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DEHYDROJUNCUSOL, A CONSTITUENT OF THE ROOTS OF *JUNCUS ROEMERIANUS*

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Key Word Index—*Juncus roemerianus*; roots; phenanthrene; dehydrojuncusol.

Abstract—Dehydrojuncusol, an uncommon simple phenanthrene derivative has been isolated from the roots of the tidal 'marsh plant', *Juncus roemerianus*. The structure of dehydrojuncusol has been determined with the help of chemical and spectral data.

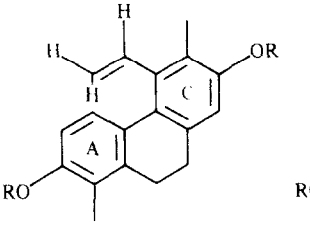
INTRODUCTION

The tidal marsh of the southeastern United States is dominated by the grass, *Juncus roemerianus* (Juncaceae), popularly known as 'needle rush'. The chemical investigation of *J. roemerianus* began from the interesting observation [1, 2] that the green biomass, most of which is not attacked by marsh herbivores, enters the detritus food chain upon death and decomposition. Subsequently, a cytotoxic compound, juncusol (**1**), followed by juncunol (**2**) and juncunone (**3**), all having the 9,10-dihydrophenanthrene skeleton, were isolated from the aerial parts of this plant [3–7]. Recently, we investigated the roots of *J. roemerianus* which resulted in the isolation of dehydrojuncusol, $C_{18}H_{16}O_2$ ([M^+] at *m/z* 264), mp 241–243°, as the major constituent along with juncusol (**1**) and juncunol (**2**). We wish to report here the structure of dehydrojuncusol as the phenanthrene derivative (**4**) based on chemical and spectral investigations. Dehydrojuncusol is the first naturally occurring nitrogen free simple phenanthrene derivative isolated from a grass and the only one containing both alkyl and vinyl substituents in the skeleton in addition to the oxygen functions. All the simple phenanthrenes discovered so far have only oxygen functions in the skeleton. However, three methylated simple phenanthrenes, one containing an additional SCH_3 group, have been encountered in the Euphorbiaceae family [8, 9]. Until recently, about 40 compounds with a nitrogen free simple phenanthrene skeleton have been found in nature. These compounds are very widely distributed having been isolated from rhizomes of various species of Dioscoreace [10, 11], trees of Combretaceae [12–14] and Euphorbiaceae [8, 9], as well as Orchidaceae [15].

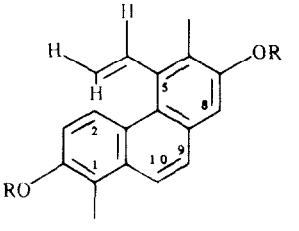
Dehydrojuncusol crystallizes from ethyl acetate–hexane in light yellow microcrystalline form. It is highly soluble in acetone, sparingly soluble in methanol and practically insoluble in chloroform. Solubility in aqueous sodium hydroxide and lack of solubility in aqueous sodium carbonate suggested the presence of phenolic hydroxy function. Formation of diacetate (**5**) $C_{22}H_{20}O_4$, ([M^+] at *m/z* 348), mp 201–203°, upon acetylation of dehydrojuncusol supports the possibility of the presence of both the oxygen atoms as hydroxy functions.

The UV spectrum of dehydrojuncusol in methanol shows λ_{max} (log ε) at 264 (4.66), 288 (4.35), and 308 (3.98) nm. The spectrum is very similar to those of 2,7-dihydroxy-3,4,6-trimethoxyphenanthrene and other similarly substituted phenanthrenes [12–14]. The IR spectrum in KBr shows bands at 3300 (OH), 1610 (Ar), 1063(C–O), 918 (vinyl), and 813 (2 adjacent Ar–H) cm^{-1}, similar to juncusol [3, 4].

