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INVESTIGATION OF THE ALKALOIDS OF VINCA MAJOR, V. PUBESCENS, AND V. ROSEA. THE STRUCTURE OF MAJDINE [1]

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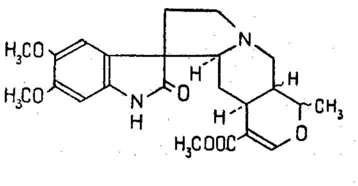
We have isolated three alkoloids from Vinca major: reserpinine, akuammine, and majdine [1].

On heating with acetic anhydride, majdine, $C_{23}H_{28}O_6N_2$, isomerizes into isomajdine with mp 204-206°, $[\alpha]_D^{18}$ – 90° (methanol). By comparing the IR and NMR spectra and other properties, it was found that majdine is possibly a stereoisomer of the hydroxyindole alkaloid carapanaubine, which has been isolated from Aspidosperma carapanaubica [2].

The mass spectra of majdine and carapanaubine were found to be identical. Consequently, majdine is a hydroxyindole base of the following structure:



The isomerization of majdine to isomajdine shows the presence in majdine of the α-orientation of the hydrogen atom at C_4 and of the β-orientation in isomajdine. Isomerization at C_4 is characteristic of the hydroxyindole alkaloids [3].

This indicates that majdine differs from carapanaubine by the configuration of the C_{15}, C_{19}, and C_{20} carbon atoms.

If we take into consideration the fact that in the δ-yohimbine and hydroxyindole bases the hydrogen at C_{15} has the α-orientation [4], the configuration of the C_{19} and C_{20} atoms in majdine remain undetermined.

A. P. Orekhov et al. [5] have isolated three bases from V. pubescens: vinine, pubescine, and a base with mp 194-195°.

The ethereal extraction of 1 kg of the above-ground parts of the plant Vinca pubescens, collected in the environs of the town of garga in the fruit-bearing season (12 October, 1959), yielded 6.35 g of total alkaloids (0.64%). They were separated with respect to their basicities into ten fractions. The third fraction yielded 200 mg of pubescine with mp 228-230°. After its purification by chromatography on alumina, it was found that it melted at 236-237°.

The IR spectra of pubescine are identical with those of reserpinine which we isolated from Vinca erecta [6]. The 6th-7th fractions gave 50 mg of vinine with mp 210-213°. After its recrystallization from acetone, it had mp 216-217°; molecular weight 428 (by mass spectroscopy).

A comparison of their mass spectra and other properties showed that vinine is identical with carapanaubine.

After the isolation of the alkaloids, the ethereal extract gave 0.59% of ursolic acid.

Ninety grams of the roots of V. rosea grown in the Botanical Garden of the UzSSR Academy of Sciences yielded 0.5% of total alkaloids, 10% of which consisted of a base with mp 256-257°, $[\alpha]_D$ – 49° (methanol), $C_{21}H_{24}ON_2$, forming a hydrochloride with mp 281-283°. A study of the UV and IR spectra and other properties of the base showed that it was ajmalicine [7].

Thus, reserpinine, akuammine, carapanaubine, ajmalicine, and the new base majdine have been isolated from Vinca major, V. pubescens and V. rosea.

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NEW FLAVONOIDS FROM THE LEAVES OF CRATAEGUS CURVISEPALA LINDM. (FAMILY ROSACEAE)

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By chromatography on polyamide columns of the total flavonoids isolated previously from the leaves of Crataegus curvisepala Lindm. (campylocalycate hawthorn) [1], two new flavonoids have been isolated: flavonoid (I) and flavonoid (II).

Flavonoid (I), $C_{15}H_{10}O_7$, mp 311-313°, formed a compound of the composition $C_{25}H_{20}O_{12}$, mp 199-201° on acetylation. On investigating the UV spectra of flavonoid (I) with the addition of sodium acetate, a bathochromic shift of 33 mμ was found in the short-wave region, which is apparently due to the presence of a strongly ionized hydroxyl group in position 7. A bathochromic shift of 19 mμ in the long-wave region of the UV spectrum of flavonoid (I) on the addition of sodium acetate and boric acid indicates the presence of hydroxyl groups in the 3'-, and 4'-positions [2].

The formation of phloroglucinol in the alkaline decomposition of flavonoid (I), and also the results of UV spectroscopy and the absence of a depression of the melting point of a mixture of flavonoid (I) and quercetin, indicates that flavonoid (I) is identical with quercetin (3, 5, 7, 3', 4'-pentahydroxyflavone).

Flavonoid (II), $C_{21}H_{20}O_{12}$, mp 238-239°, is a flavone glycoside. Hydrolysis with 2% hydrochloric acid of flavonoid (II) gave an aglycone of composition $C_{15}H_{10}O_7$ and mp 311-313°. Acetylation of the aglycone of flavonoid (II) gave a compound $C_{25}H_{20}O_{12}$ with mp 199-201°, the physicochemical properties of which did not differ from the acetylated derivative of quercetin. The methyl derivative of the aglycone of flavonoid (II), $C_{20}H_{20}O_7$, mp 152-154°, was identical with the methyl derivative of quercetin.

Among the products of the alkaline decomposition of the aglycone of flavonoid (II), paper chromatography showed the presence of phloroglucinol and 3, 4-dihydroxybenzoic acid, showing the presence in the aglycone of hydroxyl groups at the 5-, 7-, 3'-, and 4'-positions.

UV spectroscopy of the aglycone of flavonoid (II) with various additives (sodium acetate, sodium acetate + boric acid) confirmed the assumption that the aglycone of flavonoid (II) contains hydroxyl groups in the 5-, 7-, 3'-, and 4'-positions. A positive zirconium test [3] showed the presence in the aglycone of flavonoid (II) of a hydroxyl group in position 3. Thus, the aglycone of flavonoid (II) has the structure of quercetin.

Chromatography of the products of the acid hydrolysis of flavonoid (II) in the butanol-acetic acid-water (4: 1: 5) system showed the presence of galactose. A mixture of the phenylosazone of the sugar of flavonoid (II) and galactose gave no depression of the melting point (182-185°). The addition of zinc and hydrochloric acid to a solution of the aglycone of flavonoid (II) led to a characteristic red coloration. The positive zinc/hydrochloric acid reaction shows that the sugar is present in the 3- position of flavonoid (II) [4].