A Convenient Laboratory Method for Preparing *trans, trans*-9, 11-Octadecadienoic Acid[1]

WILMA J. SCHNEIDER, L. E. GAST and H. M. TEETER, Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

A convenient laboratory method to prepare *trans,trans*-9,11-octadecadienoic acid (TTA) via a polyester intermediate is described. Ricinelaidic acid was heated at 235C under vacuum for 3–4 hr to form a polyester having a mol wt of 1,500–1,600. Pyrolysis of this polyester and simultaneous distillation of the products gave crude dehydrated acids. TTA was crystallized from a 95% ethanol solution of these acids, in a yield of 35%. Of the variables affecting pyrolysis, the mol wt of polyester had the greatest effect on yield of TTA.

Introduction

As part of a study on Diels-Alder addition reactions of conjugated fatty acids, it was necessary to prepare pure TTA in quantity. By following Mangold's (8) procedure, dry vacuum distillation of ricinelaidic acid, we were able to obtain dehydrated acids that had only 37% conjugated diene.

Studies on dehydration of related hydroxy compounds (9) were reviewed to evaluate procedures and catalysts with an objective of increasing the yield and purity of TTA. Experiments with several dehydration catalysts, i.e., potassium acid sulfate, Dowex 50, zinc chloride, boric oxide, boric and tetraboric acids, confirmed that TTA was formed, but increased yields were desired.

Ricinoleic acid slowly undergoes intermolecular esterification (estolide formation) at room temp. Hawke and Kohll (3) have shown that when this acid is heated in an inert atmosphere, estolide formation is the main reaction; its rate increases with rising temp. These workers (4) also reported that when ricinoleic acid is chemically dehydrated in the presence of sodium bisulfate catalyst at 180C, the reaction proceeds in two stages: short-chain estolides and nonconjugated diethenoid acids are formed initially, but as the hydroxyl value approaches zero, rupture of the estolide chains occurs, resulting mainly in the formation of conjugated 9,11-octadecadienoic acid. Grummit and Marsh (2) reported the preparation of conjugated acids by heating ricinoleic acid with activated alumina for 3.5 hr at 225C followed by distillation of the acids. They proposed estolide formation and the generation of a new double bond by decomposition of this estolide.

We have shown that ricinelaidic acid, like ricinoleic acid, will undergo estolide formation without catalysis at temp above 200C and under vacuum. By proper control of conditions, this estolide can be conveniently prepared and pyrolyzed in simple laboratory apparatus to give TTA in good yield.

Experimental

Ricinelaidic Acid. Ricinoleic acid (Baker Castor Oil Co. P-10 acid of 90% purity) was purified by a modification of the method of Kass and Radlove (5). The crude acids were filtered through a sintered-glass funnel at room temp to remove solids and then extracted with cold petroleum ether at zero C. Residual solvent was removed to yield an oil having a neutral equivalent of 298.2 and a Wijs iodine value (I.V.) of 88.9; theoretical values for ricinoleic acid are 298.5 and 85.0, respectively. Thin-layer chromatography (TLC) showed that polyunsaturates account for the slightly high I.V.

The purified acid, 145 g was elaidinized according to the procedure of McCutchon et al. (7). The crude elaidinized mixture was dissolved in 90% aqueous acetone (6 ml/g), and the product was crystallized to yield 73 g crude elaidinized acid. Recrystallization from 90% acetone gave 58 g ricinelaidic acid, 40% yield, mp 50–51C, N.E. 298.5; I.V. 85.0. TLC showed only one component.

trans,trans-9,11-Octadecadienoic Acid. Catalytic Procedure: Ricinelaidic acid and catalyst were heated 1 hr at 200C under a 20-mm vacuum, then cooled, dissolved in diethyl ether, washed free of catalyst and dried. The solvent was removed, and the dark brown residue was vacuum distilled. Table I shows the results of dehydrating ricinelaidic acid with various catalysts. TTA was isolated by crystallization from 95% ethanol at −15C, and recrystallized once under the same conditions.

