

Colouring Matters of *Matthiola Incana*

D. S. Bhakuni*

From the seeds of *Matthiola incana* (red variety) a mucilage and an oil (Bhakuni and Joshi, *Proc. Nat. Acad. Sci. India*, 1959, **28A**, 1, 190) were isolated and studied earlier. Further chemical examination of the seeds has resulted in the isolation of two crystalline colouring substances, designated provisionally as mathiolin A, m.p. 286°, and mathiolin B, m.p. 263°, respectively.

The defatted seeds, free from mucilage, were extracted according to Bhakuni (*J. Sci. Ind. Res.*, 1961, **20B**, 297) as in the case of the seeds of the yellow variety. The mixture of the colouring matters, thus obtained after purification through organic solvents, when treated with acetone, yielded two fractions, the acetone-insoluble and the acetone-soluble. The former fraction on recrystallisation from glacial acetic acid gave mathiolin A as red plates, m.p. 286°. [Found: C, 60.96; H, 3.89; OMe, 10.22; C-Me, nil. $C_{16}H_{12}O_7$ requires C, 60.76; H, 3.79; OMe (for one), 9.81%]. The latter fraction on repeated purification through acetone-ether and finally on recrystallisation from ethyl acetate gave mathiolin B as orange-red plates, m.p. 263°. [Found: C, 61.87; H, 3.94; OMe, 9.84; C-Me, 4.24. $C_{17}H_{12}O_7$ requires C, 62.19; H, 3.65; OMe (for one), 9.45; C-Me (for one), 4.57%].

Mathiolin A

Mathiolin A dissolves in alkalis to an orange-red solution. It develops a greenish violet colour with H_2SO_4 (conc.) and a greenish colour with ethanolic ferric chloride. Routine analysis of the compound showed the presence of one OMe and the absence of C-Me groups in the molecule.

The compound on acetylation with acetic anhydride-pyridine (at 100°, for 4 hours) formed a tetra-acetate as pale yellow needles (glacial acetic acid), m.p. 165°. [Found: C, 59.34; H, 4.24; OAc, 34.6. $C_{24}H_{20}O_{11}$ requires C, 59.50; H, 4.13; OAc (for four), 35.52%]. With benzoyl chloride-pyridine it formed a tetrabenzoate, m.p. 180-82°. (Found: C, 72.33; H, 3.94. $C_{44}H_{28}O_{11}$ requires C, 72.13; H, 3.82%).

Methylation of mathiolin A with methyl sulphate in dry acetone and in presence of anhydrous potassium carbonate (refluxed for 30 min.) furnished a dimethyl ether in orange-red plates (ethyl acetate), m.p. 198°. (Found: C, 62.89; H, 4.48. $C_{18}H_{16}O_7$ requires C, 62.79; H, 4.65%).

The filtrate obtained after removal of the dimethyl ether, on further treatment with the same quantities of potassium carbonate and methyl sulphate (refluxed for 4 hours), gave a trimethyl ether in orange needles (glacial acetic acid), m.p. 176-77°. (Found: C, 63.42; H, 5.32. $C_{19}H_{18}O_7$ requires C, 63.68; H, 5.02%).

*Present address: National Botanic Gardens, Lucknow.

Mathiolin A on treating with 80% H_2SO_4 (at 100° , for 2 hours) gave a demethoxylated compound as orange-red plates, m.p. 270° . (Found: C, 59.82; H, 3.50. $\text{C}_{15}\text{H}_{10}\text{O}$, requires C, 59.60; H, 3.31%).

The compound on distillation with zinc dust furnished a colorless compound (ethanol), m.p. 204° , which showed no depression on admixture with an authentic sample of 2-methylanthracene.

The studies carried out so far on mathiolin A indicates that the compound is an anthraquinone derivative, having four hydroxyl groups out of which three are phenolic in nature and the one, which escapes methylation, appears to be alcoholic in function. It also contains one OMe group.

Mathiolin B

Mathiolin B gave an orange-coloured solution with caustic alkalies, a greenish colour with H_2SO_4 (conc.), and a violet colour with ethanolic ferric chloride. Its reaction with sodium bicarbonate indicated the presence of a carboxyl function in the molecule. Routine analysis of the compound showed the presence of one C-Me and OMe groups in the molecule.

With acetic anhydride-pyridine it formed a diacetate in yellow plates (glacial acetic acid), m.p. 176° . [Found: C, 61.02; H, 4.18; OAc, 20.32. $\text{C}_{21}\text{H}_{16}\text{O}_9$, requires C, 61.16; H, 3.88; OAc (for two), 20.87%].

The compound on methylation (in the similar manner as in case of mathiolin A) formed a monomethyl ether, m.p. 166° . (Found: C, 63.35; H, 4.18. $\text{C}_{18}\text{H}_{14}\text{O}$, requires C, 63.15; H, 4.09%) and a dimethyl ether, m.p. $152-53^\circ$. (Found: C, 64.26; H, 4.38. $\text{C}_{19}\text{H}_{16}\text{O}$, requires C, 64.04; H, 4.49%).

Demethoxylation of mathiolin B with 80% H_2SO_4 (at 100° for 2 hours) gave orange-red plates (glacial acetic acid), m.p. 253° . [Found: C, 60.84; H, 3.36. $\text{C}_{16}\text{H}_{10}\text{O}$, requires C, 61.14; H, 3.18%).

Mathiolin B on distillation with zinc dust in a stream of hydrogen furnished colorless leaflets (ethanol), m.p., 205° , which showed no depression on admixture with an authentic sample of 2-methylanthracene.

The experimental data given above suggest that mathiolin B is also an anthraquinone derivative having a C-Me group in 2-position of the basic anthraquinone nucleus. It also contains a C-Me, a carboxyl and two phenolic hydroxyl groups in the molecule. Further study of these compounds is in progress.