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THE COMPOSITION OF KETONES AND SECONDARY ALCOHOLS FROM *BRASSICA OLERACEA* WAXES

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Abstract—The ketones and oxidised secondary alcohols from *Brassica oleracea* waxes have been examined by mass spectrometry. From the spectra it was possible to estimate the proportions of 14-nonacosanone and 15-nonacosanone and show that significant amounts of the other possible structural isomers were absent. In a variety of kale the secondary alcohols contained 38% 14-nonacosanol and the ketones contained 6% 14-nonacosanone.

INTRODUCTION

NONACOSANONE and nonacosanol have been widely recognised as constituents of *Brassica oleracea* waxes,[1–4] but the position of the functional group has been the subject of some disagreement. In the ketone fraction Purdy and Truter[3] found a mixture of 15-nonacosanone and 10-nonacosanone while Macey and Barber[4] found a mixture of 15-nonacosanone and 14-nonacosanone with traces of 13-nonacosanone and 12-nonacosanone. This last result was in agreement with Horn *et al.*[5] who found 15-nonacosanone with traces of other ketones. On the other hand Laseter *et al.*[6] imply that the ketone from cabbage leaf is pure 15-nonacosanone.

Sahai and Chibnall[2] found 15-nonacosanol in the leaves of brussels sprout, but later workers found that this fraction in other varieties of *B. oleracea* also contained 10-nonacosanol[3] or 14-nonacosanol with traces of 13-nonacosanol and 12-nonacosanol.[4]

Since there was some evidence of chemical degradation in Macey and Barber's[4] results, it seemed desirable to devise a new method for determining the position of the functional group in ketones and secondary alcohols of a given chain length. This paper reports such a method using mass spectrometry and gives the composition of some secondary alcohols and ketones from *B. oleracea* waxes.

RESULTS AND DISCUSSION

The mass spectra of synthetic 15-nonacosanone and gl_6 (a previously undescribed subglaucous mutant of marrow stem kale) secondary alcohol as the ketone are given in Fig. 1. The base peak in both cases is at $m/e = 225$ and is due to homolytic fission α-to the carbonyl group. It will be noted that gl_6 secondary alcohol gives rise to peaks of equal intensity at $m/e = 211$ and $m/e = 239$ which are insignificant or absent from the spectrum of synthetic

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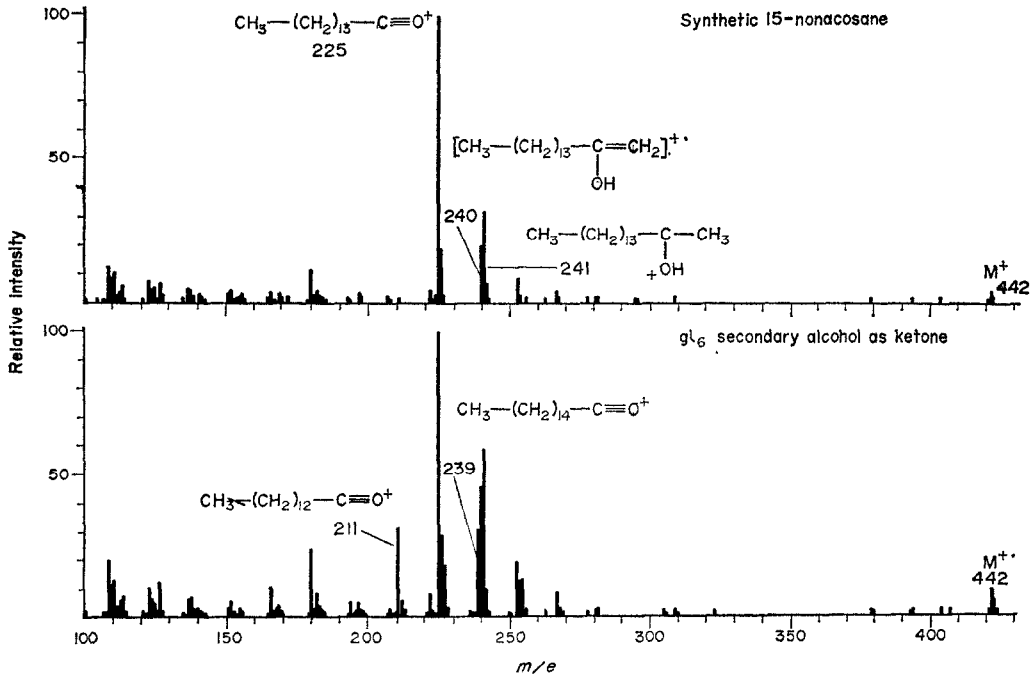

FIG 1. MASS SPECTRA OF SYNTHETIC 15-NONACOSANONE AND gl_6 SECONDARY ALCOHOL AS KETONE.

