A New Gibberellin, Gibberellin A₄

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Sirs:

In this communication, we publish the isolation and characterization of a new gibberellin which is named gibberellin A₄.

When the crude crystals of methylester of gibberellins obtained from the broth filtrate of tank culture incubating the strain No. 4 or G-4 of *Gibberella fugikuroi* in the medium composed of glycerol, ammonium chloride, monopotassium phosphate, tartaric acid, magnesium sulphate, zinc sulphate and ferric sulphate were subjected to the chromatography of alumina using a mixture of benzene-ethylacetate (5:1 by vol.) as the solvent system, a new methylester, m.p. 175-6°, different from methylesters of gibberellins A₁, A₂ and gibberellic acid, namely A₃, was obtained from the earlier eluted fraction than all known gibberellins fractions in relatively low yield. The partition chromatography through silicic acid was attempted for the purpose of obtaining the new free acid, using one mole phosphate buffer of pH 5.4 as the stationary phase and chloroform-ethylacetate mixture (1:1 by vol.) as the mobile phase and we isolated the free acid, d.p. 222°,

from, also, the earlier eluted fraction. The methylester of this free acid is identical in all respects with the methylester obtained from the chromatography of alumina described above. This new acid shows the characteristic physiological activity in about the same degree as gibberellin A₁ by our testing method against rice seedlings but inhibits the growth of root evidently.

We named this substance gibberellin A₄ and C₁₈H₂₂O₅ or C₁₉H₂₄O₅ was assigned as its molecular formula from the analytical data of itself and its derivatives and molecular weight determination. The further studies are now undergoing to determine which of above possible formulae is correct. Gibberellin A₄, C₁₈H₂₂O₅ or C₁₉H₂₄O₅, melts at 222° with decomposition and has an optical rotation $[\alpha]_D^{20} -20.8^\circ$ (c=0.34, CH₃OH); Calcd. for C₁₈H₂₂O₅, C 67.91%, H 6.97%, M.W. 318; for C₁₉H₂₄O₅, C 68.65%, H 7.28%, M.W. 332; Found, C 67.55%, H 7.35%, M.W. 334 (titration). Gibberellin A₄ monomethylester, C₁₉H₂₄O₅ or C₂₀H₂₆O₅, melts at 175-6°; Calcd. for C₁₉H₂₄O₅, C 68.65%, H 7.28%, OCH₃ 8.90%, M.W. 332; for C₂₀H₂₆O₅, C 69.34%, H 7.57%,

FIG. 1.
Gibberellin A₄

FIG. 2.
Gibberellin A₄ monomethylester

FIG. 3.
Dihydrogibberellin A₄ monomethylester

FIG. 4.
Monoacetyl gibberellin A₄ monomethylester

OCH₃ 8.52%, M.W. 346; Found, C 69.01%, H 7.28%, OCH₃ 8.09%, M.W. 342 (by Rast).

Gibberellin A₄ monomethylester gives a dihydrogibberellin A₄ methylester, m.p. 141°,

C₁₉H₂₆O₅ or C₂₀H₂₈O₅ over Adams' catalyst (Calcd. for C₁₉H₂₆O₅, C 68.24%, H 7.84%; for C₂₀H₂₈O₅, C 68.94%, H 8.10%; Found, C 68.63%, H 8.02%) and a monoacetyl gibberellin A₄

monomethylester, $C_{21}H_{26}O_6$ or $C_{22}H_{28}O_6$, m.p. 131–2°, by treatment of pyridine-acetic anhydride at room temperature (Calcd. for $C_{21}H_{26}O_6$, C 67.36%, H 7.00%; for $C_{22}H_{28}O_6$, C 68.02%, H 7.27%; Found, C 68.17%, H 7.29%).

The infrared spectra of these compounds are shown in Figures 1, 2, 3 and 4.

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Nobutaka TAKAHASHI
Yasuo SETA
Hiroshi KITAMURA
Yusuke SUMIKI

Department of Agricultural Chemistry
Faculty of Agriculture
University of Tokyo, Tokyo

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