New Procedure for converting Unsaturated Fatty Acids to their nor-Alcohols Required as Intermediates for the Preparation of Carboxy-labelled Acids

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Summary Oleic and linoleic acid have been decarboxylated to the corresponding C_{17} alcohols which can be oxidised to unsaturated C_{17} acids or reconverted into the ^{14}C-carboxy-labelled C_{18} acids.

^{14}C-Carboxy-labelled fatty acids and their esters (**3**) are usually prepared by interaction of an appropriate halide (**2**) or equivalent substrate (mesylate, tosylate) with $K^{14}CN$ followed by hydrolysis or methanolysis. For saturated acids the halide (**2**) is easily obtained from the unlabelled acid (**1**) by Hunsdiecker decarboxylation or an equivalent process.[1] This procedure is less suitable for unsaturated acids though labelled oleic and linoleic acid were first made in this way after protection of the double bond(s) by bromination or hydroxylation.[2] This approach is even less satisfactory with more highly unsaturated acids and with the improvement of synthetic procedures the required nor-halides are more frequently obtained by synthesis using acetylenic intermediates or the Wittig reaction.[3] Nevertheless there remains a need for a general procedure by which unsaturated acids (**1**) can be converted into their ^{14}C-carboxy-labelled forms and we now report a new method of preparing nor-alcohols from carboxylic acids. The former can be oxidised by chromic acid to the unlabelled nor-acid[4] or be reconverted into the labelled ester or acid *via* the mesylate and nitrile.[1,3,5]

$$\underset{(\mathbf{1})}{RCO_2H} \longrightarrow \underset{(\mathbf{2})}{RBr} \xrightarrow[\text{MeOH, H}^+]{K^{14}CN} \underset{(\mathbf{3})}{R^{14}CO_2Me}$$

A mixture of oleic acid (1·01 g) and NaOH (1·23 g), dissolved in MeOH (30 ml), and H_2O (1 ml), was electrolysed between a Pt anode and a Hg cathode for 7 h.[6] Using a supply of *ca.* 20 V the current fell from 0·8 to 0·1 A during reaction and electrolysis was stopped periodically. When restarted the current was again almost 0·8 A. The product was recovered, methylated to facilitate the separation of alcohol from unchanged acid, and separated by chromatography into hydrocarbon (25%), a methyl ether thought to be heptadec-*cis*-8-enyl methyl ether (7%), methyl oleate (14%), and heptadec-*cis*-8-enol (44%). Both the C_{17} alcohol and its methyl ether can be used for the preparation of labelled oleic acid.[7] The alcohol was identified by its t.l.c. and g.l.c. behaviour in comparison with a sample of oleyl alcohol, its i.r. spectrum which showed strong OH absorption (3340 cm^{-1}) and virtually no absorption for a *trans* alkene (970 cm^{-1}), its n.m.r. spectrum {signals at δ 0·88 ($CH_3[CH_2]_7$), 1·28 ($[CH_2]_n$), 1·99 ($-CH_2CH{=}CHCH_2-$), 3·51 ($-CH_2OH$), and 5·28 ($-CH{=}CH-$)} and by von Rudloff oxidation[8] to nonanoic acid and 8-hydroxyoctanoic acid.

Linoleic acid reacted in a similar way and furnished heptadeca-*cis*-8, *cis*-11-dienol in a slightly lower yield (21%).

We thank the S.R.C. (C.M.S.) and the University of St. Andrews (H.S.V.) for financial support.

(*Received*, 19*th August* 1974; *Com.* 1069.)

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