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SYNTHESIS OF LACHNANTHOCARPONE

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The isolation of lachnanthocarpone (X; R = R' = H), the main pigment present in the seed capsules of Lachnanthes tinctoria (Haemodoraceae), has recently been described (1). The roots of the same plant were also found to contain a number of phenalenones very closely related to the plant glycoside haemocorin (2), and having the same pattern of oxygen and phenyl substitution as haemocorin aglycone (X; R = H, R' = OMe). Haemocorin, which occurs in the related Australian genus Haemodorum is the only other phenalenone derivative so far extracted from a plant source*, and its aglycone is the only naturally-occurring phenalenone which has been obtained by synthesis (7). In the present communication we describe a synthesis of lachnanthocarpone which confirms the structure previously proposed on the basis of its spectra (1).

Cyclisation of γ-(2-methyl-4,5-dimethoxy)-phenylbutyric acid (I) [prepared as previously described (8)] with polyphosphoric acid afforded the tetralone (II) in a yield of 87%. Treatment of (II) with phenylmagnesium bromide gave the carbinol (III) (93% yield) which was dehydrated with iodine to afford the dihydronaphthalene (IV) (64% yield). Conversion of (IV) into 1-methyl-3,4-dimethoxy-5-phenylnaphthalene (V) was achieved by dehydrogenation with 2,3-dichloro-5,6-dicyano-p-benzoquinone (85% yield).

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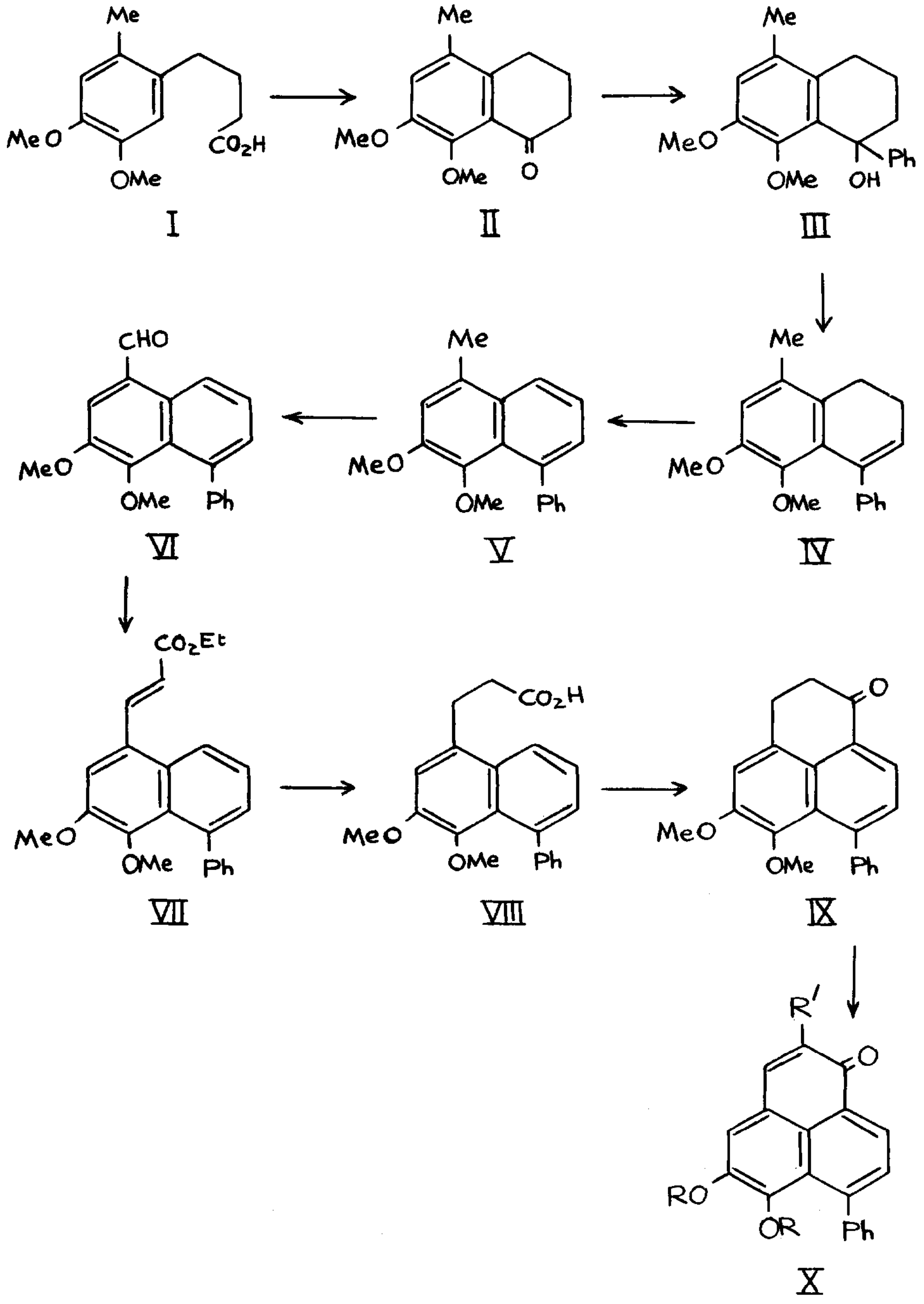
* Other pigments based on the phenalenone nucleus are formed as the products of mould metabolism. These are atrovenetin (3), herqueinone (3,4), and resistomycin (5); dimeric variants are also known, e.g. duclauxin (6).


Me
MeO
OMe
CO2H
I
Me
MeO
OMe
O
II
Me
MeO
OMe
OH
Ph
III
CHO
MeO
OMe
Ph
VI
Me
MeO
OMe
Ph
V
Me
MeO
OMe
Ph
IV
CO2Et
MeO
OMe
Ph
VII
CO2H
MeO
OMe
Ph
VIII
O
MeO
OMe
Ph
IX
R'
O
RO
OR
Ph
X

In order to convert the naphthalene (V) into a phenalenone derivative it was necessary to oxidise its methyl group. This was achieved in moderate yield (40%) by bubbling oxygen through a carbon tetrachloride solution of the naphthalene (V) containing one molar equivalent of N-bromosuccinimide, which was irradiated with a tungsten lamp, the heating effect of which was sufficient to maintain the solution at reflux temperature. In this way, 3,4-dimethoxy-5-phenyl-1-naphthaldehyde (VI) was obtained.

A Wittig reaction between the aldehyde (VI) and ethoxycarbonylmethylenetriphenylphosphorane gave the unsaturated ester (VII) in a yield of 96%. Successive hydrogenation over palladised charcoal and saponification converted the ester (VII) into the naphthalenepropionic acid (VIII) in quantitative yield. Cyclisation of the acid (VIII) to give 5,6-dimethoxy-7-phenylphenalan-1-one (IX) was achieved in a yield of 65% by treating the derived acid chloride with stannic chloride in carbon disulphide solution.

The ketone (IX) was dehydrogenated with 2,3-dichloro-5,6-dicyano-p-benzoquinone to give 5,6-dimethoxy-7-phenylphenalenone (X; R = Me, R' = H) (96% yield). Demethylation of the dimethyl ether (X; R = Me, R' = H) with pyridine hydrochloride proceeded quantitatively to afford 5,6-dihydroxy-7-phenylphenalenone (X; R = R' = H) shown to be identical with lachnanthocarpone by comparison with an authentic specimen obtained from natural sources, which was kindly provided by Dr. J.M. Edwards.

Satisfactory analyses and spectra were obtained for all the new compounds described.

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