Partial Synthesis of Gibberellin A_{15} Norketone from 7-Hydroxykaurenolide

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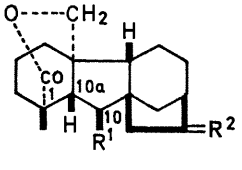
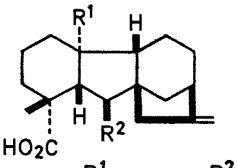
Summary The structure of gibberellin A_{15} has been confirmed by the synthesis of gibberellin A_{15} norketone from the more readily available 7-hydroxykaurenolide.

GIBBERELLIN A_{15}, a minor metabolite of *Gibberella fujikuroi*, was tentatively assigned[1] the structure (**1**). More recently, the structure (**4**) of gibberellin A_{24} was derived,[2] and rests, in part, upon that of gibberellin A_{15}. We describe a partial synthesis of gibberellin A_{15} norketone (**2**) from 7-hydroxykaurenolide[3] (**7**), which not only rigorously establishes the structure and stereochemistry of gibberellin A_{15}, and therefore also of gibberellin A_{24}, but makes the former available for further study.

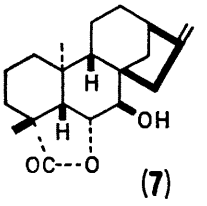
7-Hydroxykaurenolide was transformed[4] into the aldehydo-acid (**5**), which, after reduction with sodium borohydride to the alcohol (**6**)† and oxidation of the latter with osmium tetroxide–sodium metaperiodate, yielded the nor-ketone (**8**). The acetate (**9**) of the norketone (**8**) was converted into the amide (**10**) and the latter was photolysed[5] in benzene in the presence of lead tetra-acetate and iodine. Isolation of the lactonic product in the usual way[5] afforded the gummy lactone (**3**), which on oxidation with Jones' reagent gave the acid (**2**), m.p. 260—264° (decomp.), τ ($CDCl_3$) 8·81 (s, 1β-methyl), 7·70 and 7·17 (AB quartet, J 13 Hz, 10,10a-protons), 5·91 and 5·52 (AB quartet, J 13 Hz, $-CH_2-O-$). The acid was identical (m.p., i.r., and mass spectrum) with a specimen of gibberellin A_{15} norketone prepared by oxidation of gibberellin A_{15} with osmium tetroxide–sodium metaperiodate.



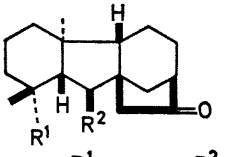
	R^1	R^2
(1)	CO_2H	CH_2
(2)	CO_2H	O
(3)	CH_2OH	O



	R^1	R^2
(4)	CHO	CO_2H
(5)	Me	CHO
(6)	Me	CH_2OH



(7)



	R^1	R^2
(8)	CO_2H	CH_2OH
(9)	CO_2H	CH_2OAc
(10)	$CONH_2$	CH_2OAc

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† All new compounds gave satisfactory elemental analyses, or accurate masses, and spectral data consistent with their structures.

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[4] B. E. Cross, K. Norton, and J. C. Stewart, *J. Chem. Soc.* (*C*), 1968, 1054.
[5] D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 1965, 181.