

Dimeric quinoline alkaloids contain a terpenoid component and belong to a comparatively small but interesting class of natural compounds. The structural and stereochemical features of these alkaloids and their division into subgroups according to the structure of the terpenoid part has been made in a review [1].

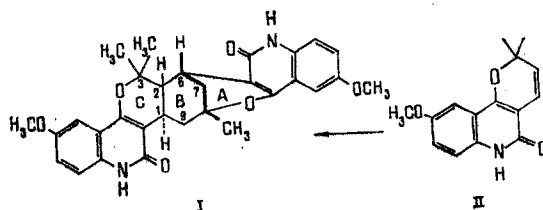
Pathways for the synthesis of these alkaloids have been considered in a number of publications [2-4]. A relatively simple synthesis of heptacyclic dimeric compounds, the so-called vepridimerines A-E is based on the thermolytic reaction of the dimethylpyrano-2-quinolone alkaloid veprisine [4]. In the present paper we describe a similar synthesis of the dimeric compound (I). The initial compound used was the pyrano-2-quinolone alkaloid haplamine (II) which is found in plants of the genus *Haplophyllum* [5-7].

Haplamine (3 g) was heated in a sealed heat-resistant tube at 220-230°C for 16 h. After cooling, the contents of the tube were chromatographed on a column of silica gel. This gave product (I), insoluble in the usual organic solvents but soluble in pyridine and acetic acid. The yield of (I) was 42% and it crystallized from glacial acetic acid with mp 300°C (decomp.) and fluoresced in UV light. The mass spectrum of (I) had the peak of the molecular ion with m/z 514.2077, composition $C_{30}H_{30}N_2O_6$, corresponding to a dimer of haplamine. The UV spectrum of the dimer obtained (λ_{max} C_2H_5OH 218, 232, 278, 288, 338, 355 nm), which did not change on acidification and alkalization, retained the absorption maxima characteristic for the 2-quinolone system [8]. The IR spectrum contained absorption bands of an amide carbonyl at 3165 and 1670 cm^{-1} . The main peaks in the mass spectrum of (I) were as follows (m/z , %): 514 (100), 499 (11), 484 (28), 471 (11), 257 (33), 242 (97), 228 (22), 216 (33), 188 (28). The presence in the spectrum of this compound of an intense peak, among others, of an ion with m/z 242.08380 having the composition $C_{14}N_2NO_3$ is typical for the fragmentation of M^+ of haplamine [6].

The PMR spectrum of (I) (CF_3COOH , ppm) contained a multiplet from six aromatic protons in the 6.93-7.37 region, two singlets from methoxy groups at 3.55 and 3.60, and three singlets from C-methyl groups at 0.83, 1.32, and 1.63. The spectrum also revealed seven protons of a cyclohexane ring at 1.03 (dd, $J = 14$ and 10 Hz, H-9); 1.65 (m, H-7), 1.99 (unresolved signal, H-2 and H-7); 2.60 (td, $J = 14$ and 4 Hz, H-1); 3.37 (m, H-6); and 3.57 (m, H-9).

A comparative analysis of the PMR spectra of (I) and of known dimeric quinoline alkaloids [1] showed that the new dimer obtained had the heptacyclic structure (I). The multiplicities and values of the chemical shifts of the signals of the protons of the cyclohexane ring of (I) were close to those of paraensidimerine F [9], geijedimerine [10], and vepridimerine E, in which the B/C rings are trans-linked, and the axial protons at C-1 and C-2 have the α - and β -orientations, respectively. In the spectra of all these compounds and of the dimer (I) the signals of the H-1 and H-9 protons were observed in a stronger field relative to those in the spectra of other heptacyclic dimers [1].

The facts given show that the new dimer obtained had structure (I).



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STUDY OF CARBOHYDRASE-CATALYZED REACTIONS WITH THE AID OF EDIAP MASS SPECTROMETRY

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The distribution of the products of the enzymatic transformation of various substrates under the action of the endo- β -(1 \rightarrow 3)-glucanase L IV from the mollusc *Spisula sachalinensis* has been investigated and the possibility has been shown of the simultaneous recording, with the aid of EDIAP mass spectrometry, of the products of hydrolysis and of transglycosylation. It has been shown that methyl gentiobioside and methyl cellobioside are acceptors in the transglycosylation reaction, as a result of which glucooligosaccharides with a mixed type of glycosidic bonds are formed. The ratio of mono-, di-, tri-, and tetrasaccharides labeled at the ends with ethylene glycol formed in the enzymatic hydrolysis of laminarin previously subjected to Smith degradation has been determined.

Workers investigating the mechanism of the action of carbohydrases and, in particular, endo-glycanases suffer from a deficiency of methods permitting the rapid evaluation of the composition and structure of the oligosaccharides formed in reactions catalyzed by these enzymes.

Since the beginning of the eighties, in addition to the method of field desorption, the methods of fast-atom bombardment and of secondary ion emission by ion bombardment have begun to be applied to oligosaccharides and glycolipids [2-5]. A common disadvantage of these methods, apart from fragmentation, in the analysis of mixtures of oligosaccharides is the fact that after the beginning of analysis the growth of the peaks of the quasimolecular ions in the mass spectrum and their subsequent disappearance take place at different rates, depending on the degree of polymerization, which complicates the evaluation of the relative concentrations of oligosaccharides in the mixture. Thus, there are practically no examples in the literature of the solution with the aid of mass-spectrometric methods of any problems connected with the study of the distribution of oligosaccharides and/or their derivatives in mixtures.

As has been shown previously, [6], the EDIAP method permits the analysis of the products of the enzymatic hydrolysis of laminarin ((1 \rightarrow 3), (1 \rightarrow 6)- β -D-glucan), consisting of a mixture of glucooligosaccharides, by direct introduction with no preliminary

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