

THE IDENTIFICATION OF BAMBOO GIBBERELLIN IN PHASEOLUS MULTIFLORUS

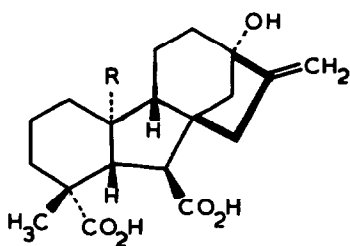
BY COMBINED GAS CHROMATOGRAPHY - MASS SPECTROMETRY

R.J. Pryce and J. MacMillan  
Department of Organic Chemistry  
The University, Bristol.

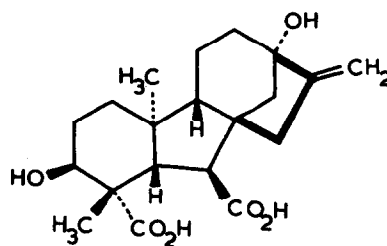
A. McCormick  
Department of Chemistry  
The University, Glasgow.

(Received in UK 17 August 1967)

We have recently described (1) the isolation of the new gibberellin  $A_{17}$  (I,  $R=CO_2H$ ) from immature seed of Phaseolus multiflorus and from its close relationship to Bamboo gibberellin (I,  $R=CHO$ ) (2) we anticipated the co-occurrence of these two gibberellins in P. multiflorus and Phyllostachys edulis (Bamboo). We now report the occurrence of Bamboo gibberellin in the seed of P. multiflorus.



(I)



(II)

Column chromatography of the crude acid extract from immature seed of P. multiflorus on celite:charcoal (2:1) has already been described (3). The total ion current trace of the methylated fraction 53, eluted with 62% acetone in water, is shown in the Figure. Scan 1 is unidentified and scans 2 and 4 corresponded to the methyl esters of gibberellins  $A_{17}$  and  $A_5$  respectively. Scan 3 was identical with the mass spectrum published (2) for Bamboo gibberellin methyl ester.

