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PSILOTIC ACID, A C_6–C_4-ACID FROM *PSILOTUM NUDUM*

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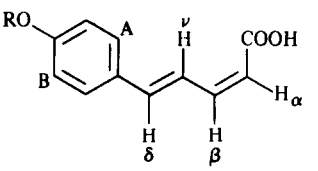
Key Word Index—*Psilotum nudum*; Psilotaceae; psilotic acid.

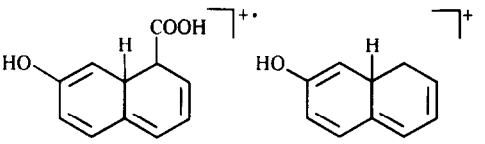
Abstract—Psilotic acid has been isolated from *Psilotum nudum* snd its structure determined as 5-(*p*-hydroxy)phenyl-2,4-diene-pent-1-oic acid on the basis of spectroscopic and chemical evidence.

Previous work on *Psilotum nudum* (L.) Griseb has resulted in the isolation of psilotin [1]. Material used in this investigation was collected from the Vindhya Hills of Madhya Pradesh, India and identified at the Botanical Gardens, Panchmani, India and National Botanical Gardens, Lucknow, India. The shrub (2 kg) was air-dried, shredded and extracted successively with petrol (bp 60–80°) and ethanol. Removal of solvent from the ethanol extract gave a gummy residue. The soluble portion obtained on refluxing this concentrate with ethyl acetate was adsorbed on a column of silica gel and eluted with benzene–ethyl acetate of gradually increasing polarity. The constituent eluted with benzene–ethyl acetate (70:30) was crystallized from methanol–ethyl acetate as a yellow solid mp 165° (**1a**).

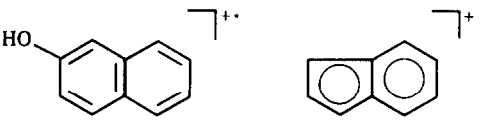
Compound **1a** is soluble in aqueous potassium hydroxide from which it can be regenerated on acidification. It exhibits two maxima in the UV at 230 nm (log ε4.6) and 329 nm (log ε5.13). These maxima show both hyper- and bathochromic shifts to 247 nm (log ε4.7) and 357 nm (log ε5.17) when the spectrum is determined in methanol–sodium methoxide. Compound **1a** is, therefore, phenolic in character [2]. The acidic nature of **1a** is evident from broad absorptions in the IR in the hydroxyl region (3020–2500 cm^{-1}) and the appearance of peaks at 1700, 1250 and 955 cm^{-1} [3]; the value at which the carbonyl peak appears further testifying to the fact that the acid is unsaturated. Absorptions at 1620, 1600 and



1a R = H
1b R = Ac



a 190(59.4%) **b** 145(100%)



c 144(44.3%) **d** 115(37.4%)

Table 1. ^{1}H NMR spectrum of **1a** (9 M/c DMSO-d_6)

Carbon No.	Proton	Chemical shift	Multiplicity	Coupling constant
2	α(1H)	5.58	*d*	$J_{\alpha,\beta}$ = 11 Hz
3	β(1H)	6.77	*dd*	$J_{\alpha,\beta}$ = 11 Hz; $J_{\beta,\gamma}$ = 11.42 Hz
4	γ(1H)	7.85	*dd*	$J_{\beta,\gamma}$ = 11.42; $J_{\gamma,\delta}$ = 15.82 Hz
5	δ(1H)	6.86	*d*	$J_{\gamma,\delta}$ = 15.82 Hz
2′,6′	A_2(2H)	6.78	*d*	$J_{A,B}$ = 8.35 Hz
3′,5′	B_2(2H)	7.35	*d*	$J_{A,B}$ = 8.35 Hz

1570 cm^{-1} indicate **1a** to be aromatic in character [4], a band at 815 cm^{-1} further suggesting the phenyl moiety to be *para*-disubstituted. Appearance of the $[M]^{+\cdot}$ in the mass spectrum of **1a** at *m/z* 190 defines its composition as $C_{11}H_{10}O_3$. ^1H NMR of **1a** reveals that two of the hydrogens present are labile and can be exchanged with deuterium. Signals arising from the remaining eight protons are spread over the low field region of the spectrum, analysis of which leads to the stereostructure **1a**. The assignments made (Table 1) are in complete agreement with those recorded for similar compounds [5]. The correspondence of the principal maxima computed for structure **1a** (333 nm) [6] with that observed (329 nm) and the appearance of fragment ions *a–d* in the mass spectrum of **1a** corroborate the proposed structure. Support is also available in the formation of a monoacetate, mp 185° (**1b**) as shown by the appearance of a peak at δ2.2 (3H, *s*) in its ^1H NMR spectrum. Low field signals in the spectrum, however, are not amenable to first-order analysis. Intermediacy of a quinone methide has been assumed to explain the formulation of psilotin [1]. Formation of **1a** can be explained on the basis of the well-charted route of chain extension of a shikimate derived acid with acetate/malonate units [7–9]. Interestingly, **1a** is, possibly, a precursor of psilotinin.

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