

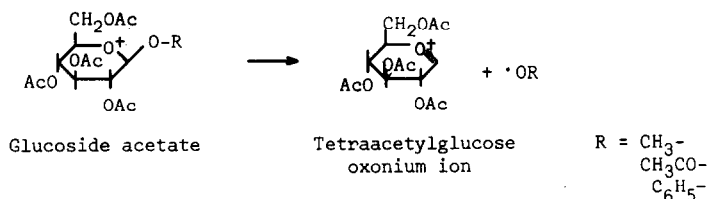
SOME OBSERVATIONS ON THE MASS SPECTROMETRY OF NATURAL
GLUCOSIDES AND THE STRUCTURE OF SALIREPOSIDE

I. A. Pearl and S. F. Darling

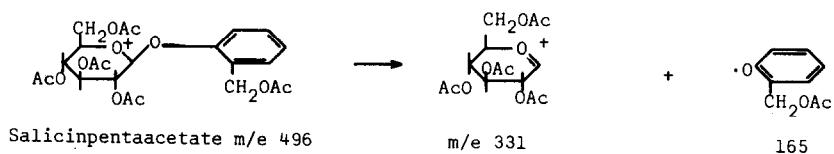
The Institute of Paper Chemistry, Appleton, Wis. 54911

(Received 23 February 1967)

In 1963 Biemann and co-workers (1) showed that glucosepentaacetate and simple glucoside acetates have mass spectra that indicate the molecular ion undergoes primary fragmentation at the C-1 bond as follows:



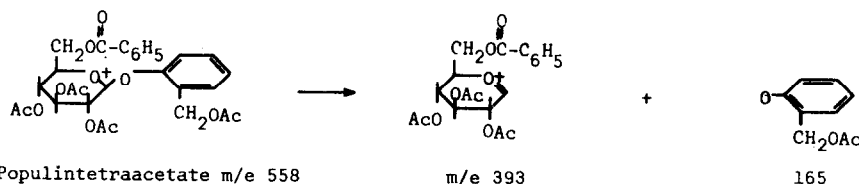
We have investigated the mass spectra of a number of natural glucoside acetates and find that in general the spectra of these acetates indicate a similar fragmentation pattern. For example, the mass spectrum of salicin pentaacetate shows a prominent line at m/e 331, the same line that Biemann found in the spectrum of glucosepentaacetate to which he assigned the oxonium ion identity as above. Because of the similarity between the mass spectra of glucosepentaacetate and salicinpentaacetate we believe that the fragmentation pattern of the two also are similar. The fragmentation of the salicinpentaacetate ion would then take place thus:



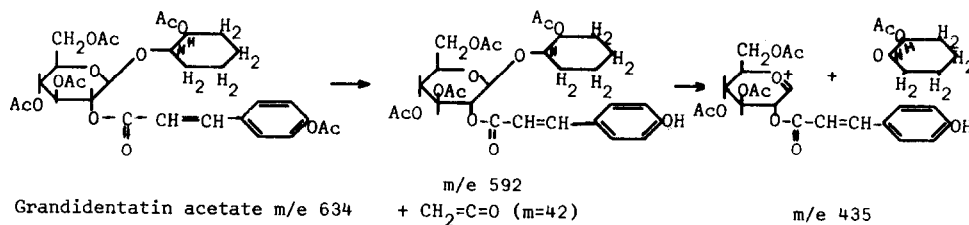
The same type of fragmentation pattern is also exhibited by salicyloylsalicin and salirepin (2) acetates. This would indicate that the basic fragmentation pattern is independent of the complexity and size of the aglucone.

Populin, tremuloidin, and salicyloyltremuloidin exhibit the same type of fragmentation pattern, but because of the presence of a benzoyl group in place of one of the acetyl groups on the

glucose moiety in these glucosides, the primary fragment has an m/e of 393 instead of m/e 331. This can be noted from the example of the fragmentation pattern for populintetraacetate.

