NMR spectra on BS-567A (Tesla) and WM-250 (Bruker) instruments with $\nu_0 = 25.142$ and 65.2 MHz in DMSO-d_6 and C_5D_5N, the ^{13}C chemical shifts being given relative to TMS; $\delta_{TMS} = \delta_{DMSO\text{-}d_6} + 39.6$ ppm, and $\delta_{TMS} = \delta_{C_5D_5N} + 123.6$ ppm. The IR spectrum was obtained on a UR-20 instrument in KBr.

The product of the reduction of dubinidinone – crystals mp 189°C (from ethanol) – was obtained by the method described in [1].

CONCLUSIONS

The existence of ring-chain tautomerism (III) of the product of the reduction of dubinidinone has been established unambiguously by ^{13}C NMR spectroscopy, (III) being the cyclic semiketal form and (II) the open-chain δ-ketol form. It has been shown that in deuteropyridine and deuterodimethyl sulfoxide solutions the tautomeric equilibrium is shifted in the direction of a predominance of the cyclic tautomer (III), while in trifluoroacetic acid the open-chain tautomer (II) predominates.

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STRUCTURE OF OXOSECODELTERINE

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Periodic acid does not oxidize delterine, an alkaloid from Delphinium ternatum. However, the further oxidation of 19-oxodelterine, obtained on oxidation by Marion's method, led to oxosecodelterine, which is a semiacetal formed through the C-7 carbonyl group and the C-10 hydroxy group. The treatment of this compound with sulfuric acid led to oxosecodemethanoldelterine.

The isolation from Delphinium ternatum of a new alkaloid, delterine, for which the structure (I) was established, has been reported previously [1]. In the present paper we give the results of the attempted periodate oxidation of delterine and that of its 19-oxo derivative, and also of an experiment on the isolation of delterine from plant raw material and its synthesis from eldelidine [1].

The attempted periodate oxidation of (I) was unsuccessful. On oxidation with potassium permanganate [2], an oxodelterine $C_{25}H_{39}NO_8$ (II) having a lactam carbonyl group in a

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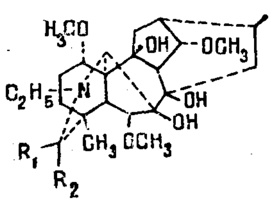
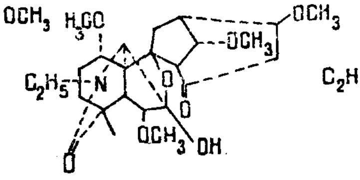
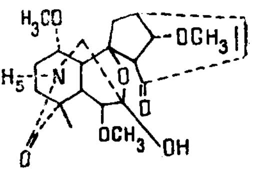


I. $R_1 = R_2$=H
II. $R_1 + R_2$=O



III



IV

6-membered ring (ν_{max}^{KBr} 1640 cm^{-1}) was obtained. The mass spectrum of (II) was characteristic for the spectra of 19-oxo compounds with a lycoctonine skeleton [3]. The oxidation of oxodelterine by periodic acid led to a dicarbonyl compound – oxosecodelterine, $C_{25}H_{37}NO_8$ (III), in the IR spectrum of which there were absorption bands of a lactam carbonyl (1630 cm^{-1}) and of a carbonyl group in a six-membered ring (1712 cm^{-1}).

The formation of various seco products is known for alkaloids with the lycoctonine skeleton and a ditertiary diol system at C_7-C_8 and C_8-C_9. Thus, the periodate oxidation of the oxo derivatives of delphatine, lycoctonine, and browniine (C_7-C_8) leads to the formation of compounds containing lactam carbonyl groups and also carbonyl groups in five-membered and six-membered rings [4]. When a diol system is present at C_8–C_9 (lappoconitine, lappaconidine) the oxoseco products each have a lactam carbon group and a carbonyl group in a five-membered ring, while the C-8 carbonyl group forms the product of the aldol condensation at C-14 [5]. In place of a C_7–C_8 diol system, the oxoseco product may form a hemiketal through the C_8=O and the C-1-α hydroxy group [6, 7].

In our case, in oxosecodelterine (III) a hemiketal was formed though the carbonyl in the five-membered ring and the C-10 hydroxy group. The NMR spectrum of (III) showed the signal of β-H-14 in the form of a poorly resolved triplet at 4.52 ppm with J = 5 Hz, which confirmed the presence of hydrogen atoms at C-9 and C-13. The treatment of oxosecodelterine with sulfuric acid gave oxosecodemethanoldelterine, $C_{24}H_{33}O_7$ (IV), which is an α,β-unsaturated ketone, the formation of which is connected with the presence in the oxoseco product (III) of a methoxy group at C-16 in the β-position to the carbonyl group [4]. IR spectrum of (IV), ν_{max}^{KBr} 1626, 1685 cm^{-1}. The NMR spectrum of (IV) contained the signals from three methoxyls [singlets at 3.28 (3 H) and 3.39 (6 H)] and of two olefinic protons in the form of a one-proton doublet at 5.96 ppm (J = 9 Hz) with additional splitting of ~1.5 Hz and a one-proton quadruplet at 6.81 ppm (J_1 = 9 Hz and J_2 = 7 Hz) with additional splitting of ~3 Hz.

