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GIBBERELLIN A_7. A NEW FUNGAL GIBBERELLIN

B.E. Cross, R.H.B. Galt and J.R. Hanson

Imperial Chemical Industries Limited,
Akers Research Laboratories, Welwyn, Herts.

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THE fungus Gibberella fujikuroi has been shown[1] to produce four gibberellins, namely, gibberellins A_1, A_2 and A_4 and gibberellic acid, whilst gibberellins A_1 and A_5 have been isolated from the immature seed of Phaseolus multiflorus.[1] We wish to report the isolation of another gibberellin from Gibberella fujikuroi. The fungus was cultured[2] until the inorganic nitrogen was exhausted from the medium, then the pH was adjusted to and maintained at 7 for 209 hours. Isolation of crude gibberellic acid as previously described[2,3] and recovery of the ethyl acetate mother liquors afforded a gum which was adsorbed on a column of charcoal-celite (1:2) and eluted with increasing concentrations of acetone in water. The fraction eluted with water containing 65% acetone gave a gum which was chromatographed on silica-celite (1:2) and eluted with increasing concentrations of ethyl acetate

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[1] For review see P.W. Brian, J.F. Grove and J. MacMillan, "The Gibberellins", in Zechmeister, Prog. Chem. Org. Nat. Prod. **18**, 350 (1960).

[2] Brit. Pat. 783611.

[3] P.J. Curtis and B.E. Cross, Chem. and Ind. 1066 (1954).

in chloroform. The fraction obtained with 20% ethyl acetate gave a new plant growth promoting acid (25 mg./l. of culture filtrate) for which we propose the name gibberellin A_7.

Analysis of gibberellin A_7 (I), m.p. 202° dec., $[\alpha]_D^{24}$ +20° (EtOH), ν_{max} 3450 (OH), 1742, 1722 (C=O), 1654 cm.$^{-1}$ (C=C), $\nu_{max}^{CH_3CN}$ 1772 (γ-lactone), 1738 (CO_2H), 1657 cm.$^{-1}$ (C=C), and its methyl ester (II), m.p. 152-153° or 168-170°, $[\alpha]_D^{23}$ +33° (EtOH), $\nu_{max}^{CHBr_3}$ 3574, 1766, 1722, 1655, 886 (=CH_2), 780, 760 and 743 cm.$^{-1}$ $(^{H}\diagdown C = C \diagup^{H})$ indicates the molecular formula $C_{19}H_{22}O_5$ for (I). Microhydrogenation revealed the presence of two double bonds; with concentrated sulphuric acid (I) gave an intense red colour (cf. gibberellic acid[4]).

Treatment of (I) with dilute mineral acid at 20° gave an aromatic acid $C_{18}H_{22}O_3$ (VI), m.p. 220-222°, ν_{max} 3415, 2634, 1678 and 1587 cm.$^{-1}$, λ_{max}^{EtOH} 269, ~272 mμ (ϵ 418, 377), which with diazomethane gave an ester $C_{19}H_{24}O_3$ (VII), m.p. 145-148°. Under similar conditions gibberellic acid (III) gives allogibberic acid[5] (VIII), suggesting that (I) has the same ring A structure as gibberellic acid, whilst the addition of water to the terminal methylene group is analogous to the

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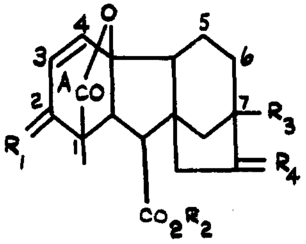
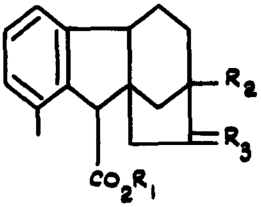
[4] B.E. Cross, J. Chem. Soc. 4670 (1954).

[5] P.W. Brian, J.F. Grove, H.G. Hemming, T.P.C. Mulholland and M. Radley, Plant Physiol. 329 (1958).



	R_1	R_2	R_3	R_4
I	H, OH	H	H	CH_2
II	H, OH	Me	H	CH_2
III	H, OH	H	OH	CH_2
IV	O	Me	H	CH_2
V	H, OH	Me	H	O

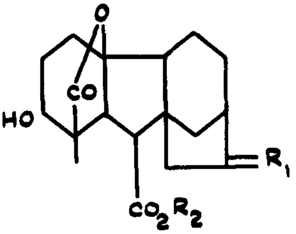


	R_1	R_2	R_3
VI	H	H	OH, Me
VII	Me	H	OH, Me
VIII	H	OH	CH_2

IX $R_1 = CH_2$ $R_2 = H$

X R_1 = OH, Me $R_2 = H$

XI R_1 = H, Me R_2 = Me



conversion[1,8] of gibberellin A_4[1,6] (IX) to gibberellin A_2[1,7] (X).

Hydrogenation of (II) over 25% palladised charcoal gave 60% of acidic products and dihydrogibberellin A_4 methyl ester[7] (XI), m.p. 148-151°, identified by mixed m.p. and infrared spectrum. The Δ^3 position of the double bond, suggested by acid rearrangement, was confirmed by the high yield of hydrogenolysis acids (cf. gibberellic acid[9]) and by the oxidation of (II) with manganese dioxide to an αβ-unsaturated ketone $C_{20}H_{22}O_5$ (IV), m.p. 139-140°, λ_{max}^{EtOH} 228 mμ (ε 6900), $\nu_{max}^{CHCl_3}$ 1776 (γ-lactone), 1724 (ester) and 1691 cm.$^{-1}$ (αβ-unsaturated ketone).

Oxidation of (I) with sodium periodate/potassium permanganate followed by spectrophotometric determination[10] of the formaldehyde showed the presence of a terminal methylene group. Ozonolysis of (II) with 1 mole of ozone yielded formaldehyde (0.43 mol.) and a nor-ketone $C_{19}H_{22}O_6$ (V), m.p. 185°, ν_{max} 3440, 1784, 1755 (5-ring ketone), 1738 cm.$^{-1}$, which although it gave a monoacetate, m.p. 187-189°, was stable to periodate and therefore not an α-ketol.

On the basis of structure (IX) for gibberellin A_4, the only

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[6] N. Takahashi, Y. Seta, H. Kitamura and Y. Sumiki, Bull. Agric. Chem. Soc. Japan, **21**, 396 (1957).

[7] Idem, ibid. **23**, 405 (1959).

[8] J.F. Grove, personal communication.

[9] B.E. Cross, J. Chem. Soc. 1960, in the press.

[10] R.U. Lemieux and E. von Rudloff, Canad. J. Chem. **33**, 1710 (1955).

structure for gibberellin A_7 consistent with these results is (I), i.e. 7-deoxygibberellic acid.

All structures are supported by satisfactory analyses; infrared frequencies refer to 'Nujol' mulls unless otherwise stated.

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