

Mass Spectrometry of Glyceryl Ether Diesters

Four glyceryl ether diesters were synthesized, purified by capillary gas chromatography, and their mass spectra studied. β Glyceryl ether diesters give intense ions corresponding to the loss of an acyloxy-methylene group from the molecular ion. α Glyceryl ether diesters give typical ions of the type

$[\text{CH}_2=\text{O}^+-\text{R}]$. Several other fragments in the mass spectra serve to distinguish between α and β glyceryl ethers. Characteristic ions reflecting the chain length of the acid and the ether moieties are also observed. No molecular ion was present.

In the course of a study on the radiolysis of simple triglycerides, a group of compounds were identified as glyceryl ether diesters. These compounds appear to be formed upon recombination of certain free radicals induced by radiation. The widespread presence of naturally occurring glyceryl ethers both free and in the form of their fatty acid diesters was previously demonstrated (Hallgren and Larsson, 1962). The present study was undertaken to evaluate mass spectrometry as a means of identifying individual glyceryl ether diesters and of determining the position of the ether group on the glycerol molecule. For this purpose the two positional isomers of both pentyl dihexanoin and hexyl dihexanoin were synthesized and their mass spectra studied.

EXPERIMENTAL

Synthesis. α and β glyceryl mono-ethers were prepared according to the method of Wood and Snyder (1967) except that HCl was used to cleave the blocking agents. The glyceryl mono-ethers were then esterified with a slight excess of hexanoyl chloride. The resulting glyceryl ether diesters were purified by gas chromatography, using a 250 ft \times 0.02 in. silicone SE-30 column operated at 220° C with a carrier gas flow rate of 15 ml/min. The capillary column provided excellent separation of traces of isomeric contaminants from the compounds studied. Under these conditions, 1-pentyl and 2-pentyl dicaproin eluted after 21.5 and 22.5 min, respectively, while 1-hexyl and 2-hexyl dicaproin eluted after 27.5 and 28.3 min, respectively. The structure of all four alkyl glycerides was confirmed by infrared analysis. Characteristic absorption bands identical to those reported by Baumann and Ulschöffer (1968) were observed.

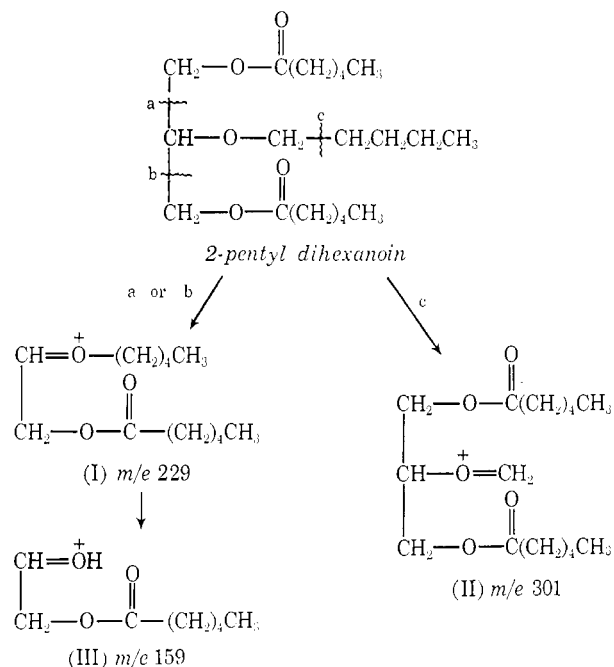
Analysis. Mass spectrometric analysis was conducted in a Hitachi Perkin-Elmer gas chromatograph-mass spectrometer, Model RMU-6A in which 50% of the effluent from the gc column was admitted *via* a heated line to a Biemann separator and then into the ion source. Both the heated line and the separator were maintained at a temperature of 220° C. The source was operated at 80 eV and the ionization chamber maintained at 250° C. A source slit opening of 0.2 mm was used. The electron multiplier was operated at 2000 V and the collector slit was 0.15 mm. A scanning time of 12 sec was used. The instrument gain was 10,000. Samples were introduced into the mass spectrometer *via* the silicone capillary column under the conditions described above.

