the two oxygen functions were present as a primary and as a tertiary hydroxyl group. In the mass spectrum of the compound the base peak at *m/z* 59 indicated the tertiary hydroxyl group was part of a hydroxy-*iso*-propyl group. Further, the NMR data showed a downfield shift of the *iso*-propyl methyls from δ 1.20 in the parent compound to 1.50 in the diacetate, which confirmed the position of the tertiary hydroxyl at C-11.

The location of the secondary alcohol group was established by oxidation with Jones' reagent to yield a ketone, mp 93–94°, which showed no UV absorption but displayed a strong IR absorption band at 1705 cm^{-1} (six-membered ring ketone). A positive Zimmermann colour test and the formation of a benzylidine derivative indicated the presence of at least one methylene group adjacent to the carbonyl function. All these observations ruled out positions C-2, C-3 and C-6 for the location of the hydroxyl group, which could only be present at one of the three remaining positions, i.e. C-1, C-8 or C-9. The ^{13}C NMR spectra of β-eudesmol (**2**) and pterocarpol (**3**) show the angular methyl group carbon signal around δ 16 ([6], Adinarayana, D. and Syamasundar, K. V. unpublished work), but the upfield shift to δ 10.2 obtained for **1** indicated that the hydroxyl group was present in the equatorial position on the γ-carbon atom to the angular methyl group [7], i.e. on C-1 or C-9. Due to the lack of gauche–gauche interactions (in the ketone) the shift to δ 16.6 in the ketone confirmed the above observation. In the mass spectrum of the ketone the fragment *m/z* 123 (derived from the exocyclic double bond ring) (Scheme 1) supported the location of the hydroxyl group at C-1. The stereochemistry of this hydroxyl group was deduced from a consideration of the NMR signal of the proton on the carbon-bearing hydroxyl, which appeared at δ 3.40 ($J = 5.5$, 10 Hz), as being equatorial. The upfield shift in the ^{13}C NMR of the angular methyl carbon to δ 10.2 was possible only if the hydroxyl group was equatorial, as in the case of brasudol (**4**) [6]. Thus the structure of the new sesquiterpene alcohol was established as selin-4(15)-en-1β,11-diol (**1**).

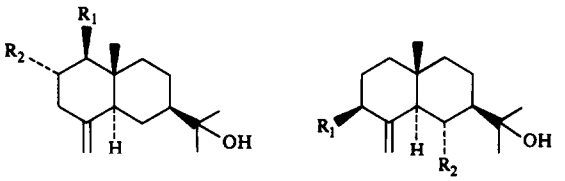
Pterocarpol (**3**), β-chenopodiol (**5**) [8] and selin-4(15)-en-3β,11-diol (**6**) [9] are the other diols with a eudesmane skeleton so far reported. There is good agreement with the spectral data of these compounds in support of the eudesmane skeleton and the position and stereochemistry of the secondary hydroxyl group on C-1 of the new sesquiterpene alcohol.

EXPERIMENTAL

Mps (Gallenkamp hot-stage melting block) are uncorr. ^1H



Scheme 1.



	R_1	R_2
1	OH	H
2	H	H
3	H	OH
4	Br	H

	R_1	R_2
5	H	OH
6	OH	H

NMR: 60 MHz in $CDCl_3$–TMS; ^{13}C NMR: 22.67 MHz and 67.89 MHz in $CDCl_3$–TMS; MS: 70 eV, direct probe.

Plant material. The main root of the plant was collected at the Mamandur forests, Andhra Pradesh, India.

Extraction and isolation. 3.75 kg of chips of the root wood was extracted exhaustively with Me_2CO. The Me_2CO extract was concd to dryness *in vacuo* and subjected to solvent fractionation with petrol (60–80°), C_6H_6, Et_2O and EtOAc.

The petrol-soluble part was chromatographed over Si gel. Fraction 1 was obtained on elution with petrol and on steam distillation it yielded β-eudesmol. Subsequent elution with petrol–EtOAc (19:1) gave pterostilbene and erythrodiol-3-monoacetate and with EtOAc yielded the sesquiterpene alcohol (**1**).

β-Eudesmol. Mp 80–81° (lit. 80–81°), $[\alpha]_D^{31}$ +38° ($CHCl_3$; *c* 0.7); IR ν_{max}^{KBr} cm^{-1}: 3280, 3090, 1640, 1470, 1450, 1440, 1370, 1260, 1182, 982, 885, 855, 793.

Pterostilbene. Mp 86–87° (lit. 87–88°). UV λ_{max}^{MeOH} nm: 220, 236, 307. The acetyl derivative, mp 126–127° (lit. 128°), was identical (mmp, IR) with an authentic sample.

Erythrodiol-3-monoacetate. Mp 238°, $[\alpha]_D^{31}$ +70° ($CHCl_3$; *c* 1.1). IR ν_{max}^{KBr} cm^{-1}: 3390 (OH), 2940, 1730 (MeCO), 1365, 1261, 1252, 1045, 970; MS *m/z* (rel. int.): 484 (49.4) $[M]^+$, 453 (64.2), 234 (68.6) and 203 (98). Hydrolysis with alcoholic KOH gave erythrodiol mp 233–235°. Diacetate (Ac_2O–pyridine) mp 186° (lit. 186°).

