ACKNOWLEDGMENT

General assistance by L. Schouten; GLC determination of triglyceride composition by J. Venekamp.

REFERENCES

1. Vander Wal, R. J., JAOCS *40*, 242–247 (1963).
2. Hilditch, T. P., "The Chemical Constitution of Natural Fats," 3rd ed., Chapman and Hall Ltd., London, 1956.
3. Scholfield, C. R., and M. A. Hicks, JAOCS *34*, 77–80 (1957).
4. Scholfield, C. R., and H. J. Dutton, *Ibid. 36*, 325–328 (1959).
5. Dutton, H. J., C. R. Scholfield and T. L. Mounts, *Ibid. 38*, 96–101 (1961).
6. Kartha, A. R. S., *Ibid. 30*, 280–282 (1953).
7. Youngs, C. G., *Ibid. 38*, 62–67 (1961).
8. Privett, O. S., and M. L. Blank, J. Lipid Res. *2*, 37–44 (1961).
9. Privett, O. S., and M. L. Blank, JAOCS *40*, 70–75 (1963).
10. Mattson, F. H., and L. W. Beck, J. Biol. Chem. *219*, 735–740 (1956).
11. Savary, P., and P. Desnuelle, Biochim. Biophys. Acta *21*, 349–360 (1956).
12. Coleman, M. H., JAOCS *38*, 685–688 (1961).
13. Vander Wal, R. J., *Ibid. 37*, 18–20 (1960).
14. Vander Wal, R. J., *Ibid. 37*, 595–598 (1960).
15. Huebner, V. R., *Ibid. 38*, 628–631 (1961).
16. Kuksis, A., and M. J. McCarthy, Can. J. Biochem. Physiol. *40*, 679–686 (1962).
17. Abstracts of Papers 37th Annual Fall Meeting Minneapolis, JAOCS *40*, September 1963.
18. de Vries, B., "Separation of Triglycerides by Column Chromatography on Silica Impregnated with Silver Nitrate," *Ibid. 41*, 403–406 (1964).
19. de Vries, B., and G. Jurriens, J. Chromatog. *14*, 525–526 (1964).
20. Jurriens, G., B. de Vries and L. Schouten, J. Lipid Res. *5*, 267–268 (1964).
21. Jurriens, G., B. de Vries and L. Schouten, *Ibid. 5*, (1964).
22. Quinlin, P., and H. J. Weiser, JAOCS *35*, 325–327 (1958).

[Received March 3, 1964—Accepted August 13, 1964]

Preparation of Malonaldehyde Acetals by Ozonolysis of Polyunsaturated Fatty Esters[1]

P. FITTON, E. H. PRYDE and J. C. COWAN, Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Malonaldehyde acetals were prepared in more than a 70% yield by ozonolysis of the methyl esters of linseed oil, safflower oil and linoleic acid, and by ozonolysis of linseed oil alone. Malonaldehyde tetramethyl acetal could not be separated readily from caproaldehyde dimethyl acetal by fractional distillation. However, conversion of the methyl acetals to propylene glycol acetals resulted in sufficient spread in boiling points for their effective separation by distillation.

Introduction

IN OUR LABORATORIES, studies have been made on the reaction of ozone with unsaturated fatty acids and on the chemistry of the products, as part of a program to increase the utilization of linseed and soybean oils.

It has previously been reported (5) that ozonolysis of methyl oleate in methanol at 0C, followed by reduction, usually by zinc and acetic acid, gives the products expected by cleavage of the 9,10 double bond, pelargonaldehyde and methyl azelaaldehydate, in high yields. Methyl azelaaldehydate is, of course, also formed by the ozonolysis of all fatty acids in which the first site of unsaturation is at C_9. It is, therefore, a readily accessible product from the ozonolysis of oils rich in these unsaturated acids, such as linseed and soybean oils. Methyl azelaaldehydate is a potentially important monomer intermediate, and preliminary studies on polymers from pentaerytheritol acetal have already been reported (7).

Since methyl azelaaldehydate is produced only from the first 9 carbon atoms of the fatty acid molecule, an investigation was started to recover useful reactive products from the other half of the molecule. Ozonolysis of methyl linoleate would be expected to give 1 mole of caproaldehyde, 1 mole of malonaldehyde, and 1 mole of methyl azelaaldehydate. Similarly, methyl linolenate should give 1 mole of propionaldehyde, 2 moles of malonaldehyde, and 1 mole of methyl azelaaldehydate. Accordingly, malonaldehyde should be a major product of the ozonolysis of oils rich in these acids. As a simple β-dialdehyde it should be a reactive and potentially useful product.

Malonaldehyde has been prepared previously as its tetraalkyl acetal by the acid-catalyzed condensation of an allyl-alkyl ether with a trialkylorthoformate (3), a method limited by the high cost of the orthoformate ester, by the ozonolysis of 1,4-dibutoxybut-3-ene (2), and by the ozonolysis of the esters of fatty acids (1). Ozonolysis of methyl linoleate in methanol at 0C, followed by reduction with hydrogen and a 3% palladium-on-barium-sulfate catalyst reportedly (1) gave a mixture of aldehydes. Treating this mixture with a catalytic amt of H_2SO_4 in methanol gave the methyl acetals. These were separated by distillation in good yields; however, the products were not characterized, and no mention was made of impurities. Attempts were made to repeat this work.

