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ONE-POT SYNTHESIS OF NIDORELLAURENAL AND ITS ONE-STEP CONVERSION TO METHYL NIDORELLAURINATE, A CONSTITUENT OF *NIDORELLA AURICULATA*[1]

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Abstract : Nidorellaurenal (4) is obtained in a one-pot reaction, involving heating of the known carbinol (8) with selenium dioxide in dimethyl sulphoxide. Conversion of 4 to methyl nidorellaurinate (6), the natural product from *Nidorella auriculata*, has been achieved by Corey's one-step procedure.

Bohlmann and Fritz[2] recently isolated from *Nidorella auriculata* DC an aromatic sesquiterpene ester which was named methyl nidorellaurinate[3] and its structure assigned as (6) from spectral data. The biogenetic parallelism that exists between nuciferal (3), an aromatic sesquiterpene aldehyde isolated from *Torreya nucifera*[4] and nidorellaurenal (4), the aldehyde corresponding to the naturally occurring ester[2](6)is striking. Both the sesquiterpene aldehydes (3) and (4) can be visualised as isoprenologues of p-cymene (1). The terminally functionalized isopentenyl moiety (2) is attached to C-9 of p-cymene (1) in nuciferal (3), while it is attached to C-7 of p-cymene in nidorellaurenal (4). The novelty of the unusual linkage of isoprene unit and our earlier synthesis of nuciferal (3) in these laboratories[5] prompted usto undertake the synthesis of nidorellaurenal (4) and convert it further to methyl nidorellaurinate (6).

Heating (125-130°,4h) of the known 3-(p-isopropylphenyl)propyl dimethyl carbinol[6](8) with selenium dioxide in dimethylsulphoxide[7], followed by purification afforded in a one-pot reaction nidorellaurenal (4) in 25% yield resulting from concurrent dehydration[8] of the carbinol to the olefin (7) and its regiospecific oxidation[5,9] of the terminal (E)-methyl group to furnish the (E)-enal (4). One-step oxidation of the enal (4) by Corey's procedure[10] gave in 83% yield methyl nidorellaurinate (6), the spectral features of which showed identity with that of the natural product[2]. Oxidation of the aldehyde (4, with alkaline silver oxide[5,9a] gave nidorellaurenic acid (5). Stepwise dehydration[11] of the carbinol (8) to the olefin (7), followed by oxidation[7] of the olefin slightly raised the overall yield of the enal (4) to 37%. Elemental analysis[12] and spectral data (IR and PMR) are in agreement with the structural assignments of the compounds synthesized (4, 5, 6 and 7).

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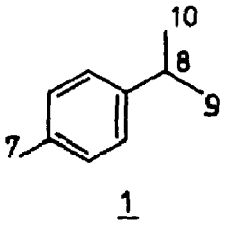

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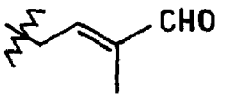

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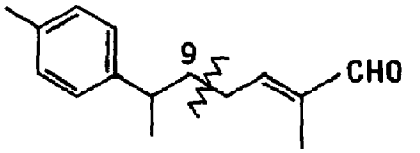

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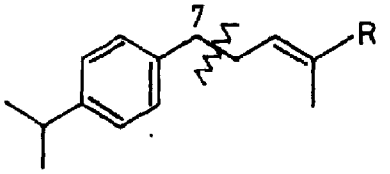

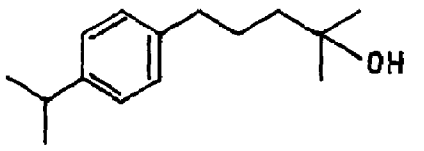

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4, R = CHO 6, R = CO_2CH_3

5, R = CO_2H 7, R = CH_3

References and notes

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12. Elemental analysis of the compounds (5) and (6) are in agreement with the calculated values (C ± 0.16, H ± 0.36).

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