

## A New Coumarin from *Citrus paradisi* Macf.

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Phytochemical examination of the peel of grapefruit resulted in the isolation of five compounds namely friedelin,  $\beta$ -sitosterol, 7(3',7',11',14'-tetramethyl)pentadec-2',6',10'-trienyloxycoumarin, limonin and cordialin B. These compounds have been characterized on the basis of spectral data, and 7(3',7',11',14'-tetramethyl)pentadec-2',6',10'-trienyloxycoumarin is a hitherto unreported compound.

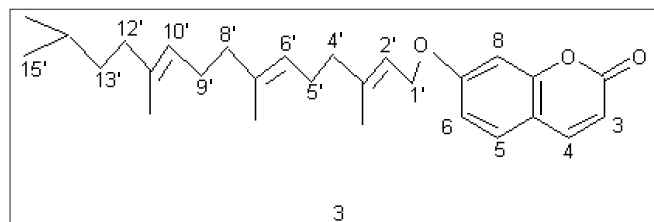
**Key words:** *Citrus paradisi*, Rutaceae, coumarin, friedelin,  $\beta$ -sitosterol, limonin, cordialin B

*Citrus paradisi* commonly known as grapefruit and *pahari nimbu* belongs to the family Rutaceae. It is synonymous with *C. decumana* var. *racemosa*, *C. decumana* var. *paradisi* Nichols and *C. racemosa* Macf. The juice of the grapefruit is used for building up resistance to common cold and wound infections<sup>1</sup>. There is report of only one compound i.e. 6,7-dimethoxycoumarin<sup>2</sup> from grapefruit peel. In view of existing scanty data, the present study was undertaken (fig 1).

Melting points were determined on Ganson Electrical Melting Point Apparatus. IR spectra were recorded on Hitachi 570 Infrared Spectrophotometer using KBr. <sup>1</sup>H NMR spectra were recorded on Bruker AC-300F 300 MHz NMR Spectrophotometer using TMS as an internal standard. Chemical shifts are given in  $\delta$  (ppm) and CDCl<sub>3</sub> was used as a solvent for recording NMR spectra. Fruits of *C. paradisi* (10 kg) were procured from Landscape, HAU, Hisar.

The peel of the fruits was removed and air dried. The peel was then refluxed with hot methanol for 6 h and the process was repeated 4 times. Extractives were concentrated on water bath under reduced pressure and the viscous mass thus obtained was mixed with silica gel (60-120 mesh), dried on water bath and subjected to column chromatography. Petroleum ether was used as a solvent in packing the column. Five compounds were isolated.

Compound A crystallized from methanol, 25 mg, mp 268<sup>o</sup> (literature mp 267.3-269.5<sup>o</sup>)<sup>3</sup>. It gave pale brown color on reaction with Ac<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>; IR<sub>v<sub>max</sub></sub> (KBr, cm<sup>-1</sup>): 1720; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 2.25-1.20 (25 H,



**Fig. 1:** Structure for the coumarin isolated from *Citrus paradisi*

m, 11\*CH<sub>2</sub> and 3\*CH), 1.17 (3 H, s, CH<sub>3</sub>), 1.04 (3H, s, CH<sub>3</sub>), 1.00 (6H, s, 2\*CH<sub>3</sub>), 0.95 (3 H, s, CH<sub>3</sub>), 0.86 (6H, s, 2\*CH<sub>3</sub>), 0.72(3H, s, CH<sub>3</sub>); GCMS: 426 (M<sup>+</sup>). This data settled compound A to be friedelin (1)<sup>3</sup>.

Compound B crystallized from methanol, 20 mg, mp 136<sup>o</sup> (literature mp 136-137<sup>o</sup>)<sup>4</sup>. It responded to Liebermann-Burchard Reaction. IR<sub>v<sub>max</sub></sub> (KBr, cm<sup>-1</sup>): 3427; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 5.34 (1H, br, H-6), 3.51 (1H, m, H-3), 2.28-1.13 (29H, m, 11\*CH<sub>2</sub>, 7\*CH), 0.92 (6H, s, 2\*CH<sub>3</sub>), 0.83 (3H, s, CH<sub>3</sub>), 0.80 (3H, s, CH<sub>3</sub>), 0.78 (3H, s, CH<sub>3</sub>), 0.68 (3H, s, CH<sub>3</sub>); GCMS: 414 (M<sup>+</sup>). This data confirmed compound B to be  $\beta$ -sitosterol (2)<sup>5</sup> using a direct comparison.

