

## A NEW QUINONE FROM AERIAL PARTS OF *EHRETIA LAEVIS*

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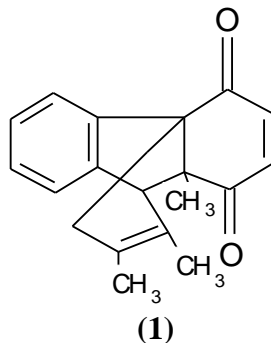
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A new naphthoquinone derivative named lewisone (**1**) was isolated from the aerial parts of Indian plant *Ehretia laevis* collected from northern region, along with the known compounds, n-octatricontane, baurenol acetate, baurenol and ursolic acid. The structure of the new naphthoquinone was determined by spectroscopic analysis of its acetylated derivative and comparison with known compounds.

### EXPERIMENTAL AND DISCUSSION

The genus *Ehretia*, family Boraginaceae, is reported to be medicinally useful in indigenous system of medicine.<sup>1</sup> Earlier investigations of some species of *Ehretia* have yielded long chain aliphatic unsaturated acids, ursolic acid, a triterpine baurenol, a pyrazolidine alkaloid ehretinine and a naphthoquinone microphyllone<sup>2-5</sup> but no work has been reported on *E. laevis* (sub family Erhetoioideae). As part of our studies on north Indian plants, we have examined the benzene extract of the fresh leaves, stem and bark of *E. laevis* collected from village Ranhera, Bullandsahar, India. The benzene soluble fraction of the plant was further extracted with petroleum ether. Silica gel column chromatography followed by preparative TLC of this extract of *E. laevis* afforded a new novel naphthoquinone derivative for which we propose the name lewisone (**1**), as well as the previously reported known compounds: n-octatricontane, baurenol acetate, baurenol and ursolic acid. These known compounds were characterized by comparison of their spectral data with those reported earlier.<sup>2-5</sup> The structure of this new compound was

determined by MS, UV, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR and was further confirmed by the reductive acetylation.



The new 1,4-naphthoquinone lewisone (**1**), melting point 128-30°C, gave a positive Craven's test, a positive colour reaction with 2,4-dinitrophenylhydrazine and redox reaction with alkaline sodium dithionite for quinones. MS showed  $\text{M}^+$  ( $m/z$ ) peak at 278 and the elemental analysis showed its molecular formula as  $\text{C}_{19}\text{H}_{18}\text{O}_2$ . The IR spectrum of lewisone showed a peak at  $1654\text{ cm}^{-1}$  for naphthoquinone carbonyl group, peaks at  $860$  and  $770\text{ cm}^{-1}$  for cis-disubstituted olefins and ortho-disubstituted benzene ring respectively. The UV spectrum of (**1**) was found to be similar to that for the 1,4-naphthoquinones.<sup>6</sup> The  $^1\text{H}$  NMR of (**1**) showed singlets at  $\delta$  0.87, 1.24 and 1.61 for three methyl groups of  $\text{C}_{4a}$ ,  $\text{C}_7$  and  $\text{C}_6$  positions, a multiplet at  $\delta$  2.2-2.4 for  $\text{C}_8$  methylene group, singlets at  $\delta$  3.80 and 6.94 for methine proton at  $\text{C}_5$  position and two quinonoid protons respectively and a multiplet between  $\delta$  7.22-7.79 for four aromatic protons.  $^{13}\text{C}$  NMR of (**1**) exhibited peaks at  $\delta$  180 for  $\text{C}_1$  and  $\text{C}_4$  carbonyl carbon atoms,  $\delta$  138 for  $\text{C}_2$  and  $\text{C}_3$  quinonoid carbon atoms,  $\delta$  135 and 134 for tetra substituted  $\text{C}_9$  and  $\text{C}_{10}$  aromatic carbon atoms,  $\delta$  132 for aromatic  $\text{C}_{11}$  and  $\text{C}_{14}$  carbon atoms,  $\delta$  131 and 129 for aromatic  $\text{C}_{11}$  and  $\text{C}_{13}$  carbon atoms,  $\delta$  126 and 125 for disubstituted olefin carbons  $\text{C}_7$  and  $\text{C}_6$ ,  $\delta$  65

and 59 for tetra substituted bridge carbons C<sub>4</sub> and C<sub>8</sub>,  $\delta$  42 for methine carbon at C<sub>5</sub> position,  $\delta$  32 for methylene carbon C<sub>8</sub>,  $\delta$  31, 27 and 24 for methyl carbons C<sub>11</sub>, C<sub>16</sub> and C<sub>15</sub> respectively.

