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LAGERENYL ACETATE AND LAGERENOL, TWO TETRACYCLIC TRITERPENOIDS WITH THE CYCLOARTANE SKELETON FROM *LAGERSTROEMIA LANCASTERI*

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Key Word Index—*Lagerstroemia lancasteri*; Lythraceae; triterpenoids; lagerenyl acetate; lagerenol; 2α-hydroxy-3β-*E*-*p*-coumaryloxy-urs-12-en-28-oic acid; 2α-hydroxyursolic acid; germanicyl acetate; friedelin; β-sitosterol.

Abstract—Lagerenyl acetate and lagerenol, two new tetracyclic triterpenoids with the cycloartane skeleton, together with four other triterpenoids 2α-hydroxy-3β-*E*-*p*-coumaryloxy-urs-12-en-28-oic acid (jacoumaric acid, isolated as its monoacetylmethylcarboxylate derivative), 2α-hydroxyursolic acid (isolated as its diacetate), germanicyl acetate and friedelin, and sitosterol were isolated from the leaves and twigs of *Lagerstroemia lancasteri*. The structures of lagerenyl acetate and lagerenol were established as 3β-acetoxycycloart-24-one and 3β-hydroxycycloart-24-one, respectively, on the basis of spectral and chemical evidence.

INTRODUCTION

The family Lythraceae is well-known for producing alkaloids [1]. *Lagerstroemia lancasteri* [2], a tall hybrid shrub of this family, has not been previously chemically investigated. Our investigation on the petrol and chloroform extracts of the leaves and twigs of this plant resulted in the isolation of two new and four known triterpenoids and sitosterol, but no alkaloid could be isolated. The present paper gives an account of the isolation of all the constituents and establishment of the structures of the new triterpenoids.

RESULTS AND DISCUSSION

Extensive chromatography of the petrol and chloroform extracts of the leaves and twigs of *L. lancasteri* over silica gel afforded two new tetracyclic triterpenoids with the cycloartane skeleton, designated lagerenyl acetate (**1**) and lagerenol (**2**), in addition to sitosterol and four known triterpenoids, viz. 2α-hydroxy-3β-*E*-p-coumaryloxy-urs-12-en-28-oic acid (**3**) (jacoumaric acid, isolated as its monoacetylmethylcarboxylate derivative, **5**), 2α-hydroxyursolic acid (**4**) (isolated as its diacetate, **9**), germanicyl acetate and friedelin.

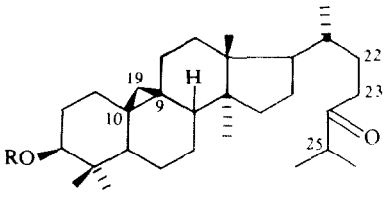
Lagerenyl acetate, mp 122–123°, $C_{32}H_{52}O_3$ (M^+ at *m/z* 484), $[\alpha]_D^{30}$ +57.8° ($CHCl_3$), has been assigned the structure **1** from chemical and spectral evidence It gave a positive Liebermann–Burchard test for triterpenoids and no colouration with TNM. Its IR spectrum showed the presence of aliphatic ester (1735 and 1235 cm^{-1}) and ketomethylene (1712 and 1450 cm^{-1}) [3] groups and a cyclopropane ring (1030 cm^{-1}) [4]. The ^1H NMR spectrum (80 MHz, $CDCl_3$) indicated the presence of the 9,10-cyclopropane ring (δ0.30 and 0.55, each 1H, *d*, *J* = 4 Hz, H_2-19) [5], an equatorial C-3 acetoxy group (2.05, 3H, *s*, OCOMe; 4.58, 1H, *m*, $W_{1/2}$ = 10 Hz, H-3α) a side chain moiety (2.38, 2H, *t*, *J* = 4.8 Hz, H_2-23; 2.50, 1H, *septet*, *J* = 7 Hz, H-25; 1.10, 6H, *d*, *J* = 7 Hz, H_3-26 and H_3-27), five methyl groups on the cycloartane skeleton (0.85, 0.90 and 0.96) [5] and methylenes and methines having 22 protons (1.2–1.7, *m*). The appearance of peaks at *m/z* 302, 203, 175 and 122 in the mass spectrum of lagerenyl acetate for the ions **a**–**d**, respectively, indicated the presence of the 9,10-cyclopropane ring and the attachment of the acetoxy group to ring A [6]. The fragment ion peak at *m/z* 127 for the C-17 side chain (ion **e**) was also obtained.