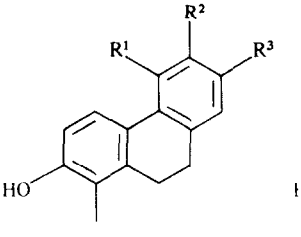
In addition to the molecular ion at *m/z* 264, the mass spectrum of dehydrojuncusol showed significant peaks at *m/z* 249 $[M-15]^+$, 234 $[249-15]^+$, 218, 205, and 189. The formation of the peaks at *m/z* 249 and 234 is indicative of the presence of two aromatic Me groups as in juncusol [3, 4].

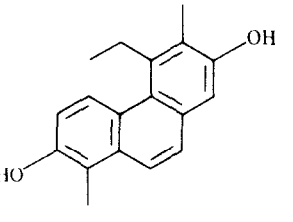


1 R = H
8 R = Ac



4 R = H
5 R = Ac





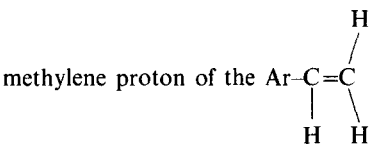
6

2 R^1 = —CH=CH_2, R^2 = H, R^3 = Me
3 R^1 = —Ac, R^2 = OH, R^3 = Me
7 R^1 = —CH=CH_2, R^2 = H, R^3 = OH

The ^{1}H NMR spectrum of dehydrojuncusol in $(CD_3)_2CO$/TMS supports the presence of two aromatic Me groups in the molecule. In addition to two sharp singlets at δ 2.34 (3H, Ar–Me) and 2.45 (3H, Ar-Me), the spectrum shows ABX type of signals at 5.15 (1H, *dd*, J_{AX} = 18 Hz, J_{AB} = 2 Hz), 5.60 (1H, *dd*, J_{BX} = 12 Hz, J_{AB} = 2 Hz), and 7.33 (1H, *dd*, J_{AX} = 18 Hz, J_{BX} = 12 Hz) for Ar–CH=CH_2 group, two pairs of *ortho* aromatic proton doublets, one at 7.06 (1H, *d*, *J* = 9 Hz), and 8.78 (1H, *d*, *J* = 9 Hz) and the other at 7.46 (1H, *d*, *J* = 9 Hz) and 7.77 (1H, *d*, *J* = 9 Hz), an isolated aromatic proton signal at 7.27 (1H) and a broad 2H singlet at 3.03 for two OH groups.

Catalytic hydrogenation of dehydrojuncusol produces a dihydro compound (**6**), $C_{18}H_{18}O_2$ ([M]$^+$ at *m/z* 266), mp 233–235°. The ^{1}H NMR spectrum of the dihydroderivative in $CDCl_3$/TMS shows, in addition to other signals, a 3H triplet at δ 1.55 (*J* = 7 Hz) and a 2H quartet at 3.33 (*J* = 7 Hz) for an ethyl group in place of the ABX signals for a Ar–CH=CH_2 group.

In the ^{1}H NMR spectrum of dehydrojuncusol, the



methylene proton of the Ar–C=C group, *trans* to the

methine proton, appears at a higher field at δ5.15 (J_{AX} = 18 Hz) relative to the methylene proton which appears at 5.60 (J_{BX} = 12 Hz), *cis* to the methine proton. This situation is identical to the methylene protons of the vinyl group in juncusol (**1**) and opposite to those in the related compound effusol (**7**), isolated from *J. effusus* [16]. The most likely position of the vinyl group in dehydrojuncusol, therefore, is C-4 or C-5 in a phenanthrene skeleton with a substitution *ortho* to it, as in ring C of juncusol (**1**).

The lowfield shift of one of the proton doublets at δ 8.78 (*J* = 9 Hz) in the ^{1}H NMR spectrum of dehydrojuncusol is characteristic of the C-4 or C-5 proton of phenanthrenes [10–12]. As this proton is *ortho*-coupled with the proton at 7.06 (*J* = 9 Hz), it appears that C-3 and C-4 of dehydrojuncusol are unsubstitued. Consequently, there should be substituents at C-1 and C-2 of ring A, as in juncusol (**1**). The second pair of *ortho*-coupled proton doublets at 7.46 and 7.77 are typical of the C-9 and C-10 protons of phenanthrenes when C-1 and C-8 are unsymmetrically substituted [8, 9].

