STEREOCHEMISTRY OF ALKHANIN AND ALKHANOL

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The stereochemistry of alkhanin and alkhanol — sesquiterpene lactones isolated from *Artemisia fragrans* — has been established.

We have previously [1, 2] described two sesquiterpene lactones isolated from *Artemisia fragrans* Willd., which we called alkhanin and alkhanol. A third substance isolated from the same plant raw material had the composition $C_{15}H_{22}O_4$, mp 202-203°C. Its IR spectrum showed the presence of OH groups (3450 cm^{-1}), a γ-lactone ring (1760 cm^{-1}), and a double bond (1650 cm^{-1}). Acetylation led to a diacetyl derivative $C_{19}H_{26}O_6$ with mp 193-194°C, the IR spectrum of which showed the bands of a CO group of a γ-lactone ring (1760 cm^{-1}), of the CO groups of acetyl residues (1740, 1720, 1255, and 1240 cm^{-1}), and of a double bond (1655 cm^{-1}). The spectrum lacked the band of an OH group.

The NMR spectrum of the substance had the following signals: s 0.76 ppm (3 H, $CH_3-\overset{|}{\underset{|}{C}}-$ at C-10), d 1.20 ppm (3 H, J = 6 Hz, $CH_3-CH<$ at C-11), s 4.96 and 5.14 ppm (1 H each, $CH_2=C<$ at C-4), m 3.36 ppm (1 H, at C-1), t 4.38 ppm (1 H, at C-3), d 2.98 ppm (1 H, J = 10 Hz, at C-5), t 4.05 ppm (1 H, J = 10 Hz, at C-6), s 3.88 ppm (H; OH group), d 4.28 ppm (J = 8 Hz, H,OH group).

A comparison of the physicochemical properties and the IR and NMR spectra of the substance and those of erivanin [3, 4] showed their identity.

Indian workers [5], by oxidizing dihydroreynosin with selenium dioxide, obtained 1,3-dihydroxysantenolide, isomeric with erivanin. 1,3-Dihydroxysantenolide differs from erivanin in the stereo-position of the OH group at C-1, i.e., the OH group at C-1 in erivanin has the α orientation [6] and in isoerivanin the β orientation [5].

As reported previously [1], on acetylation alkhanin forms α-santonin. A comparison of the melting points and IR spectra of an authentic [4] sample of natural dihydroerivanin with those of tetrahydroalkhanin showed their identity. After recrystallization, the tetrahydroalkhanin had mp 220-222°C. Consequently, the stereochemistry of alkhanin and of erivanin at C-1, C-3, C-6, C-7, C-10, and C-11 are the same, i.e., the OH group at C-1 in the alkhanin molecule, like that in erivanin, has the α orientation. This position of the OH group is confirmed by the spin—spin coupling constants of H-1. The signal of the proton at C-1 in the NMR spectrum of alkhanin appears in the form of a quartet with spin—spin coupling constants of 4 and 6 Hz.

As compared with the analogous singlet of alkhanol, the signal of the angular methyl group in the NMR spectrum of diacetylalkhanol is shifted downfield by 0.11 ppm, and in the spectrum of the diacetyl derivative of erivanin it is shifted by 0.15 ppm. The same signal in the NMR spectra of alkhanol and erivanin taken in benzene solution is shifted upfield (in comparison with the spectra of deuterochloroform solution) by 0.38 and 0.40 ppm, respectively.

On this basis, it may be assumed that the OH group in the alkhanol molecule is present in the axial position. The results of an analysis of the NMR spectra of alkhanol and its diacetate show the correctness of the hypothesis put forward. Thus, in the NMR spectrum of diacetylalkhanol (Fig. 1), taken in benzene solution, H-1 appears in the form of a quartet at 4.62 ppm with spin—spin coupling constants of 5 and 3 Hz and is not shifted in comparison with the spectrum of $CDCl_3$, while the H-3 signal is shifted downfield by 0.08 ppm and appears in the form of a multiplet at 5.24 ppm. The multiplet splitting of the latter is

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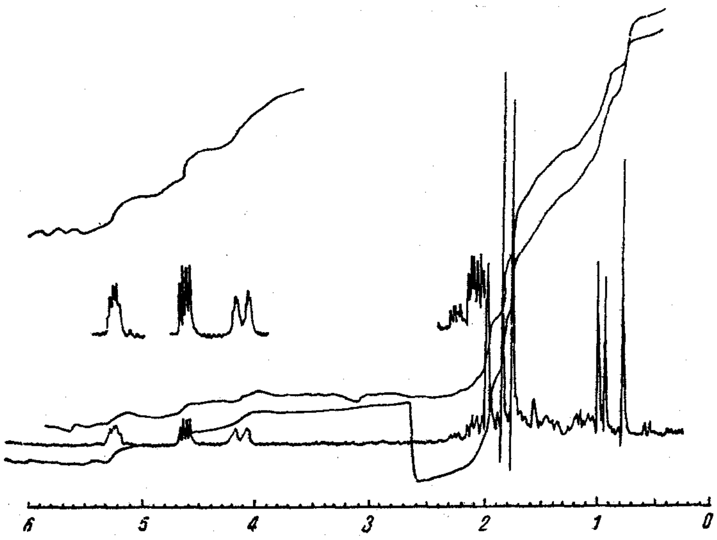


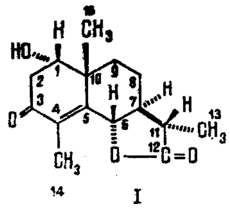
Fig. 1. NMR spectrum of diacetylalkhanol in benzene solution.

probably caused not only by interaction with the protons of the C-2 but also by allyl interaction with the vinyl methyl group.

