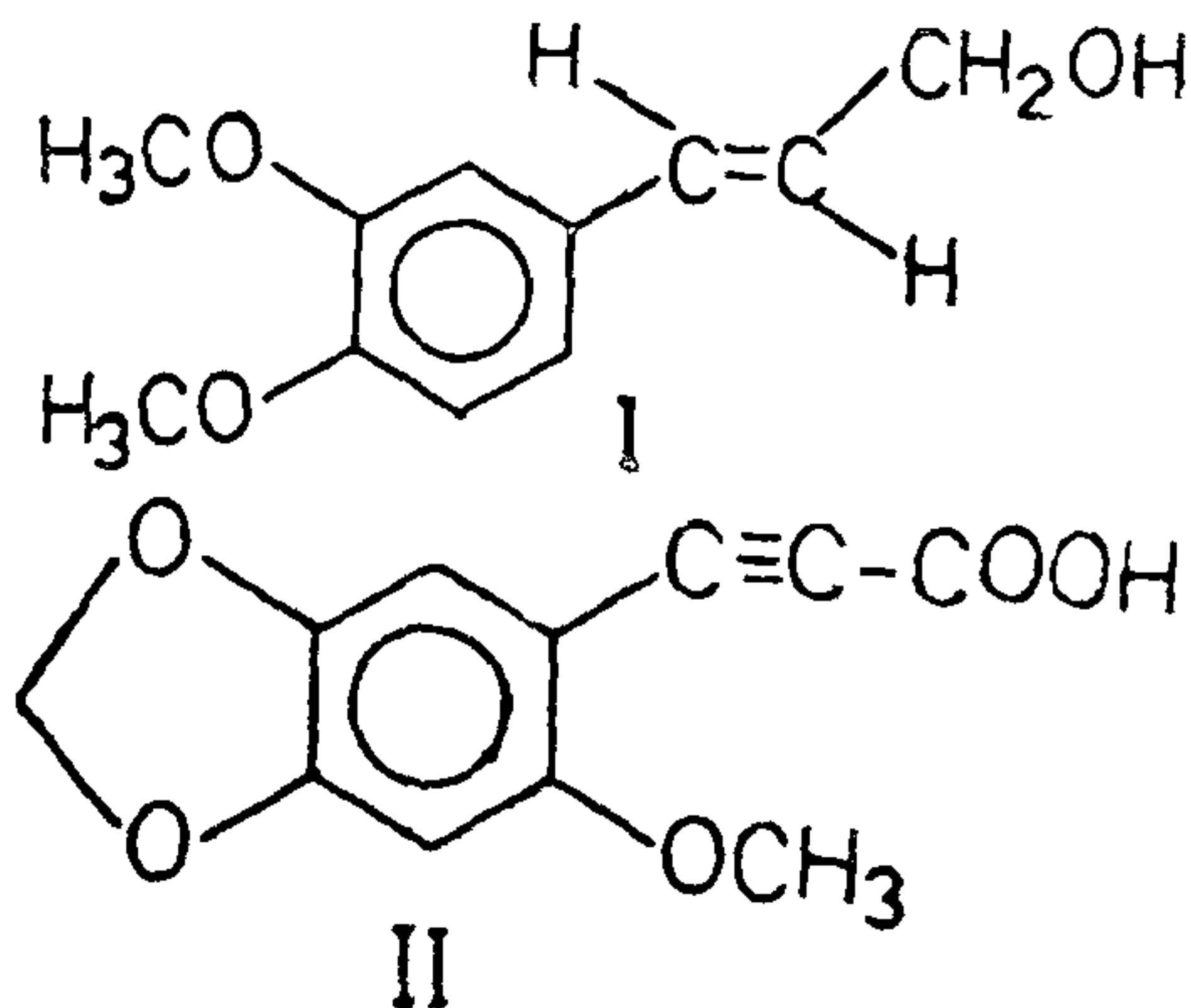


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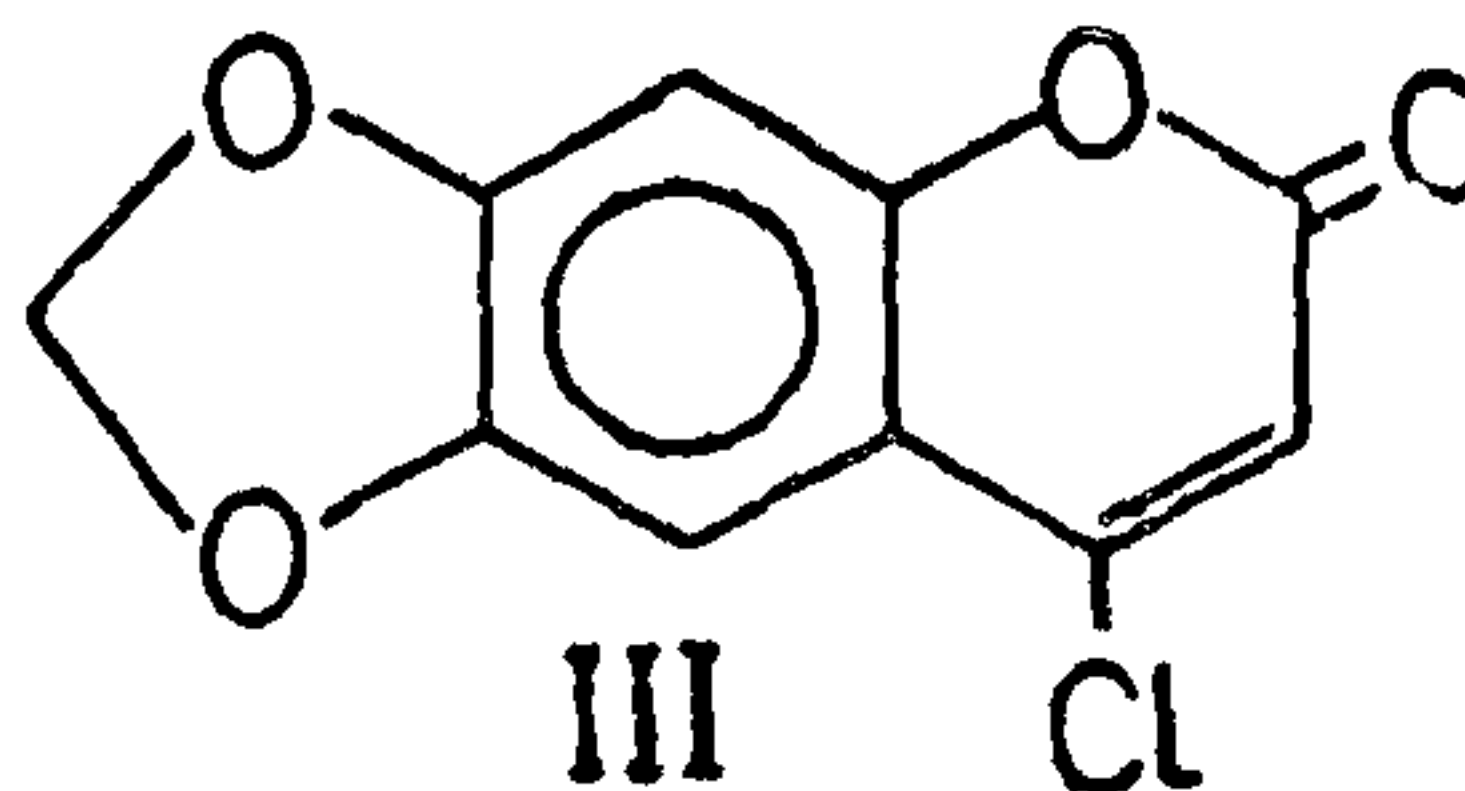
SYNTHESIS OF 4-CHLOROAYAPIN

KLEMM'S synthesis¹ is a general procedure applicable for unsymmetrical 1-aryltetralins. It was proposed to adopt this synthesis for 1-aryltetralins with an ortho substituent in the 1-aryl group as in hypophyllanthin². Accordingly, trans-3,4-dimethoxycinnamyl alcohol (I) and 2-methoxy-4,5-methylenedioxyphenylpropionic acid (II) were obtained by well known procedures. The propionic acid (II) was synthesised from 2-methoxy-4,5-methylenedioxybenzaldehyde through the corresponding cinnamic acid. It crystallised from alcohol as colourless needles, m.p. 136-38°, I.R. ν 2220 cm^{-1} (C=C), 1675 cm^{-1} (COOH) and 925 cm^{-1} (O-CH₂-O).



To esterify the alcohol (I) with the acid (II) it was converted into the acid chloride by refluxing with thionylchloride according to the Klemm's procedure¹. The acid chloride was then refluxed with alcohol (I) in dry benzene employing pyridine. The product was worked up as usual which crystallised from benzene petroleum ether as colourless plates, m.p. 179-80°, (C₁₀H₈O₄Cl), +ve Beilstein test. Surprisingly it was found to be an α : β -unsaturated lactone from its I.R. spectrum (1730 cm^{-1}) and exhibited all the characteristics of a coumarin, such as bluish violet fluorescence in conc H₂SO₄. From its NMR spectrum it contained one methylenedioxy group [(δ , 6.21, 2H (s))] and one olefinic hydrogen [(δ , 6.68, 1H (s)]

which can be located at C-3 of a coumarin system. The C-8 hydrogen is noticed at δ 7.00 and C-5 hydrogen at δ 7.42. These values support the structure (III).



This coumarin can be named as 4-chloroayapin³. In the first step the triple bond of the propionic acid (II) is being reduced to double bond by the addition of HCl, a byproduct during the reaction with thionylchloride. In the next step during the esterification process the ortho methoxyl is suffering facile demethylation and obviously converted into the coumarin (III). Such kind of demethylations are reported in literature^{4,5}.

The reaction was repeated without alcohol (I). It gave a product, m.p. 155°, +ve Beilstein test. It was found to be an α , β -unsaturated acid (I.R. 970 cm^{-1} , 1675 cm^{-1}). It did not exhibit bluish violet fluorescence. It is difficult to visualise the role of alcohol in the formation of coumarin in the above reported reaction.

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SYNTHESES OF LAXANTHONES-II AND THEIR DERIVATIVES

CONSTITUTIONS previously assigned to the two isomeric xanthonés, laxanthone-II and isolaxanthone-II isolated from *Lawsonia inermis* have now been confirmed as I and II by their syntheses.