EXPERIMENTAL

The homogeneity of the substances was checked by chromatography in a thin layer of alumina in the hexane–ether (1:1), ether, and ether–methanol (100:1) systems and on type KSK silica gel in the chloroform–methanol (40:1) system. NMR spectra were taken in deuterochloroform on a JNM-4H-100/100 MHz instrument with HMDS as internal standard (values given in the δ scale); mass spectra were taken on a MKh-1303 instrument fitted with a system for direct introduction into the ion source; and IR spectra on a UR-20 instrument (tablets with KBr).

Isolation of the Alkaloids. After 3.8 kg of the air-dry epigeal part of Delphinium ternatum, collected in the vegetation phase, had been moistened with a 5% solution of sodium carbonate, the alkaloids were exhaustively extracted with chloroform at room temperature. Seven extractions were made. The extracts were treated with 5% sulfuric acid and the combined acid solutions were washed with ether and then, with cooling, they were made alkaline with soda and were extracted with ether and with chloroform. This gave an ether-washing fraction A (1.91 g), an alkaline ether fraction B (11 g), and an alkaline chloroform fraction C (1.92 g) of total alkaloids, which corresponds to 0.39% on the weight of the air-dry plant. Fraction B was dissolved in ethanol and the solution was acidified with 10% perchloric acid. The precipitate of methyllycaconitine perchlorate that deposited (3.5 g) was separated off. The mother solution, after the separation of the perchlorate, was made alkaline with soda, diluted with ether, and extracted successively with petroleum ether, benzene, ether, and chloroform. The ether fraction was chromatographed on a column of alumina (1:100). Elution with hexane–ether (1:1) led to the isolation of 0.56 g of a base with mp 116-118°C, and with hexane–ether (1:40) to 0.6 g of delterine (I) with mp 73-75°C.

Oxodelterine (II). A mixture of 0.31 g of delterine, 10 ml of acetone, and 5 ml of water was stirred at room temperature for 5 min. Then 0.31 g of potassium permanganate in 30 ml of 50% aqueous acetone was added to the mixture. The reaction mixture was shaken for 20 min. The excess of potassium permanganate was decomposed with sodium sulfite, and the manganese dioxide was separated off. The acetone was distilled off on the water bath and the residual solution was acidified with 5% sulfuric acid and was extracted repeatedly with chloroform. The residue from the distillation of the chloroform (0.23 g) was chromatographed on alumina. The substances were eluted with chloroform and with chloroform–methanol (100:1). The chloroform–methanol fractions yielded 0.14 g of oxodelterine with mp 209-210°C (acetone), M^+ 481.

Oxosecodelterine (III). A mixture of 0.14 g of (II) and 0.14 g of periodic acid in 18 ml of methanol–water (1:5) was stirred with a magnetic stirrer for 5 days. Then the methanol was distilled off, and the aqueous solution was made alkaline with sodium carbonate and extracted with chloroform. The residue after the elimination of the chloroform was chromatographed on alumina. The chloroform–methanol eluates yielded 90 mg of a product with mp 168-170°C, M^+ 479.

Oxosecodemethanoldelterine (IV). A solution of 0.07 g of (III) in 2 ml of ethanol and 10 ml of 30% sulfuric acid was heated on the steam bath for 5 h. The cooled reaction mixture was made alkaline with soda and extracted with chloroform. The solvent was distilled off and the residue was chromatographed on alumina, elution with chloroform giving (IV).

Synthesis of Delterine from Eldelidine. 6-O-Methyleldelidine. A mixture of 0.3 g of eldelidine, 6 ml of methyl iodide, and 0.15 g of sodium hydride in 25 ml of dioxane was boiled for 8 h and was then filtered. The filtrate was evaporated, the residue was dissolved in 5% sulfuric acid, and the solution was washed with ether and was made alcohol with soda, with cooling, and was then extracted with ether. After elimination of the ether the alkaline ethereal fraction was chromatographed on alumina. Elution with hexane–ether (1:1) led to the isolation of 0.2 g of a product with mp 132-134°C, M^+ 479.

6-O-Methyldemethyleneeldelidine (Delterine). A mixture of 0.15 g of 6-O-methyleldelidine and 25 ml of 10% sulfuric acid was heated on the steam bath for 10 h. Then, with cooling, the reaction mixture was made alkaline with soda and was extracted with ether. After the solvent had been driven off, the residue was chromatographed on alumina, elution with hexane–ether (1:25) leading to a product with mp 73-75°C, which was shown to be identical with a sample of delterine by a mixed melting point, TLC, and IR spectroscopy.

CONCLUSIONS

The structure of oxosecodelterine, which contains a hemiketal grouping, has been established on the basis of chemical transformations and spectral characteristics.

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