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STRUCTURE OF JUNCUNOL, A NOVEL 9, 10-DIHYDROPHENANTHRENE FROM JUNCUS ROEMERIANUS

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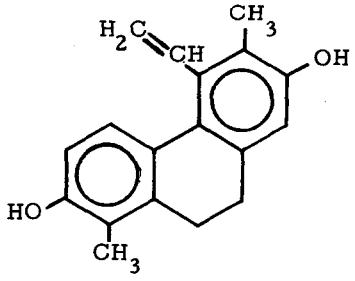
Juncus roemerianus (NO Juncaceae) is the most dominant amongst a group of plants, commonly known as 'marsh grass', which grow all along the coastal plain of Southern and Southeastern United States. The 95% ethanolic extract of the aerial part of J. roemerianus was evaluated by us which resulted in confirmed level activity against the National Cancer Institute's murine P388 lymphocytic leukemia (PS system). The $CHCl_3$ extract of this plant, upon column chromatography and crystallization yielded, inter alia, juncunol, $C_{18}H_{18}O(M^+250)$[2], mp 144°, and a cytotoxic compound juncusol[3]. In this communication, we wish to report the structure of juncunol as a novel 9, 10-dihydrophenanthrene derivative 1a. Juncunol is only the second example of a relatively rare 9, 10-dihydrophenanthrene derivative encountered in nature with a vinyl substituent in the ring system.



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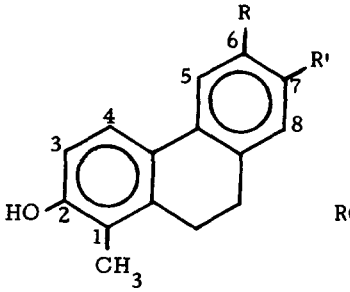
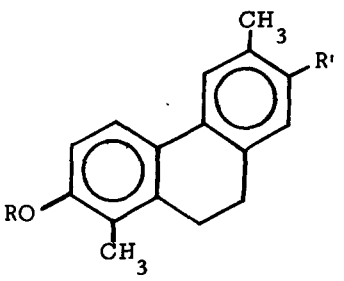


1a, R=CH_3; R' = -CH=CH_2
1b, R= -CH=CH_2; R' =CH_3



2, R=H, R' =CH_2CH_3
3, R=Ac; R' = -CH=CH_2

The ir spectrum of juncunol in KBr exhibits peaks at 3500 (OH), 1620, 1600(Ar), and 915 (mono-substituted double bond) cm^{-1}. The 100MHz ^1H nmr spectrum of juncunol in $CDCl_3$ (TMS) shows a 4H singlet at 2.65 ppm, typical of the methylene protons of the 9, 10-dihydrophenanthrene ring system[4]. The spectrum also shows two singlets at 2.26(3H, Ar-CH_3) and 2.36(3H, Ar-CH_3), ABX type of signals for a vinyl group at 5.20(1H, J_{AX}=10Hz, J_{AB}=2Hz), 5.66(1H, J_{BX}=17 Hz, J_{AB}=2Hz), and 6.86(1H, J_{AX}=10Hz, J_{BX}=17Hz), 4 aromatic proton peaks, two of which are ortho related at 6.60(J=8Hz) and 7.36(J=8Hz), and the remaining two are para related at 6.88 and 7.22, and a broad signal at 4.40(1H, OH) ppm. The lowfield shifts of two of the aromatic protons to 7.36 and 7.22

ppm in the nmr spectrum of juncunol are characteristics of the protons at C-4 and C-5 in 9, 10-dihydrophenanthrene skeleton. As the former is an ortho coupled proton and the latter has a proton para to it, the C-3, C-4, C-5 and C-8 in juncunol must be unsubstituted. Catalytic hydrogenation of juncunol affords a dihydro compound (2), $C_{18}H_{20}O$, mp 116°. The absence of the ABX type of signals and the appearance of a quartet at 2.85(2H, J=Hz, Ar-$C\underline{H}_2$-CH_3) and a triplet at 1.28(3H, J=6Hz, Ar-$CH_2C\underline{H}_3$) in the ^{1}H nmr spectrum of the dihydro compound confirms the presence of a vinyl group in the parent compound.

Acetylation of juncunol with acetic anhydride in pyridine produces a monoacetate (3), $C_{20}H_{20}O_2$, mp 102-104°, confirming the presence of the oxygen atom as OH function in the parent compound. In the ^{1}H nmr spectrum of juncunol in pyridine-d_5, the ortho coupled aromatic proton at C-3 shifts downfield to 7.03 ppm ($\delta_{pyridine}$-$\delta_{chloroform}$=43Hz) and one of the CH_3 groups shifts downfield to 2.48 ppm ($\delta_{pyridine}$-$\delta_{chloroform}$=22Hz). These significantly large pyridine induced solvent shifts must be attributed to the orientations of the C-3 proton and the CH_3 group in question ortho to OH function[5]. Therefore, the OH group must be placed at C-2 and, consequently, one CH_3 group must be placed at C-1 in juncunol. Thus, the remaining CH_3 group and the vinyl group must be placed at C-6 and C-7 leading to two possible alternative structures 1a or 1b of juncunol. We prefer structure 1a for juncunol because of the following biogenetic consideration: As juncunol occurs with juncusol (4) in J. roemerianus and since the properties of juncunol resemble those of juncusol, it is reasonable to assume that the remaining CH_3 group in juncunol is present at C-6, as in 4. Consequently, the vinyl group must be present at C-7 in juncunol.

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