Lipids. Part III. Determination of Hydrogenation Selectivity in the Synthesis of* cis-*Fatty Acids.*

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Reversed-phase partition chromatography is suitable for the analysis of mixtures of acetylenic, ethylenic, and saturated acids encountered in the synthesis of *cis*-long-chain fatty acids by catalytic semihydrogenation. Selectivity of four catalysts for production of undec-10-enoic acid from undec-10-ynoic acid is examined.

AT the present time, the most important synthetical process for introducing a *cis*-ethenoid linkage is catalysed semihydrogenation of the corresponding acetylene. The process suffers from two major drawbacks. First, the reaction is not fully stereospecific (*i.e.*, small amounts of *trans*-isomer are also formed) and, secondly, it is not completely selective (*i.e.*, some olefin is saturated before all the acetylene has disappeared). Analytical methods using infrared or Raman techniques are suitable for determination of *trans*- in the presence of *cis*-material (cf. Shreve, Heather, Knight, and Swern, *Analyt. Chem.*, 1950, **22**, 1261). Selectivity is less easily estimated by infrared methods : because of the lack of suitable vibrations it is often difficult to determine small amounts of acetylenic or saturated acids when much olefinic acid is present. Partition chromatography is now applied to the estimation of acetylenic, ethylenic, and saturated long-chain fatty acids in mixtures.

Howard and Martin's reversed-phase technique (*Biochem. J.*, 1950, **46**, 532; Popják and Tietz, *ibid.*, 1954, **56**, 46; Silk and Hahn, *ibid.*, p. 406), which employs a column of paraffin supported on silane-treated kieselguhr with acetone–water mixtures as eluant, has recently been applied to the separation of a wide range of plant fatty acids (W. Mary L. Crombie, Comber, and Boatman, *ibid.*, 1955, **59**, 309). It is also suitable for the present purpose. Test mixtures such as might be encountered in synthesis of oleic, petroselinic, and undec-10-enoic acids by semihydrogenation were found to be separable, and analyses are summarised in Table I. It is likely that the method is applicable to acids of chain lengths C_{10}—C_{24} with unsaturation at most points along the chain except $C_{(2)}$. The presence of a little *trans*-impurity in the *cis*-fatty acid causes no difficulty as resolution of the two stereoisomers is incomplete and they appear as one band.

To illustrate the capabilities of the method a few catalytic hydrogenation products

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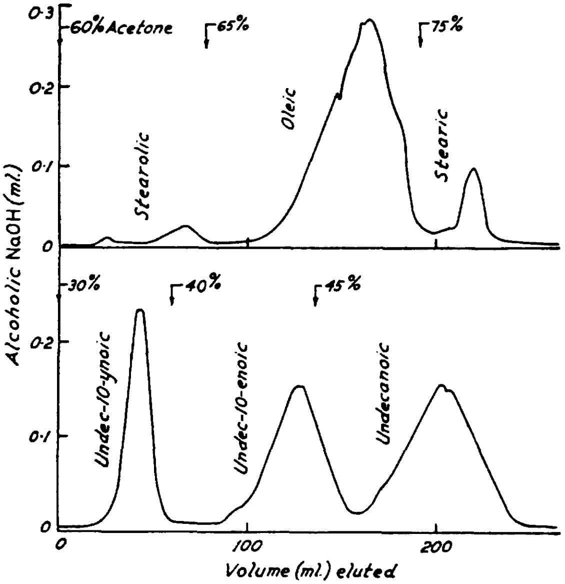
from undec-10-ynoic acid have been examined. In this work correlation between measured hydrogen uptake and product analysis is not quantitative. The products appear to have been hydrogenated rather more than the burette readings indicate and this probably reflects inability to apply adequate corrections with the standard laboratory equipment used: furthermore the system cannot be allowed to come to equilibrium if hydrogenation must be interrupted at a certain level. Hydrogen volumes absorbed must therefore be accepted as approximate and are recorded to the nearest 5%.

TABLE 1. *Analysis of mixtures of acetylenic, olefinic, and saturated long-chain acids.*

Acid	Composition (%)	Found (%)	Acid	Composition (%)	Found (%)
Stearolic	5·4	3·7	Tariric	1·6	1·2
Oleic	85·1	86·7	Petroselinic	95·4	95·5
Stearic	9·5	9·6	Stearic	3·0	3·2
Undec-10-ynoic	6·2	6·0	Tariric	2·9	3·4
Undec-10-enoic	85·4	86·1	Petroselinic	88·1	86·3
Undecanoic	8·4	7·9	Stearic	9·0	10·5



Upper curve: Separation of test mixture (*see Table* 1).

The unmarked first peak is due to a trace of autoxidised material in the oleic acid.

*Lower curve: Separation of products from partial hydrogenation of undec-*10*-ynoic acid with Adams's catalyst* (*see Table* 2).

The arrows indicate points at which the concentration of the eluting solvent (acetone–water) was changed. Successive effluent volumes of 2 ml. were titrated.

