



## CHEMICAL EXAMINATION OF *CITRUS SINENSIS* STEMS VARIETY BLOOD RED

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### ABSTRACT

Chemical examination of *Citrus sinensis* roots var. blood red has afforded seven compounds, which have been identified as methyl tritriacontanoate, pentanoic acid, nobiletin, sinestein, 5, 4'-dihydroxy-7, 3'-dimethoxy flavanone 3-O- $\beta$ -glucoside and glucose.

**Key words:** *Citrus sinensis*, Rutaceae, Methyl tritriacontanoate, Pentanoic acid, Nobiletin, Sinestein, 5,4'-dihydroxy-7, 3'-dimethoxy flavanone 3-O- $\beta$ -glucoside, Glucose.

### INTRODUCTION

*Citrus sinensis* (L.) var. blood red (family: Rutaceae<sup>1</sup>) is known as sweet orange or mosambi. It migrated to India from China in the 13<sup>th</sup> century<sup>2</sup>. Sweet oranges are now cultivated throughout the world<sup>3</sup>. The plant is known to cure skin and dental diseases<sup>4</sup>. In view of the fact that there is no previous examination of its stems, we have undertaken the present study.

### EXPERIMENTAL

Stems (3 Kg) of the plant were procured from Botanical Gardens, Hisar, and these were chopped into small pieces, which were dried in shade for 24 h under a fan. The extraction was done with hot methanol. Extractives were subjected to column chromatography using silica gel (60-120 mesh). The elution was started with petroleum ether. Polarity was increased slowly. Seven compounds could be isolated.

Melting points were determined on Ganson Electrical Melting Point Apparatus;

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$^1\text{H}$  NMR on Bruker AC 300 MHz NMR Spectrometer; IR on Hitachi 570 Infra Spectrophotometer; and Mass Spectra on VG 70 S 11-250 J GCMS-DS Spectrometer.

## RESULTS AND DISCUSSION

The data obtained for the seven compounds are given as below. Characterizations are based on comparison of the data obtained with those of existing literature data.

**Compound A (Methyl tritriacontanoate, 1):** It was obtained on elution with benzene-petroleum ether (1 : 19). It crystallized out from methanol as a colourless solid, 20 mg, mp 80°C (lit<sup>5</sup> M.P. 80-82 °C). IR ( $\nu_{\text{max}}$ , nujol,  $\text{cm}^{-1}$ ): 1738.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 3.59 (s, 3 H,  $\text{COOCH}_3$ ), 1.33-1.18 (60 H, m, 30 x  $\text{CH}_2$ ), 0.89 (3 H, t,  $J$  7.5 Hz,  $\text{CH}_2\text{-CH}_3$ ). GCMS ( $m/z$ , relative abundance): 508 ( $\text{M}^+$ , 24).

**Compound B (Methyl triacontanoate, 2):** It was obtained on elution with benzene-petroleum ether (1 : 9). It crystallized out from MeOH, 18 mg, M.P. 70°C (lit<sup>6</sup> M.P. 71°C). IR ( $\nu_{\text{max}}$ , nujol,  $\text{cm}^{-1}$ ): 1732.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 3.60 (s, 3 H,  $\text{COOCH}_3$ ), 2.47 (2 H, t  $J$  7.5 Hz,  $\text{CH}_2\text{-COO}$ ), 2.00-0.90 (54 H, m, 27 x  $\text{CH}_2$ ), 0.94 (3 H, t,  $J$  7.5 Hz,  $\text{CH}_2\text{-CH}_3$ ). GCMS ( $m/z$ , relative abundance): 466 ( $\text{M}^+$ , 14).

**Compound C (Pentacosanoic acid, 3):** The elution with benzene-petroleum ether (1 : 1) yielded this compound. It crystallized out from methano, 20 mg, M.P. 77°C (lit<sup>7</sup> M.P. 78-79°C). IR ( $\nu_{\text{max}}$ , nujol,  $\text{cm}^{-1}$ ): 1706, 3410.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) : 2.28 (2 H, t,  $J$  7.5 Hz,  $\text{CH}_2\text{COO}$ ), 2.10-1.18 (44 H, m, 22 x  $\text{CH}_2$ ), 0.81 (3 H, t,  $J$  7.5 Hz,  $\text{CH}_2\text{-CH}_3$ ) GCMS ( $m/z$ , relative abundance): 380 ( $\text{M}^+$ , 35).

