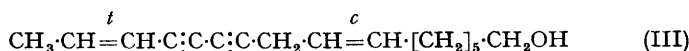
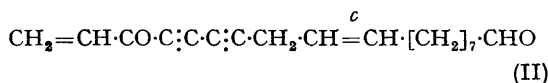
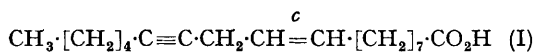


A Synthesis of Crepenynic Acid

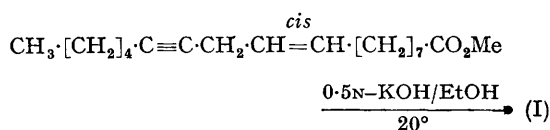
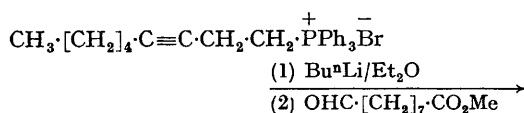
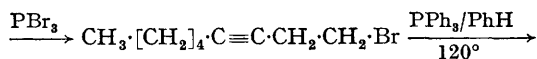
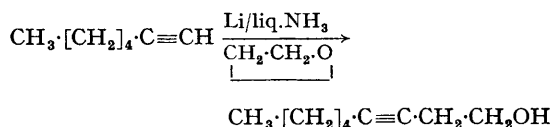
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CREPENYNIC ACID (I), first isolated from seed oils of *Crepis* species (Fam. Compositae),¹ has been encountered in other plants and fungi and is probably widely distributed. The methylene-interrupted unsaturation of (I) is common to a wide variety of naturally occurring polyacetylenes, e.g., (II) and (III), and an attractive scheme was devised² involving the acid (I) as a key intermediate in the biosynthesis of polyacetylenes from fatty acids. In support of this view, oleic acid has been shown³ to be a precursor of both crepenynic acid and dehydromatricarianol (IV) in the fungus *Tricholoma grammopodium*, although no direct relationship between the two metabolites was established.



As specifically-labelled crepenynic acid was needed for biosynthetic studies, several synthetic routes have been examined, that outlined here being

the most successful; the route is a modification of that used⁴ for the synthesis of methyl linoleate.



The natural and synthetic methyl esters of (I) had the same retention times on g.l.c. under a variety of conditions and identical infrared, nuclear magnetic resonance, and mass spectra. No evidence of the presence of the *trans*-isomer

synthesised earlier,⁵ was found. The crepenynic acid now obtained was a low-melting solid (m.p. 10.5–11°), it gave the known epoxyacetylenic acid, m.p. 37–38°, on treatment with peracetic

acid¹ and methyl linoleate (75%) on partial hydrogenation of the methyl ester with Lindlar catalyst.

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¹ K. L. Mikolajczak, C. R. Smith, jun., M. O. Bagby, and I. A. Wolff, *J. Org. Chem.*, 1964, **29**, 318.

² J. D. Bu'Lock, "Comparative Phyto-chemistry," ed. T. Swain, Academic Press, London, 1966, p. 79.

³ J. D. Bu'Lock and G. N. Smith, *J. Chem. Soc. (C)*, 1967, 332.

⁴ L. D. Bergelson and M. M. Shemyakin, *Angew. Chem. Internat. Edn.*, 1964, **3**, 250.

⁵ M. de Gaudemaris and P. Arnaud, *Bull. Soc. chim. France*, 1962, 315.