The [M]$^+$ of dehydrojuncusol is 264; which is two mass units less than that of juncusol. Moreover, the co-occurrence with juncusol, the presence of identical substituents, such as, two Ar–Me, two phenolic OH and a vinyl group as in juncusol, and the absence of the typical 4H singlet for the C-9 and C-10 methylene protons of juncusol [3, 4] and the presence of two more *ortho* aromatic protons in the ^{1}H NMR spectrum suggested the possibility of dehydrojuncusol to be the C-9, C-10-dehydro derivative of the former. Therefore, juncusol diacetate (**8**) was dehydrogenated with DDQ. Alkaline hydrolysis of the product showed two spots on the TLC plate with very close R_f values. The TLC comparison of the DDQ dehydrogenated product with authentic samples of juncusol and dehydrojuncusol indicated that the former was partly converted to the latter. The more polar compound was then separated by PLC and the product was found to be identical (mmp, TIC, IR) with natural dehydrojuncusol. More than 30% conversion was not observed after a prolonged treatment of juncusol diacetate with DDQ in boiling benzene. This is to be expected because the presence of a vinyl group at the angular C-5 position of juncusol prevents the 9,10-dihydrophenanthrene ring system of juncusol from attaining a planar geometry necessary for the facile DDQ dehydrogenation reaction. Therefore, the possibility of dehydrojuncusol being an artefact produced during the extraction and subsequent work up of the plant material can be ruled out. Therefore, dehydrojuncusol should be represented by structure **4**.

EXPERIMENTAL

Extraction of the roots of J. roemerianus. Dried and ground roots (1.75 kg) of *J. roemerianus* were extracted with 95% EtOH at room temp. until the last extract was colourless. The extract was evapd and the dark brown residue (70.3 g) was equillibrated with $CHCl_3-H_2O$ (1:1) in a separatory funnel. The organic layer was then dried and evapd to give a dark brown residue (27 g). The residue, dissolved in a minimum volume of CH_2Cl_2, was charged on a dry column (300 g) of silica gel (70–230 mesh, Aldrich) and CH_2Cl_2 was used as mobile phase. The combined fractions were designated fractions A (300 ml), B (450 ml), C (600 ml), D (250 ml), E (1,200 ml), F (300 ml), G (600 ml), H (900 ml).

Isolation of juncunol (**2**). Fraction B upon evapn gave a residue (0.7 g) which after rechromatograpy and PLC in the usual way furnished juncunol (0.11 g), mp 140–142°, which was identified by comparison of its spectral characteristics (IR, ^{1}H NMR) with those published in the literature [5].

Isolation of dehydrojuncusol (**4**) *and juncusol* (**1**). Fraction F upon evapn gave a dark crystalline residue (1.35 g) which showed two close spots on TLC plates; the upper spot was designated X and the lower major spot was designated Y. The residue was recrystallized several times from EtOAc–*n*-C_6H_{14} and the mother liquor became enriched in Y while the residue X, after several recrystallizations, furnished juncusol (0.063 g), mp 176–177°, identified by comparison (mmp, TLC, IR, ^{1}H NMR) with an authentic sample isolated earlier [16]. The combined mother liquors, enriched in Y, was subjected to PLC and the two bands were separated. The lower band after usual work-up followed by several crystallizations from EtOAc–*n*-C_6H_{14} gave light yellow microcrystals of dehydrojuncusol (0.11 g), mp 241–243°: λ_{max}^{MeOH} (log ε) 211 (4.45), 264 (4.66), 288 (4.35), and 308 (3.98) nm; IR major bands at 3300, 2930, 1610, 1063, 918, and 813 cm^{-1}; ^{1}H NMR (acetone-d_6) δ2.34, 2.45, 3.03, 5.15, 5.60, 7.27, 7.33, 7.46, 7.76, 8.78 ppm; MS *m/z* 264 [M]$^+$ (100%), 249, 234, 218, 205, 189 (Calcd for $C_{18}H_{16}O_2$: C, 81.81; H, 6.06. Found: C, 81.63; H 6.10%).

