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SESQUITERPENE LACTONE FROM *SALMALIA MALBARICA**

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Key Word Index—*Salmalia malbarica*; Bombacaceae; cadalane; sesquiterpene lactone; gossypol; methoxy hemigossypol.

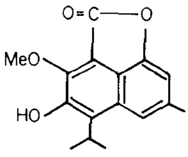
Abstract—A new cadalane type sesquiterpenoid, 1, 6-dihydroxy-3-methyl-5-(1-methylethyl)-7-methoxy-8-carboxylic acid (8 → 1 lactone) has been isolated from a 50% aqueous methanolic extract of 6–9 months old cultivated roots of *Salmalia malbarica* (*Bombax malbaricum*).

INTRODUCTION

Roots of *Salmalia malbarica* are known to possess[1] stimulant action and they form the chief ingredient of an indigenous aphrodisiac medicine, musla-semul, administered in cases of impotence. Earlier chemical investigations had led to the isolation and characterization of gossypol, hemigossypol derivatives[2] and structurally allied naphthaquinone derivatives[3] from this source. Here we report the isolation of a new sesquiterpenoid lactone structurally allied to hemigossypol. The residue from a 50% aqueous methanol extract of young roots of *S. malbarica* on chromatography over Si gel and further purification by crystallization yielded a pure principle coded as SM-I.

RESULTS AND DISCUSSION

Compound SM-I, colourless needles from benzene mp 206°, acetate mp 165°. The ^{1}H NMR $(CD_3)_2CO$, 60 MHz spectrum of the compound showed an aromatic methyl group at δ 2.42 (3 H, *s*). A doublet for isopropyl methyl groups resonated at 1.42 along with a methine septet at 3.66 ($J = 6$ Hz). Other signals included one singlet for a methoxyl group at δ 4.3, two broad singlets at 7.07 and 7.57 assigned to *meta*-coupled aromatic protons and a phenolic hydroxyl signal at 9.8 which collapsed on shaking with deuterated water. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ϵ): 210 (4000), 253 (7800), 263 (7500), 243 (2800), 351 (3000), 392 sh. IR$_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400 (–OH), 1755 (five-membered lactone C=O), 1634 (C=C). The high resolution mass spectrum of the compound showed its molecular composition to be $C_{16}H_{16}O_4$ (found: 272.1092; calculated: 272.1095). Other fragments at *m/z* 257 $[M - Me]^+$ and 229 $[M - Me - CO]^+$ were noteworthy. The spectral data of the compound showed it to be closely related to a methoxyhemigossypol derivative, with the difference that the compound lacked one phenolic hydroxyl and aldehyde group and in addition contained a five-membered lactone carbonyl. Consideration of physical and spectral characteristics along with biogenetic considerations led us to believe that the aldehyde group of hemigossypol had been oxidized and the carboxyl then lactonized with OH-1. Lactonization with OH-7 would yield a thermodynamically unstable species. A critical comparison of ^{1}H NMR shifts of 6-methoxy hemigossypol[4] and SM-I showed the methoxyl signal to be very lowfield and the methine proton of the isopropyl group slightly upfield in SM-I. This could happen only if the methoxyl group is attached to C-7 rather than C-6. In a 7-methoxy compound, such as SM-I, the methoxyl group will shift downfield due to the deshielding effect of the lactone carbonyl. Relief from Van der Waal steric repulsion due to the bulkier electron cloud of a methoxyl group will make the methine proton of the isopropyl group resonate at slightly higher field. This was shown by comparison of the ^{1}H NMR spectrum of thymol and its methyl ether. In the methyl ether the methine proton of the isopropyl group resonated at δ 2.98 while in the parent compound the signal was recorded at 2.87. This spectral data established SM-I (**1**) to be an oxidation product of 7-methoxy hemigossypol rather than the 6-methoxy isomer. The occurrence of 7-methoxy hemigossypol has not been reported previously in nature.



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EXPERIMENTAL

Mps are uncorr. Spectra were obtained in EtOH (UV), $(CD_3)_2CO$ (^{1}H NMR), KBr pellets (IR). ^{1}H NMR spectra were measured at 60 MHz and MS at 70 eV.

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Extraction. Roots (5.6 kg) of young cultivated plants grown from seeds collected from a local (Himachal Pradesh, India) wild source, were cut into small pieces, dried at 30° and powdered. The powdered drug was soaked in aq. MeOH (50%) for 48 hr. The percolate was concd to dryness under red. pres. The residue (230 g) was dissolved in hot MeOH and the soln allowed to stand overnight at room temp. when a solid (5 g) separated out. The solid was charged on a column of Si gel and subjected to graded elution with C_6H_6–EtOAc. Elution with C_6H_6–EtOAc (4 : 1) gave a solid found to be homogenous on TLC (R_f 0.25; C_6H_6–EtOAc, 10 : 3). The solid on crystallization from C_6H_6 gave colourless needles (SM-I), mp 206°, MS 272.1096, $C_{16}H_{16}O_4$, m/z (rel. int.): 257 (78.4), 229 (20.8), UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ϵ): 210 (4000), 253 (7800), 263 (7500), 343 (2700), 351 (3000), 392 sh. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400 (–OH), 1755 (γ-lactone C=O), 1635 (C=C). ^{1}H NMR, $(CD_3)_2CO$: δ 1.42 (6H, *d*, $J = 6$ Hz), 2.42 (3H, *s*, aromatic Me), 3.66 (1H, *sep*, $J = 6$ Hz), 4.3 (3H, *s*, –OMe), 7.07 and 7.57 (2 × 1H, *br s*, *meta*-coupled aromatic protons) and 9.8 (1H, *s*, –OH). Acetylation of the compound in pyridine with Ac_2O gave a colourless monoacetyl derivative (^{1}H NMR and IR) which was recrystallized from petrol, mp 165°.

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FURANOEREMOPHILANES FROM *LOPHOLAENA SPECIES*[*]

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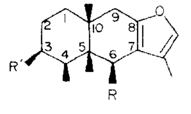
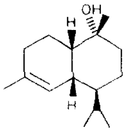
Key Word Index—*Lopholaena coriifolia*; *L. disticha*; *L. segmentata*; Compositae; sesquiterpenes; furanoeremophilanes.

Abstract—Three additional *Lopholaena* species afforded several furanoeremophilanes, two of them not reported previously.

Lopholaena, a genus with *ca* 20 taxa, is restricted to southern and tropical Africa. Only two species have been studied chemically[1] although we have now investigated three further species. The roots of *Lopholaena coriifolia* (Sond.) Phill. et C. A. Smith afforded caryophyllene and the furanoeremophilanes **1**[2], **2**[3], **3**[4], **5**[5], **6**[6] and **7**. The structure of the latter could be deduced from the ^{1}H NMR spectrum (Table 1) which was similar to that of **5**. The chemical shifts of H-3 and H-6 further showed that the ester group was at C-3. The aerial parts gave germacrene D, bicyclogermacrene, α-humulene, caryophyllene,



	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
R	H	OH	OAc	OAng	OH	OH	OH	OAng	OMeacr	OMeacr	H
R′	H	H	H	H	OAng	OSen	OMeacr	OAng	OMeacr	OAng	OAng



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[*] Part 443 in the series "Naturally Occurring Terpene Derivatives". For Part 442 see Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, 1989.