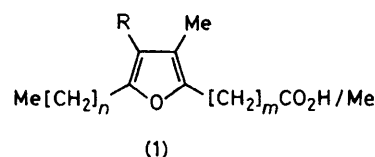


## Conversion of Linoleic and Latex Furanoid Acid to Fish C<sub>18</sub> Dimethyl Furanoid Isomers

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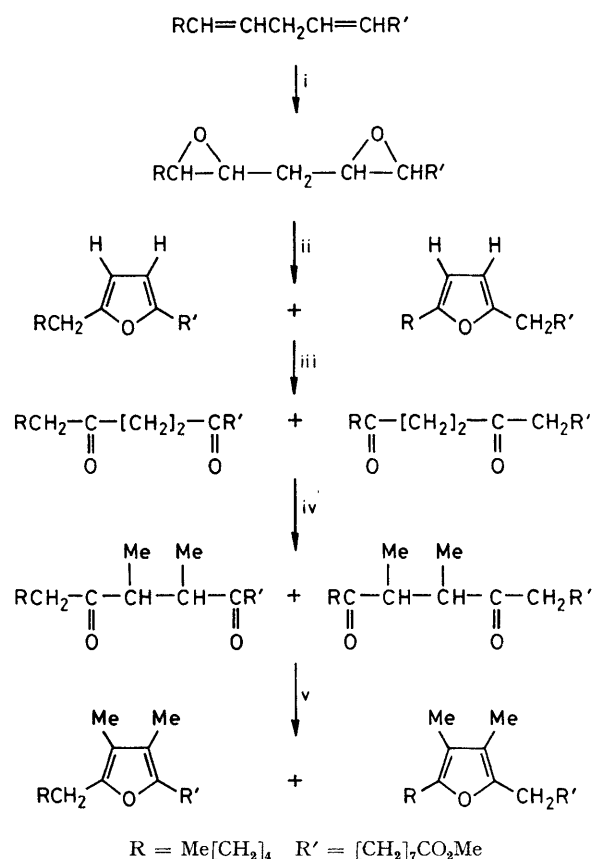
**Summary** Methyl 9(10),12(13)-dioxo-octadecanoate (derived from methyl linoleate) and 10,13-dioxo-11-methyloctadecanoate (derived from the latex of the rubber plant) were methylated at the methylene carbons located between the two oxo-groups (using MeI, KOH in DMSO) and cyclodehydration furnished a mixture of methyl 9(10),-12(13)-epoxy-10(11),11(12)-dimethyloctadeca-9(10),11(12)-dienoates and methyl 10,13-epoxy-11,12-dimethyloctadeca-10,12-dienoate respectively.



R = H, Me; n = 2 or 4; m = 8, 10, or 12

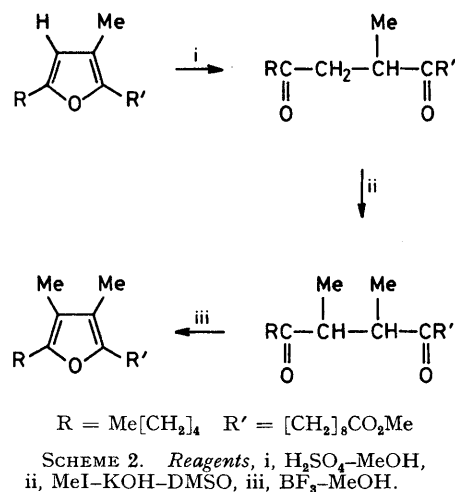
FURANOID fatty acids (**1**; R = H) containing methyl substituents at the 3- and 4-position of the furan system have been found in the lipid extracts of a number of fish species.<sup>1,2</sup> Schlenk *et al.*<sup>3</sup> have reported the total synthesis of one of the natural C<sub>20</sub> furanoid acids (**1**: R = H, n = 4, m = 10). Lie Ken Jie and co-worker<sup>4</sup> have synthesised a naturally occurring C<sub>20</sub> furanoid ester (methyl 12,15-epoxy-13-methylicos-12,14-dienoate) by two-carbon chain extension of methyl 10,13-epoxy-11-methyloctadeca-10,12-dienoate isolated from the latex of the rubber plant (*Hevea brasiliensis*).<sup>5</sup> We now describe another partial synthesis of another naturally occurring C<sub>18</sub> dimethyl furanoid ester (**1**; R = Me, n = 4, m = 8) from methyl linoleate and from methyl 10,13-epoxy-11-methyloctadeca-10,12-dienoate.

The epoxidation of methyl linoleate gave the methyl 9,12-diepoxystearate, which was readily converted into a mixture of two positional C<sub>18</sub> furanoid fatty ester isomers on treatment with NaI, Pr<sup>n</sup>I in dimethyl sulphoxide (DMSO) (40% yield).<sup>6</sup> Acid methanolysis of the mixture of furanoid esters gave the corresponding methyl dioxostearates (80%).<sup>7</sup> Methyl substitution of the relatively more reactive hydrogens of the carbon atoms situated between the two oxo-functions was achieved by treatment of the methyl dioxostearates with methyl iodide in DMSO catalysed by KOH for 48 h (75%).<sup>8</sup> Cyclodehydration of the product with 14% BF<sub>3</sub>-MeOH complex furnished a 1:1 mixture of methyl 9,12-epoxy-10,11-dimethyloctadeca-9,11-dienoate (**1**; R = Me, n = 5, m = 7) and methyl 10,13-epoxy-11,12-dimethyloctadeca-10,12-dienoate (**1**; R = Me, n = 4, m = 8) (50%) (Scheme 1).

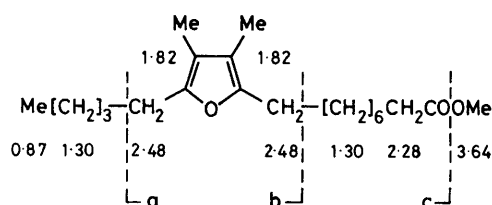


SCHEME 1. Reagents, i, *m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>3</sub>H, ii, NaI-Pr<sup>n</sup>I-DMSO, iii, H<sub>2</sub>SO<sub>4</sub>-MeOH, iv, MeI-KOH-DMSO, v, BF<sub>3</sub>-MeOH.

Pure methyl 10,13-epoxy-11,12-dimethyloctadeca-10,12-dienoate (**1**; R = Me, *n* = 4, *m* = 8) was prepared by acid methanolysis of methyl 10,13-epoxy-11-methyloctadeca-10,12-dienoate (obtainable from the latex of the rubber plant), followed by methylation and cyclodehydration of



the dimethyldioxo-intermediate to furnish (**1**; R = Me, *n* = 4, *m* = 8) (Scheme 2). Its methyl ester exhibited  $\nu_{\text{max}}$  (cm<sup>-1</sup>): 1740s (C=O ester), 1580, 1640m (C=C furan), and 1010m (furan ring breathing).



Methyl ester of (**1**; R = Me, *n* = 4, *m* = 8) showing <sup>1</sup>H n.m.r. assignments (δ). Mass spectral analysis: fragment (*m/z*), *M*<sup>+</sup> = 336(59%), *a* = 279(100), *b* = 179(43), *c* = 305(108).

The Research Grants Committee and the Lipid Research Fund of Hong Kong University provided financial assistance.

(Received, 19th June 1981; Com. 717.)

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