MASS-SPECTROMETRIC CHARACTERISTICS OF THE MOLECULAR SPECIES OF COTTON-PLANT PHOSPHATIDYLCHOLINE

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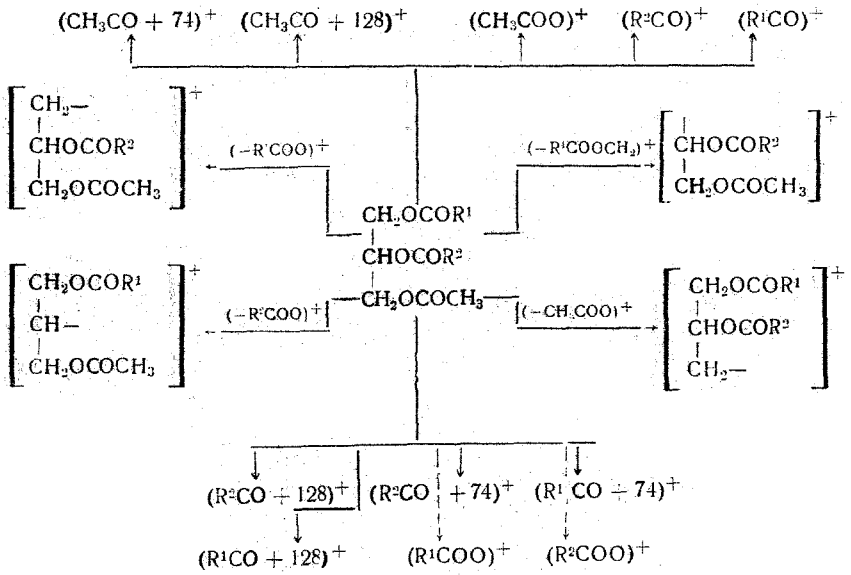
Investigations of the molecular species of phospholipids are necessary to elucidate their functions in the vital activity of cells.

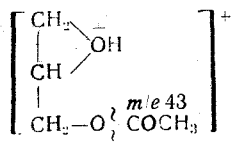
We have determined the molecular species of phosphatidylcholine (PC) by a combination of enzymatic hydrolysis and their separation on silver-treated plates in a thin layer followed by lipolysis of the subfractions obtained [1]. This method is complex and lengthy, and at the present time communications have appeared on the analysis of the molecular forms of phospholipids by a combination of GLC and mass spectrometry of the compounds in the form of their trimethylsilyl derivatives and acetates [2-5].

We have determined by the mass-spectrometric method the molecular species of the subfractions of the monoacetyldiglyceride derivatives of PC (monoenes, dienes, triens, and tetraenes) obtained by separating the monoacetyldiglycerides (MADGs) according to their degree of unsaturation on a silver-impregnated layer.

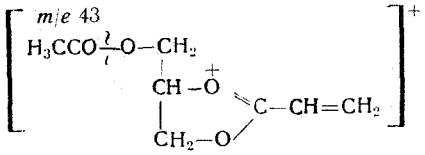


Scheme of the fragmentation of a monoacetyldiglyceride

The mass spectra of the MADGs were interpreted in the same way as suggested for triglycerides [6] and MADGs [3] according to the manner of their fragmentation. As can be seen from the scheme, the fatty acids were identified by the peaks of the corresponding ions $(M-R^{1,2}CO)^-$ and $(R^{1,2}CO)^+$. The fatty acids in position 2 were identified from the $(R^2OCOCH-CH_2-OCOCH_3)^+$ ion. In addition to the ion with m/e 43 $(CH_3CO)^+$, there were two peaks with m/e 117 and 171



