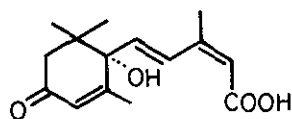


POTASSIUM TRANSPORT IN PLANT LEAVES;
SYNTHESIS OF ROSEOSIDE TETRAACETATE.

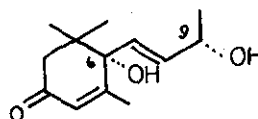
Kenneth L. Stuart and Yvonne G. Whittle,
Department of Chemistry, University of the West Indies,
Kingston 7, Jamaica.

The plant hormones vomifoliol and abscisic acid appear to be involved in the transport of potassium in plant leaves. A novel transport mechanism is proposed. The first synthesis of roseoside tetraacetate is reported.

It is now well established that potassium is intimately involved in the opening and closing of stomata in plants^{1,2,3} and two structurally related plant hormones, namely abscisic acid (1) and vomifoliol (2) are implicated^{4,5}.

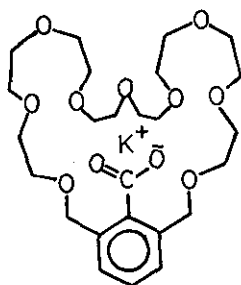


1

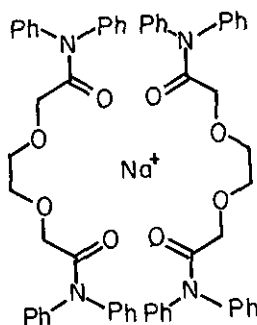


2

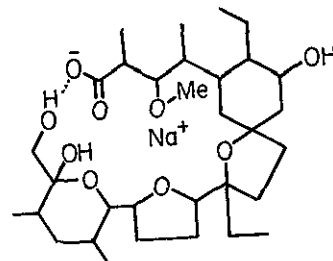
High ion selectivity has not only been realised by highly organised cryptates such as compound (3), but also demonstrated for open chain synthetic ether amides like compound (4)⁶. The role of hydrogen bonding can also be of importance in ion selectivity as was shown in the preparation of a selective transporting membrane⁷. Incorporation of the macrocyclic antibiotic monensin (5) into the membrane allowed sodium ions to be moved against a concentration gradient.



3

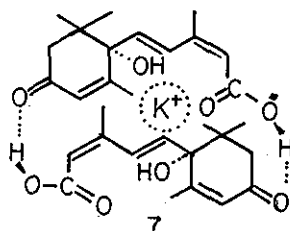
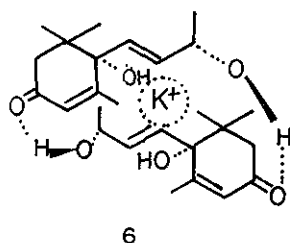


4



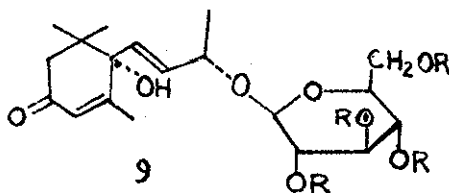
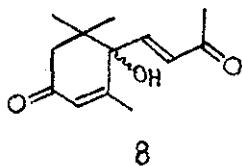
5

By invoking enzyme mediated head-to-tail hydrogen bonded dimers [(6), and (7)] it is possible with the aid of Corey-Pauling-Koltun molecular models to see how vomifolliol and cis-trans-abscisic acid respectively could be used in potassium transport in concert with a membrane bound light sensitive shuttle situated in leaf guard cells⁸. We now propose this novel transport mechanism in the leaves of plants.



As might be expected, the keto compound (8) and trans-trans-abscisic acid show no stomatal activity⁵.

Vomifoliol has been shown to occur widely in plants⁹, and the glycoside roseoside (9, R = H) has so far been isolated from Vinca rosea¹⁰, Betula alba, Cydonia oblonga and Chaneromeles japonica¹¹.



Because of the low solubility of vomifoliol in aqueous media at physiological pH values, we are of the view that vomifoliol may be transported as its glucoside to its site of action in the stomata and transformed by a β -glucosidase to the active compound (6). For this reason we synthesised a diastereomeric mixture of roseoside tetraacetate (9, R = Ac) for subsequent base hydrolysis to roseoside diastereomers. Vomifoliol (a mixture of the 6S - 9S, 6R - 9R, 6S - 9R and 6R - 9S diols) was first prepared from α -ionone by a method similar to that reported earlier¹². Although these compounds have been separated into their

racemic pairs by high speed liquid chromatography in small amounts¹³, we were unable to do this on the scale necessary for the subsequent glucosidation step.

Then a modified Koenig-Knorr reaction with β -bromoglucose¹⁴ was performed on the synthetic vomifoliol. Treatment of the product with pyridine/acetic anhydride followed by plc separation gave a non-crystalline but tlc homogeneous product (20% yield) that had NMR, MS, IR and UV data in good agreement with those of roseoside tetraacetate.

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