The conformational calculations were made on a ES-1061 computer by the MM2 program [11] with full optimization of the geometry of the molecules and the use of the parameters of the potentials present in this version of the program with the exception of the parameters for the O1—C12—C11 valence angle and the C6—O1—C12—C11, C7—C11—C12—O1, C13—C11—C12—O1 and C13—C11—C12—O2 torsional angles, which were taken from other literature sources [12, 13].

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TERPENOIDS OF Artemisia splendens

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d-Camphor, ℓ-borneol, stearic acid, β-sitosterol, austricin, and a new sesquiterpene lactone which has been called splendolide have been isolated from the epigeal part of Artemisia splendens Willd. The structure of splendolide has been established as 1β-hydroxy-6βH,7αH-eudesma-4,11(13)-dien-6,12-olide.

There is no information in the literature on the chemical composition of Asia Minor wormwood Artemisia splendens Willd. By column chromatography on silica gel of the total extractive substances obtained from the epigeal part of Asia Minor wormwood (gathered in the Nakhechevan ASSR, Shakhbuz region, environs of the village of Bichenek) we have isolated six substances (I-VI).

Substance (I) — $C_{10}H_{16}O$, mp 178-179°C (sublimation). The IR spectrum of (I) showed the absorption band of a carbonyl group in the region of characteristic frequencies (1755 cm^{-1}). The PMR spectrum had the signals of quaternary methyl groups at 0.80, 0.89, and 0.94 ppm. No signals belonging to any protons were observed in the 3.00-10.00 ppm region.

Substance (II) — $C_{10}H_{18}O$, mp 201-202°C (sublimation). The IR spectrum of (II) had the bands of an OH group (3350 cm^{-1}). The hydroxy group was undoubtedly secondary, since the PMR spectrum contained a one-proton doublet at 4.00 ppm (J = 10 Hz) with greatly broadened ($W_{\frac{1}{2}}$ = 6 Hz) components. A singlet (9 H) belonged to three quaternary methyl groups. There were no signals in the 4.20-10.00 ppm region of the spectrum. The oxidation of (II) with chromium trioxide led to substance (I), which was identified from its IR spectrum in the absence of a depression of the melting point in a mixed sample.

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Substance (III) – $C_{15}H_{18}O_4$, mp 149-151°C. According to its IR spectrum it was a sesauiterpene lactone. Thus, the IR spectrum of (III) showed the absorption bands of an OH group (3370, 3535 cm^{-1}), of a γ-lactone ring (1770 cm^{-1}), of a conjugated ketone group in a five-membered ring (1690 cm^{-1}), and of double bonds (1635, 1645 cm^{-1}).

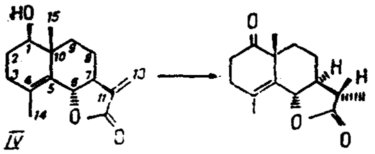
The acetylation of substance (III) led to a monoacetyl derivative $C_{17}H_{20}O_5$, mp 193-195°C. The IR spectrum of the latter contained the absorption bands of a γ-lactone ring (1795 cm^{-1}) of an acetyl group (1745 and 1250 cm^{-1}) of a ketone in a five-membered ring conjugated with two double bonds (1695 cm^{-1}), and of double bonds (1645 and 1628 cm^{-1}). The UV spectrum showed a maximum (255 nm, log ε 4.22) characteristic for a cyclopentadienone of the type of ferulidin [1], badkhvzin [2], etc. [3].

A direct comparison of the physicochemical properties (composition, melting point, etc.) and IR spectra of compounds (I), (II), and (III) with those of authentic samples, and also the NMR spectra of (I) and (II) permitted the compounds under investigation to be identified as d-camphor, ℓ-borneol, and austricin (deacetylmatricarin).

Substance (IV) – $C_{15}H_{20}O_3$, mp 151-152°C, was a new sesquiterpene lactone, and it has been given the name of splendolide. In the IR spectrum of splendolide were found absorption bands of a hydroxy group (3460 cm^{-1}), of a CO group in a γ-lactone ring (1765 cm^{-1}) and of double bonds (1675, 1650 cm^{-1}). The NMR spectrum of (IV) showed singlets of an angular methyl group (1.10 ppm) and of a vinyl methyl group (1.85 ppm). The substance contained two double bonds, one of which was methylenic and was present at a lactone ring. A confirmation of this was the detection in the NMR spectrum of one-proton doublets at 5.40 ppm (J = 3.5 Hz) and 6.12 ppm (J = 3.5 Hz). The second double bond (trisubstituted or tetrasubstituted) was present at C_3–C_4 or C_4–C_5, respectively. The absence of additional signals characteristic for olefinic protons from the spectrum, together with the presence of the signal of a vinyl methyl group indicated its tetrasubstituted nature and its presence at C_4–C_5. The lactone proton appeared in the form of a doublet with broadened components at 4.53 ppm (J = 11.5 Hz). The doublet splitting of the signal was caused by interaction with one vicinal proton and showed the C_6–C_7 position of the lactone ring.

