A similar ion is observed in the mass spectrum of (II), which shows that the acetoxy (or, in (I), the hydroxy] group is present in ring D. In the mass spectrum of the oxime of the base (IV), an ion with m/e 255 corresponds to this ion (A).

On the basis of the facts given above, structure (I) may be put forward as the most probable for regelinone.

Regelinone is the first representative of the oxohomoproaporphine bases.

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ACETYLBROWNIINE — A NEW ALKALOID FROM *Delphinium oreophilum*

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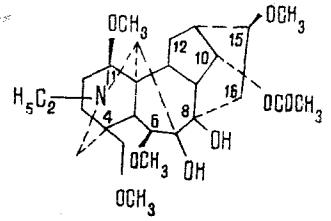
We have investigated the epigeal part of *Delphinium oreophilum* [1, 2] collected in the budding stage in the Dzhungarian Ala-Tau. The total alkaloids amounted to 0.8% of the weight of the air-dry plant. On separating the combined material, we isolated two bases, one of which was obtained in the form of the perchlorate with mp 181-183°C and was identified on the basis of IR spectra, thin-layer chromatography, and a mixed melting point with an authentic sample as methyllycaconitine perchlorate. The second base, with mp 129-130°C, was isolated by separating the mother liquors of the combined alkaloids according to their basicities.

This alkaloid had the composition $C_{27}H_{43}NO_8$ (I). Its IR spectrum contained absorption bands at 3480 and 3430 cm^{-1} (hydroxy groups) and 1743 cm^{-1} (carbonyl of an ester group). The NMR spectrum of the base (JNM-4H-100/100 MHz, $CDCl_3$, internal standard HMDS, δ scale) contained the signals of an ethyl group (three-proton triplet at 0.99 ppm), or an acetoxy group (three-proton singlet at 2.01 ppm) and of four methoxy groups (three-proton singlets at 3.16, 3.21, 3.25, and 3.34 ppm), and a signal with an intensity of one-proton unit at 4.72 ppm (triplet, J = 5 Hz). The position of this signal and the spin—spin coupling constant are characteristic for a proton geminal to an acetoxy group at C_{10} [3, 4].

A direct comparison of the spectral characteristics and the physicochemical constants of (I) with those of browniine monoacetate [5] showed their complete identity.

This is the first time that monoacetylbrowniine has been isolated from a plant.



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PREPARATION OF THE [Ala-B^{15}, Ala-B^{16}] and [Phe-B^{16}] ANALOGS OF BOVINE INSULIN

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In connection with the study of the influence of changes in the structure of insulin on its biological activity, we have obtained previously unknown semisynthetic analogs of bovine insulin — [Ala-B^{15}, Ala-B^{16}] insulin (I) and [Phe-B^{16}] insulin (II) — by combining the A-chain isolated from natural bovine insulin with the corresponding synthetic analogs of the B chain of insulin [1]. The protected chains were demasked by sodium in liquid ammonia in the presence of sodium amide [2], and were then subjected to oxidative sulfitolysis [3], as a result of which the following bis-S-sulfonate analogs of the B chain were obtained: (III), in which the leucine-B^{15} and tyrosine-B^{16} residues have been replaced by two alanine residues, and (IV), in which the tyrosine-B^{16} has been replaced by a phenyl alanine residue.

Amino-acid analyses of the bis-S-sulfonates: (III) Lis 0.9, His 1.6, Arg 1.1, Asp 0.7, Thr 0.6, Ser 0.6, Glu 3.1, Pro 0.8, Gly 3.0, Ala 4.1, Val 3.0, Leu 2.7, Tyr 0.8, Phe 2.8; (IV) Lis 1.2, His 1.6, Arg 1.1, Asp 1.0, Thr 0.9, Ser 0.4, Glu 2.8, Pro 1.0, Gly 3.0, Ala 2.0, Val 2.8, Leu 3.7, Tyr 1.0, Phe 4.0.

The bis-S-sulfornate of (III) was subjected to ion-exchange chromatography on SP-Sephadex C-25. After this, the bis-S-sulfornate of (III) [(IV) without preliminary purification] was made to recombine with a four-fold excess of the tetramercapto form of the A-chain of bovine insulin previously prepared by treating the tetra-S-sulfonate of the A-chain of bovine insulin with 2-mercaptoethanol. The combination of the corresponding chains and the isolation of the insulin analogs was carried out by the method of Katsoyannis [4]. Compound (II) was purified by ion-exchange chromatography on CM-Sephadex C-25.

The electrophoretic mobilities of the compounds obtained were compared with the mobilities of natural bovine insulin (electrophoresis on "Khromatograficheskaya M" paper, pH 2.6; 720 V, 10 mA; standard — bovine insulin).

According to the results of disk electrophoresis in polyacrylamide gel, compound (I) was homogeneous, and compound (II) contained impurities, and therefore compound (II) was purified by disk electrophoresis in polyacrylamide gel. This process was carried out by Davis's method [5] at pH 8.3 with a concentration of the separating gel of 7.5%. After electrophoresis, the appropriate sections of the gel were comminuted and eluted with 7% aqueous acetic acid for 16 h. Compound (II) was isolated from the eluate in the form of the picrate, which was then converted into the hydrochloride.

Amino-acid analyses: (I) His 2.0, Lis 1.2, Arg 1.3, Asp 2.5, Thr 1.3, Ser 2.6, Glu 6.5, Pro 0.9, Gly 4.5, Ala 5.4, Val 4.5, Ile 0.8, Leu 5.0, Tyr 2.6, Phe 3.4; (II) His 1.6, Lis 1.1, Arg 1.2, Asp 2.7, Thr 1.2, Ser 2.6, Glu 6.6, Pro 1.0, Gly 4.4, Ala 2.7, Val 4.5, Ile 0.7, Leu 6.0, Tyr 2.7, Phe 4.4.

The biological activity in testing for convulsive effects in mice, in comparison with the activity of international standard insulin, was 5.5% for (I) and 33% for (II). The prep-

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