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Chemical constituents from *Clerodendron serratum*

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A new compound, serratin, was isolated from the essential oil of *Clerodendron serratum* along with lupeol. The structure of the compound has been elucidated on the basis of chemical analysis and spectroscopic methods including IR, MS, and NMR techniques.

Keywords: Verbenaceae; *Clerodendron serratum*; serratin; lupeol

1. Introduction

Clerodendron is one of the major genera of Verbenaceae and many of the species are reported to occur in India [1–3]. The occurrence of flavonoids [4–6], diterpenoids [7,8], and sterols [9] has been reported earlier from *Clerodendron* genus. They are found to have pesticidal properties and antifeeding principles. This prompted us to investigate an Indian species *Clerodendron serratum* in search of antifeeding principles and led to the isolation of a new compound, named as serratin (**2**) (Figure 1) along with lupeol (**l**). *C. serratum* is used in medicine for fevers, rheumatism, and dyspepsia, and the leaves are used for external applications in cephalalgia and ophthalmia [10]. The occurrence of glucose, D-(−)-mannitol, saponins, and oleanolic, quaretaroic, and serratagenic acids has been reported earlier [11].

2. Results and discussion

The plant *C. serratum* collected during November 2002 was shade-dried and hydrodistilled to yield a yellow oil (1 g, 0.02%). The oil in column chromatography led to the isolation of compounds **1** and **2**. Compound **1** was identified as lupeol by comparing its melting point and spectral data (IR, NMR, and MS) and its monoacetate with literature values [12] and running co-TLC of the monoacetate with an authentic sample.

Compound **2** with mp 42°C and $[\alpha]_D^{20} + 4.25$ (MeOH) was analyzed for $C_{27}H_{40}0_2$ from the ion peak at *m/z* 396 (14%) $[M]^+$. Its UV spectrum showed absorption maxima at 214 and 238 nm, suggesting the presence of a heteroannular diene. A purple color with vanillin–H_2SO_4 and a positive Lebermann–Burchard test indicated the steroidal nature of the compound. The compound responded positively to Zimmerman test for 3-keto steroids. In the IR spectrum, the broad absorption bands at 3400 and 1712 cm^{-1} were indicative of the hydroxyl functionality and cyclohexanone moiety in the molecule. In addition, the bands at 1635, 1600, and 870 cm^{-1} indicated the presence of double bonds and an isopropenyl side chain [13,14]. The ^1H NMR spectrum of **2** exhibited two two-proton broad singlets at δ 2.20 and 2.10, respectively, attributable to methylene, adjacent to the carbonyl group, three broad singlets

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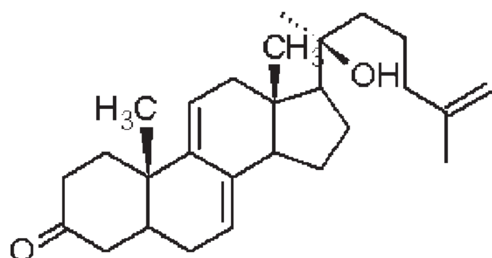

Figure 1. The structure of **2**.

at δ 0.77, 0.98, and 1.02, respectively, integrating for three protons each ascribable to C-18, C-19, and C-20 methyl groups. The two olefinic protons as broad singlets at δ 4.61 and 4.78 and a methyl linked to the double bond at δ 1.70 as well as a significant ion in the mass spectrum at *m/z* 41 indicated the presence of an isopropenyl moiety in the side chain [15]. The other two olefinic proton multiplets at δ 5.35 and 5.45 were due to the heteroannular diene of the ring system [16–18]. The presence of a heteroannular diene excluded the possibility of the usual 5,6 double bond. The 7,9(11) conjugated diene system was supported by its mass fragments [19,20] at *m/z* 41, 70, 110, 124, 174, 168, 222, 272, 286, 326, 269 [$M^+ - C_8H_{15}O$], 309 [$M^+ - H_2O—C_5H_9$], and 378 [$M^+ - H_2O$] (Figure 2). Further, one proton broad singlet at δ 4.10 (exchangeable with D_2O) and no other signals between δ 2 and 4 region revealed the presence of an —OH group attached to a tertiary carbon atom and its probable position is with C-20 [13,21,22],

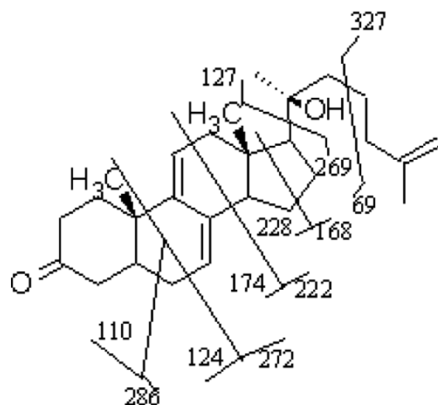

Figure 2. The key EI-MS fragment ions for **2**.

which is further supported by the mass spectrum. The presence of the carbonyl group in ring A was determined at C-3 on biogenetic grounds also. According to the above spectral evidence and the ^{13}C NMR spectral data (Table 1) the compound was assigned the structure **2**.

