SUMMARY

1. The oxidation of cembrene with chromium trioxide in aqueous sulfuric acid (the Jones reagent) and in aqueous acetone has given norcembr-2,7,11-trien-4-one, norsolanadione, (3E, 8E)-5-isopropyl-8-methyltrideca-3,8-diene-2,12-dione, and five new compounds the structures of which have been established on the basis of their spectra.

2. Oxidation with chromium trioxide in aqueous acetone, in contrast to oxidation with the Jones reagent, takes place stereospecifically—the C11–C12 double bond of cembrene is not affected.

LITERATURE CITED


ALKALOIDS OF Haplophyllum perforatum

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We are studying for the first time the alkaloids of the epigeal part of the plant Haplophyllum perforatum growing in the Dzhungarian Ala–Tau, Kazakh SSR. The plant, collected in the flowering period, was extracted with methanol. The methanolic extract was separated into acid, neutral, and basic fractions. From the basic fraction, comprising 0.32% of the weight of the dry plant, we obtained evoxine (I) [1], and the new alkaloids glycopidine (II) [2], and methylevoxine (III) [3], and from a neutral fraction the lignane eudesmin, the known alkaloids flindersine (IV) [4] and 7-isopentenyloxy-γ-fagarine (V) [5], and a new base—haplamine (VI) [6], which proved to be the main component (0.143% of the dry weight of the plant) of the mixture of bases. No alkaloids were found in the acid fraction. The total amount of bases obtained was 0.48% of the weight of the dry plant, and of these 1/3 was represented by the alkaloids isolated from the neutral fraction of the extract. Thus, the combined alkaloids of this plant can be evaluated both qualitatively and quantitatively only after separation of the basic and the neutral fractions of the extract.

Of the substances isolated, only evoxine and the lignane eudesmin had been obtained from this plant previously [7, 8]. Furthermore, we did not detect skimmianine, which is present in the plant H. perforatum

growing in Babatage [9] and in the Kitab region of the Kashkad'ya oblast [7]. The combined alkaloids of
H. perforatum from different growth sites are completely different, which is a convincing example of the de-
pendence of the qualitative and quantitative compositions of the alkaloids of plants of one species on the growth
site [10].

Since doubt has been expressed in the literature concerning the native nature of evoxine [11], we extracted
the alkaloids without the use of an acid. However, as in the case of methanolic extraction, we obtained (I).
These facts show that evoxine is a natural alkaloid and not an artefact.

We have previously proposed for haplamine the structure of 6-methoxyflindersine (VI) on the basis of the
spectral characteristics of the alkaloid and of its decomposition product (VII) [6]. The latter was synthesized
from p-anisidine and diethyl malonate by a known method [12]. According to TLC and its melting point and IR
spectrum, the synthetic 4-hydroxy-6-methoxy-2-quinolone was identical with substance (VII). Their O,N-di-
ethylmethyl derivatives (VIII) also gave no depression of the melting point. Thus, it was shown that the methoxy
group in haplamine is present in position 6.

The presence of an α,α-dimethylpyran ring was confirmed by the formation of a dihydro derivative (IX)
(Scheme 1), the spectral characteristics of which are close to those of dihydroflindersine (X). In the NMR
spectrum of (IX) (Fig. 1), as in the spectrum of (X) [13], in place of the signals of olefinic protons two two-
proton triplets are observed at 7.53 and 8.32 ppm (J = 6.5 Hz), which is typical for the protons of the γ- and β-
methylene groups of an α,α-dimethyldihydropyran ring [14]. The other signals observed in the NMR spectrum
of haplamine [6] are retained in the spectrum of (IX). Under the conditions of mass spectrometry, the molec-
ular ion of dihydrohaplamine with m/e 259 decomposes with the formation of the stable ions(M-43)+, (M-55)+,
and (M-56)+, which is characteristic for substances containing an α,α-dimethyldihydropyran ring unsubstituted
in the β position [15]. The IR spectra of haplamine taken in an KBr tablet and in chloroform solution show a
strong absorption band at 1660 cm⁻¹ (amide carbonyl) and a weak maximum at 3155 cm⁻¹ (NH group). Conse-
quently, haplamine has the lactam structure both in the crystalline state and in solution. The considerable dis-
placement in the low-frequency direction of the absorption band of the NH group, which is typical for cyclic
amides [16] is due to strong intermolecular hydrogen bonds, which are retained in solutions in solvents of low
polarity [17].

The methylation of haplamine with methyl iodide formed not a N-methyl derivative, as in the case of
flindersine [18], but an O-methyl derivative (XI), mol. wt. 271 (mass spectrometry) (see Scheme 1), the IR spect-
rum of which lacked the absorption band of an amide carbonyl. On this basis, structure (XI) was proposed for
the methylation product, and this was confirmed by its partial synthesis from haplamine. The action of phos-
phoric trichloride on haplamine formed the 2-chloro derivative, the treatment of which with sodium methoxide
yielded 2-O-methylhaplamine, identical with the product of the methylation of haplamine according to its melt-
ing point, TLC, and IR spectrum.

Like flindersine [18], haplamine is not acetylated under the usual conditions. When compound (VI) was
heated with acetic anhydride in the presence of p-toluenesulfonic acid, the 2-O-acetyl derivative (XII) was ob-
tained (see Scheme 1), as was shown by the presence in the IR spectrum of (XII) of an absorption band at 1765
cm⁻¹ corresponding to the characteristic vibrations of a Ar-OCOCH₃ group. In the NMR spectrum of 2-O-
acetylhaplamine (Fig. 2), the protons of the benzene ring appear in the form of sharp signals at (ppm) 2.40
(doublet, 1 H, Jortho = 9 Hz–H-8); 2.92 (quadruplet, 1 H, Jortho = 9 Hz, Jmeta = 3 Hz–H-7); and 3.32 (doublet,
1 H, Jmeta = 3 Hz–H-5). These facts show that the signal in the weak field does not always refer to H-5 [13].

Scheme 1. Transformations of haplamine (VI).