The gross unselectivity of Adams's platinum catalyst is shown in the Figure (see also Table 2). Even when 1·2 mol. of hydrogen have been absorbed there is still a large residue of unchanged acetylenic acid: it is unsuitable for synthetical work. Raney nickel (W4) has also given poor results in the present case. Palladium on barium sulphate has much higher selectivity, but Table 2 shows that after approximately one mol. of hydrogen has

TABLE 2. *Hydrogenation of undec-*10*-ynoic acid.*

Catalyst	Solvent	Measd. H_2 absorption (mol.)	$\cdot C⋮CH$ (%)	$\cdot CH{:}CH_2$ (%)	$\cdot CH_2\cdot CH_3$ (%)
Adams platinum	EtOAc	1·15	21·5	35·5	43
Raney nickel (W4)	Pet [b]	0·85	32·0	36·0	32
Palladium–barium sulphate	EtOAc	1·2	Nil	67	33
,, ,,	,,	1·0	4·5	87	8·5
Lindlar Pb–Pd–$CaCO_3$ [a]	,,	1·05 [c]	Nil	91	9·0
,, ,,	Pet [b]	1·1 [c, d]	Nil	91·5	8·5
,, ,,	,,	1·0 [d]	Nil	94·5	5·5
,, ,,	,,	0·85 [d]	9·0	88·0	3·5

[a] Poisoned with quinoline in the usual way. [b] Light petroleum (b. p. 80—100°), treated with Raney nickel before use. [c] Absorption ceased spontaneously. [d] Experiments on a macroscale.

been absorbed 8·5% of saturated impurity is present even though a little acetylenic material remains unchanged.

If undec-10-ynoic acid is hydrogenated with quinoline-poisoned lead–palladium–calcium carbonate (Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446) in ethyl acetate, absorption of gas ceases when rather more than one mol. has been used. At this stage no acetylenic acid remains but 9% of undecanoic acid is present. The same result was obtained in light petroleum, with a much smaller amount of catalyst. By interruption of the reaction a little before hydrogenation ceases spontaneously, the quantity of saturated acid is reduced but even when 9% of acetylenic acid remains unhydrogenated small amounts of saturated acid have been formed. Despite the inconvenience of removing quinoline from the product, Lindlar's system is the best catalyst for this semireduction and the slowing of gas absorption near uptake of one mol. facilitates manipulation. Dr. B. C. L. Weedon has allowed the author to examine a specimen of stearolic acid hydrogenated with Lindlar catalyst until absorption ceased. This contained no acetylenic acid and less than 2% of stearic acid, so selectivity seems almost complete in this case which involves an internal triple linkage.

EXPERIMENTAL

Materials.—Undec-10-enoic acid (commercial) was purified to m. p. 25—25·5° by fractional melting (lit., m. p. 24·5°). Undec-10-ynoic acid, prepared by A. G. Jacklin by bromination and dehydrobromination of undec-10-enoic acid, was crystallised from light petroleum (b. p. 60—80°) to m. p. 43—44° (lit., m. p. 43°). Undecanoic acid, m. p. 28·5—29·0° (lit., m. p. 28·5°), was prepared by complete hydrogenation of undec-10-ynoic acid. The acids were chromatographically homogeneous. The author is grateful to Dr. B. C. L. Weedon for gifts of some acids mentioned in Table 1. Petroselinic acid, from a natural source, contained impurity which was speedily eluted during chromatography: a correction was made for this.

Hydrogenation.—For semimicro-work (30—100 mg.) an apparatus with magnetic stirring similar to Ogg and Cooper's (*Analyt. Chem.*, 1949, **21**, 1400) was used. The solvent volume was 5 ml. Catalysts: Adams catalyst was from a commercial source (Johnson & Matthey); palladium (5%) on barium sulphate was prepared according to Houben ("Die Methoden der Organische Chemie," Thieme, Leipzig, Vol. II, p. 500), and Raney nickel (W4) according to Pavlic and Adkins (*J. Amer. Chem. Soc.*, 1946, **68**, 1471) and aged for 4 weeks. Amounts used were 10% of the sample weight for Adams catalyst, and 25% for palladium–barium sulphate and Raney nickel. With Lindlar catalyst a weight equal to that of the sample was employed after addition of a minute drop of quinoline. Catalysts were equilibrated with hydrogen before use. Figures for hydrogen absorption in Table 1 are calculated on the volume of hydrogen required for complete hydrogenation of undec-10-ynoic acid to undecanoic acid as determined experimentally.

Macro-experiments were carried out in a small standard laboratory hydrogenator, with mechanical shaking. Samples were approx. 500 mg. In experiments with light petroleum (5 ml.; b. p. 80—100°) the weight of Lindlar catalyst was 10% of the sample weight and the quinoline added was 40% of the catalyst weight. Semi-reduction was achieved in about 30 min.

Chromatography.—The technique was essentially as described by Howard and Martin (*loc. cit.*). In a few cases, where the amount of saturated acid was low, its presence was confirmed by Bertram oxidation (which converts unsaturated compounds into acids which are eluted speedily), followed by chromatography (W. Mary L. Crombie, Comber, and Boatman, *loc. cit.*). As the oxidation conditions cause loss of some undecanoic acid this provides only a qualitative check.

The possibility of employing infrared spectroscopy for analysis of mixtures of undec-10-enoic acid containing small amounts of undec-10-ynoic and undecanoic acids was examined. No reliable estimate of small quantities of saturated acid was possible, though because of the terminal position of the acetylenic linkage an approximate figure for undec-10-ynoic acid could be obtained by use of the C⋮C–H stretching frequency.

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