15-nonacosanone. These peaks are readily explained as the products of homolytic fission if it is assumed that gl_6 secondary alcohol contains 14-nonacosanol as well as 15-nonacosanol.

Table 1 gives the intensities of the peaks at $m/e = 211$ and $m/e = 239$ for ketones from various *B. oleracea* waxes, indicating the presence of 14-nonacosanone in each case.

TABLE 1. RELATIVE INTENSITIES OF PEAKS FROM MASS SPECTRA OF KETONES FROM *B oleracea* WAXES

	Relative intensities*	
	$m/e = 211$	$m/e = 239$
Synthetic 15-nonacosanone	1	–
Glaucous kale ketone	6	4
gl_6 Ketone	4	3
gl_6 Secondary alcohol as ketone	32	31

* m/e 225 = 100.

The mass spectra of the ketones listed in Table 1 were examined for peaks due to the homolytic fission of 13-nonacosanone, 12-nonacosanone and 10-nonacosanone but no evidence could be adduced for the presence of these compounds. Thus the maximum possible amounts of these compounds in the samples examined would be of the order of 1 %.

Assuming that only 14-nonacosanone and 15-nonacosanone are present the percentage composition of the ketones can be approximated from the formula:

$$\% \text{ 14-nonacosanone} = \frac{\text{relative intensity } 211 + \text{relative intensity } 239}{\text{relative intensity } 211 + \text{relative intensity } 225 + \text{relative intensity } 239} \times 100;$$

and similarly for 15-nonacosanone.

Using the figures given in Table 1 and correcting for the small peak at $m/e = 211$ found in synthetic 15-nonacosanone, the percentage compositions listed in Table 2 were calculated.

TABLE 2. COMPOSITION OF KETONES FROM *B. oleracea* WAXES

	% 15-Nonacosanone	% 14-Nonacosanone
Glaucous kale ketone	92	8
gl_6 Ketone	94	6
gl_6 Secondary alcohol as ketone	62	38

The glaucous kale ketone analysed above has been previously analysed by Macey and Barber.[4] They found 78% 15-nonacosanone and 16% 14-nonacosanone, the remaining 6% being 13-nonacosanone and 12-nonacosanone. In this and other chemical analyses a greater proportion of the shorter chain acids than expected, as well as some unidentified fatty acids[7] were found, suggesting chemical degradation of the acids during the alkaline hydrolysis of the amide. If this is the case, their value of 78% for the proportion of 15-nonacosanone would be an underestimate, thus indicating that the value of 92% given above is of the right order. Their value of 52% 15-nonacosanol[4] may also be an underestimate. The marked difference found between secondary alcohol and ketone is similar to that found here.

Laseter *et al.*[6] published a mass spectrum of the ketone from cabbage leaf (*B. oleracea* var. Round Dutch) which they imply to be pure 15-nonacosanone. An analysis of the spectrum by the method used above suggests that this ketone is actually a mixture containing approximately 15% 14-nonacosanone and 85% 15-nonacosanone.

The work of Kolattukudy *et al.*[8–10] has suggested that the ketones and secondary alcohols of *B. oleracea* waxes are formed by the specific oxygenation of a preformed chain, longer than C_{18}, at a position corresponding to C_{15} in the final product. If this is the case the mechanism could be desaturation followed by a fairly unspecific hydration to account for the 40% 14-nonacosanol that we have found. The ketone could then be formed from the secondary alcohol by a fairly specific dehydrogenation to give approximately 90% 15-nonacosanone. Chibnall and Piper[11] have previously suggested hydration of a double bond as a possible origin for the functional groups in ketones and secondary alcohols of *B. oleracea*.

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EXPERIMENTAL

The ketones and secondary alcohols were isolated from gl_6 wax by column chromatography on TLC silica gel.[12] An Et_2O solution of the secondary alcohols was shaken with acidified $K_2Cr_2O_7$[3] for 2 days to oxidise them to the corresponding ketones. Traces of unoxidised secondary alcohols were removed by preparative TLC. An Et_2O solution of the ketones was also shaken with acidified $K_2Cr_2O_7$[3] to remove contaminating aldehydes. The pure ketones were then recovered by eluting them from a florisil column with benzene. Both fractions were tested for purity by TLC and GLC prior to mass spectrometry. The glaucous kale ketone was a sample previously isolated by Macey and Barber[4] and the synthetic 15-nonacosanone was kindly supplied by Dr. R. Jaeger.

The spectra were obtained on an MS 12 Mass Spectrometer operating with an electron bombardment energy of 70 eV.

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