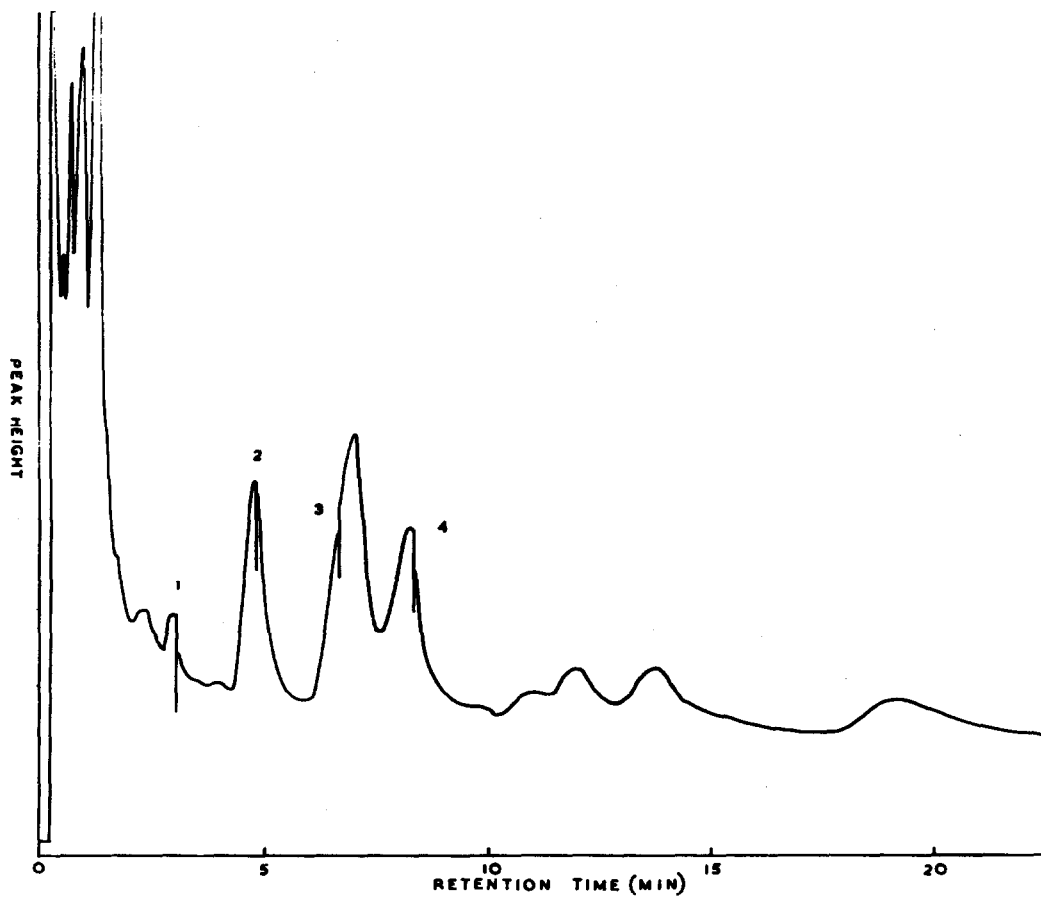


FIG. Total ion current trace of methylated fraction 53.

(1% QF-1 column, 6' x 1/8" i.d.; helium carrier gas at 30 ml./min.; isothermal at 190°)

Three C<sub>20</sub>-gibberellins have now been isolated from green plants, namely Bamboo (I, R=CHO), Lupinus-I (II) (4), and A<sub>17</sub> (I, R=CO<sub>2</sub>H) and all possess a 7-hydroxyl group in contrast to the fungal C<sub>20</sub>-gibberellins A<sub>12</sub>, A<sub>13</sub>, A<sub>14</sub>, and A<sub>15</sub>. 7-Hydroxylation may therefore occur at a much earlier stage in the biosynthesis in green plants than in G. fujikuroi (5,6,7) and this view is supported by the recent finding that (-)-kaurene is converted into steviol in Stevia rebaudiana (8,9). Similarly a comparison of the known C<sub>19</sub>-gibberellins suggests that in general 7-hydroxylation precedes oxidation in ring A in green plants but not in the fungus. A possible exception in the C<sub>20</sub>-gibberellins may be the unidentified gibberellin A<sub>x</sub> of citrus fruit and banana fruit if the statement (10) that it is the same as the unknown fungal gibberellin (Compound B) (11) can be substantiated because Compound B has recently (12) been identified as gibberellin A<sub>14</sub> by gas chromatography and combined gas chromatography - mass spectrometry.

---

G.c.-m.s. determinations were determined at the  
S.R.C. g.c.-m.s. unit at Glasgow University.

We thank the Science Research Council for a Research  
Studentship (to R.J.P.), and the Agricultural Research  
Council for financial support.

#### REFERENCES

1. R.J. Pryce and J. MacMillan, Tetrahedron Letters, in press.
2. N. Murofushi, S. Iriuchijima, N. Takahashi, S. Tamura, J. Kato, Y. Wada, E. Watanabe, and T. Aoyama, Agr. Biol. Chem. (Tokyo), 30, 917 (1966).
3. B.D. Cavell, J. MacMillan, R.J. Pryce, and A.C. Sheppard, Phytochemistry, 6, 867 (1967).
4. K. Koshimizu, H. Fukui, T. Kusaki, T. Mitsui, and Y. Ogawa, Tetrahedron Letters, 2459 (1966).
5. T.A. Geissman, A.J. Verbiscar, B.O. Phinney, and G. Cragg, Phytochemistry, 5, 933 (1966).
6. A.J. Verbiscar, G. Cragg, T.A. Geissman, and B.O. Phinney, Phytochemistry, 6, 807 (1967).
7. R.D. Bennett, E.R. Lieber, and E. Heftmann, Phytochemistry, 6, 1107 (1967).
8. J.R. Hanson, private communication.
9. B.E. Cross, in press.
10. R.A. Khalifah, Plant Physiol., 41, 771 (1966).
11. K.C. Jones, Ph.D. Thesis, University of California, Los Angeles, 1965.
12. K.C. Jones, C.A. West, and B.O. Phinney, Phytochemistry, in press.