On hydrolysis with 1% potassium hydroxide–methanol compound **1** afforded lagerenol (**2**), mp 92°, $[\alpha]_D^{30}$ +44° ($CHCl_3$), IR ν_{max}^{KBr} 3340 cm^{-1} (OH), which was found to be identical with another triterpenoid of this plant in all respects (mmp, $[\alpha]_D$, co-TLC and IR). The ^1H NMR and mass spectral features of the latter compound were also fully consistent with structure **2**. The ^1H NMR spectrum clearly indicated the β-equatorial nature of the C-3 hydroxyl group (δ3.30, *dd*, *J* = 10 and 5 Hz). The mass spectrum exhibited peaks for ions **a**–**e**. Again acetylation of lagerenol, isolated from the plant, afforded **1**. The mp and $[\alpha]_D$ values of lagerenyl acetate and lagerenol were very close to those of 3β-acetoxycycloart-24-one mp 123°, $[\alpha]_D$ +53° ($CHCl_3$) and 3β-hydroxycycloart-24-one, mp 92–94°, $[\alpha]_D$ +44.5° ($CHCl_3$), respectively, both obtained from 3β-acetoxy-24-methylenecycloartane [3].

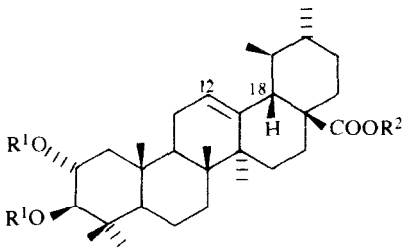
The other constituents were identified either by direct comparison with authentic samples or by comparison of the physical (mp and $[\alpha]_D$) and spectral (IR, ^1H NMR and mass spectra) data of the compounds and/or their derivatives with those reported in the literature (see Experimental). To our knowledge, *L. lancasteri* is the first plant of the family Lythraceae elaborating the above types of triterpenoids.

EXPERIMENTAL

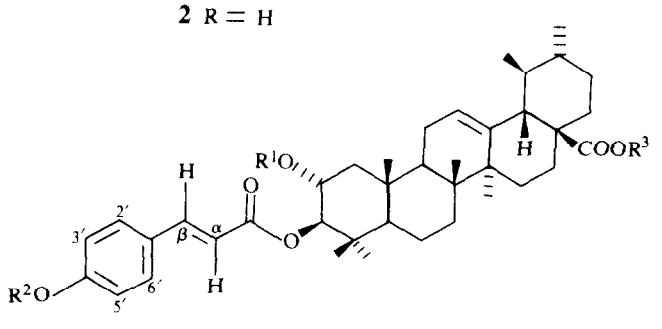
Mps: uncorr.; IR: KBr; UV: 95% EtOH; ^1H NMR: δ-values in ppm downfield from TMS; MS: 70 eV; Si gel (100–200 mesh) for



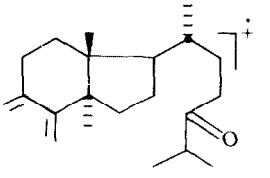
1 R = Ac
2 R = H



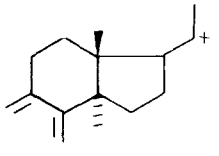
4 $R^1 = R^2 = H$
8 $R^1 = H, R^2 = Me$
9 $R^1 = Ac, R^2 = H$



3 $R^1 = R^2 = R^3 = H$
5 $R^1 = Ac, R^2 = H, R^3 = Me$
6 $R^1 = R^2 = Ac, R^3 = Me$
7 $R^1 = R^2 = H, R^3 = Me$



a



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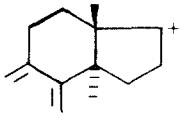
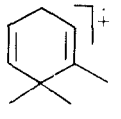
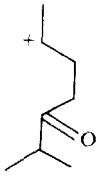


c



d



e

chromatography unless otherwise stated; spots visualized in UV light and on exposure to I_2 vapour; homogeneity of compounds established by TLC and MS.