The hydroxy group in the molecule of splendolide is secondary, since a one-proton quartet was found in the NMR spectrum at 3.57 ppm (J_1 = 10, J_2 = 6 Hz), which is characteristic for a gem-hydroxylic proton. The ratio of the areas of the components of the quartet (1:1:1:1) showed interaction with only two vicinal protons. The spin-spin coupling constants of 10 and 6 Hz indicated that the OH had the equatorial orientation.

The magnitude of the chemical shift of the angular methyl group showed that the OH group in the splendolide molecule was located in the α position relative to the angular methyl group, i.e., it was present at C_1, as in artesin [4], artemin [5, 6], and dihydrotaurin [6]. Consequently, the OH group and the tetrasubstituted double bond in the lactone under investigation were present in the same ring. Signals (4H) in the 2.0-2.3 ppm region corresponding to the protons of two methylene groups located in the α position to an OH group and a double bond could serve as confirmation of this. Thus, according to the facts given above, splendolide has the structure of 11,13-dehydroartesin [4].



IV

The reduction of splendolide by $NaBH_4$ in methanol followed by the chromium trioxide oxidation of the product obtained led to substance (V), $C_{15}H_{18}O_3$, mp 116-117°C the IR spectrum of which showed the bands of a γ-lactone ring (1787 cm^{-1}) and of a ketone grouping in a six-membered ring (1728 cm^{-1}). Consequently, splendolide has the structure of 1β-hydroxy-6βH, 7αH-eudesma-4,11(13)-dien-6,12-olide.

In addition, from Asia Minor wormwood we have isolated substances (VI), $C_{13}H_{36}O_2$, mp 69-79°C, and (VII), $C_{29}H_{50}O$, mp 137-138°C, which have been identified by a comparison of their IR spectra as stearic acid [7] and β-sitosterol, respectively.

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrophotometer in paraffin oil, and NMR spectra on a Varian HA-100D spectrometer in $CDCl_3$, 0 — TMS.

Isolation of the Terpenoids. The resin obtained by three extractions (three days each time) of 535 g of the epigeal part of Asia Minor wormwood (24 g; 4.48% yield) was chromatographed on a column of silica gel (3 × 120 cm., SG 40/100, Chemapol). The volume of each fraction was 100 ml. Elution was performed with hexane, hexane—benzene (2:1) and (1:1), benzene—chloroform (1:1), and chloroform.

Fractions 56-60, eluted by hexane—benzene (2:1) yielded a substance $C_{10}H_{16}O$, mp 178-179°C (d-camphor). Fractions 109-115, eluted by hexane—benzene (1:1) yielded a substance $C_{10}H_{18}O$ with mp 201-202°C (ℓ-borneol). Fractions 165-171, eluted by benzene, gave a substance $C_{18}H_{36}O_2$ with mp 69-70°C (stearic acid). From fractions 146-150, eluted by benzene, was isolated a substance $C_{29}H_{50}O$ with mp 137-138°C (β-sitosterol). Fractions 336-338, eluted by benzene yielded a substance $C_{15}H_{20}O_3$, mp 151-152°C (splendolide). Fractions 969-974, eluted by chloroform, gave a substance $C_{15}H_{18}O_4$ with mp 149-150°C (austricin).

Acetylation of Austricin. A solution of 0.1 g of the substance in 3 ml of pyridine was treated with 3 ml of acetic anhydride. The mixture was left at room temperature for 24 h and was then evaporated on the water bath. The residue was worked up by a known method [8]. This gave a substance $C_{17}H_{20}O_5$ with mp 193-195°C.

Reduction of Splendolide with $NaBH_4$. A solution of 0.1 g of splendolide in 15 ml of methanol was treated with 0.15 g of sodium tetrahydroborate. The mixture was left at room temperature for 10 min and was then diluted with water, acidified with 20% H_2SO_4, and extracted with diethyl ether. The ethereal layer was separated off and was washed three times with water, dried with Na_2SO_4, filtered, and evaporated. The residue (a viscous oil) was dissolved in a mixture of diethyl ether and hexane. The crystals that deposited were filtered off and recrystallized from aqueous ethanol, mp 117-118°C.

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