

2-Alkylcyclobutanones From the Radiolysis of Triglycerides

ABSTRACT

A cyclic compound was isolated from the radiolytic products of each of the simple triglycerides containing C_6 , C_8 , C_{10} , C_{12} , C_{14} , C_{16} and C_{18} fatty acids. In each case the compound was identified as the 2-alkylcyclobutanone of the same carbon number as the precursor fatty acid. A mechanism is proposed for the production of these compounds which involves the formation of a six-membered ring intermediate, cyclization and cleavage at the acyl-oxy bond.

In the course of a recent investigation on the radiolysis of tricaproin, an odorous compound was isolated which eluted after *n*-hexanal on SE-30 gas chromatograph (GC) columns, and

gave rise to a mass spectral pattern very similar to that of hexenal. Aldehydes with the same chain length as the triglyceride fatty acids and possessing an additional double bond had been tentatively identified by Dubravcic and Nawar (1) in seven higher triglycerides which were irradiated at 6 Mrads and 25 C. However when attempts were made to determine the position of unsaturation by ozonolysis in the compound isolated from tricaproin, it was discovered that this compound did not contain a double bond. The compound was finally identified conclusively as 2-ethylcyclobutanone. Its retention on two different GC columns, and its IR and mass spectra (shown in Figure 1) were identical to those of an authentic sample synthesized in the laboratory by the method of Hanach and Herterich (2).

The corresponding compounds were conse-

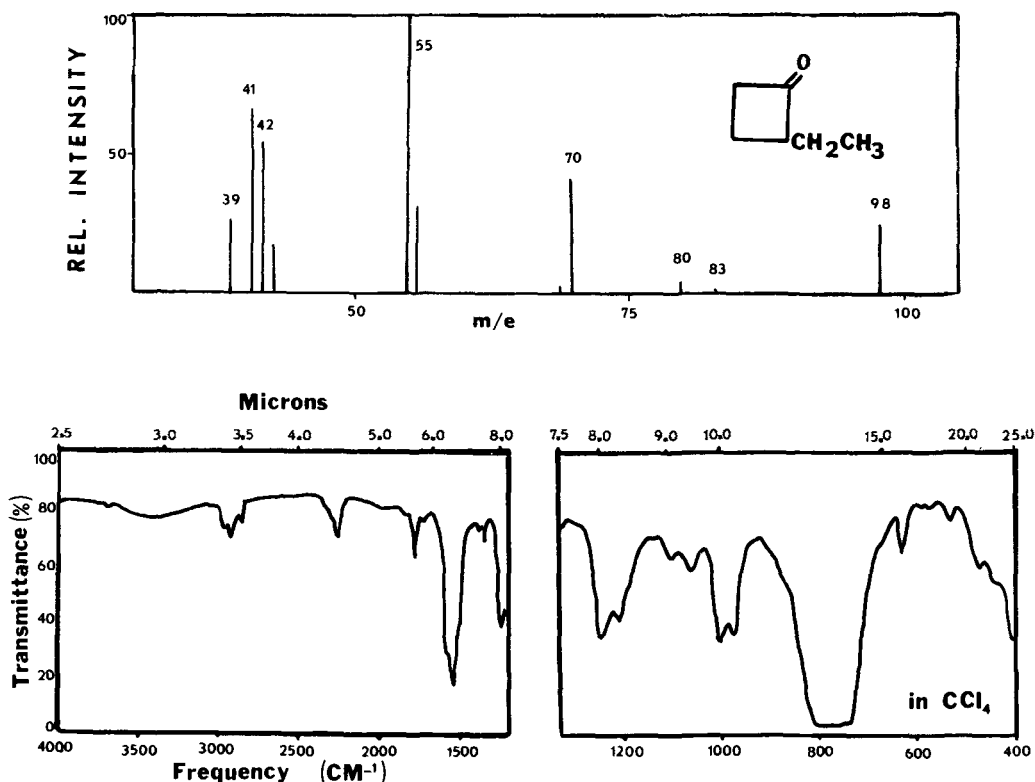
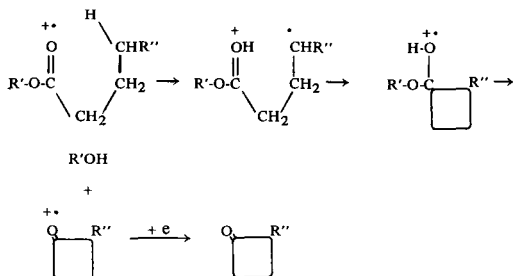


FIG. 1. Mass and IR spectra of 2-ethylcyclo-butanone.

quently isolated from the radiolytic products of the simple triglycerides tricaprylin, tricaprin, trilaurin, trimyristin, tripalmitin and tristearin. The triglycerides were irradiated and analyzed as previously described by Nawar et al. (3), and in each case the compound eluting on SE-30 immediately following the *n*-alkanal of the same chain length as the triglyceride fatty acid was subjected to IR and mass spectral analyses. In addition the compound recovered from tripalmitin was analyzed by NMR and that recovered from trimyristin was analyzed by high resolution mass spectrometry. All of these compounds, which were previously suspected of being unsaturated aldehydes, were found to be 2-alkylcyclobutanones of the same carbon number as the esterified fatty acid. Tributyrin did not yield a cyclobutanone upon irradiation.

It is proposed that these compounds may result from cleavage at the acyl-oxy bond via the formation of a six-membered ring intermediate as follows:



R' is the glyceryl moiety plus two acyl groups, and R'' is the remainder of the fatty acid chain. This pathway is similar to the mechanism leading to the formation of methylcyclobutanol in the photolysis of 2-pentanone (4).

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REFERENCES

1. Dubravcic, M.F., and W.W. Nawar, *JAACS* 45:565 (1968).
2. Hanach, M., and I. Herterich, *Tetrahedron Letters* 32:3847 (1966).
3. Nawar, W.W., J. Champagne, M. Dubravcic and P. LeTellier, *J. Agr. Food Chem.* 17:645 (1969).
4. Ausloos, P., and R.E. Rebbert, *J. Am. Chem. Soc.* 83:4897 (1961).

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Phospholipids of Fish Gills

ABSTRACT

Lipids were extracted from gill filaments of nine species of fish. Individual phospholipids as a percentage of the total were determined. These data revealed a pattern which did not appear to vary between pre- and postspawning salmon or among fish living at greatly differing ocean depths.

During two expeditions of the R/V Alpha Helix we had the opportunity to analyze individual phospholipids in gills of several species of fish. The gill primarily functions in respiration and osmoregulation, i.e., transport of gases and ions across membranes. Pink and coho salmon (*Oncorhynchus gorbuscha* and *O.*

kisutch) were netted in coastal waters of British Columbia. Kelp bass (*Paralabrax clathratus*), sand bass (*P. maculatofasciatus*), whitefish (*Caulolatilus princeps*), and sheepshead (*Pimelometopon pulchrum*) were caught with hook and line in 25-50 m water off Isla de Guadalupe (Mexico). Pacific rattail (*Corphaenoides acrolepis*), flatnose codling (*Antimora rostrata*), and sablefish (*Anaplopoma fimbria*) were caught by sunken traps or lines which were subsequently released to the surface from depths of 2000-3000 m. Sablefish were caught off San Diego, the other two species near Isla de Guadalupe.

Gills were removed immediately from the freshly caught fish. Gill filaments were clipped from the arches with surgical scissors and then extracted with chloroform-methanol 2:1 v/v by the method of Folch et al. (1). Phospholipids in the extracts were isolated by silicic acid column