Tetrahedron Letters,Vol.24,No.36,pp 3859-3860,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain 

# TYPHASTEROL (2-DEOXYCASTASTERONE) · A NEW PLANT GROWTH REGULATOR FROM CAT-TAIL POLLEN

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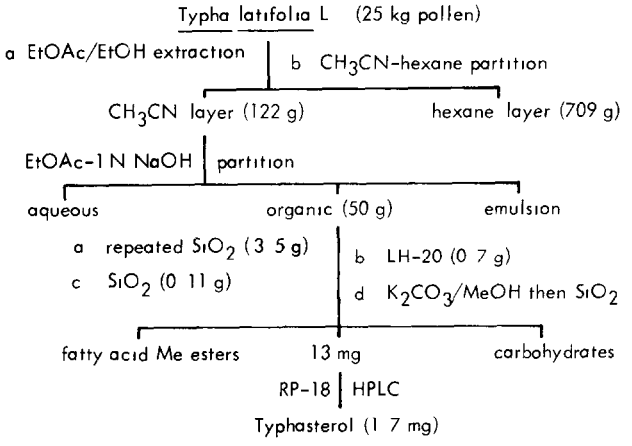
Summary Typhasterol, a new plant growth promoting substance from Typha latifolia L was determined to be (22R,23R,24S)-3α,22,23-trihydroxy-24-methyl-5α-cholestan-6-one

Since the isolation of brassinolide 1[1] from rape pollen, two other steroidal plant growth promoters, castasterone 2[2] and dolicholide 3[3] have been found in chestnut insect gall and Dolichos lablab seeds, respectively We had tried to isolated a new auxin from corn germ oil[4] by monitoring biological activity with the lamina joint tests[5] In this letter, we report the isolation of typhasterol 4 (2-deoxycastasterone) from cat-tail pollen utilizing this assay system (Scheme 1) Extraction of this pollen as well as the corn germ oil stimulate the growth of celely[6]



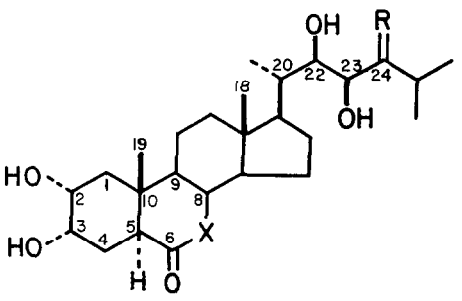

Scheme 1 Isolation of Typhasterol 4

Typhasterol (mp 227-230°C, from $CHCl_3$-MeOH) proved to be the first naturally occurring[7] 2-deoxy steroidal plant growth hormone FAB mass spectroscopy gave an ion at m/z 471 (M + Na, base peak) High resolution EI MS gave the molecular ion at m/z 448 3548 ($C_{28}H_{48}O_4$) and a base peak at m/z 348 2630 ($C_{22}H_{36}O_3$, C-22/23 cleavage + H-transfer)

The proton NMR (360MHz, $CDCl_3$) revealed two broad doublets ($W_{1/2}$=5 Hz, J=9 Hz) at 3 56

and 3.72 ppm, as well as methyl group resonances at 0 69 (s, 13-Me), 0 76 (s, 10-Me), 0 85, 0 92, 0 95, and 0 97 ppm (d, 20-, 24-, and 25-Me's) Since these values are identical (± 0 01 ppm) with those reported for 2[2], the same 22R, 23R, and 24S configuration can be assigned to the side chain The remaining two oxygens were accounted for by an axial C-3 hydroxyl group (3β-H 4 17 ppm, bs $W_{1/2}$= 8 Hz) and the 6-keto moiety (CD in $CH_2Cl_2$ $\Delta\varepsilon_{294}$ -2 2) Interestingly, in place of the usual double doublet pattern described for 5α-H in 1 ~ 3[2], a five line pattern centered at 2 76 ppm was observed (X part of an ABX system)[8] Furthermore, 5α-H exhibited long-range coupling to 10-Me (W-type) and 7α-H[9], thus verifying the trans A/B ring junction That this is not an artifact resulting from epimerization during isolation (Scheme 1) was demonstrated by obtaining the same material following a more tedious (repeated HPLC) isolation procedure

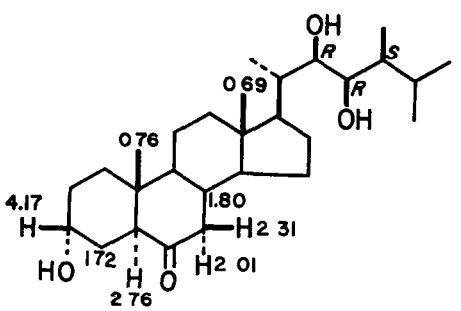
Typhasterol displayed similar activity to brassinolide in the rice lamina joint bending test[5] In addition to being of biosynthetic interest, it is worth noting that 4 retains plant growth promoting activity[6] despite the lack of a hydroxyl group at C-2




1 R = β-$CH_3$, H X = -$OCH_2$-

2 R = β-$CH_3$, H X = -$CH_2$-

3 R = $CH_2$ X = -$OCH_2$-

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Acknowledgement We thank Professor K Munakata for helpful discussion and Professor N Ikekawa for a sample of authentic 1 Physical measurements by Drs T Iwashita, J Pawlak, K Mizukawa, and H Naoki are gratefully acknowledged

References and Notes

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7 Both 4 and the ethyl analog of 4 have been synthesized by Professor Ikekawa and his coworkers
8 This pattern could be simulated with the following parameters $\nu_A - \nu_B$= 0, $J_{AB}$= 14, $J_{AX}$= 13, $J_{BX}$= 4 Hz
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(Received in Japan 27 April 1983)