as 4',5,7-trihydroxy-3',6-dimethoxyflavone, which has been detected previously in the wormwoods <u>A. frigida, A. xerophytica</u>, and <u>A. arctica</u> [6, 7].

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## COMPONENTS OF Launaea asplenifolia

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We have studied the components of the epigeal part of <u>Launaea asplenifolia</u> Hook (family Asteraceae) growing in the region of Saharanpur (India). There is no information on the chemical study of this plant in the literature.

The dried and comminuted epigeal part of the plant was extracted with ethanol. The concentrated ethanolic extract was diluted with water and was then shaken out successively with petroleum ether and ethyl acetate. By column chromatography, the petroleum ether extract yielded compound (I). Th ethyl acetate extract was distilled, and the residue was dried in vacuum and separated into fractions soluble in chloroform (fraction A), in ethyl acetate (B), and in methanol (C). Fraction A was chromatographed on silica gel with elution by chloroform and by chloroform-methanol. This gave compounds (II), (III), and (IV). In the same way, fraction B yielded compound (V).

Fraction C was concentrated and left in the cold. After a week, a crystalline compound (VI) had precipitated.

Compound (I),  $C_{30}H_{50}O$ , mp 212-214°C (from ethanol); acetate with mp 216-217°C; benzoate with mp 286-287°C; PMR spectrum (CDCl<sub>3</sub>),  $\delta$ : 0.8-1.8 (18 H, signals of six CH<sub>3</sub> groups); 1.3-1.45 (>CH<sub>2</sub> groups); 1.73 (3 H, s, >C=C-CH<sub>3</sub>); 3.2 (1 H, m, -CHOH); 4.63 (2 H, d, 8 Hz, >C=CH<sub>2</sub>). Mass spectrum m/z M+ 426 (98%,  $C_{30}H_{50}O$ ), 411, 408, 393, 384, 207, 219, 220, 218, 189, 122 (100%), 81, 28.

Compound (II) crystallized from methanol in the form of pink crystals;  $\lambda_{max}^{CH_3OH}$  274, 300, 440, 554;  $\lambda_{max}^{C_2H_5}$ )H (1% HCl) 276, 355, 558;  $\lambda_{max}^{A1C1}$  277, 305, 580 nm.

Compound (III) crystallized from methanol in the form of yellow crystals;  $\lambda_{max}$ CH<sub>3</sub>OH 265, 297, 335; (S + CH<sub>3</sub>ONa 275, 325, 380; +AlCl<sub>3</sub>, 276, 300, 350, 385; +AlCl<sub>3</sub>/HCl 276; 299, 341, 380; +CH<sub>3</sub>COONa 274, 300; 376; +CH<sub>3</sub>COONa/H<sub>3</sub>BO<sub>3</sub> 268, 301, 336 nm. PMR spectrum,  $\delta$ : 6.0 (1 H, d, J = 2 Hz, H-6); 6.2 (1 H, s, H-3); 6.4 (H, d, J = 2 Hz, H-8); 6.7 (2 H, d, J = 9 Hz, H-3', 5'); 7.6 (2 H, d, J = 9 Hz, H-2', 6').

Compound (IV) crystallized from methanol in the form of yellow crystals.  $\lambda_{max}$ CH<sub>3</sub>OH 240, 253, 268, 291, 353; +CH<sub>3</sub>ONa 260, 336, 405; +AlCl<sub>3</sub> 278, 301, 431; +AlCl<sub>3</sub>/HCl 265, 276, 285, 363, 384; +CH<sub>3</sub>COONa 270, 326, 388; +CH<sub>3</sub>COONa/H<sub>3</sub>BO<sub>3</sub> 262, 328, 370 nm. PMR spectrum,  $\delta$ : 6.1 (1 H, d, J = 2 Hz, H-6); 6.3 (1 H, s, H-3); 6.5 (1 H, d, J = 2 Hz, H-8); 6.8 (1 H, J = 9 Hz, H-5'); 7.4 (1 H, d, J = 2 Hz, H-2'); 7.5 (1 H, q, J = 9 Hz, H-6').