Extraction. Air-dried and powdered leaves and twigs (1 kg) of *L. lancasteri*, collected from Royal Agri-Horticultural Society, Calcutta, in April 1978, were extracted in a Soxhlet apparatus with petrol (60–80°) and $CHCl_3$ in succession (40 hr each). The residues obtained by concn of the extracts were found to be devoid of alkaloidal constituents (negative Dragendorff's test) and were separately chromatographed over silica gel (60–120 mesh), elution being carried out with solvents and solvent mixtures of increasing polarities.

Germanicyl acetate. The light yellow solid from the petrol–C_6H_6 (3:1) eluates of the main chromatogram of the petrol extract was repeatedly chromatographed over Si gel. The petrol–C_6H_6 (9:1) fractions afforded germanicyl acetate as colourless flakes (0.10 g), mp 268° ($CHCl_3$–MeOH), $[\alpha]_D^{30}$ +15° ($CHCl_3$; *c* 0.107), positive L–B test and TNM colouration. The IR and ^1H NMR spectral data were similar to those reported in the lit. for germanicyl acetate [7, 8]; MS *m/z* (rel. int.): 468 $[M]^+$ (37) ($C_{32}H_{52}O_2$), 453 (26.8), 408 (12.5), 393 (5.4), 249 (3.6), 218 (19.6), 205 (41.4), 204 (100), 189 (69.6) and 177 (64.3). Hydrolysis with 1% KOH–MeOH yielded germanicol, mp 178°, $[\alpha]_D^{30}$ +9° ($CHCl_3$; *c* 0.064) [9].

Friedelin. The light yellow residue from the petrol–C_6H_6 (1:1) eluates of the above main chromatogram was repeatedly chromatographed over silica gel to afford friedelin as colourless needles (0.015 g), mp 255° ($CHCl_3$–MeOH), $[\alpha]_D^{30}$ −22° ($CHCl_3$; *c* 0.084), identical with an authentic sample in all respects (mmp, co-TLC, IR).

Lagerenyl acetate (**1**). The gummy yellow residue obtained from the early C_6H_6 eluates of the main chromatogram of the petrol extract was rechromatographed over silica gel. The petrol–C_6H_6 (1:3) eluates afforded **1**, crystallizing from $CHCl_3$–MeOH as colourless flakes (0.025 g), mp 122–123°, $[\alpha]_D^{30}$ +57.8° ($CHCl_3$; *c* 0.099); IR ν_{max}^{KBr} cm^{-1}: 2945, 1735, 1712, 1450, 1375, 1360, 1235 and 1030; MS *m/z* (rel. int.): 484 $[M]^+$ (19.1) ($C_{32}H_{52}O_3$), 424 (100), 409 (46.9), 355 (18.4), 302 (45.2), 222 (20.8), 203 (34.9), 175 (48.6), 127 (34.3), 122 (16.2), 121 (34.9), 107 (40.3), 95 (46.9), 71 (44.4) and 43 (68.5).

Sitosterol. The later C_6H_6 eluates of the main chromatogram of the petrol extract furnished sitosterol, crystallizing from

Cl_3–MeOH in flakes (0.10 g), mp 137° alone and the mp ined undepressed upon admixture with an authentic sample. *gerenol* (**2**). The residue from the C_6H_6–$CHCl_3$ (1:1) eluates e main chromatogram of the petrol extract was rechromato- ıed over silica gel. The C_6H_6–$CHCl_3$ (1:1) eluates afforded stallizing from $CHCl_3$–MeOH as colourless plates (0.005 g),)2°, $[\alpha]_D^{30}$ +44.6° ($CHCl_3$; *c* 0.094); IR ν_{max}^{KBr} cm^{-1}: 3340, 1455, 1378, 1362 and 1030 (cyclopropane ring) [4]; IMR (80 MHz, $CDCl_3$): δ0.35 and 0.59 (each 1H, *d*, 4.5 Hz, H_2-19), 0.82, 0.90 and 0.97 (15H, five methyls), 1.12 *d*, *J* = 7 Hz, H_3-26 and H_3-27), 1.2–1.7 (*m*, methylene and ine Hs), 2.41 (2H, *t*, *J* = 4.8 Hz, H_2-23), 2.54 (1H, *septet*, *J* Hz, H-25), 3.30 (1H, *dd*, *J* = 10 and 5 Hz, H-3); MS *m/z* (rel. 442 $[M]^+$ (30.1) ($C_{30}H_{50}O_2$), 424 (100), 409 (45.9), 355 (19), 49.6), 222 (11.8), 203 (33), 175 (50.9), 127 (33.6), 122 (16.1), 43.3), 107 (47.8), 95 (61.4), 71 (56.1) and 43 (100).

