

## STERYL ACETATES IN *RHODODENDRON* WAXES

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**Key Word Index**—*Rhododendron*; Ericaceae; leaf wax; steryl acetates; sitosterol; stigmasterol; chemotaxonomy.

**Abstract**—Sitosteryl acetate was found to be a component of the leaf waxes of seven *Rhododendron* species. One species, *R. augustinii*, also contained stigmasteryl acetate.

### INTRODUCTION

Leaf surface waxes have been often examined as potential characters for chemical taxonomy, principally using the hydrocarbon fraction [1]. Other compounds found in these waxes include, aldehydes, ketones, acetates,  $\beta$ -diketones, primary and secondary alcohols, esters, various diterpenes and triterpenes including triterpene acetates [1–3]. Sterols have also been isolated from several waxes [3–5], but to our knowledge, the present communication represents the first description of the isolation of steryl acetates from a leaf wax. Such compounds, however, have been isolated from plants on one or two occasions [6].

### RESULTS AND DISCUSSION

*Rhododendron* leaf surface waxes, obtained by chloroform washing, were examined by TLC, GLC and, in some cases, by GC–MS. Most waxes contained hydrocarbons and triterpenoids plus other components whose distribution was more variable. In a few cases TLC demonstrated the presence of a component having the same  $R_f$  as stigmasteryl acetate ( $\text{CHCl}_3$  or petrol– $\text{CHCl}_3$ , 7:3). Examination of these fractions by GLC and GC–MS [7] confirmed the presence in six species of 24-ethyl-5-cholesten-3 $\beta$ -yl (sitosteryl or clonasteryl) acetate and in one species 24-ethyl-5,22(E)-cholestadien-3 $\beta$ -yl (stigmasteryl or poriferasteryl) acetate was also present. We have not determined the stereochemistry at C-24, but in the light of general experience of the occurrence of sterols in

plants it is probable that these two compounds are respectively sitosteryl acetate [24(R)isomer] and stigmasteryl acetate [24(S)isomer]. Sitosteryl acetate was present in the waxes from *R. megaratum* (13%), *R. cinnabarinum* (9%), *R. concatenans* (14%) and *R. keysii* (21%) (all sub-section Cinnabarina), *R. Manipurensis* (47%) (sub-section Madenia), *R. moupinense* (sub-section Moupinensia) (ca 5%) and *R. augustinii* (25%) (sub-section Triflora). The latter species also contained stigmasteryl acetate (16.5%). Several other species contained trace amounts of sitosteryl acetate.

The apparently very limited distribution of this class of compound in leaf waxes suggests that their role in chemical taxonomy will also be limited. The composition of the three members of the subsection Cinnabarina suggests a common origin for these species which is further confirmed by the presence in all three of the  $\beta$ -diketone nonacosane-8,10-dione and other as yet unidentified compounds, plus also a relative absence of triterpenoids. *R. augustinii* is clearly unique in its genetic composition and it would be interesting to investigate any known or suspected hybrids derived from it. No other members of the triflora (five were examined in all) contained detectable sterol and in fact this subsection is chemically heterogeneous. It would also be worthwhile examining species having a similar geographical origin to *R. manipurensis* and *R. moupinense* for steryl acetates since it is possible that the isolated occurrence of these compounds in such species may be due to derivation from a common original

gene pool. *R. manipurens* was the only species out of 8 members of the subsection *Maddenia* in which any steryl acetates could be detected. This species is considered by some authorities [8] to be identical with *R. maddenii*. However, steryl acetate could not be detected in the latter species and there is therefore some justification for maintaining two separate species, although it is possible that the example of *R. manipurens* in Edinburgh is a hybrid.

This report appears to be the first concerning the occurrence of significant amounts of steryl esters in leaf waxes. It seems pertinent to suggest that the location of such compounds known to occur in other species [6] be examined as it is possible that acetylation of sterols may be associated with their secretion on to the leaf surface.

#### EXPERIMENTAL

Rhododendron leaves were harvested from the Royal Botanic Garden, Edinburgh and were extracted by washing

with  $\text{CHCl}_3$  for 1 min. TLC, GLC and GC-MS analyses were as previously described [7]. Garden accession numbers were: *R. megeratum* (699558), *R. cinnabarinum* (380362), *R. concatenans* (250167), *R. keyssii* (698677), *R. manipurens* (754074), *R. Moupinense* (699651), and *R. augustinii* (698380).

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