The value of the spin–spin coupling constant for H-1 and H-3 and also the behavior of the signals in the NMR spectrum in benzene solution determine the position of the OH groups in the alkhanol molecule (II) as axial [7].

On passing from deuterochloroform solution to benzene solution, the doublet of the secondary methyl group in the lactone ring in the spectrum of diacetylalkhanol shifts upfield by 0.25 ppm. The size of the shift shows the possible α-position of the methyl group at C-11 [8]. The signal of the lactone proton in the NMR spectra of alkhanol and its derivatives appears in the form of a doublet with a spin–spin coupling constant of 10 Hz. This shows the trans-linkage of the lactone ring.

All the facts given above indicate a possible similarity of the stereochemistry of alkhanol at C-1, C-3, C-6, C-7, C-10, and C-11 with the stereochemistry of the analogous asymmetric centers of alkhanin (I) and erivanin. A proof of this idea is the production by the hydrogenation of alkhanol [2] of a dihydro derivative $C_{15}H_{24}O_4$ with mp 220-222°C identified from its IR spectrum as tetrahydroalkhanin (dihydroerivanin).



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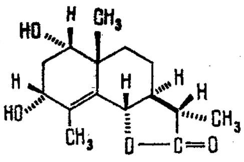

II

EXPERIMENTAL

The IR spectra were taken in paraffin oil on a UR-20 spectrophotometer and the NMR spectra on a Varian HA-100/D spectrometer in $CDCl_3$ and C_6H_6 solutions. The chemical shifts are given on the δ scale. TMS was used as internal standard.

SUMMARY

The stereochemistry of alkhanin and alkhanol has been established.

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LACTONES OF *Ferula gigantea*

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The following substances have been isolated from an acetone extract of *Ferula gigantea* B. Fedtsch.: a coumarin — umbelliferone, $C_9H_6O_2$, mp 230-233°C; and sesquiterpene lactones — talassin A, $C_{25}H_{30}O_7$, mp 188-191°C; malaphyllinin, $C_{24}H_{24}O_7$, mp 231-235°C; malaphyll, $C_{29}H_{32}O_9$, mp 212-213°C; and malaphyllin, $C_{26}H_{28}O_9$, mp 216-218°C. Structures have been proposed for three new sesquiterpene lactones on the basis of an analysis of their spectral characteristics.

Species of *Ferula* belonging to the section Palaeonartex Korov. contain various sequiterpenes. In view of this, it appears of interest to study *F. gigantea* B. Fedtch. [1] (subsection Tumidae M. Pimen. et J. Baranova); *F. inflata* Korov. and *F. latifolia* Korov. are assigned to this species according to the literature [2]. The material for investigation was collected close to the settlement of Shurobad, Kulyab oblast, Tadzhikistan at the type site of *F. inflata*.

Chromatography on silica gel of an acetone extract of the roots of the *Ferula* yielded eight compounds: I) $C_{25}H_{30}O_7$, mp 188-191°C; II) $C_{27}H_{28}O_7$, mp 263-266°C; III) $C_{24}H_{24}O_7$, mp 231-235°C; IV) $C_{28}H_{30}O_8$, mp 232-234°C; V) $C_9H_6O_3$, mp 230-233°C; VI) $C_{25}H_{26}O_8$, mp 192-193°C; VII) $C_{29}H_{32}O_9$, mp 212-213°C; VIII) $C_{26}H_{28}O_9$, mp 216-218°C.

On the basis of the identity of its IR spectrum and PMR spectrum with corresponding spectra of an authentic sample, compound (V) was identified as umbelliferone. The remaining substances were, according to their spectral characteristics, sesquiterpene lactones.

An analysis of spectral characteristics (Table 1) enabled the main structural elements of the molecules of these compounds to be determined. Strong absorption bands at 1789-1795 cm^{-1} in the IR spectra of these compounds show the presence of a γ-lactone grouping. A guaiadienone grouping is responsible for the presence in the UV spectra of these substances of absorption maxima in the 251-264 nm region (log ε 4.25-4.53) and for absorption bands in the IR spectra at 1689-1697 cm^{-1} (C=O of an α,β-unsaturated cyclopentanone), 1640-1645 and 1620-1625 cm^{-1} (—C=C—), and in the PMR spectra of six-proton singlets with 2.20-2.28 ppm (2 CH_3—C=) and a broadened singlet at 6.22-6.28 ppm, $W_{1/2}$ = 4.0 Hz $(=CH-\underset{\underset{O}{\|}}{C}-)$. In addition to the C=O groups of a cyclopentanone and a γ-lactone, the molecules of the sesquiterpene lactones contain two other carbonyls, of ester groups, as follows both from the IR spectra (two absorption bands in the 1745-1710 cm^{-1} interval, sometimes overlapping one another) and also from the presence in the ^{13}C NMR spectra of four singlet signals of carbonyl carbons in the 165-174 ppm region.

The closeness of the characteristics of the PMR spectra of the lactones described to one another and to the spectra of talassin A [3], olgin, and olgoferin [4], isolated pre-

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