RESULTS AND DISCUSSION

The mass spectra of the four glyceryl ether diesters are shown in Figure 1. The fragmentation patterns of these compounds are characteristic and involve principal fragmen-

tation processes of both glycerides and alkyl ethers. The position of the ether moiety on the glycerol can be established based on mass spectral data.

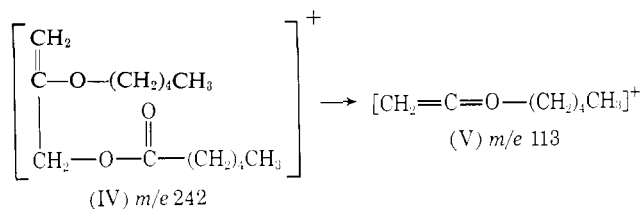
β Ethers. As typical of unsymmetrical ethers (Budzikiewicz *et al.*, 1967) α -cleavage of the molecular ion is a favored decomposition mode, which can give rise to two ions depending upon the site of the α -bond fission. Thus the 2-alkyl dihexanoin gives ions I (m/e 229 for the 2-pentyl diglyceride and m/e 243 for the 2-hexyl diglyceride), and II



(m/e 301 for both compounds). The peak at m/e 229 is quite intense since species I can arise from fission at two locations (a and b) both of which are favored over cleavage at c. As in alcohols, the more highly substituted fragment is lost preferentially. Further decomposition of ion I with rearrangement of a hydrogen atom produces fragment III at m/e 159 in the spectra of both the 2-pentyl and the 2-hexyl diglycerides. This mechanism is confirmed by the presence of a metastable peak at m/e 110.40 in the spectrum of 2-pentyl hexanoin and at m/e 104.04 in the spectrum of 2-hexyl hexanoin. These values are identical to the calculated values corresponding to metastable transitions $229 \rightarrow 159^+$ and $243 \rightarrow 159^+$ (Beynon *et al.*, 1965).

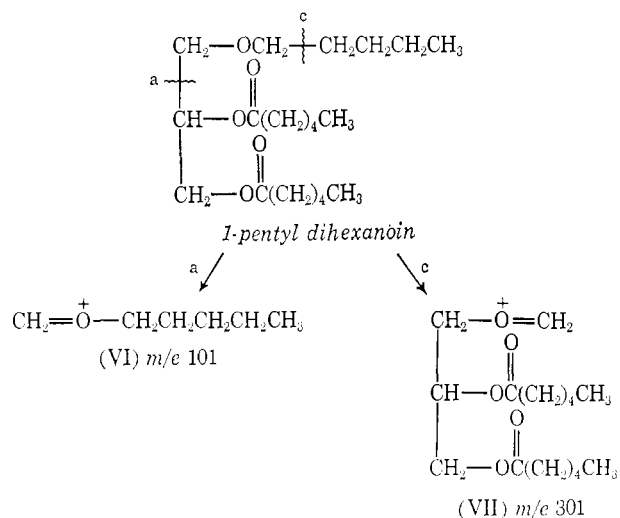
The loss of hexanoic acid from the molecular ion of 2-pentyl dihexanoin produces the peak at m/e 242 (256 for the

hexyl diester) due to the ion IV which would preferentially undergo α -cleavage to give



the peak at *m/e* 113 (127 for the hexyl diester) representing ion V. This fragment (*m/e* 113) may alternatively arise from the loss of hexanoic acid from ion I (*m/e* 229). The small peaks at *m/e* 143 and *m/e* 127 in the spectrum of 2-pentyl dihexanoin may arise from the loss of an acyl [$\text{CH}_3(\text{CH}_2)_4\text{CO}$] and the loss of an acyloxy [$\text{CH}_3(\text{CH}_2)_4\text{COO}$] group, respectively, from the ion IV (*m/e* 242).

α Ethers. If the ether group is located in the primary position of the glycerol, α -cleavage at (a) produces ion VI (*m/e* 101 for the 1-pentyl diglyceride and *m/e* 115 for the 1-hexyl diglyceride).



The less preferred fission at (c) produces the small fragment VII at *m/e* 301 for both compounds.

The peak at *m/e* 242 (M-RCOOH) is more pronounced in the 1-pentyl dihexanoin than in the 2-pentyl isomer. Loss of an acyl group from this fragment may produce the intense peak at *m/e* 143 (*m/e* 157 for the hexyl diglyceride), and loss of the acyloxy group gives the peak at *m/e* 127 (141 for the hexyl diglyceride).

