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Berberis ALKALOIDS.
XXXVIII. TURCAMINE — A NEW ISOQUINOLINE ALKALOID FROM *Berberis turcomanica*

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The new isoquinoline alkaloid turcamine (1) has been isolated from the leaves of Berberis turcomanica, *and its structure has been established as 8-hydroxy-7-methoxy-2-methyltetrahydroisoquinoline. A relationship has been found between a substituent at C-8 and the multiplicities of the signals from C-5 and C-6.*

Continuing an investigation of the alkaloids of the leaves of *Berberis turcomanica* Kar. [1], from the ether fraction of bases we have isolated corypalline [2] and base (1) with mp 100-102°C. The known alkaloid corypalline was identified from its spectral characteristics and also by direct comparison with an authentic specimen.

The mass spectrum of base (1) contained intense peaks of ions with *m/z* 192 ($[M - 1]^+$, 100%) and 150 (50). The mass-spectrometric fragmentation of (1) was close to that of corypalline and showed that base (1) was a simple tetrahydroisoquinoline containing OCH_3 and OH groups in ring *A*. The presence of $(M - 1)^+$ as the strongest ion witnessed the absence of a substituent at C-1 [3].

The PMR spectrum of (1) revealed signals of N-methyl and methoxy groups in the form of three-proton singlets and of two methylene groups in the form of a multiplet in the 2.60-3.10 ppm region, and also a two-proton singlet from the protons at C-1. In the aromatic region of the spectrum there were the signals of two *ortho*-protons in the form of one-proton doublets with a spin-spin coupling constant $J = 8.5$ Hz at 6.65 and 6.86 ppm.

Starting from the results given above, it could be assumed that the substituents in (1) were located at C-5 and C-6 or at C-7 and C-8. The latter is more likely from biogenetic considerations, since the alkaloid oblongine, in which substituents in ring *A* are present in positions 7 and 8, has previously been isolated from barberries, and no 5,6-disubstituted compounds have ever been found among simple isoquinoline alkaloids. The mutual arrangement of the substituting groups in (1) was found definitively from the results of an analysis of the literature. The properties of synthesized 8-hydroxy-7-methoxy- and 7-hydroxy-8-methoxy-N-methyltetrahydroisoquinolines (1 and 2, respectively) have been described [2]. The melting point and PMR spectrum of the alkaloid that we had isolated corresponded to (1). Consequently, base (1) is a new alkaloid isolated from a natural source for the first time, and we have called it turcamine.

On analyzing literature information on the PMR spectra of tetrahydroisoquinolines and 1-benzylisoquinolines 7,8-disubstituted in ring *A*, we noted a definite regularity in the multiplicity of the signals from the H-5 and H-6 protons: it depends not on the neighboring substituent at C-7 but on the substituent at C-8. Thus, in compounds (1), (3) and (6)-(8), in which the substituent group at C-8 is hydroxyl, the signals of the protons at C-5 and C-6 appear in the form of two one-proton doublets with SSCCs of 7.5-9.0 Hz. Such doublets are observed in the PMR spectra of gortchakoine (6) [5], juziphine (7) [6], and norjuziphine (8) [7]. In compounds (2), (4), (5), and (9)-(11), in the structure of which the C-8 position is occupied by an OCH_3 group, however, the corresponding protons each give a singlet in the 6.10-7.10 ppm interval [8, 9].

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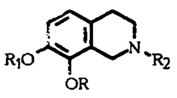
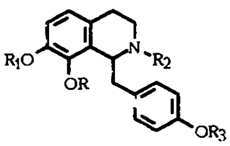


1-5

1. R=H, R_1=R_2=CH_3;
2. R=R_2=CH_3, R_1=H;
3. R=R_1=H, R_2=CH_3;
4. R=R_1=CH_3, R_2=H;
5. R=R_1=R_2=CH_3



6 - 11

6. R=H, R_1=R_2=R_3=CH_3;
7. R=R_3=H, R_1=R_2=CH_3;
8. R=R_2=R_3=H, R_1=CH_3;
9. R=R_1=R_2=R_3=CH_3;
10. R=R_2=R_3=CH_3; R_1=H;
11. R=R_1=R_2=CH_3; R_3=H

Thus, on the basis of spectral characteristics and an analysis of the literature, we propose for turcamine the structure of 8-hydroxy-7-methoxy-2-methyltetrahydroisoquinoline (**1**).

EXPERIMENTAL

For general observations, see [1].

Isolation of Turcamine. The mother solution (0.1 g) obtained in the separation of the ether fraction [1] of *B. turcomanica* leaves was rechromatographed on a column of alumina in a ratio of 1:40. Elution with chloroform—methanol (24:1) yielded 10 mg of corypalline in amorphous form. From the enriched fractions, 6 mg of turcamine was isolated preparatively (on plates with Al_2O_3 in the chloroform—methanol (9:1) system).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 193 (M^+, 15), 192 ($M-1^+$, 100), 178 ($M-15^+$, 40), 177, 150 (50), 149.

PMR spectrum (100 MHz, $CDCl_3+CDCl_3+CD_3OD$ (1:1), ppm, δ, J, Hz, 0 – HMDS): 2.38 (3H, s, N-CH_3), 3.76 (3H, s, OCH_3), 2.60-3.10 (4H, m, H-3, H-4), 3.34 (2H, s, H-1), 6.65, 6.86 (each 1H, d, J = 8.5, H-5, H-6).

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