Estolide Procedure. A typical procedure was as follows: 100 g ricinelaidic acid were placed in a 250-ml round-bottom flask fitted with a short Claisen distillation head, thermometer, vacuum adapter and receiver. The flask was warmed to melt the acid, placed under a 1-mm vacuum, and then carefully lowered into a Wood's metal bath at 235C. Temp was maintained at 235C for a selected time (estolide formation) and then increased slowly until smooth distillation occurred (pyrolysis). A bath-to-head differential of approx 100C was required for smooth distillation of the pyrolysis products. Highest temp reached during the latter part of the distillation were: bath 325C and head 240C. Most of the product distilled at 200–225C/0.5–0.8 mm. The distillate was semisolid at room temp. The dehydrated acids were dissolved in 95% ethanol (3 ml/g) and allowed to crystallize at −15C.

A twice-recrystallized product had an absorptivity (a) of 123.7 (methanol) and 114.1 (isooctane) at 231

TABLE I

Catalytic Dehydration of Ricinelaidic Acid at 200C

Reaction	Catalyst	Diene conjugation,[a] %	Yield,[b] %	mp C
A	5% $NaHSO_4$	41.5		
B	20% Dowex 50 [c]	41.1		
C	1% $ZnCl_2$	40.8	9.8	47–49
D	1% H_3BO_3	35.1		
E	1% B_2O_3	45.3		
F	20% H_3BO_3	51.7	21.3	53–54
G	13% $H_2B_4O_7$	57.4	23.4	51–52

[a] *In distilled dehydration mixture.*
[b] Based on ricinelaidic acid.
[c] *Sulfonated polystyrene ion-exchange resin.*

---

[1] Paper II in the series on "Reactions of Conjugated Fatty Acids," presented at AOCS meeting in Atlanta, 1963.

[2] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, USDA.

TABLE II

Preparation of *trans,trans*-9,11-Octadecadienoic Acid via Polyester Intermediate

Reaction[a]	Estolide preparation		Dehydrated acids			*trans,trans*-9,11-Octadecadienoic acid	
	Time of reaction, hr	Product mol wt[b]	Yield,[c] %	Neutral equivalent	Total diene conjugation, %	Yield,[c,d] %	mp,[d] C
H	1	780	86.6	333	49.2	26.0	47–49.5
J	1	705	89.5	302	46.7	28.1	48.5–50
K	2	1165	84.7	307	53.5	31.0	50–51
L	2	1172	92.7	339	47.9	28.2	48–49
M	3	1385	76.0	280	54.1	30.8(25.9)[e]	47.5–49(53–53.5)[e]
N	3	1540	83.0	280	62.6	35.1(28.7)[e]	49–50(53–53.5)[e]
P	4	1605	85.1	293	61.7	32.9(27.6)[e]	50(53–53.5)[e]
Q	4	1650	88.2	299	52.3	36.2(25.5)[e]	48.5–49.5(53)[e]
R	6	1800	88.4	308	54.4	35.3	48–49.5
S	17	2025	74.3	289	56.4	24.4	48.5–50

[a] H–R carried out at 235C under 1-mm vacuum; S carried out at 195C atmospheric pressure, under N_2.
[b] Calculated from neutral equivalent.
[c] Yield based on estolide.
[d] Once-crystallized product.
[e] Recrystallized once from 5 ml 95% ethanol/g.

mμ. IR spectroscopy of this product showed a strong absorption at 987 cm^{-1}, a = 1.240 (carbon disulfide) attributed to *trans,trans* conjugated diene.

Table II lists data for experiments based on this method of preparation. Mol wt of the estolides were calculated from the neutral equivalent on the assumption of one carboxyl/molecule. Conjugated diene values were determined in isooctane at 231 mμ based on a = 110 (10).

Discussion

Data on the catalytic dehydration of ricinelaidic acid show in Table I. Conjugated diene values of 41% were found in the dehydrated acid products when such dehydration catalysts as sodium bisulfate, Dowex 50 or zinc chloride were used to dehydrate ricinelaidic acid. In reactions A, B and C, the yields of TTA were low, and the isolated products were impure. Apparently in these reactions TTA was difficult to crystallize from the mixture of dehydrated acids. However when boric acid or tetraboric acid was used (F,G), significantly higher diene values, 52–57%, were obtained. In those reactions, TTA could be isolated much more easily by crystallization; however, yields were still only fair, and several recrystallizations were required to obtain a sufficient pure product for our use.

