THE ISOCOUMARIN ARTEMIDINAL FROM Artemisia dracunculus

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Continuing a chemical investigation [1] of a chloroform extract of the epigeal part of Artemisia dracunculus L. by chromatography on columns of alumina and silica gel we have isolated a substance with the composition $C_{10}H_6O_3$ which we have called artemidinal. This substance is stable to the action of mineral acids, but it dissolves in dilute alkalis on heating.

The absorption curve of the substance in the UV region possesses maxima characteristic for isocoumarins [1, 2] at 230, 242, 256, 264, 275, and 322 nm (log ε 4.41, 4.19, 3.94, 3.84, and 3.77).

The IR spectrum has bands at 1720 cm^{-1} (C=O of an α-pyrone ring), 1685 cm^{-1} (C=O of a carbonyl group), 1630 (C=C of a lactone ring), 1605, 1560, and 1480 cm^{-1} (C=C of a benzene ring), and a strong absorption band at 762 cm^{-1} (ortho-disubstituted benzene ring).

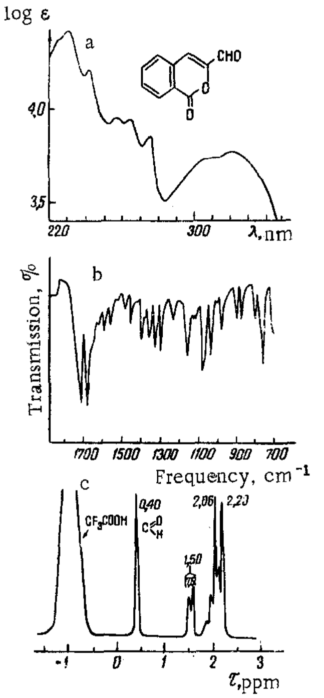

Fig. 1. UV (a), IR (b), and NMR (c) spectra of artemidinal.

The IR spectrum of the oxime of the compound has a band at 1685 cm^{-1}, and the band of the remaining carbonyl is shifted to 1737 cm^{-1}.

The NMR spectrum, taken in trifluoroacetic acid, has a one-proton singlet at τ 0.40 ppm; this represents the proton of an aldehyde group, the presence of which was confirmed by the formation of a silver mirror [3].

In the region of aromatic protons there are a one-proton doublet at 1.5 ppm, J=7.5 Hz, and a three-proton multiplet with a center at 2.06 ppm relating to the remaining three protons of the benzene ring. The shift of one of the protons of the benzene ring by 0.56 ppm in the downfield direction is explained by the influence of a carbonyl group in the β position relative to this proton [4]. A one-proton singlet at 2.20 ppm corresponds to the proton of an α-pyrone ring.

It is known [5, 6] that in coumarin systems a proton present in the β position with respect to a carbonyl group $(-\underset{\substack{|\\ H}}{C}=\underset{|}{C}-\underset{|}{C}=O)$ gives a signal in the 2-2.5 ppm region.

Where there is an oxygen atom adjacent to the β proton $(-O-\underset{|}{C}=\underset{\substack{|\\ H}}{C}-\underset{|}{C}=O)$ [7], the signal will be present in the region below 2.0 ppm; consequently, the aldehyde group in artemidinal is in position 3 (Fig. 1).

From its IR spectrum, R_f value, and a mixed melting point, we showed that artemidinal was identical with an aldehyde isolated from the products of the potassium permanganate oxidation of the isocoumarin artemidin [1].

Thus, artemidinal is isocoumarin with an aldehyde group at C_3.

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EXPERIMENTAL

The NMR spectrum was taken on a JNM-4H-100 instrument (the shifts are given from the HMDS signal taken as 10), the UV spectrum on an SF-4A instrument and the IR spectrum on a UR-10 instrument.

Isolation of Artemidinal. A chloroform extract from the epigeal part of Artemisia dracunculus L. (collected in July at the village of Nura, Pamir-Alai) (110 g) was treated with ether, and the soluble part was shaken with a 5% aqueous solution of sodium bicarbonate.

The ethereal fraction, after evaporation of the solvent, was chromatographed on neutral alumina (activity grade IV, 1:10) and was subsequently eluted with petroleum ether, benzene, ether, and methanol. IR spectra showed the presence of a carbonyl group in the benzene and ethereal eluates.

The benzene and ethereal eluates were combined and rechromatographed on silica gel (1:30). Elution was performed first with petroleum ether and then, until the artemidin had been removed completely, with benzene, and subsequently with chloroform. The first portion of the chloroform eluate (300 ml), after distillation, gave a yellow residue which was recrystallized from benzene and chloroform. Crystals deposited in the form of colorless needles with mp 175-176°C, having the composition $C_{10}H_6O_3$ and mol. wt. 174 (mass spectrometry). On a nonfixed layer of silica gel in the chloroform–ether (9:1) system, the R_f value was 0.5. We prepared the oxime of artemidinal, with mp 203-204°C [3].

Oxidation of Artemidin. A solution of 0.2 g of artemidin in 2 ml of acetone was treated dropwise with 50 ml of an acetone solution containing 0.36 g of potassium permanganate. The mixture was left at room temperature for 20 h, after which it was filtered and the filtrate was evaporated. The artemidinal was isolated preparatively on a nonfixed layer of silica gel in the chloroform–ether (9:1) system.

SUMMARY

Artemidinal, $C_{10}H_6O_3$, which is isocoumarin with an aldehyde group at C_3, has been isolated from the epigeal part of Artemisia dracunculus.

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