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A LABDANE DITERPENOID AND STEROL FROM *LAGERSTROEMIA LANCASTERI*

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Key Word Index—*Lagerstroemia lancasteri*; Lythraceae; labdane diterpenoid; sterol; lagerstronolide; stigmast-4-ene-3β,6α-diol.

Abstract—A new labdane diterpenoid, lagerstronolide, having a β-substituted γ-butyrolactone moiety, and stigmast-4-ene-3β,6α-diol were isolated together with sitosterol glucoside from *Lagerstroemia lancasteri*. The structures of the new compounds were determined by means of spectral and chemical analysis. This is the first report of labdane diterpenoid in the Lythraceae family.

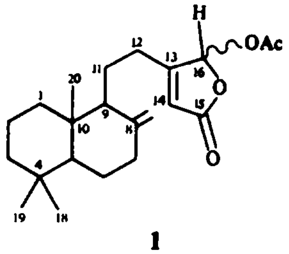
INTRODUCTION

Earlier work on the leaves and twigs of *Lagerstroemia lancasteri* afforded six triterpenoids and sitosterol [1]. Further investigation of this plant led to the isolation of a new diterpenoid named lagestronolide (**1**) and a 3,6-dihydroxysterol (**2**) and the known sitosterol glucoside in addition to the previously reported compounds [1].

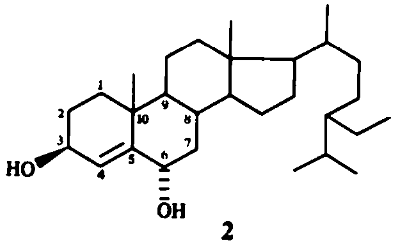
RESULTS AND DISCUSSION

Lagerstronolide (**1**), mp 162°, $C_{22}H_{32}O_4$ (M^+ at m/z 360.2301) $[\alpha]_D$ $-7.3°$, gave a positive Legal test indicating the presence of an α,β-unsaturated γ-lactone moiety [2]. Its UV spectrum showed a maximum at 213 nm (ε10000) and its IR spectrum showed bands at 1785, 1765 (β-substituted γ-acetoxybutenolide [3]) 1645 and 885 cm^{-1} (exo-cyclic methelene group [4]). The ^{1}H NMR spectrum (100 MHz) of compound **1** which showed singlets at δ0.78 (3H), 0.80 (3H), and 1.00 (3H) for three tertiary methyl groups and two broad singlets at δ4.63 and 5.10 respectively are in accordance with the structure **1** having an exocyclic methelene group located at C-8 [4]. The absolute configuration of **1** was not certain but a labdane was more likely, as the optical rotation was opposite in sign to that of a similar *ent*-labdane derivative [3]. The methylene and methine protons appeared as multiplets in the region δ1.2–1.65 and 1.85–2.40, respectively. The presence of a β-substituted γ-acetoxybutenolide moiety was also demonstrated by the proton signals ascribed to the olefinic and oxygen bearing methine proton at δ6.81 and 5.91 (*s*, 1H each) [3] and the acetoxy methyl group appeared as a singlet at δ2.16. The presence of ion peaks at m/z 360, 300, 285 and 109 [3] in the mass spectrum of lagerstronolide confirmed its structure as **1**.

Compound **2** was isolated from the $CHCl_3$–MeOH (19:1) eluant as colourless needles, mp 220° (M^+ at m/z 430). Its IR spectrum showed the presence of hydroxyl groups (3300 cm^{-1}) and the ^{1}H NMR spectrum showed the olefinic proton at δ5.50 (1H, *br s*, $W_{1/2}$ = 3 Hz) and the carbinol methine protons appeared at 4.18 (H-3, *m*, $W_{1/2}$ = 13 Hz) and 4.10 (H-6, *t*, J = 7 Hz), respectively. Compound **2** on oxidation with CrO_3–AcOH [5] followed by *in situ* reduction with Zn dust [6] afforded the known compound 5α-stigmastane-3,6-dione (**3**), mp 199° (M^+ at m/z 428) [7]. The hydroxyl group at C-6 has been assigned as equatorial (α) from the J-value (7 Hz) of the H-6 signal. The hydroxyl group at C-3 is β and equatorially oriented on the basis of biogenetic consideration. The structure of **2** was also supported by its mass spectral fragmentations (see experimental). Thus the structure of compound **2** was established to be stigmast-4-ene-3β,6α-diol. The structure of sitosterol glucoside was elucidated by its hydrolysis to sitosterol and glucose.



1



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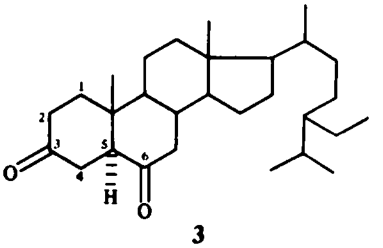

3

EXPERIMENTAL

NMR: solvent $CDCl_3$; TMS as int. standard; mps uncorr. The TLC spots were exposed to I_2 vapour for detection. Petrol, 60–80°. The plant material was collected from Royal Agri-Horticultural Society, Calcutta.

Isolation—Extraction of the leaves and twigs of *Lagerstroemia lancasteri* (1 kg) was carried out as described earlier [1]. The $CHCl_3$ concentrate was chromatographed over silica gel (60–120 mesh) and 100 fractions of 250 ml each were collected using solvent and solvent mixture of increasing polarities. Fractions were mixed together according to their TLC behaviour.

Lagerstronolide (**1**). The earlier petrol–C_6H_6 (1 : 3) fractions afforded compound **1** crystallizing from $CHCl_3$–MeOH as needles (10 mg); TLC (silica gel); R_f 0.45 (benzene); $[\alpha]_D$ $-7.09°$ ($CHCl_3$; c 0.2); IR ν_{max}^{KBr} cm^{-1}: 3000, 1460, 1380, 1212, 1055, 982, MS m/z (rel. int.): 360 $[M]^+$ (2), 300 $[M - AcOH]^+$ (11), 285 $[M - AcOH - Me]^+$ (100). (Calcd for $C_{22}H_{32}O_4$: 360.2301; found 360.2301).

Stigmast-4-ene-3β,6α-diol (**2**). The earlier $CHCl_3$–MeOH (19 : 1) eluants afforded compound **2** crystallizing from MeOH as needles (20 mg); TLC (silica gel) R_f 0.45 ($CHCl_3$–MeOH, 19 : 1); $[\alpha]_D$ $+21.50°$ ($CHCl_3$; c 0.5); IR ν_{max}^{KBr} cm^{-1}; 3300, 2945, 2865, 1452, 1375, 1025, ^{1}H NMR ($CDCl_3$, 100 MHz): δ0.6–1.0 (6 × Me), 1.2–1.75 (methylene and methine H); MS m/z (rel. int.): 430 $[M]^+$ (28), 412 (100), 397 (37), 271 (24), 229 (29), 175 (99), 136 (25) [8].

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