3. Experimental

3.1 General experimental procedures

IR spectrum was recorded on a Perkin-Elmer 1650 spectrometer in $CHC1_3$; ^1H NMR spectrum in $CDC1_3$ with TMS as the internal standard on Bruker WH 400 instrument and ^{13}C NMR spectrum in $CDC1_3$ on Bruker WH l00 MHz instrument were recorded; and mass spectra were run at 70 eV. Elemental analysis was carried out using Perkin-Elmer 240C model analyzer. Silica gel was used for chromatography.

3.2 Plant material

The leaves of *C. serratum* was collected from Udhagamandalam, The Nilgiris district of Tamilnadu, India in November 2002. A voucher specimen is preserved in Botany Department of Government Arts College, Udhagamandalam, The Nilgiris, Tamilnadu, India.

3.3 Extraction and isolation

Leaves of *C. serratum* (17 kg) collected in Udhagamandalam, The Nilgiris, were shade-dried, powdered (4 kg), and hydrodistilled in a Clevenger apparatus (3 h). The volatile distillates and water were taken out from the Clevenger apparatus in a separating funnel. Petroleum ether was added to dissolve the oil. The solution was saturated by shaking with sodium chloride. Then, the lower aq. layer was drawn off. The organic layer containing the oil was dried using anhyd. sodium sulfate. The solvent was evaporated to get pure yellow oil (1 g, 0.02%).

The oil (1 g) dissolved in minimum amount of petroleum ether (bp 40–60°C) was applied to a column of silica gel (100 g)

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Table 1. ^{13}C NMR spectral data of compound **2** in $CDCl_3$.

C	Signal (d)
1	32.0
2	22.6
3	216.5
4	21.3
5	55.4
6	18.2
7	129.2
8	147.0
9	152.0
10	37.1
11	132.0
12	25.1
13	36.2
14	56.2
15	24.4
16	28.4
17	56.4
18	12.1
19	21.5
20	74.5
21	19.0
22	33.9
23	30.8
24	36.4
25	150.9
26	20.2
27	109.3

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set in pet. ether. The column was eluted successively with pet. ether and a pet. ether–chloroform mixture. The fractions (25 ml) were collected and monitored by TLC using the benzene and ethyl acetate solvent system, leading to the isolation of **1** (180 mg, 18% yield) from fractions 32–56 and recrystallized as colorless needles from chloroform. Fractions 71–84 yielded compound **2** (150 mg, 15% yield) which was recrystallized from benzene.

3.3.1 Lupeol

Mp 210°C; $[\alpha]_D^{20} + 27$ ($CHCl_3$), R_f 0.71 (C_6H_6:EtOAc, 9:1).

3.3.2 Lupeol acetate

A mixture of pyridine, acetic anhydride (4 ml each), and 80 mg of **1** was warmed slightly and kept overnight. On usual work up, it yielded a solid acetate derivative with mp 187°C, R_f 0.94 (C_6H_6:EtOAc, 9:1).

*3.3.3 Serratin **2***

Mp 42°C; $[\alpha]_D^{20} + 4.25$ (MeOH); UV: (MeOH) 214, 238 nm; IR ($CHC1_3$): 3400, 1712, 1635, 1600, 1360, 870 cm^{-1}; ^1H NMR ($CDC1_3$) δ: 2.10 (2H, brs, H-2), 2.20 (2H, brs, H-4), 0.77, 0.98, 1.02 (each 3H, s, H-18, H-19, H-20), 4.61 and 4.78 (2H, brs, $=CH_2$), 1.70 (3H, s, $=C-CH_3$), 5.35 and 5.45 (each 1H, m, $-C=C-H$); ^{13}C NMR (Table 1); EI-MS: *m/z* 396 (14), 378 (22), 326 (31), 309 (27), 269 (25), 286 (56), 272 (48), 222 (70), 168 (100), 174 (82), 124 (40), 110 (52), 70 (51), 41 (69). Elemental analysis: found: C, 81.72; H, 10.23% (calcd for $C_{24}H_{40}O_2$: C, 81.81; H, 10.10%).

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