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Annemarie Wegmann, May 1978

analytical chemistry

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The fact that active sites in a mass spectrometer source can cause changed fragmentation patterns has been largely overlooked in the past. These sites can have several origins (*1*). In the case described here, marked effects were observed after the source of a MAT-711 double focusing mass spectrometer was electropolished (2) by a commercial company. After this treatment, the overall sensitivity increased, but changed fragmentation patterns were observed with various compounds such as free sterols and indole alkaloids.

To prove that the pattern change was due to active sites in the source, test substances were introduced via gold crucibles and different sample concentrations applied by gradually increasing the temperature of the solid probe rod. Drastic fragmentation changes were obtained with low sample concentrations (low temperature), but all spectra improved with increased sample concentration until they reached the originally known pattern (see Table I and bar-plots, Figures 1, 2, 3, and 4).

These results demonstrate that a larger number of molecules have to be present to cover the active sites in the source so as to yield a reproducibly satisfactory spectrum.

To minimize the effects of active sites when only very small amounts of sample material are available, perfluorokerosene (PFK) was tried as a "source filler" to increase the sample concentration in the gas phase. This added material ("source filler") seems to act by coating the active sites in the source, allowing more of the sensitive molecules to get ionized without

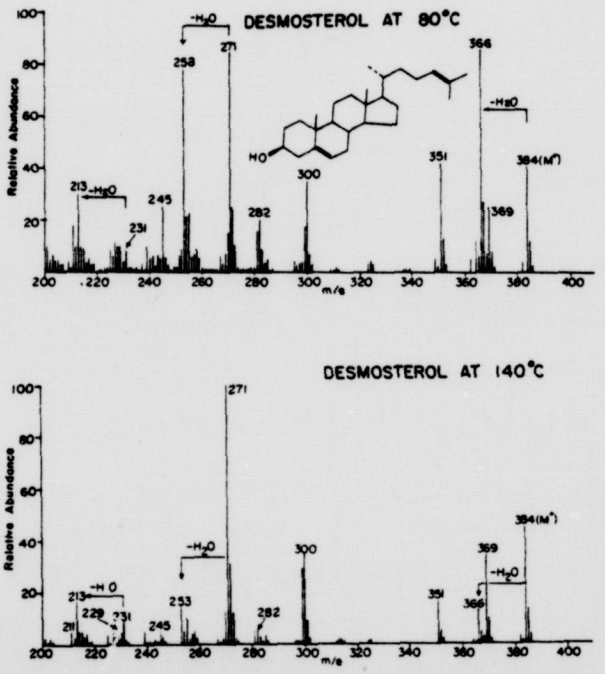

Figure 1. Mass spectra of desmosterol at 80 °C and 140 °C (low and high sample concentration)

Table I. Change of Ratio of Dehydration and Dehydrogenation at Various Sample Concentrations

Temperature, °C	Desmosterol		Cholesterol		Fucosterol	
	$M^+/M^+ - 18$	$M^+/M^+ - 2$	$M^+/M^+ - 18$	$M^+/M^+ - 2$	$M^+/M^+ - 18$	$M^+/M^+ - 2$
90	0.5	10.6	1.5	8.5	2	8.4
100	0.9	8.7	1.8	14.1	2.6	10.5
110	1.2	10.4	2.3	20	3.2	16
120	2.2	22	3	32	3.5	18.1
130	2.1	19.5	2.3	31	3.6	22.8
140	3.3	19.5	2.6	33.5	4.2	17.5[a]

[a] Could be thermal decomposition at this temperature.

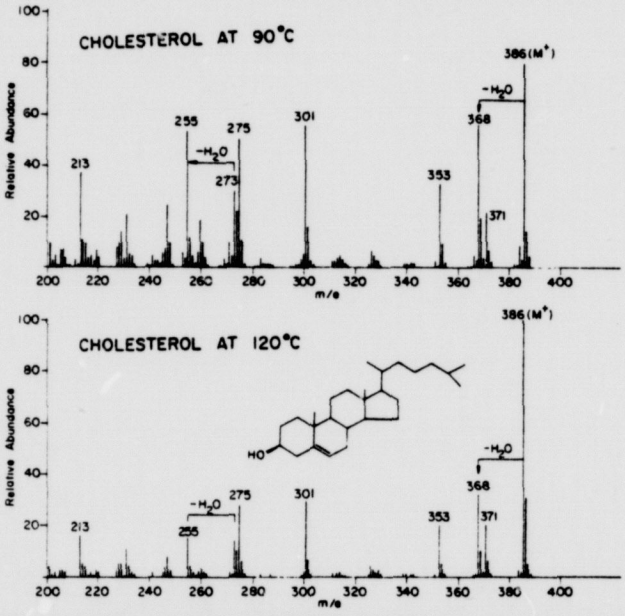

Figure 2. Mass spectra of cholesterol at 90 °C and 120 °C (low and high sample concentration)