**Compound D (Nobiletin, 4):** It was obtained on elution with ethyl acetate-benzene (1 : 9). It crystallized out from MeOH, 60 mg, M.P. 135°C (lit<sup>8</sup> M.P. 134°C). It gave yellow colour with Mg / HCl. IR ( $\nu_{\text{max}}$ , nujol,  $\text{cm}^{-1}$ ): 1629.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 7.57 (1 H, dd,  $J$  7.5 Hz, 2, 5 Hz, H-6'), 7.48 (1 H, d,  $J$  2,5 Hz, H-2'), 7.06 (1 H, d,  $J$  2,5 Hz, H-5'), 6.63 (1 H, s, H-3), 4.10, 4.03, 3.96, 3.93 (4 x 3 H, 4 s, 4 x OMe), 3.91 (6 H, s, 2 x OMe). GCMS ( $m/z$ , relative abundance): 402 ( $\text{M}^+$ , 100).

**Compound E (Sinenstein, 5):** It was obtained on elution with ethyl acetate-benzene (1 : 3). It crystallized out from MeOH, 20 mg, M.P. 177°C (lit<sup>9</sup> M.P. 178-179°C). It gave yellow colour with Mg/HCl. IR ( $\nu_{\text{max}}$ , nujol,  $\text{cm}^{-1}$ ): 1651.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 7.38 (1 H, d,  $J$  2.5 Hz, H-2'), 7.01 (1 H, dd,  $J$  7.5 Hz, 2,5 Hz, H-6'), 6.59 (1 H, s, H-8), 6.90 (1 H, s, H-3),

6.84 (1 H, d, J 7.5 Hz, H-5'), 4.01, 3.96, 3.95, 3.92 (5 x 3 H, 5 s, 5 x OMe), GCMS (m/z, relative abundance): 372 (M<sup>+</sup>, 100).

**Compound F (5,4'-dihydroxy-7,3'-dimethoxy flavanone 3-O-β-glucoside, 6):** It was obtained on elution with methanol-ethyl acetate (1 : 9). It crystallized out from ethyl acetate, 90 mg, M.P. 210°C (lit<sup>10</sup> M.P. 210°C). It gave yellow colour with Mg/HCl. GCMS (m/z, relative abundance): 494 (M<sup>+</sup>, 3). Molisch test: +ve; Kiliani hydrolysis: glucose, which was confirmed by direct comparison with an authentic sample. Acetate: compd F + Ac<sub>2</sub>O + Py. <sup>1</sup>H NMR of the glucodide acetate (δ, CDCl<sub>3</sub>): 7.19 (1 H, dd, J 7.5, 2.5 Hz, H-6'), 7.10 (1 H, d, J 2.5 Hz, H-2'), 7.08 (1 H, d, J 7.5 Hz, H-5'), 6.40 (1 H, d, J 2.5 Hz, H-8), 6.25 (1 H, d, J 2.5 Hz, H-6), 3.82 (6 H, s, 2 x OMe), 5.21-2.70 (9 H, m, H-2, H-3, 7 glu H), 2.02, 2.00, 1.99, 1.97 (4 s, 4 x 3 H, 4 x OAc).

**Compound G (Glucose, 7):** It was obtained on elution with methanol-ethyl acetate (1 : 4). It crystallized out from ethyl acetate, 50 mg, M.P. 148°C (lit<sup>11</sup> M.P. 146-150°C). IR (ν<sub>max</sub>, nujol, cm<sup>-1</sup>): 3365. GCMS (m/z, relative abundance): 180 (M<sup>+</sup>, 3).

Though all the seven compounds turned out to be already known compounds yet the chemistry of the stems of this plant has been revealed.

## ACKNOWLEDGEMENT

Authors are grateful to Botanical Gardens, Hisar, for the supply of plant material; and to PU, Chandigarh, for providing the spectral data.

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*Accepted : 28.08.2012*