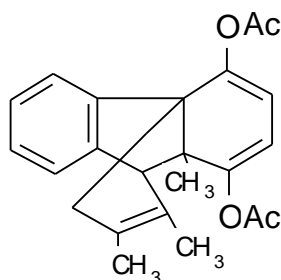
All the above evidence and the comparison with microphyllone, led to the identification of structure of lewisone (**1**) as 4a, 5, 8, 8a-tetrahydro-4a, 6, 7-trimethyl-5, 8a-*o*-benzeno-1, 4-naphthoquinone. Compound **1** on reductive acetylation with zinc dust and acetic anhydride gave compound **2**, which did not give colour reaction with 2,4-dinitrophenylhydrazine. The spectral data of compound **2**, confirmed its structure as 1,4-diacetoxy-4a, 5, 8, 8a-tetrahydro-4a, 6, 7-trimethyl-5, 8a-*o*-benzenonaphthalene.

M. ps. are uncorrected. <sup>1</sup>H NMR was taken at 90 MHz and <sup>13</sup>C NMR at 22.61 MHz. Aerial parts of *E. laevis* were collected from village Ranhera, district Bulandsahar, Uttar Pradesh, India In the month of September 1992. The fresh stem, bark and leaves (5 kg) were cut into very small pieces and exhaustively extracted with benzene. The solvent was removed under reduced pressure and the dark green residue (10 g) was chromatographed over a silica gel column using petroleum ether (b.p. 60-80°). Earlier fractions gave semi-solid n-octatricontane (R<sub>f</sub> 0.90, benzene). Then elution with benzene-petroleum ether (1:19) gave baurenol acetate, baurenol and ursolic acid, which were separated by preparative TLC. Finally, the elution with benzene-petroleum ether (1: 4) gave yellow solid (500 mg). The quinone was visualised on TLC by spraying with 10% 2,4-dinitrophenylhydrazine solution and then heating to give purple spot.

**Lewisone (1):** Recrystallisation from methanol yielded 480 mg lewisone (**1**) as yellow plates; m.p. 128-30°C;  $[\alpha]_D^{20} +9.5^\circ$  (CHCl<sub>3</sub>); R<sub>f</sub> 0.60 (benzene); found: C, 81.72; H, 6.82;

for  $C_{19}H_{18}O_2$ ;  $\lambda_{max}$  (MeOH) 204, 244, 324 nm;  $\nu_{max}$  (nujol) 1654, 1400, 1180, 860, 770  $cm^{-1}$ .

**Acetylation of (1).** A mixture of lewisone (**1**, 100 mg), zinc dust (200 mg) and freshly distilled acetic anhydride (15 ml) was refluxed for 4 h (checked by TLC). The reaction mixture was then poured in ice-water (100 ml). The organic layer was extracted with  $CHCl_3$ , washed with water and dried over  $MgSO_4$ .  $CHCl_3$  was distilled off under reduced



(2)

pressure and the residue left was purified by preparative TLC to give diacetate (**2**; 125 mg) as colourless needles, m. p. 46° (methanol),  $R_f$  0.85 (benzene); found: C, 74.72; H, 7.10 for  $C_{23}H_{24}O_4$ ;  $\lambda_{max}$  (MeOH) 220, 276 nm;  $\nu_{max}$  (nujol) 1700, 1460, 1140, 790  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , TMS)  $\delta$  0.90 (s, 3H,  $C_4$ -CH<sub>3</sub>), 1.84-2.10 (m, 12H,  $C_{6,7,14}$ -CH<sub>3</sub>), 2.24-2.40 (m, 2H,  $C_8$ -CH<sub>2</sub>), 4.20 (s, 1H,  $C_5$ -H), 7.20-7.60 (m, 6H,  $C_{2,3,10,11,12,13}$ -H);  $m/z$ : 334  $M^+$ .

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