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DERIVATIVES OF PHLOROACETOPHENONE FROM THE LICHEN PSEUDOVERNIA FURFURACEAE

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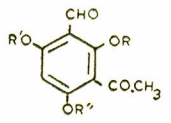
Abstract. The isolation of two derivatives of phloroacetophenone has been described. The natural occurrence of one of which is being reported for the second time only and the other is a new compound.

Pseudovernia furfuracea (L) Zopf. (*Parmelia furfuracea*) is a green leafy lichen abundantly growing in Azad Kashmir (Northern Pakistan) in the area of Neelam valley. Previously isolation of depsides, depsidones, sugars, aromatic acids and sterols have been reported from this source.[1,2] We isolated two derivatives of phloroacetophenone from this lichen, the structures of which are discussed below.

The compound, m.p. 142-44°, was identified as 4,6-dihydroxy-2-methoxy-3-methyl acetophenone on the basis of following evidence. It analysed for $C_{10}H_{12}O_4$. It gave green colour with ferric chloride in alcohol. IR (KBr) 1635 cm-1 (*o*-hydroxyketone) and 3340 cm-1 (OH). NMR 60 mc ($CDCl_3$) gave signals (all singlets) at τ7.90 (CH_3), 7.56 ($CO.CH_3$), 6.08 (OCH_3), 4.72 (free OH), 3.77 (aromatic proton) and—2.0 (bonded OH). Both the hydroxyl protons readily exchanged with D_2O. The mass spectrum showed M + peak at m/e 196 and other significant peaks at 164 (M-32; CH_3OH), 136 (M-60; OH, $COCH_3$), 107 (M-89; CH_3, $COCH_3$, OCH_3). A literature survey showed that this compound has been synthesized[3] and its natural occurrence, also from a lichen, recently reported by Italian workers. Spectral data and m.p. of our compound is in close agreement with the published work.[4]



I R' = R'' = H, R = C_2H_5
II R = R'' = H, R' = C_2H_5
III R = R' = H, R'' = C_2H_5

The compound, m.p. 92-94°, gave scarlet colour with ferric chloride in alcohol. The NMR 100 mc ($CDCl_3$) showed signals centered at τ 8.52 (t, *J* 7 Hz. CH_3). and 5.55 (q.*J* 7Hz, CH_2, indicating the presence of an ethoxy group. [5,6] The $COCH_3$ protons resonated as a singlet at τ 7.44. A signal at τ — 0.50 showed the presence of CHO group.[7] Two singlets at τ —2.56 and —3.14 showed the presence of two OH groups which are both bonded. Both readily exchanged with D_2O. A signal for aromatic proton resonated at τ 3.70. IR spectrum (nujol) showed a weak band at 1615 cm-1 and a strong peak at 1655 cm-1. It is known[7,9] that frequency shift of carbonyl group in acetophenones to *o*-hydroxyacetophenones is larger than from benzaldehydes to *o*-hydroxybenzaldehydes. We, therefore, attribute the absorbance at 1615 and 1655 cm-1 to the carbonyl groups of $COCH_3$ and CHO respectively. The compound analysed for $C_{11}H_{12}O_5$. Mass spectrum showed M+ at m/e 224 (56%). Other significant peaks were observed at 196 (M-28 CO) 24%, 178 (M-46 C_2H_5OH) 27%, 150 (M - 74 $CO.C_2H_5OH$) 100%), 179 (M - 45 OC_2H_5) 12% and 123 (M - 101 $COCH_3C_2H_5CHO$) 7%. On the basis of above spectral data the structures I, II, III are possible.

In analogy with 4,6-dihydroxy-2-methoxy-3-methylacetophenone isolated from the same source we propose 4,6-dihydroxy-2-ethoxy-3-formylacetophenone I as the structure of the natural product.

Experimental

Pseudovernia furfuracea was collected in August 1973 from the Neelam valley in Azad Kashmir. The lichen (0.78 kg) was successively extracted with hexane and EtOH at room temperature for 30 days. The concentration of ethanolic extract at reduced pressure gave a mixture of colourless crystals which were separated and identified as atranorin and chloroatranorin, both already known from this lichen.[10] The mother liquors (6.5 g) from the above mixture were chromatographed on silica (150.0 g) column. Elution with C_6H_6 and crystallization from MeOH gave colourless needles 4,6-dihydroxy-2-methoxy-3-methyl acetophenone (0.04 g), m.p. 142-44°. Calc. for $C_{10}H_{12}O_4$: C, 61.22 ;H, 6.16%. Found: C, 61.41; H, 6.31%). Further elution with C_6H_6 and crystallization from MeOH gave colourless microneedles of 4,6-dihydroxy-2-ethoxy-3-formylacetophenone (0.023 g) m.p. 92-94°. ($C_{11}H_{12}O_5$ requires: C, 58.92; H, 5.39%. Found: C, 58.84; H, 5.22%.

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