Fragments Common to Both α and β Ethers. The peak at *m/e* 71 corresponds to the alkyl ion [$\text{CH}_3(\text{CH}_2)_4$] $^+$. This fragment is more intense in the pentyl diglycerides since it results from both the acid and the ether moieties. In the hexyl dihexanoin the peak at *m/e* 71 corresponds to the alkyl ion from the acid moiety, while a fragment at *m/e* 85 represents the alkyl ion from the ether moiety.

For all four compounds the base peak at *m/e* 99 represents the acylium ion [$\text{CH}_3(\text{CH}_2)_4\text{CO}$] $^+$. The loss of an acyloxy group from the molecular ion [$\text{M}-\text{RCOO}$] $^+$, as is common in the fragmentation of triglycerides (Barber *et al.*, 1964), gives ions at *m/e* 243 for the pentyl diglycerides and *m/e* 257 for the hexyl diglycerides.

The peak at M-56 is due to McLafferty rearrangement and is analogous to the rearranged methyl acetate ion peak at *m/e* 74 in the spectra of methyl esters (Budzikiewicz *et al.*, 1967). The fragment is formed on 2,3-cleavage with simultaneous migration of one hydrogen atom from the fragment lost. A

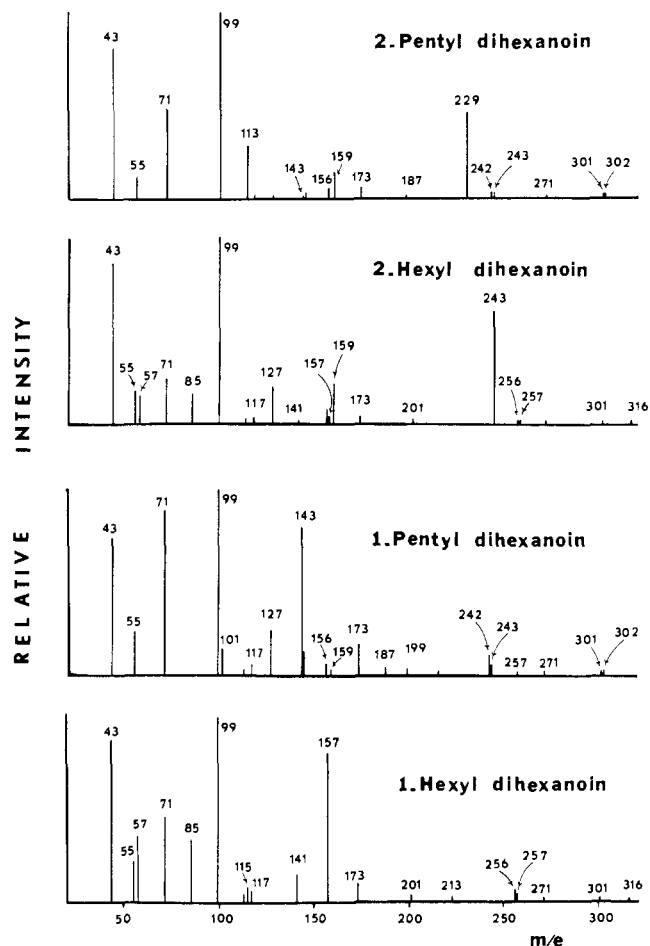


Figure 1. Mass spectra of glyceryl ether diesters

similar rearrangement involving the loss of 56 mass units from the [$\text{M}-\text{RCOO}$] $^+$ ion results in the formation of the peaks a *m/e* 187 and *m/e* 201 in the spectra of the pentyl and hexyl diglycerides, respectively.

The peak at *m/e* 271 represents the loss of the ether alkoxy group [$\text{M}-\text{RO}$] $^+$ from the molecular ion of all four compounds. The peak at *m/e* 173 corresponds to the ion [$\text{RCO} + 74$] $^+$ typical in the spectra of triglycerides (3), and the peak at *m/e* 117 represents the rearrangement ion [$\text{CH}_3(\text{CH}_2)_4\text{COO} + 2\text{H}$] $^+$ typical of hexanoate esters (Sharkey *et al.*, 1959).

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