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GIBBERELLIN A_{24}, AN ALDEHYDIC GIBBERELLIN FROM GIBBERELLA FUJIKUROI

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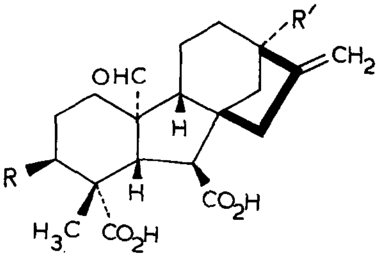
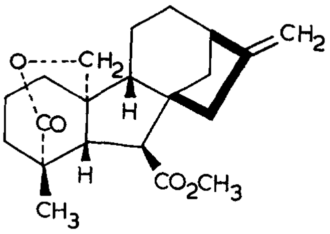
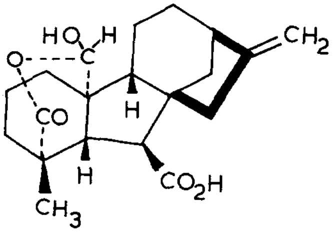
Two aldehydic C_{20}-gibberellins have been isolated recently from plant sources: gibberellin A_{19} (I, R=H, R′=OH) from bamboo shoots (1) and gibberellin A_{23} (I, R=R′=OH) from young seed of *Lupinus luteus* (2). We now report the isolation of gibberellin A_{24} (I, R=R′=H), the first fungal C_{20}-gibberellin with an aldehydic function.



(I)



(II)



(III)

Gibberella fujikuroi (M419) was cultured at pH7 as described by Cross *et al.* (3); the gum recovered from the gibberellin mother liquors was adsorbed on silica gel and placed on a column of Celite:charcoal (2:1). By gradient elution with increasing concentrations of acetone in water, gibberellin A_{24} was obtained in fractions eluted with 63 to 66.5% acetone in water. Further purification of these fractions by thin layer chromatography on silica gel with light petroleum (b.p. 60-80°):ethyl acetate:acetic acid (800:200:1), afforded gibberellin A_{24} which crystallised from acetone:light petroleum (b.p. 60-80°) in needles, m.p. 199-203°. The dimethyl ester, obtained with diazomethane, crystallised from methanol in needles, m.p. 94-95°. Although the isolated yield of pure gibberellin A_{24} was about 4 mg. per litre of culture fluid gas chromatography of a methylated aliquot of the crude mother liquors showed the presence of 30-35 mg. per litre of culture filtrate.

The molecular formula $C_{20}H_{26}O_5$ for gibberellin A_{24} was established by combustion analyses of the acid and methyl ester and by the high resolution mass spectrum of the dimethyl ester. A 100 Mc/sec. n.m.r. spectrum of the dimethyl ester in $CDCl_3$ revealed the following significant signals: (a) a singlet at 0.38τ characteristic of a tertiary aldehydic proton; (b) two broad singlets at 5.16 and 5.23τ typical of exocyclic methylene protons; (c) an AB-quartet (J, 13 c./sec.) centred at 6.19 and 7.81τ (double irradiation); (d) two methoxyl singlets at 6.34 and 6.43τ; and (e) a tertiary methyl singlet at 8.88τ. The AB-quartet is typical of a gibberellin in which the 10-proton is deshielded by diaxial carbonyl substituents at positions 1 and 4a (1,4,5). Like the n.m.r. spectrum, the mass spectra of gibberellin A_{24} and the dimethyl ester are typical of a C_{20}-gibberellin; the spectrum of the dimethyl ester bore a close resemblance to that published (1) for gibberellin A_{19} dimethyl ester and showed significant peaks at M^+, $(M-CH_4O)^+$, $(M-C_2H_4O_2)^+$ and $(M-C_4H_8O_4)^+$, each of which showed a subsequent loss of CO. Two positions are possible for the tertiary aldehydic function; structure (I, R=R´=H) is selected for gibberellin A_{24} since borohydride reduction, followed by methylation, afforded gibberellin A_{15} methyl ester (II).[6]

The lactol structure (III) for gibberellin A_{24} in the solid state was indicated by the infrared spectrum which showed a band at 3400 cm.$^{-1}$, absent in the spectrum of the dimethyl ester. An equilibrium between the free aldehyde (I) and the lactol (III) explained the unexpected n.m.r. spectrum of gibberellin A_{24} in d_5-pyridine which contained no aldehydic proton signal but showed two very broad resonances assigned to the average chemical shift of exchanging carboxylic and hydroxyl protons (ca. 0.5τ; 2H) and aldehydic and lactol methine protons (ca. 1.9τ; 1H). Consistent with this interpretation of the n.m.r. spectrum, the 10-proton doublet was broadened and shifted up-field (ca. 6.2τ) compared to the sharp doublet (5.9τ) in the spectrum of the dimethyl ester in the same solvent. An inspection of molecular models shows that the lactol must have the R-configuration at the anomeric centre and that the two other aldehydic gibberellins, A_{19} (I, R=H, R´=OH) and A_{23} (I, R=R´=OH), should also form lactols readily.

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