

Chemical constituents of *Viburnum grandifolium*

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Isorhamnetin, rhamnetin, quercetin, quercetin-3-*O*-rhamnoside and apigenin-7-*O*-neohesperidoside have been isolated from the leaves of *Viburnum grandifolium*.

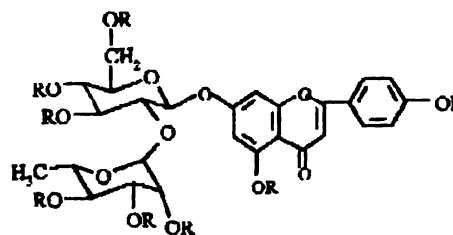
The plants of genus *Viburnum* (Fam. Caprifoliaceae) are reputed for their medicinal values¹. About seventeen species have been tested for their toxicity². The medicinal importance and rarity of work on *Viburnum grandifolium* increased our interest to carry out a comprehensive investigation on the plant. Earlier report from this plant dealt with the isolation of luteolin-3'-*O*- β -D-xylosyl(1 $\rightarrow$ 2)glucoside and apigenin-7-*O*- β -D-xylosyl(1 $\rightarrow$ 2)glucoside³. We now report the isolation of isorhamnetin, rhamnetin, quercetin, quercetin-3-*O*-rhamnoside and apigenin-7-*O*-neohesperidoside from its leaves.

The leaves collected from Kashmir were air-dried and powdered. After defatting with petroleum ether, they were extracted with methanol. Examination of the concentrate by TLC over silica gel plates [solvent system used — toluene : ethyl formate : formic acid, 5 : 4 : 1 (I); benzene : pyridine : formic acid, 36 : 9 : 5 (II); ethyl acetate, ethyl methyl ketone : acetic acid : water, 5 : 3 : 1 : 1 (III)] showed it to be a mixture of five major compounds along with some minor ones. Therefore, it was chromatographed over a silica gel column. Elution of the column with benzene-ethyl acetate (9 : 1-1 : 1) afforded a mixture of three compounds (with marked differences in their R_f values) which were separated into individual components by PTLC using solvent-I. They were labelled as Vg-1, Vg-2 and Vg-3.

Vg-1 (100 mg), yellow shining needles, m.p. 305°; Vg-2 (80 mg), pale yellow needles, m.p. 295° and Vg-3 (100 mg), yellow shining crystals, m.p. 311-112° were characterized⁴ as isorhamnetin, rhamnetin and quercetin, respectively, by comparison of m.p. and spectral data with those of authentic samples and also by co-chromatography. Further elution of the column with EtOAc-MeOH (9 : 1-7 : 3) yielded a mixture of two more components which were separated into pure compounds by PTLC using solvent-III and they were labelled as Vg-4 and Vg-5.

Vg-4 (300 mg) was crystallized from CHCl_3 -MeOH as yellow granular crystals, m.p. 190°, $\text{C}_{21}\text{H}_{20}\text{O}_{11}$. The glyco-

sidic nature of Vg-4 was evidenced by positive Molish test. It gave positive test with Mg/HCl. Hydrolysis with 6% HCl yielded an aglycone and sugar, characterized respectively as quercetin and rhamnose by R_f value and co-chromatography with authentic samples. Vg-4 was identified as quercetin 3-*O*-rhamnoside⁵ by comparison of UV-spectra of the glycoside with that of the aglycone using different shift reagents. It was further confirmed by ^1H NMR and mass spectral analysis of the acetate of the glycoside.



1a R = H

1b R = Ac

Vg-5 (250 mg), yellow granular crystals, m.p. 197° (CHCl_3 -MeOH), $\text{C}_{27}\text{H}_{31}\text{O}_{14}$, gave positive Molish test and Shinoda's test. On hydrolysis with 6% HCl, it gave an aglycone, m.p. 345-346°, identified as apigenin by comparing its m.p. and spectral data with those of an authentic sample; the sugars were identified as rhamnose and glucose by copaper chromatography and GLC of alditol acetate. Partial hydrolysis of Vg-5 with 1% H_2SO_4 (1 h) yielded a partial glycoside and rhamnose indicating rhamnose as terminal sugar. The partial glycoside on further hydrolysis (acidic and enzymatic) afforded apigenin and glucose (identified by co-chromatography). Structure of Vg-5 was confirmed by acetylation of the glycoside with Ac_2O /py to afford an acetate (1b), m.p. 216°, ^1H NMR (90 MHz, CDCl_3) δ 1.20 (3H, d, J 6 Hz, rham. CH_3), 1.79-2.08 (18H, m, 6 $\times$ OAc), 2.39 (3H, s, 4'-OAc), 2.50 (3H, s, 5-OAc), 3.81-4.46 (5H, m, H-2'', 5'', 6'', 5'''), 4.90 (1H, d, J 2 Hz, H-1''' (rham)),

5.30 (1H, d, J 9.5 Hz, H-1'' (glu)), 4.66–5.60 (5H, m, H-3'', 4'', 2''', 3''', 4'''), 6.51 (1H, s, H-3), 6.66 (1H, d, J 2.5 Hz, H-6), 6.78 (1H, d, J 2.5 Hz, H-8), 7.19 (2H, d, J 9 Hz, H-3', 5'), 7.85 (2H, d, J 9 Hz, H-2', 6'). On the basis of the above facts, Vg-5 was characterized as apigenin-7-*O*-neohesperidoside (**1a**)⁶.

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