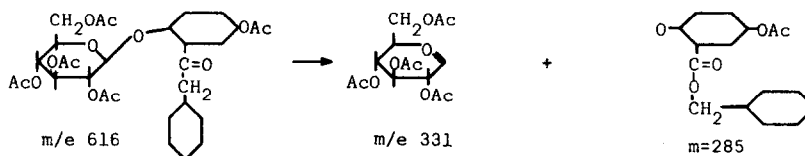


A slight deviation from this general primary fragmentation pattern is found in the case of the acetates of grandidentatin and 1-O-p-coumaroyl- β -D-glucose. The spectra of these substances show a line of low intensity at $M-42$ in addition to the major line that would be expected by rupture of the C-1 bond. We attribute this peak to the loss of one of the acetyl groups as ketene (mass 42) either before or concurrently with the rupture of the C-1 bond. In the case of grandidentatin acetate the fragmentation would look like this.



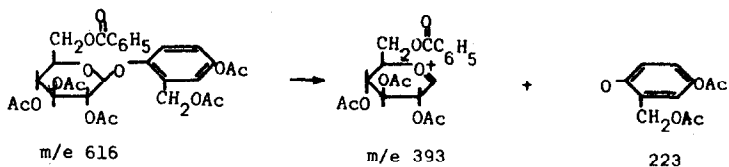
The loss of one acetyl group so readily is not unreasonable when one considers that in these compounds one acetyl group is situated on the p -hydroxyl of the coumaric acid group since it is well known that the peak representing loss of ketene is the base peak in the mass spectrum of phenyl acetate.

Among other glucoside acetates we have examined are those of trichocarpin and salireposide. Trichocarpin was shown to be the benzylester of gentisic acid glucoside by Loeschcke and Francksen (3) in 1963. Based on the behavior of the other glucosides one would expect the acetate of trichocarpin to fragment as follows.

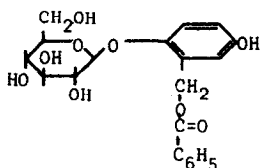


The mass spectrum of the acetate of trichocarpin is in complete agreement with this pattern.

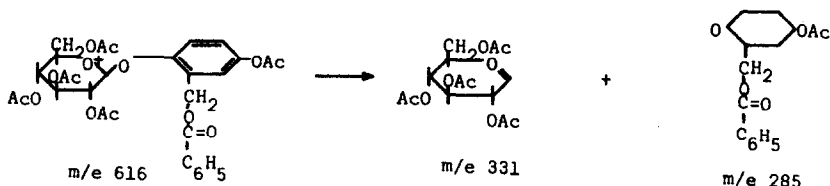
The mass spectrometric examination of salireposide acetate gave unexpected results. According to the structure reported by Thieme (4) in 1964, the acetate should show a prominent line at m/e 393 like other glucosides that have a benzoyl on the glucose moiety, thus;



However, the mass spectrum of salireposide acetate shows no trace of a line at this mass but does have a prominent line at m/e 331. This is strong evidence that the benzoyl group is not attached to the glucose part of the molecule but probably resides on one of the hydroxyls of the aglucone, gentisyl alcohol. Since salireposide exhibits properties of a free phenolic compound, the benzoyl group is more likely on the methylol group of the gentisyl alcohol. Accordingly, the structure of salireposide would be as follows:



and the fragmentation pattern of its acetate would take the following course.



We have been able to confirm this supposition by enzymatic hydrolysis of salireposide in such a manner as to rupture the molecule at the glucosidic linkage without disturbing the benzoyl ester bond. In this manner we have isolated glucose as one of the products of the hydrolysis and benzoylgentisyl alcohol as the other product. The benzoylgentisyl alcohol forms a nice crystalline diacetate melting at 62.5-63° and its mass spectrum is entirely consistent with its structure.

We are now in the process of examining other natural glucosides and their acetates by mass spectrometry, and several detailed papers in this field are in preparation.

REFERENCES

- (1) K. Biemann, D. C. DeJongh, and H. K. Schnoes, J. Amer. Chem. Soc. 85, 1763 (1963).
- (2) We have given the name salirepin to the compound heretofore known as debenzoylated salireposide. We have isolated this compound from certain bark extracts and believe a generic name like salirepin will be more convenient than the use of the complicated expression, debenzoylated salireposide.
- (3) V. Loeschcke, and H. Francksen, Naturwissenschaften 51, 140 (1964).
- (4) H. Thieme, Naturwissenschaften 51, 291 (1964).

All of our mass spectrograms were made by the Morgan Schaffer Corp. of Montreal, Quebec, Canada except those of 1-O-p-coumaroyl- β -D-glucose and its acetate which were made through the kindness of Mr. Will Major of the Perkin-Elmer Corp. of Norwalk, Conn.