Compound (V) crystallized from methanol and was not hydrolyzed by dilute hydrochloric acid. When 100 g of the substance was boiled with FeCl<sub>3</sub> (0.8 g in 3.2 ml of water) for 6 h, D-glucose was formed, this being identified by paper chromatography.  $\lambda_{max}$ CH<sub>3</sub>OH 271, 301,

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335; +CH<sub>3</sub>ONa 279, 330, 396; AlCl<sub>3</sub> 277, 305, 351, 385; +AlCl<sub>3</sub>/HCl 278, 302, 343, 384; +CH<sub>3</sub>COONa 281, 300, 380; +CH<sub>3</sub>COONa/H<sub>3</sub>BO<sub>3</sub> 270, 330, 345 nm. PMR spectrum,  $\delta$ : 3.5 (6 H, glucose); 6.2 (1 H, d, J = 2 Hz, H-6); 6.3 (1 H, s, H-3); 6.8 (2 H, d, J = 9 Hz, H-3', 5'); 7.9 (2 H, d, J = 9 Hz, H-2', 6').

Compound (V) crystallized from methanol and was hydrolyzed by dilute HCl with the formation of D-glucose (paper chromatography).  $\lambda_{max}$  CH<sub>3</sub>OH 255, 268, 350; +CH<sub>3</sub>ONa 262, 303, 398; AlCl<sub>3</sub> 275, 298, 330, 432; +AlCl<sub>3</sub>/HCl 270, 293, 357, 388; +CH<sub>3</sub>COONa 260, 265, 404; +CH<sub>3</sub>COONa/H<sub>3</sub>BO<sub>3</sub> 259, 370 nm. PMR spectrum,  $\delta$ : 3.6 (6 H of glucose); 5.0 (H-l of glucose); 6.2 (1 H, d, J = 2 Hz, H-6); 6.3 (1 H, s, H-3); 6.8 (1 H, d, J = 9 Hz, H-5'); 7.3 (1 H, d, J = 2 Hz, H-2'); 6.4 (1 H, q, J = 2 Hz, H-6').

When the compound was methylated (dimethyl sulfate +  $K_2CO_3$ ) followed by hydrolysis of the product obtained, 7-hydroxy-3,4,5-trimethoxyflavone was formed. On the basis of the spectral characteristics and chemical transformations given above and of a comparison with authentic samples, compounds (I-VI) were identified, respectively, as lupeol [1, 2], delphinidin [3, 4], apigenin [3, 4]; luteolin [3, 4], vitexin [3-5], and luteolin 7-0-glucoside [3, 4, 6].

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## NARINGIN AND ISORHOIFOLIN FROM GRAPEFRUIT LEAVES

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The flavonoid compounds of the leaves of the grapefruit Citrus paradisi Macf. variety Duncan, have been investigated. Samples collected in the Sukhumi experimental station of subtropical crops of VNIIR [All-Union Scientific-Research Institute of Plant Breeding], were fixed with steam and were dried. The leaves (0.5 kg) were comminuted and extracted with 80% methanol on the boiling water bath. The extracts were combined and were evaporated in vacuum to drive off the methanol, and the aqueous residue was treated repeatedly with chloroform. By two-dimensional paper chromatogrphy (direction I: butan-1-ol-acetic acid-water (4:1:5); direction II: 2% acetic acid), more than 10 flavonoid compounds were detected in the extract obtained. Fractionation of the combined flavonoids was carried out on a column of polyamide sorbent. Water and water-ethanol in various proportions were used as eluents. The fraction of flavanone glycosides (eluted from the polyamide with 30% ethanol) was rechromatographed on a column of microcrystalline cellulose (with elution by water) and yielded substance (I). The fraction of flavone and flavonol glycosides (eluted from the polyamide by 50% ethanol) was separated on a column of Sephadex LH-20 (with elution by the acetone-ethanol-water (2:1:1) system). From the subfractions so obtained, substance (II) was isolated by paper chromatograp! (Filtrak FN-13) in 5% acetic acid.

On the basis of qualitative reactions and spectral investigations in the UV region [1, 2] it was established that substances (I) and (II) were flavanone and flavone derivatives, respectively. The products of the acid hydrolysis [3] of substances (I) and (II) were shown by PC in various solvent systems to contain naringenin (substance (I)) and apigenin (substance (II)), D-glucose and L-rhamnose (substances (I) and (II)). The oxidative degradation (IV) of substances (I) and (II) led to disaccharides: neohesperidose (2-0- $\alpha$ -rhamnosyl-D-glucose) and to rutinose (6-0- $\alpha$ -L-rhamnosyl-D-glucose), respectively. The results obtained in a study of UV spectra are taken in the presence of ionizing and complex-forming reagents

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