

## Short Communications

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### CONSTITUENTS OF SAXIFRAGA CILIATA

#### Part II.\* Structure of Saxin

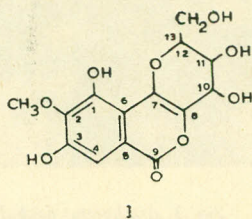
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In an earlier communication, a bitter principle isolated from the roots of *Saxifraga ciliata*<sup>1</sup> was shown to have similar physical properties as those of bergenin reported from other plant materials.<sup>2</sup> The bitter principle designated as saxin, has been subjected further to some spectral studies which are described here. In the IR spectrum taken in KBr pellet saxin gave main absorption peaks at<sup>†</sup> 3430s, 3395s, 3385s, 3260ms, 3210ms, 3040m, 2980m, 2940m, 2895m, 1702s, 1612m, 1525mw, 1505w, 1461ms, 1370m, 1347s, 1335ms, 1330ms, 1345m, 1290m, 1265mw, 1232m, 1215m, 1203m, 1178m, 1140m, 1137m, 1124ms, 1110ms, 1087s, 1068ms, 1040m, 1022m, 1010m, 990ms, 990ms, 964m, 907w, 858m, 813mw, 789mw, 765m, 722mw, 710w, 672mw, 648m, 622m, 592m, 585m, 565w, 538m, 594mw cm<sup>-1</sup>. In UV absorption spectra taken in methanol, saxin gave peaks at 217 and 272 m $\mu$  ( $\epsilon$  30,100; 8,900).

Bergenin has been assigned revised structure I by Hay and Haynes.<sup>3</sup>

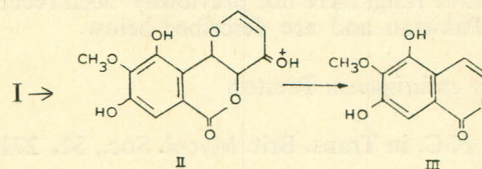


The IR and UV absorption of bergenin has been reported to be 1699 cm<sup>-1</sup> and  $\lambda_{max}$  220, 275 m $\mu$  ( $\epsilon$  26,300; 8,300) respectively. Anhydrous bergenin absorbed at 1712 and 1682 cm<sup>-1</sup> (nujol mull). Anhydrous saxin gave peaks at 1725 and 1690 cm<sup>-1</sup> in KBr pellet. Bergenin pentaacetate gave IR peaks at 1780 and 1745 cm<sup>-1</sup> (nujol mull) and UV absorption peaks at 210 and 254 m $\mu$  ( $\epsilon$  29,000; 10,200). This compares well with the IR peaks of saxin pentaacetate at 1775s, 1750 inflexion and 1735 cm<sup>-1</sup> (KBr) and UV absorption peaks at 210 and 253 m $\mu$  ( $\epsilon$  28,600 and 9,300).

The PMR spectra of saxin acetate taken in dimethyl sulphoxide, gave bands at 7.92 (aliphatic acetate

methyls), 7.62 (aromatic acetate methyls), 6.59 (two protons at C-13 of primary acetate), 6.10 (methoxyl methyl), 5.95 and 5.79 (3 protons at C-7, 8 and 12), multiplet between 5.30 and 4.27 (protons at C-10 and 11) and 2.18  $\tau$  (aromatic proton at C-4). The PMR spectrum of saxin itself taken in the same solvent gave peaks with absorptions between 6.89 and 6.53 (hydroxyl protons), 6.43 (two protons at C-13 of primary hydroxyl), 6.13 (methoxyl methyl), 5.92 and 5.79 (3H at C-7, 8 and 12) 5.02 and 4.88 (2H at C-10 and 11), 2.90  $\tau$  (aromatic proton at C-4).

The mass spectra of saxin gave its molecular ion peak at 328 which corroborates the molecular formula of anhydrous saxin C<sub>14</sub>H<sub>16</sub>O<sub>9</sub>. The base peak at 208 is obviously formed by elimination of the carbon atoms 10, 11, 12 and 13 thus leaving behind substituted isocoumarin molecule, C<sub>10</sub>H<sub>8</sub>O<sub>5</sub> (III). The other major fragment at 279 is formed by elimination of carbon-13 and dehydration at C-11 to give II.



#### Experimental

The spectral analyses were carried out by Physico-chemical Measurements Unit, Berks, U.K., and PCSIR Laboratories, Karachi. The m.p.s. have been taken on Koffler block and are corrected.

**Anhydrosaxin.** Crystalline saxin (70 mg) was taken in a glass tube and slowly heated in a paraffin oil-bath to 155°C. The crystals melted above 140°C and resolidified. It was powdered with a spatula and heated to 150-160°C. After about 30 min it attained a constant weight which did not change after another 30 min heating. The total weight lost during the heating amounted to 4.5 mg (theoretical 3.7 mg). The solid residue was allowed to cool in a vacuum-desiccator. Anhydrosaxin melted at 239-41°C.

Saxin crystals<sup>1</sup> when heated on Koffler block started melting (with bubbling) at 159°C and completed its decomposition at about 161°C. It resolidified as platelets above 171°C and remelted at 239-42°C.

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#### References

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2. I. Bergenin, A.E. Chichibabin, A.V. Kirsanov, A.I. Korelev and N.N. Vorozhtov Jr., Ann., **469**, 93(1929).
3. J. Evelyn Hay and L. J. Haynes, J. Chem. Soc., 2231 (1958).

\*For Part I, see *Saxifraga Ciliata*, Pakistan J. Sci. Ind. Res., **4**(2), 79-80 (1961).

†Intensity of the bands are designated as strong (s), medium strong (ms), medium (m), medium weak (mw) and weak (w).