,3β-Diacetoxyurs-12-en-28-oic acid (**9**) *and methyl 2α-ıxy-3β-*E*-p-coumaryloxy-urs-12-en-28-oate* (**5**). The light ı residue from the $CHCl_3$–MeOH (17:1) eluates of the main matogram exhibited two very close spots on TLC. It was lated (Ac_2O–pyridine, room temp., 16 hr) and the less polar uct obtained by usual work-up was chromatographed over gel.

ıe $CHCl_3$–MeOH (97:3) eluates afforded **9** as a colourless rphous solid (0.025 g), mp 227°, $[\alpha]_D^{30}$ +17.12° ($CHCl_3$; *c*), positive L–B test and TNM colouration; IR ν_{max}^{KBr} cm^{-1}: (ester C=O), 1698 (COOH), 1240 and 1032; ^{1}H NMR MHz, $CDCl_3$): δ0.78, 0.91 and 1.08 (21H, seven methyls), -1.75 (methylene and methine Hs), 1.98 and 2.06 (each 3H, *s*, OO-2 and MeCOO-3), 2.20 (1H, *d*, *J* = 12 Hz, H-18) [10], (1H, asymmetrical *d*, *J* = 10 Hz, H-3), 5.15 (1H, *m*, $W_{1/2}$ Hz, H-2), 5.25 (1H, *m*, $W_{1/2}$ = 10 Hz, H-12); MS *m/z* (rel. 556 $[M]^+$ (0.4) ($C_{34}H_{52}O_6$), 436 (4.7), 307 (1.1), 248 (100), (41.8), 189 (20.9) and 133 (43.0). Hydrolysis of **9** with 1% H–MeOH afforded 2α-hydroxyursolic acid (**4**) as an amorph- solid, mp 238–240° (*d*) [lit. [11] 243–245° (d)] (R_f com- ble to that of the starting material).

ıe $CHCl_3$–MeOH (19:1) eluates afforded a crude solid which d not be purified even after several chromatographies. This ı showing the presence of a carboxyl group in its IR spectrum 5 cm^{-1}) was methylated with CH_2N_2 and the product was matographed over silica gel. The $CHCl_3$–MeOH (49:1) eluates ished **5**, crystallizing from EtOAc–petrol in colourless need-).09 g), mp 281°, $[\alpha]_D^{30}$ + 10.82°, positive L–B test and TNM uration, violet with $FeCl_3$–EtOH. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), , 1705, 1695, 1600 and 1585 (aromatic), 1260, 1235, 1160, 975 825 (*p*-disubstituted C_6H_6). UV λ_{max}^{EtOH} nm (log ε): 316 (4.37) 239 (4.05) shifted to 372 (4.49), 312 (3.80) and 245 (3.90) on tion of alkali; this is reminiscent of a *p*-hydroxy-*E*-cinnamoyl ;ty [12] (316 → 372). ^{1}H NMR (80 MHz, $CDCl_3$): δ0.76, 0.97 and 1.09 (21H, seven Mes), 1.25–1.75 (*m*, methylene and ıine Hs), 1.91 (3H, *s*, MeCOO-2), 2.20 (1H, *d*, *J* = 12 Hz, H- 10], 3.60 (3H, *s*, MeOCO-17), 4.85 (1H, asymmetrical *d*, *J* 0.6 Hz, H-3), 5.18 (1H, *m*, $W_{1/2}$ = 16 Hz, H-2), 5.25 (1H, *m*, = 10 Hz, H-12), 5.67 (1H, *br s*, disappeared on D_2O shake, 4'), 6.25 (1H, *d*, *J* = 16.5 Hz, H-α), 6.82 (2H, *d*, *J* = 8.8 Hz, H- ıd H-5'), 7.38 (2H, *d*, *J* = 8.8 Hz, H-2' and H-6') and 7.60(1H, *J* = 16.5 Hz, H-β); MS *m/z* (rel. int.): 674 $[M]^+$ (3) $_{58}O_7$), 614 $[M-HOAc]^+$ (4.48), 467 [614 OC_6H_4–CH=CH–CO]$^+$ (2), 450 [614 – HOC_6H_4–CH H–COOH]$^+$ (7.4), 262 (47), 203 [262 – $CO_2Me]^+$ (65), 147 $)C_6H_4$–CH=CH–C≡O]$^+$ (100) and 133 (35).