Compound C (3) crystallized from methanol, 50 mg, mp 70<sup>o</sup>. IR<sub>v<sub>max</sub></sub> (KBr, cm<sup>-1</sup>): 1700; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 7.64 (1H, d, *J* 10 Hz, H-4), 7.36 (1H, d, *J* 7.5 Hz, H-5), 6.82 (2H, m, H-6, H-8), 6.25 (1H, d, *J* 10 Hz, H-3), 5.50 (1H, 1H, t, *J* 7.0 Hz, H-2'), 5.10 (2H, t, *J* 7.0 Hz, H-6', H-10'), 4.61 (2H, d, *J* 7.0 Hz, 2\*H-1'), 2.34 (4H, m, 2\*H-5', 2\*H-9'), 2.10 (6H, t, *J* 7.0 Hz, 2\*H-4', 2\*H-8', 2\*H-12'), 1.75 (3H, s, CH<sub>3</sub>), 1.72 (3H, s, CH<sub>3</sub>), 1.65 (3H, s, CH<sub>3</sub>), 1.30-0.86 (9H, m, 2\*CH<sub>3</sub>, CH<sub>2</sub>, CH); GCMS: 422 (M<sup>+</sup>).

Compound D crystallized from methanol, 40 mg, mp 297 (literature mp 298)<sup>3</sup>. IR<sub>v<sub>max</sub></sub> (KBr, cm<sup>-1</sup>): 1758,1708; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 7.41 (2H, m, H-2', H-5'), 6.30 (1H, m, H-3'), 5.46 (1H, s, OCHCOO), 4.77-4.47 (2H, m, 2\*OCH), 4.02 (2H, s, OCH<sub>2</sub>), 2.98-1.77 (10H, m, 4\*CH<sub>2</sub>, 2\*CH), 1.29 (3H, s, CH<sub>3</sub>), 1.17 (6H, s, 2\*CH<sub>3</sub>), 1.07 (3H, s, H<sub>3</sub>); GCMS: 470 (M<sup>+</sup>). The data proposed compound D to be limonin (4)<sup>3</sup>.

Compound E crystallized from methanol, 50 mg, mp 114<sup>o</sup> (literature mp 114-115<sup>o</sup>)<sup>3</sup>. It responded to Liebermann-Burchard Reaction. IR<sub>v<sub>max</sub></sub> (KBr, cm<sup>-1</sup>): 3358; Acetate: compd.+Ac<sub>2</sub>O+Py; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 5.34 (1H, m, =CH), 4.28 (1H, m, CH-O), 4.10 (1H, m, CH-O), 3.65(1H, m, CH-O), 3.39(1H,

m, CH-O), 2.32-1.08 (20H, m, 8\*CH<sub>2</sub>, 4\*CH), 2.08 (3H, s, OAc), 2.04 (3H, s, OAc), 2.01 (3H, s, OAc), 2.00 (3H, s, OAc), 1.23 (3H, s, CH<sub>3</sub>), 1.10 (3H, s, CH<sub>3</sub>), 0.98 (3H, s, CH<sub>3</sub>), 0.92 (3H, s, CH<sub>3</sub>), 0.88 (3H, s, CH<sub>3</sub>), 0.86 (3H, s, CH<sub>3</sub>), 0.67 (3H, s, CH<sub>3</sub>), GCMS: 490 (M<sup>+</sup>). A comparison with literature data<sup>3</sup> suggested this compound to be cordialin B (5).

Compound C showed fluorescence under UV indicating it to be a coumarin. The IR spectrum of the compound exhibited the presence of a carbonyl group at 1700 cm<sup>-1</sup> which was a further support towards the coumarin nucleus. MS suggested its molecular mass to be 422. <sup>1</sup>H NMR of the compound in CDCl<sub>3</sub> showed a doublet at δ 7.64 (*J* 10 Hz) which was typical of H-4 of a coumarin. Another doublet was observed at δ 7.36 (*J* 7.5 Hz) which could be H-5 of a coumarin. There was a multiplet at δ 6.82 for two protons which represented H-6 and H-8 of the nucleus. A doublet at δ 6.25 (*J* 10 Hz) was assignable to H-3. A triplet at δ 5.50 (*J* 7.0 Hz) could be H-2' of an aliphatic chain attached at C-7 of the nucleus. Another triplet at δ 5.10 (*J* 7.0 Hz) for two protons could be due to H-6' and H-10'. A doublet at δ 4.61 (*J* 7.0 Hz) was assignable to 2 protons at C-1'. A multiplet at δ 2.34 for 4 protons could be 2\*H-5' and 2\*H-9'. A triplet at δ 2.10 (*J* 7.0 Hz), representing 6 protons, could be 2\*H-4', 2\*H-8 and 2\*H-12'.

Three singlets at δ 1.75, 1.72 and 1.65, each for 3 protons, could be due to 3 methyls, one each at C-3', C-7' and C-11'. A multiplet in the range 1.30-0.86 for 9 protons could be 2 methyls, one methylene and one methine. The data suggested the compound to be 7(3',7',11',14'-tetramethyl)pentadec-2',6',10'-trienyloxycoumarin (3) which is a hitherto unreported compound.

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