74 + 43 = 117



43 + 128 = 171

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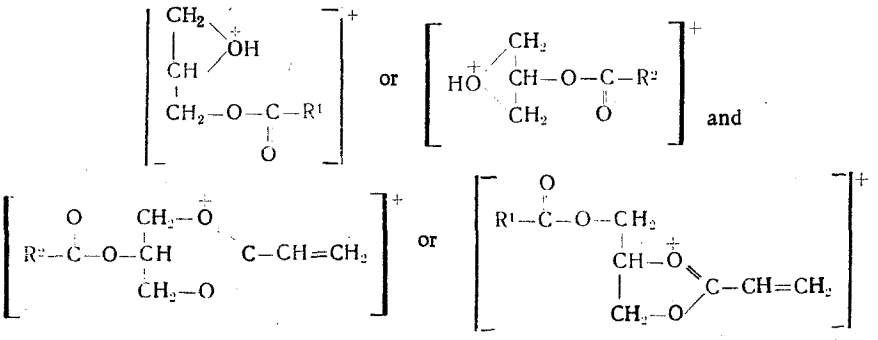
characteristic and common for all molecular species, and the presence of the peaks of $(RCO^{1,2} + 74)^+$ and $(RCO^{1,2} + 128)^+$



characterizes the bond of the fatty acids with the glycerol moiety.

Below we give the mass spectra of the subfractions (the mass numbers of the ions are given in m/e and the intensities in percentages relative to the maximum peak are shown in parentheses).

Tetraenic subfraction: 658 (100); 640 (2); 599 (11); 391 (2); 379 (70); 377 (10); 363 (2); 337 (19); 263 (55); 171 (21); 117 (75); 43 (84), which corresponds to the molecular species 3-acetyl-1,2-dilinoleoylglycerol (M^+ 658).

Trienic subfraction: 660 (100); 658 (58); 642 (6); 601 (23); 599 (6); 393 (6); 381 (75); 379 (37); 365 (6); 339 (5); 171 (6); 117 (6); and 43 (60). These results correspond to the following molecular ions: 3-acetyl-2-linoleoyl-1-oleoylglycerol (M^+ 660) and 3-acetyl-1,2-dilinoleoylglycerol (M^+ 658).

Dienic subfraction: 662 (3); 644 (2); 636 (2); 634 (7); 618 (2); 616 (4); 575 (12); 395 (11); 383 (21); 381 (100); 379 (84); 369 (5); 367 (2); 355 (70); 339 (2); 313 (4); 267 (3); 239 (19); 171 (10); 117 (34); and 43 (60). These results correspond to the following molecular ions: 3-acetyl-2-linoleoyl-1-stearoylglycerol (M^+ 662), 3-acetyl-2-oleoyl-1-palmitoylglycerol (M^+ 636), and 3-acetyl-2-linoleoyl-1-palmitoylglycerol (M^+ 634).

Monoenic subfraction: 662 (2); 644 (3); 636 (8); 634 (3); 618 (10); 616 (4); 603 (3); 577 (50); 381 (69); 379 (80); 367 (4); 365 (3); 355 (100); 341 (1); 339 (10); 313 (10); 265 (61); 171 (26); 117 (70); 43 (85). These results correspond to the following molecular ions: 3-acetyl-2-oleoyl-1-palmitoylglycerol (M^+ 634), 3-acetyl-2-oleoyl-1-palmitoylglycerol (M^+ 636), and 3-acetyl-1,2-dioleoylglycerol (M^+ 662).

When a species was the main one, it gave the M^+ 100% peak (tetranes and trienes), and when there were several species in the subfractions, we again observed the presence of the molecular ions (dienes and monoenes), but here the main species gave a stronger peak than the others.

The investigations showed that by the mass-spectrometric method it is possible to establish the nature of the subfractions qualitatively and to determine a number of molecular species differing from one another.

The subfractions of the monoacetyldiglycerides were obtained by a method described previously [1]. The mass spectra were recorded on an MKh-1303 instrument fitted with a system for direct introduction of the sample into the ion source at 150-160°C and an ionizing voltage of 40 V.

SUMMARY

The quantitative identification of the molecular species of phosphatidylcholine in the form of their monoacetyldiglycerides has been performed by a mass-spectrometric method.

LITERATURE CITED

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2. M. Barber and T. O. Merren, Tetrahedron Lett., 18, 1063 (1964).
3. Hasegawe Kiyozo and Suzuki Tatsuga, Lipids, 8, 631 (1973).