Diacetate of dehydrojuncusol (**5**). The diacetate was prepared from dehydrojuncusol in the usual way with Ac_2O in pyridine and crystallized from C_6H_6–*n*-C_6H_{14}, mp 200–201°; (Calcd for $C_{22}H_{20}O_4$: C, 75.86, H, 5.75: Found: C, 75.67, H, 5.60%). IR ν_{max}^{KBr} cm^{-1}: 3070, 2930, 1755, 1610, 900, and 820; ^{1}H NMR ($CDCl_3$/TMS): δ 2.36 (3H, *s*), 2.38 (6H, *s*), 2.53 (3H, *s*), 5.33 (1H, *dd*, J_{AX} = 18 Hz, J_{AB} = 2 Hz), 5.72 (1H. *dd*, J_{BX} = 11 Hz, J_{AB} = 2 Hz), 7.10 (1H, *d*, *J* = 9 Hz), 7.29 (1H, *s*), 7.67 (1H, *d*, *J* = 9 Hz), 7.98 (1H, *d*, *J* = 9 Hz), and 9.12 (1H, *d*, *J* = 9 Hz) ppm.

Dihydro derivative of dehydrojuncusol (**6**). Dehydrojuncusol (0.05 g) in MeOH (30 ml) and 10% Pd-C (0.05 g) was hydrogenated for 2 hr in a Parr hydrogenation apparatus. Removal of the catalyst by filtration and concentration of the methanolic solu-

tion to a small vol. gave transparent crystals on standing which were recrystallized from MeOH, (0.023 g), mp 233–235°; IR $\nu_{max}^{KBr}cm^{-1}$: 3290, 1610, 890, 840, and 790; ^1H NMR (acetone-d_6): δ 1.55 (3H, *t*, $J=7$ Hz), 2.45 (3H, *s*), 2.55 (3H, *s*), 3.13 (2H, *br s*), 3.33 (2H, *q*, $J=7$ Hz), 7.17 (1H, *s*), 7.22 (1H, *d*, $J=9$ Hz), 7.45 (1H, *d*, $J=9$ Hz), 7.75 (1H, *d*, $J=9$ Hz), and 8.35 (1H, *d*, $J=9$ Hz); MS *m/z*: 266 $[M]^+$, 251, 236, 207, 189, 165, 118.

Conversion of juncusol to dehydrojuncusol. A mixture of juncusol diacetate (0.06 g) prepared according to ref. [3] and DDQ (0.06 g) in C_6H_6 (5 ml) was refluxed for 12 hr. After cooling, filtration, and evapn, the residue was directly hydrolysed in 2% KOH in MeOH (3 ml). The product after usual work-up gave a solid which proved to be a mixture juncusol and dehydrojuncusol when compared with authentic samples of these two compounds on TLC. Therefore, the product was subjected to PLC and the lower band, the minor product, after recovery and crystallization froL EtOAc–*n*-C_6H_{14} was found to be identical (mmp, IR and MS) to the natural dehydrojuncusol.

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AN IMPROVED HIGH YIELD SYNTHESIS OF DEHYDRODIEUGENOL

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Key Word Index—Neolignan; oxidative dimerization of eugenol.

Abstract—The oxidative coupling of eugenol with potassium ferricyanide in ammonium hydroxide produces the known neolignan, dehydrodieugenol in almost quantitative yield.

INTRODUCTION

Because of the importance of phenolic oxidative coupling reactions, classified as biogenetic type synthesis [1], oxidative coupling reactions have been the subject of most of the natural product chemists in this field. Amongst the known oxidizing agents employed for the last three decades [2], iron compounds, such as $FeCl_3$ and $K_3Fe(CN)_6$ are the most widely used phenol oxidants [3]. The ferricyanide–ferrocyanide is an unique system, the redox potential of which is unaffected by pH. Except in strong acid solutions, its oxidizing capacity is somewhat superior in alkaline than in acidic medium [4]. In the half reaction, the oxidizing species is a complex electron abstracting ion, which mimics biological systems of cytochrome type, where a 'one

$$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}$$

electron transfer' is involved. The primary action of potassium ferricyanide as a 'one electron abstracter' on a phenol, such as PhOH, is to generate the phenoxy radical. Through spreading the odd electron by resonance