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GIBBERELLIN A_9

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A more detailed examination of the crude acidic metabolites produced in the fermentation of Gibberella fujikuroi described in our earlier communication[1] has revealed the presence of a new acid. The gummy fraction eluted from the charcoal-celite column[1] with water containing 80% acetone has been rechromatographed on silica-celite (1:2). Elution with 10% ethyl acetate in light petroleum afforded a plant growth promoting acid for which we propose the name gibberellin A_9.

Gibberellin A_9 (I), which formed needles from acetone - light petroleum (b.p. 60-80°), m.p. 208-211° dec., $[\alpha]_D^{22}$ -12° (EtOH), ν_{max}^{Nujol} 3098 (OH of carboxyl), 1740, 1723, 1659 and 893 cm $^{-1}$, and its methyl ester (II), m.p. 136°, $[\alpha]_D^{22}$ -15° (EtOH), ν_{max}^{Nujol} 1777 (γ-lactone), 1738 (ester), 1659 and 873 ($=CH_2$) cm $^{-1}$, gave analyses consistent with the formula $C_{19}H_{24}O_4$ for the acid (I). Microhydrogenation of (II) revealed the presence of one double bond, shown to be a terminal methylene

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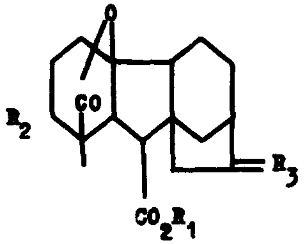
[1] B.E. Cross, R.H.B. Galt and J.R. Hanson, Tetrahedron Letters No. 15, 18 (1960).

group exocyclic to a 5-membered ring by ozonolysis of (II) to formaldehyde (0.6 mol.) and a nor-ketone (III), $C_{19}H_{24}O_5$, m.p. 204-207°, ν_{max}^{Nujol} 1772 (γ-lactone), 1738 (ester and 5-ring ketone) cm $^{-1}$. Structure (I) for gibberellin A_9, suggested by the above results, was established by degradation of gibberellin A_4 (IV)[2,3] to (III). The tosylate (V) of gibberellin A_4 methyl ester nor-ketone (VI)[4] with boiling collidine gave a Δ^2-olefin, $C_{19}H_{22}O_5$, m.p. 160-161°, which on catalytic hydrogenation afforded a product identical in all respects with gibberellin A_9 methyl ester nor-ketone (III).



	R_1	R_2	R_3
I	H	H	CH_2
II	Me	H	CH_2
III	Me	H	O
IV	H	OH	CH_2
V	Me	TsO	O
VI	Me	OH	O
VII	Me	AcO	O

The structures of gibberellins A_7 and A_9 are both dependent upon that of gibberellin A_4 which has been related[3] to gibberellin A_1 ——

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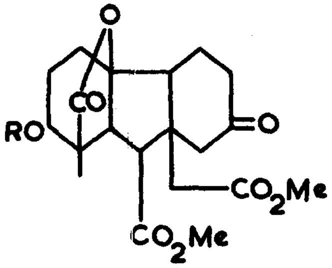
[2] P.W. Brian, J.F. Grove and J. MacMillan, "The Gibberellins" in Zechmeister, Prog. Chem. Org. Nat Prod. **18**, 350 (1960).

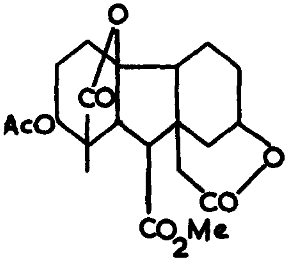
[3] H. Kitamura, N. Takahashi, Y. Seta, A. Kawarada and Y. Sumiki, Bull. Agric. Chem. Soc. Japan **23**, 344 (1959).

[4] N. Takahashi, Y. Seta, H. Kitamura and Y. Sumiki, ibid. **23**, 405 (1959).

and hence to gibberellic acid[5,2] — by Sumiki and his co-workers. We have confirmed this relationship by a new series of reactions. Acetylation of the keto-ester (VIII), derived from gibberellic acid,[6] yielded the acetate (IX), m.p. 193-195°, which on hydrogenation (Adams catalyst) in acetic acid containing a trace of perchloric acid afforded the δ-lactone (X), m.p. 193-194°, $\nu_{max}^{CHBr_3}$ 1774 and 1738 (broad) cm $^{-1}$. Baeyer-Villiger oxidation of the acetate of gibberellin A_4 methyl ester nor-ketone (VII), m.p. 189°, $\nu_{max}^{CHBr_3}$ 1771, 1738 cm $^{-1}$, with perbenzoic acid gave the same δ-lactone (X).



(VIII) R=H
(IX) R=Ac



(X)

All structures are supported by satisfactory analyses.

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[5] J.F. Grove, P.W. Jeffs and T.P.C. Mulholland, J. Chem. Soc. 1236 (1958).

[6] B.E. Cross, J. Chem. Soc. 3022 (1960).