'ethyl 2α-acetoxy-3β-(E-O-*acetyl*-p-*coumaryloxy*)*-urs-12-en-ate* (**6**). Acetylation of **5** (0.01 g, Ac_2O–pyridine, 2 hr at 80°) rded a diacetate (**6**), crystallizing from $CHCl_3$–petrol as urless needles (0.008 g), mp 209°; IR ν_{max}^{KBr} cm^{-1}: 2940, 1770 (phenolic acetate), 1738 (br, ester C=O), 1600 and 830 (*p*-disubstituted C_6H_6); UV λ_{max}^{EtOH} nm (log ε): 281 (4.35) and 225 (4.38); ^{1}H NMR (80 MHz, $CDCl_3$): δ0.76–1.09 (21H, seven Mes), 1.2–1.7 (*m*, methylene and methine Hs), 1.90 (3H, *s*, MeCOO-2), 2.30 (3H, *s*, MeCOO-4'), 3.60 (3H, *s*, MeOCO-17), 4.87 (1H, asymmetrical *d*, *J* = 10.3 Hz, H-3), 5.20 (1H, *m*, $W_{1/2}$ = 16 Hz, H-2), 5.25 (1H, *m*, $W_{1/2}$ = 10 Hz, H-12), 6.38 (1H, *d*, *J* = 16 Hz, H-α), 7.10 (2H, *d*, *J* = 8.5 Hz, H-3' and H-5'), 7.55 (2H, *d*, *J* = 8.5 Hz, H-2' and H-6') and 7.67 (1H, *d*, *J* = 16 Hz, H-β); MS *m/z* (rel. int.): 716 $[M]^+$ (2) ($C_{44}H_{60}O_8$), 656 $[M-HOAc]^+$ (5), 467 [656 – $AcOC_6H_4$–CH=CH–CO]$^+$ (3), 450 [656 – $AcOC_6H_4$–CH =CH–COOH]$^+$ (11), 262 (100), 203 [262 – $CO_2Me]^+$ (85), 147 (67) and 133 (45).

*Methyl 2α-hydroxy-3β-*E*-p-coumaryloxy-urs-12-en-28-oate* (**7**). Deacetylation of **5** (0.01 g) with K_2CO_3 (1%) in MeOH–H_2O (1:1, 20 ml) (5 min on water bath followed by 25 min at room temp.) afforded **7** as an amorphous solid (0.005 g), mp 296°, IR and MS data similar to those of jacoumaric acid methyl ester [13]. Due to the paucity of **7**, study of its other spectral features could not be done.

Methyl 2α-hydroxyursolate (**8**). Compound **5** (0.04 g) was hydrolysed by refluxing with 1% KOH–MeOH (50 ml) for 2 hr to afford, after usual work-up, methyl 2α-hydroxyursolate (**8**) as colourless needles (0.015 g), mp 215° ($CHCl_3$–petrol), $[\alpha]_D^{30}$ + 60° ($CHCl_3$; *c* 0.103), positive L–B test and TNM colouration, IR ν_{max}^{KBr} cm^{-1}: 3440, 2940, 1725 (ester C=O), 1640 (C=C), 1450, 1370, 1360 and 985; ^{1}H NMR (80 MHz, $CDCl_3$): δ0.72–1.15 (21H, seven Mes), 1.25–1.70 (*m*, methylene and methine Hs), 2.24 (1H, *d*, *J* = 12 Hz, H-18), 2.98 (1H, *d*, *J* = 11 Hz, H-3), 3.60 (3H, *s*, MeOCO-17), 3.60 (1H, *m*, H-2), 5.25 (1H, *m*, $W_{1/2}$ = 10 Hz, H-12); $[M]^+$ at *m/z* 486 ($C_{31}H_{50}O_4$). The mp, $[\alpha]_D$ and IR data of **8** are similar to those reported earlier [11]. The other product of hydrolysis on methylation with CH_2N_2 afforded methyl *p*-methoxy-*E*-cinnamate, as colourless needles, mp 90° ($CHCl_3$–petrol), identified by direct comparison (mmp and ^{1}H NMR data) with an authentic sample [14].

Methyl 2α-hydroxyursolate (**8**) was also obtained by methylation of 2α-hydroxyursolic acid (**4**) with CH_2N_2.

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