

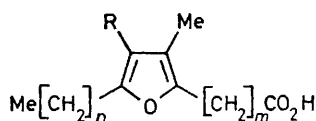
Synthesis of a Fish C₂₀ Furanoid Fatty Acid from the Lipid Extract of the Latex of the Rubber Plant (*Hevea brasiliensis*)

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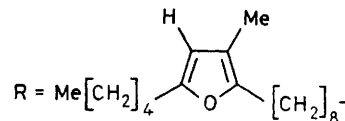
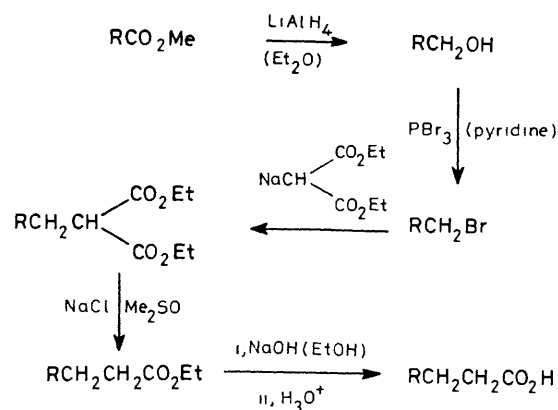
Summary 10,13-Epoxy-11-methyloctadeca-10,12-dienoic acid, isolated from the latex of the rubber tree, was chain-extended by two carbons to give the naturally occurring 12,15-epoxy-13-methyleicosa-12,14-dienoic acid in high yield.

FURANOID fatty acids (1—8) are not found in seed oils, but occur in high concentrations in the lipid extracts of the liver and testes of certain fish species during spawning.¹ The role of this unique class of fatty acids in nature remains vague; however, these compounds are believed to be associated with the reproductive system or sexual maturity of the fish. Recently the triglyceride fraction of the latex of the rubber tree (*Hevea brasiliensis*) was reported to contain more than 90% of a single C₁₈ furanoid fatty acid, *viz.* 10,13-epoxy-11-methyloctadeca-10,12-dienoic acid (2)²



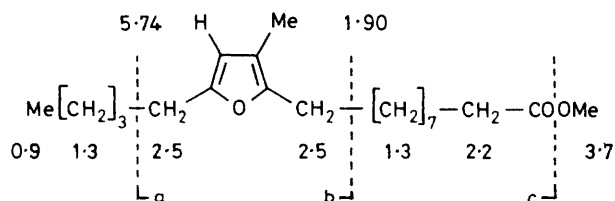
	<i>n</i>	<i>m</i>	R
(1)	2	8	Me
(2)	4	8	H
(3)	4	8	Me
(4)	2	10	Me
(5)	4	10	H
(6)	4	10	Me
(7)	4	12	H
(8)	4	12	Me

In an effort to produce pure furanoid fatty acids for detailed physical, chemical, and biochemical studies, Lie Ken Jie and Lam,³ and Gunstone *et al.*⁴ have synthesised series of disubstituted furanoid fatty acids for such purposes. Schlenk *et al.*⁵ have lately reported the total synthesis of the acids (5) and (6).



SCHEME

Since the acid (2) is available from the latex of the rubber tree, the extension of the chain by 2 carbons would readily lead to the production of the acid (5) in large quantities (Scheme). Thus, the methyl ester of (2) was treated with lithium aluminium hydride in anhydrous diethyl ether to give the corresponding furanyl alcohol (100% yield). Bromination of the latter with PBr₃ in pyridine allowed complete conversion of the alcohol into the bromide (46% yield). The reaction of sodio diethyl malonate with the derived bromide gave the furanyl diester (85%) which was decarboxylated in a mixture of dimethyl sulphoxide and sodium chloride under reflux



Methyl ester of (5) showing ^1H n.m.r. assignments (δ). Mass spectral analysis: fragment (m/z), M^+ = 350 (30%), a = 293 (10), b = 165 (100), c = 319 (5).

yielding the ethyl ester of the acid (5) (97%).⁶ Base hydrolysis of the ethyl ester furnished the required (5).

The methyl ester derivative of (5) exhibited ν_{max} (cm^{-1}): 3100w, (C-H, furan), 1740s, (C=O ester), and 1010m, (furan ring breathing).

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¹ R. L. Glass, T. P. Krick, and A. E. Eckhardt, *Lipids*, 1974, **9**, 1004; R. L. Glass, T. P. Krick, D. M. Sand, C. H. Rahn, and H. Schlenk, *ibid.*, 1975, **10**, 695; R. L. Glass, T. P. Krick, D. L. Olson, and R. L. Thorson, *ibid.*, 1977, **12**, 828.

² H. Hasma and A. Subramaniam, *Lipids*, 1978, **13**, 907.

³ M. S. F. Lie Ken Jie and C. H. Lam, *Chem. Phys. Lipids*, 1977, **20**, 1; 1978, **21**, 275.

⁴ F. D. Gunstone and R. C. Wijesundera, *Chem. Phys. Lipids*, 1979, **24**, 193.

⁵ C. H. Rahn, D. M. Sand, Y. Wedmid, H. Schlenk, T. P. Krick, and R. L. Glass, *J. Org. Chem.*, 1979, **44**, 3420.

⁶ A. P. Krapcho and A. J. Lovey, *Tetrahedron Lett.*, 1973, 957.