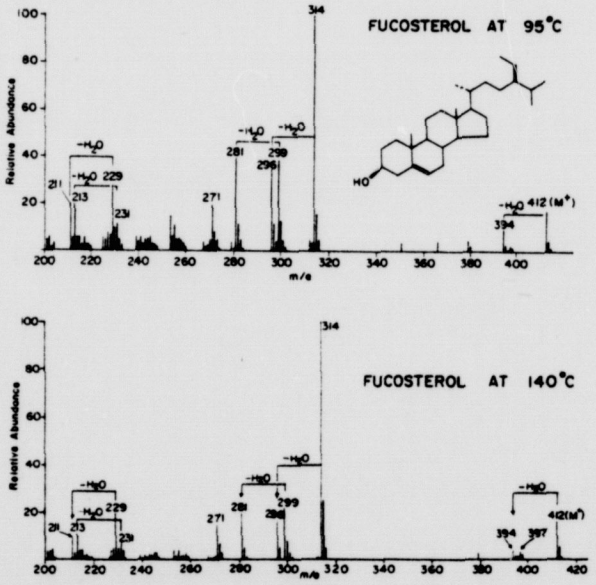

Figure 3. Mass spectra of fucosterol at 95 °C and 140 °C (low and high sample concentration)

decomposition. To check the effectiveness of different "source fillers", methyl stearate was also tried. The results of such treatment are shown in Table II.

These tables show that the addition of PFK caused a decrease of dehydration in all cases, and a decrease of dehydrogenation in all cases except for cholesterol at the lower concentrations (temperatures). The effects of the "source

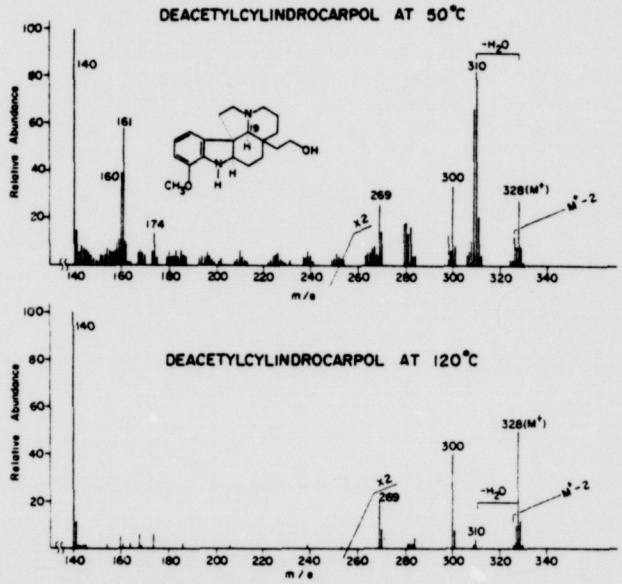

Figure 4. Mass spectra of deacetylcylindrocarpol at 50 °C and 120 °C (low and high sample concentration)

Table II. Dehydration and Dehydrogenation of Sterols with and without "Source Filler" at Concentration Extremes (Temperatures)

°C	Cholesterol	$M^+/M^+ - 18$	$M^+/M^+ - 2$
90	without "source filler"	1.5	8.5
90	PFK added	1.8	8.5
140	without "source filler"	2.6	33
140	PFK added	2.8	53

°C	Desmosterol	$M^+/M^+ - 18$	$M^+/M^+ - 2$
90	without "source filler"	0.5	10.6
90	Methyl stearate added	0.9	7.4
90	PFK added	0.9	12.9
140	without "source filler"	3.3	19.5
140	PFK added	4.3	28.7

filler" were most pronounced with Desmosterol. Adding methyl stearate showed a discrepancy in the dehydrogenation effect of sterols at 90 °C, and its effectiveness cannot be verified at higher temperatures because of its volatility.

To eliminate the possibility of ion source phenomena due to crucible surface effects, each comparative trial (with and without "source filler") was performed with the same crucible. The source pressure (3) was also maintained as constant as possible at readings between 4 and 5×10^{-6} Torr.

CONCLUSION

To determine small amounts of sensitive compounds, a source has to be totally inert. If active sites are present the

spectra quality decreases drastically. Dehydrogenation ($M^+ - 2$) and dehydration were observed in mass spectral data on free sterols and indole alkaloids. This problem was solved by repeated source silylation in the GC/MS mode, and/or by using perfluorokerosene (PFK) as a "source filler" for the solid probe mode. Since PFK as a "source filler" generally does not cause overlapping fragmentation patterns, it is an appropriate additive for such purposes, particularly when computerized background deduction is available.

ACKNOWLEDGMENT

The author is grateful to C. Djerassi for encouragement to publish these findings and for reading the manuscript.

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RECEIVED for review November 28, 1977. Accepted February 13, 1978. Work supported by the National Institutes of Health (RR-00612 and AM-04257).