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Berberis ALKALOIDS.

XXXV. AN INVESTIGATION OF *Berberis turcomanica*

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We have investigated the alkaloid composition of young shoots of *Berberis turcomanica* Kar. gathered in the incipient fruit-bearing phase in the region of Kara-Kala, Turkmenia. The extraction and separation of the mixture were performed as described in [1]. The total amount of alkaloids was 0.85%, of which 0.36% was berberine (**1**). The level of (**1**) in *B. turcomanica* in the flowering and fruit-bearing stages did not differ from its levels in other Central Asian species of barberry [2], which permits young shoots of *B. turcomanica* to be recommended as an additional source of raw material for obtaining berberine. In addition to (**1**), from the total quaternary bases we isolated columbamine, and, from the mixture of tertiary alkaloids, oxyacanthine and isoboldine. The alkaloids were identified from their spectral characteristics and by direct comparison with authentic samples. This is the first time that isoboldine has been isolated from this species.

When the mother solutions [1] were rechromatographed on columns of Al_2O_3, we obtained compounds (**2**) with mp 150-151°C and (**3**) with mp 231-233°C. The UV spectrum of (**2**) showed four absorption maxima at (nm) 238, 280, 314, and 327. The mass spectrum showed the peaks of ions with *m/z* 339 (M^+, 70), 338 (80), 325 (20), 324 (100), and 308 (20). The PMR spectrum, taken in chloroform, included the signals of four OCH_3 groups at (ppm) 3.72, 3.77, 3.86, and 3.95, of seven aromatic protons at 6.73 (3H, br.s), 6.98, 7.29 (1H each, s), 7.36 and 8.32 (1H each, d, J = 6 Hz), and of a methylene group at 4.47 (2H, s). From these facts [3] and also the results of TLC and the absence of a depression of a mixed melting point, base (**2**) was identified as papaverine. This is the first time that papaverine has been isolated from the Berberidaceae family.

Compound (**3**) gave a positive reaction with the Dragendorff reagent. Its mass spectrum contained the peaks of ions with *m/z* 450 (30), 449 (100), 435 (25), 419 (80), 299 (95) and 151 (50). The UV spectrum contained absorption bands in the 234 and 296 nm regions. The IR spectrum lacked absorption bands corresponding to hydroxy and carbonyl groups. The PMR spectrum revealed four groups of signals: in the aromatic region a singlet at (ppm) 6.80, two doublets from methylene groups at 4.69 and 3.46 (J = 14 Hz), and a singlet from an OCH_3 group at 3.76 with an intensity ratio of 2:1:1:6. Such a grouping of equivalent protons indicated a high symmetry of compound (**3**). This was confirmed by its ^{13}C NMR spectrum, which

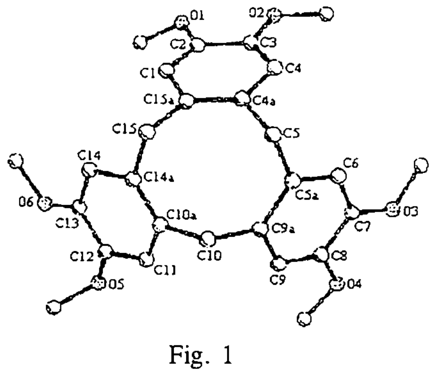

Fig. 1

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included only five signals for carbon atoms. To determine its structure, compound (**3**) was subjected to x-ray structural analysis, and it was found that (**3**) was cyclotriveratrylene (CTV), the spatial structure of which is shown in Fig. 1. Assignment of the signals in the ^{13}C NMR spectrum: 113.0 (d, C-1), 147.6 (s, C-2), 132.7 (s, C-4a), 36.3 (t, C-5), 55.9 (q, OCH_3).

CTV has been obtained by the condensation of veratrole with formaldehyde or from veratryl alcohol by heating with concentrated acids; however, a definitive structure for (**3**) has been established only much more recently [4]. Since we used no concentrated acids in the extraction of the raw material and the separation of the mixture of alkaloids, we consider that CTV is a native compound that we are the first to have isolated from a plant. It is likely that the biosynthesis of (**2**) and (**3**) in the plant proceeds in parallel from a common precursor, However, it is not excluded that (**3**) is the final product of the transformations of benzylisoquinoline alkaloids, since there have been reports of the formation of CTV on the oxidation of laudanosine [5].

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