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# A NEW GIBBERELLIN IN THE SEED OF PHASEOLUS MULTIFLORUS

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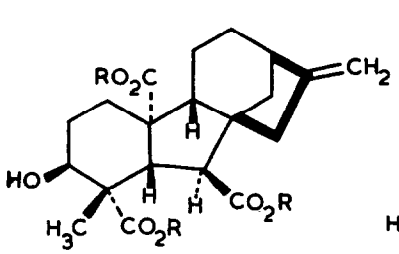
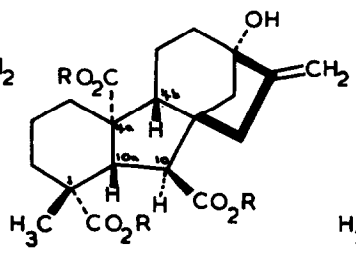
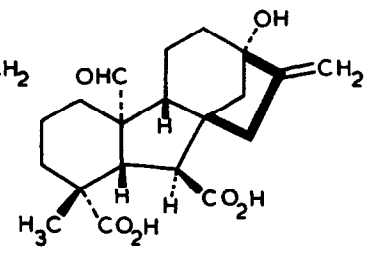
In an earlier paper (1) we showed that gibberellins $A_1$, $A_4$, $A_5$, $A_6$, and $A_8$ could be directly identified in immature seed of Phaseolus multiflorus by combined gas chromatography–mass spectrometry (g.c.-m.s.) of a methylated crude extract and its trimethylsilylation product. However, the peaks tentatively assigned previously (2) to gibberellin $A_{13}$ methyl ester (I, R=$CH_3$) and its trimethylsilyl ether by gas chromatography (g.c.) alone were found to be those of the corresponding derivatives of an isomer of gibberellin $A_{13}$. We now report the isolation of this new gibberellin (II, R=H) which we name $A_{17}$*.




(I)




(II)




(III)

Column chromatography of the total crude acid extract on celite:charcoal (2:1) has already been described (2). Fraction 55, eluted with 64% acetone in water, and shown by g.c. of a methylated aliquot to contain a high concentration of the new gibberellin, was

*Gibberellin $A_{16}$ methyl ester has recently been isolated from Gibberella fujikuroi by R.H.B. Galt, Tetrahedron, submitted.

further purified by column chromatography on celite:silica gel (2:1) and by thin layer chromatography on silica gel with chloroform:ethyl acetate:acetic acid (15:5:1). The material, eluted from the former with 60-85% ethyl acetate in chloroform and from the latter at Rf ca. 0.4 to 0.6, was precipitated from ethyl acetate by petroleum ether to give gibberellin $A_{17}$ as an amorphous solid m.p. 140-150° with a purity of 90% by g.c. analysis. The methyl ester showed a parent ion in the mass spectrum at m/e 420 with composition $C_{23}H_{32}O_7$ and was clearly a trimethyl ester from its nuclear magnetic resonance (n.m.r.) spectrum (see Table). The infrared spectrum of a chloroform solution of the trimethyl ester showed the following features: a broad hydroxyl (ca. 3500 $cm.^{-1}$); a composite carbonyl (1723 $cm.^{-1}$); and an exocyclic methylene (1663 and 906 $cm.^{-1}$). Gibberellin $A_{17}$ was therefore a tribasic hydroxy acid, $C_{20}H_{26}O_7$.

TABLE

N.m.r. Resonances (τ values) and Assignments

| Acid | Methyl Ester | | Intensity | Assignment |
|---|---|---|---|---|
| $(CD_3)_2CO$ | $CDCl_3$ | $C_6D_5N$ | | |
| 8.84 | 8.91 | 8.77 | 3 | $CH_3-C\lesssim$ |
| 6.19 | 6.28 | 5.95 | 1 | 10 - H |
| 4.97,5.24 | 4.94,5.17 | 4.58,5.05 | 1,1 | $CH_2=C\lesssim$ |
| - | 6.36,6.41,6.46 | 6.43,6.43,6.52 | 3,3,3 | $CH_3OC(=O)\lesssim$ |

Structure (II, R=H) is deduced for gibberellin $A_{17}$ from the n.m.r. data shown in the Table for the acid and trimethyl ester. The revealing resonances are those of the 10-proton and the exocyclic methylene protons. As in Bamboo gibberellin (III) (3) and in gibberellin $A_{13}$ (I, R=H), the 10-proton doublet ($J_{10,10a}$ 12 c./sec.) occurs at characteristically low field, deshielded by the 1,4a-diaxial carboxyl and aldehyde groupings (4). The significant difference in the chemical shifts of the exocyclic methylene protons, one of which shifts to even lower field in pyridine solution reveals the presence of a 7-hydroxyl group (5). The stereochemistry shown in (II, R=H) for gibberellin $A_{17}$ is assumed by analogy and is supported by the n.m.r. evidence discussed above.

Structure (II, R=H) differs from that of gibberellin $A_{13}$ (I, R=H) only in the position of the hydroxyl group. This close relationship is reflected in the similarity of their mass spectra and in the expected and significant intensity differences, particularly of the $[M-18]^+$ peak in the methyl esters. The possible biosynthetic link between gibberellin $A_{17}$ (II, R=H) and Bamboo gibberellin (III) is obvious and the co-occurrence of these two gibberellins in P. multiflorus and Phyllostachys edulis (Bamboo) is anticipated. The biological properties of gibberellin $A_{17}$ are under current study and will be reported in the full paper.

It is noteworthy that the detection and isolation of gibberellin $A_{17}$ was effected without the guidance of bioassay.

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