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ISOLATION AND STRUCTURAL STUDIES ON THE ALKALOIDS IN FLOWERS OF *CATHARANTHUS ROSEUS*

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The flowers of *Catharanthus roseus* (L.) G.Don enjoy the reputation in the folklore of possessing hypoglycemic properties and are, therefore, administered to diabetic patients. While a large amount of work has been carried out on the alkaloidal contents of the leaves of *C. roseus* (1-6), little work has been done on the flowers of this plant. We report here the isolation of ten alkaloids from its flowers: vinblastine, coronaridine, 11-methoxytabersonine, tetrahydroalstonine, ajmalicine, catharanthine, mitraphylline, vindorosine, vindoline, and a new alkaloid that appears to be isomeric to vincristine.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded on Jasco-IRA-1, ir spectrophotometer, Shimadzu uv-240, uv spectrophotometer, Finnigan MAT 312, mass spectrometer and Brücker WP-100 SY nmr spectrometer.

Leaves and other plant tissues were carefully removed from the flowers of *C. roseus*. The flowers (73 kg) were then extracted with EtOH, the extracts concentrated to a dark brown gum, and the material partitioned between 5% HOAc and $CHCl_3$. The acid-soluble portion was basified with NH_3 and extracted into $CHCl_3$ to afford the crude alkaloids (34 g). These were redissolved in 5% HCl solution and extracted into $CHCl_3$ at various pH values.

The alkaloids obtained at pH 4 were loaded on a flash chromatography column (neutral alumina) and eluted with increasing polarities of petroleum ether (40-60°)-C_6H_6 (F_1), C_6H_6 (F_2), C_6H_6-$CHCl_3$ (1:1) (F_3), $CHCl_3$ (F_4), $CHCl_3$-EtOAc (1:1) (F_5), EtOAc (F_6), and MeOH (F_7).

THE FRACTIONS.—Fraction (F_3) (9 g) was again loaded on a silica column and eluted with 80% $CHCl_3$-20% petroleum ether (40-60°). The eluates were concentrated and subjected to preparative tlc on silica plates in 80% petroleum ether-20% Me_2CO to afford a compound identified as coronaridine (8 mg) by comparison of its spectral data with those reported in the literature (7). Further elution of the same column with $CHCl_3$-EtOAc (1:1) afforded another fraction that was subjected to preparative tlc on silica plates in 72% petroleum ether-28% Me_2CO to afford 11-methoxytabersonine (5 mg) which was identified by comparison of its ir, uv, nmr ($CDCl_3$) and mass spectra with those reported in the literature (8).

Fraction (F_4) (11 g) was chromatographed on an alumina column and eluted with petroleum ether and then with $CHCl_3$. The $CHCl_3$ eluates afforded a mixture of alkaloids that were purified by preparative tlc on silica plates in 70% petroleum ether-30% Me_2CO. The faster-moving alkaloid was identified as tetrahydroalstonine (10 mg) by comparing its spectral data with those reported in the literature (9). The slower-moving alkaloid was identified as ajmalicine (20 mg) by direct tlc comparison with an authentic sample and by comparison of spectral data (10). Further elution of the same column with EtOAc gave another fraction containing an alkaloid that was further purified by preparative tlc on silica plates in 68% petroleum ether-32% Me_2CO. The alkaloid was identified as vindorosine (15 mg) by comparison of spectral data (11) (ir, uv, nmr, ms).

Fraction (F_5) (8 g) was loaded on a silica column and eluted with EtOAc-EtOH (1:1) to give a fraction containing two alkaloids that were separated by preparative tlc on silica plates in 55% petroleum ether-45% Me_2CO. The faster-moving alkaloid was identified as catharanthine (13 mg) by direct chromatographic comparison with an authentic sample isolated by us from the leaves of *C. roseus* as well as by comparison of spectral data (12). The slower-moving alkaloid was similarly identified as mitraphylline (13) (5 mg).

Another fraction obtained on elution of the column with the same solvent system was found to contain one major compound that was separated and purified by preparative tlc on silica plates in 50% Me_2CO-

50% petroleum ether. This was identified as vindoline (30 mg) by chromatographic and spectroscopic comparison with an authentic sample (14).

Fraction (F_7) (6 g) was chromatographed on a silica column (200 g) and eluted with increasing polarities of petroleum ether, EtOAc, and MeOH. The eluates of 70% EtOAc-30% MeOH (200 ml) was concentrated and purified by preparative tlc on silica plates in 60% Me_2CO-40% petroleum ether to afford an alkaloid (18 mg) which was identified as vinblastine.

Comparison of the spectral data with those reported in the literature (15,16) for vinblastine as well as chromatographic comparison with an authentic sample of vinblastine isolated from *C. roseus* leaves in several solvent systems confirmed the identity of the binary compound as vinblastine.

Another band faster moving to vinblastine isolated from the same plates afforded a new alkaloid that had a mass spectrum virtually identical to that of vincristine. Direct tlc comparison with an authentic sample of vincristine, however, showed that the isolated compound was faster running to vincristine in 60% Me_2CO-40% petroleum ether, the two being distinctly separable on mixed tlc. Further work on the new compound, which appears to be isomeric to vincristine, is continuing.

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HORDENINE AND *N*-METHYL-4-METHOXYPHENETHYLAMINE FROM *ERIOGONUM* SPECIES

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A screening program (1) found several *Eriogonum* species (Polygonaceae, Buckwheat family) to contain alkaloids. Because this was the first report of alkaloids in the genus *Eriogonum*, we have identified the major alkaloidal components in four species.

Species	Plant Part	Alkaloids Found
E. alatum Torr.	roots	hordenine
	above ground	none
E. annuum Nutt.	whole plant	hordenine, *N*-methyl-4-methoxyphenethylamine
E. campanulatum Nutt.	roots	hordenine
	above ground	hordenine, *N*-methyl-4-methoxyphenethylamine
E. inflatum Torr. & Frem.	whole plant	hordenine