Data on the pyrolysis of ricinelaidic estolides show in Table II. The factor that proved most important in the preparation of TTA via the pyrolysis of estolide intermediate was its mol wt. The temp of 235C was chosen for preparing the estolide because it ensured a relatively short reaction time but did not cause significant pyrolysis. Vacuum facilitated removal of water formed during esterification. By increasing the reaction time, higher mol wt were obtained.

While dehydrated acids from estolides (Table II) may arise primarily from the pyrolysis of ester linkages, Hawke and Kohll (3) show from calculations of mol wt distribution based on Florey's principle of linear polycondensation (1) that polyesters having mol wt of 1,500 contain as much as 18–20 mole percentage of monomeric hydroxy acid. Hawke and Kohll (4) suggest that, with ricinoleic acid dehydrations using sodium bisulfate catalyst, intramolecular dehydration of monomer acid occurs and leads mostly to the production of nonconjugated diethenoid acids, whereas pyrolysis of estolide linkages leads mainly to conjugated acids. Similarly, ricinelaidic estolides would contain monomeric acids in varying amounts, depending on the mol wt. Thus, the possibility for both direct dehydration and estolide pyrolysis reactions exists. This suggestion appears to be substantiated by comparing reactions H and J with N (Table II). In H or J the lower mol wt estolides contain more monomeric acid and are pyrolyzed to give products containing less conjugated diene that those from experiment N. Apparently, intramolecular dehydration leading to nonconjugated acids is more important in H and J.

Maximum amount of distillate is obtained by the use of a very short Claisen head. In certain reactions, e.g., H and L, pyrolysis of low-mol-wt estolides gave dehydrated acids with somewhat higher neutral equivalents. TLC showed that estolides and ricinelaidic acid were present in these distillates. These contaminants were apparently carried over by evolution of water resulting from dehydration or esterification of ricinelaidic acid, which would be present in appreciable amounts in low-mol-wt estolides. The higher temp and lower pressure of distillation, in comparison to the conditions of original estolide formation, would encourage these reactions of the monomer acid as well as promote relatively violent evolution of the water so formed.

A 3-hr reaction appears to be the min time to ensure an estolide of suitable mol wt. Maximum yield of TTA was obtained from an estolide having a mol wt of 1,500–1,600 as shown in the 3–4 hr reactions. IR analysis of the methyl ester of these acids (N) disclosed the absence of hydroxyl at 3,570 cm^{-1} and indicated complete dehydration. When the reaction mixture was heated an additional 3 hr, the yield of TTA did not improve significantly (compare R and N). The decreased yield of TTA caused by low yield of dehydrated acids possibly is attributed to formation of polymeric products that cannot be pyrolyzed (S).

ACKNOWLEDGMENT

Spectral data by G. E. McManis, Jr.; assistance in the experimental work from Mary F. Gibbons and encouragement during the course of the study from J. C. Cowan.

REFERENCES

1. Flory, P. J., Chem. Rev. *39*, 137–197 (1946).
2. Grummit, O., and D. Marsh, JAOCS *30*, 21–25 (1953).
3. Hawke, F., and E. A. Kohll, J. S. African Chem. Inst. *12*, 1–16 (1959).
4. Hawke, F., and E. A. Kohll, *Ibid.*, 17–25.
5. Kass, J. P., and S. B. Radlove, J. Am. Chem. Soc. *64*, 2253–2257 (1942).
6. Lorette, N. B., and J. H. Brown, Jr., J. Org. Chem. *24*, 261–262 (1959).
7. McCutchon, M. A., R. T. O'Connor, E. F. DuPré, L. A. Goldblatt and W. G. Bickford, JAOCS *36*, 115–118 (1959).
8. Mangold, C., Monatsh. Chem. *15*, 309–310 (1894).
9. Rheineck, A. E., "Progress in the Chemistry of Fats and Other Lipids," ed. R. T. Holman, W. O. Lundberg and T. Malkin, Vol. 5, Pergamon Press, London, 1958, pp. 170–178.
10. Spectroscopy Committee of AOCS, 1956–1957 Report. JAOCS *34*, 600–603 (1957).

[Received March 26, 1964—Accepted May 18, 1964]