Selin-4(15)-en-1β,11-diol (**1**). Mp 156–157°, $C_{15}H_{26}O_2$ (Found C, 75.8; H, 10.92. $C_{15}H_{26}O_2$ requires C, 75.6; H, 10.9%.) $[\alpha]_D^{31}$ +56.4° ($CHCl_3$; *c* 1.5). IR ν_{max}^{KBr} cm^{-1}: 3340 (OH), 1650 and 885 (exo-$\rangle C{=}CH_2$); ^1H NMR ($CDCl_3$): δ 0.68 (3H, *s* angular Me), 1.20 (6H, *s*, *iso*-propyl Me's), 3.40 (1H, *q*, J = 5.5, 10 Hz) and 4.77 and 4.50 (2H, 2*br s*, $\rangle C{=}CH_2$); MS *m/z* (rel. int.): 238 (0.4) $[M]^+$, 222 (0.43), 220 (1.3), 179 (8.9), 162 (72), 147 (65), 134 (11), 133 (8), 121 (11.6), 120 (13), 119 (13.8), 107 (9.8), 105 (10.3), 95 (9.3), 91 (10.3), 81 (10.8), 79 (13.4), 59 (100), 55 (14.6), 43 (13.1), ^{13}C NMR ($CDCl_3$): δ 10.2 (C-14), 22.17 (C-8), 24.8 (C-6), 27.0 and 27.2 (C-12 and C-13), 31.5 (C-2), 34.2 (C-3), 37.0 (C-9), 40.1 (C-10), 47.5 (C-7), 48.9 (C-5), 72.5 (C-11), 79.1 (C-1), 108.0 (C-15), 148.6 (C-4).

Monoacetate of **1**. This was prepared using pyridine and Ac_2O at room temp. for 24 hr. Mp 79–80°. IR ν_{max}^{KBr} cm^{-1}: 3340 (OH), 1730, 1245 (acetoxyl), 1650 and 890; ^1H NMR ($CDCl_3$): δ 0.78 (3H, *s*, angular Me), 1.21 (6H, *s*), 2.02 (3H, *s*, MeCO), 4.43–4.47 (3H, *m*, exo-$\rangle C{=}CH_2$ and H-1).

Diacetate of **1**. This was prepared by refluxing 100 mg **1**

with 2 ml Ac_2O and 0.5 ml pyridine at reflux temp. for 3 hr. It was obtained as a viscous oil and showed no OH absorption (IR). ^1H NMR ($CDCl_3$): δ 0.81 (3H, *s*), 1.50 (6H, *s*), 2.05 and 2.11 (6H, 2*s*, MeCO), 4.65–4.90 (3H, *m*, exo-$\diagdown\!\!\diagup C{=}CH_2$ and H-1).

Jones' oxidation of **1**. **1** (200 mg) dissolved in Me_2CO(20 ml) was stirred with Jones' reagent for 30 min at 20°. Usual work-up yielded the ketone, mp 95–96°. IR ν_{max}^{KBr} cm^{-1}: 3340 (OH), 1705 (C=O), 1650 and 890; ^1H NMR ($CDCl_3$): δ 0.98 (3H, *s*), 1.22 (6H, *s*), 5.01 and 5.22 (2H, 2*s*); MS *m/z* (rel. int.): 236 (2.5) $[M]^+$, 221 (2.1), 203 (2.5), 178 (32.3), 163 (12.6), 149 (9.5), 135 (17.7), 123 (29.1), 119 (11.4), 107 (10.1), 105 (12.6), 93 (19.6), 91 (24.6), 79 (29.1), 77 (21.5), 59 (100); ^{13}C NMR ($CDCl_3$): δ 16.6 (C-14), 22.1 (C-8), 24.6 (C-6), 27.1 and 27.6 (C-12 and C-13), 32.3 (C-9), 34.5 (C-3), 38.1 (C-2), 48.0 and 48.4 (C-7 and C-10), 48.7 (C-5), 72.5 (C-11), 108.9 (C-15), 146.8 (C-4), 214.5 (C-1).

Hydrogenation of **1**. To 200 mg **1** in 6 ml MeOH 200 mg of Pd–C (5%) catalyst was added and hydrogenated for 2 hr. Usual work-up and crystallization (petrol–EtOAc) gave the dihydro-compound, mp 93–94°. IR ν_{max}^{KBr} cm^{-1}: 3340 (OH); MS *m/z* (rel. int.): 225 (5), 207 (3.7), 205 (4.4), 189 (7.5), 181 (56.2), 164 (32.5), 149 (43.7), 136 (21.2), 135 (17.5), 123 (63.7), 122 (29.4), 121 (29.4), 109 (41.2), 107 (42.5), 97 (25), 95 (51.2), 93 (37.5), 83 (30), 81 (87.5), 69 (48.7), 67 (56.2), 59 (100).

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