Results

The methyl esters of linseed oil fatty acids were ozonized and the product was reduced. Reduction was slow if a 3% palladium-barium sulfate catalyst was used. Lindlar catalyst (4) gave better yields more rapidly. In Figure 1 are shown analyses by gas-liquid chromatography (GLC) of the acetals produced from both catalysts in the reduction of ozonolysis products of linseed oil esters. As clearly seen, the amt of malonaldehyde formed relative to the other products is high when Lindlar catalyst is used.

If the ozonolysis product was reduced with zinc and acetic acid, a more complex mixture of products was obtained, and of this mixture, malonaldehyde was only a minor constituent.

The aldehydes in methanol were converted to their methyl acetals by standing overnight with a catalytic amt of H_2SO_4, after which time the acid was removed by stirring the product for 2 hr with a large excess of sodium carbonate. This step was necessary to remove every trace of acid; otherwise failure to do so always led to much polymerization during distillation of the acetals. Fractionation of the acetals was not as straightforward as one would be led to believe from reference 1, and complete fractionation could not be achieved even when a spinning band distillation column was used with a reflux ratio of 120:1. Malonaldehyde tetramethyl acetal fractions were always contaminated with 5–10% of caproaldehyde dimethylacetal, and methyl azelaaldehydate fractions always contained ca. 10% dimethyl azelate (6).

Other alcohols were tried as common ozonization solvents and acetalating agents without much success.

---

[1] Presented at the AOCS Meeting, Minneapolis, 1963.

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

With ethanol, the products could still not be separated, and with such glycols as propylene and 2-methylpentan-2, 4-diol, the yields of malonaldehyde were decreased drastically. However, when a mixture of malonaldehyde tetramethyl acetal and caproaldehyde dimethyl acetal was heated in propylene glycol with a trace of acid, the propylene glycol acetals that formed could be separated by a 3-in. Vigreaux column. Since the reaction can be run in methanol, the malonaldehyde-caproaldehyde methyl acetal mixture separated from methyl azelaaldehydate by a relatively crude distillation. The malonaldehyde tetramethyl acetal mixture was heated in propylene glycol with a trace of H_2SO_4; after 4 hr, the malonaldehyde dipropylene glycol acetal was readily isolated by distillation. The yields were good: malonaldehyde, 70% and methyl azelaaldehydate, 90%.

Malonaldehyde was characterized as its dianil, identical to a sample prepared from authentic 1,1,3,3-tetraethoxypropane (8).

Experimental

Gas-liquid chromatograms were run on an F&M Model 500 programmed temp chromatograph, using a 2-ft silicone rubber column and a flow rate of 50 ml/min. The temp was increased from 75C at a rate of 11C/min.

Ozonolysis of Methyl Esters of Safflower Oil. Methyl safflowerate (69% methyl linoleate) (40 g) was dissolved in absolute methanol (450 ml) and a stream of ozonized oxygen was passed through the solution cooled to 0C until an aliquot of the solution no longer decolorized a solution of bromine in methanol. Lindlar catalyst (0.5 g) was added and a stream of hydrogen was bubbled through the stirred solution, which was cooled in an ice water bath until a filtered aliquot did not liberate iodine from an aqueous potassium iodide solution. After filtering, concd H_2SO_4 (0.5 ml) was added and the solution was allowed to stand overnight at room temp.

Solid sodium carbonate (20 g) was added and the mixture was stirred for 2 hr. After filtration the methanol was removed to leave a light yellow oil which was then distilled in a 2-in. Vigreaux column to give the following fractions:

Fraction 1, bp 83–127C/20 mm (75% yield of a crude mixture of malonaldehyde and caproaldehyde methyl acetals); fraction 2, bp 63–69C/0.1 mm, 2.51 g; fraction 3, bp 84–87C/0.1 mm, 26.75 g (95% yield of crude methyl azelaaldehydate dimethyl acetal).

Fraction 1 was dissolved in propylene glycol (100 ml), concd H_2SO_4 (0.5 ml) was added, and the mixture was heated on a steam bath for 4 hr. After cooling, the product was diluted with ether (100 ml), then solid sodium carbonate was added to neutralize the acid, and after having been washed with aqueous sodium carbonate the solution was dried. Removal of ether left a light yellow oil, which distilled into the following fractions:

Fraction 1A, bp 37–43C/0.95 mm, 1.7 g; fraction 1B, bp 43–56C/0.95 mm, 4.59 g (caproaldehyde propylene glycol acetal); fraction 1C, bp 76–82C/0.95 mm, 3.46 g; fraction 1D, bp 84–87C/0.95 mm, 10.62 g (malonaldehyde dipropylene glycol acetal). Fraction 1C contained 50% of malonaldehyde dipropylene glycol acetal, and fraction 1D, 95% by GLC analysis on a 2-ft silicone column. The total yield of malonaldehyde dipropylene glycol acetal was 65%.

Ozonolysis of Methyl Esters of Linseed Oil. The methyl esters of linseed oil (13.3% methyl linoleate and 51.1% methyl linolenate) (72 g) were ozonized in methanol at 0C. The ozonolysis products were reduced, and the acetals formed as above. Fractionation of the resulting oil gave malonaldehyde tetramethyl acetal (65–70C/0.3 mm, 33.12 g, 71%) and methyl azelaaldehydate dimethyl acetal (110–115C/0.3 mm, 46.61 g, 91%).

The malonaldehyde tetramethyl acetal fraction was shown by GLC analysis to contain 10% of caproaldehyde dimethyl acetal.

Ozonolysis of Linseed Oil. Linseed oil (36 g) was dissolved in ethyl acetate (400 ml), and methanol (100 ml) was added. The mixture was then saturated

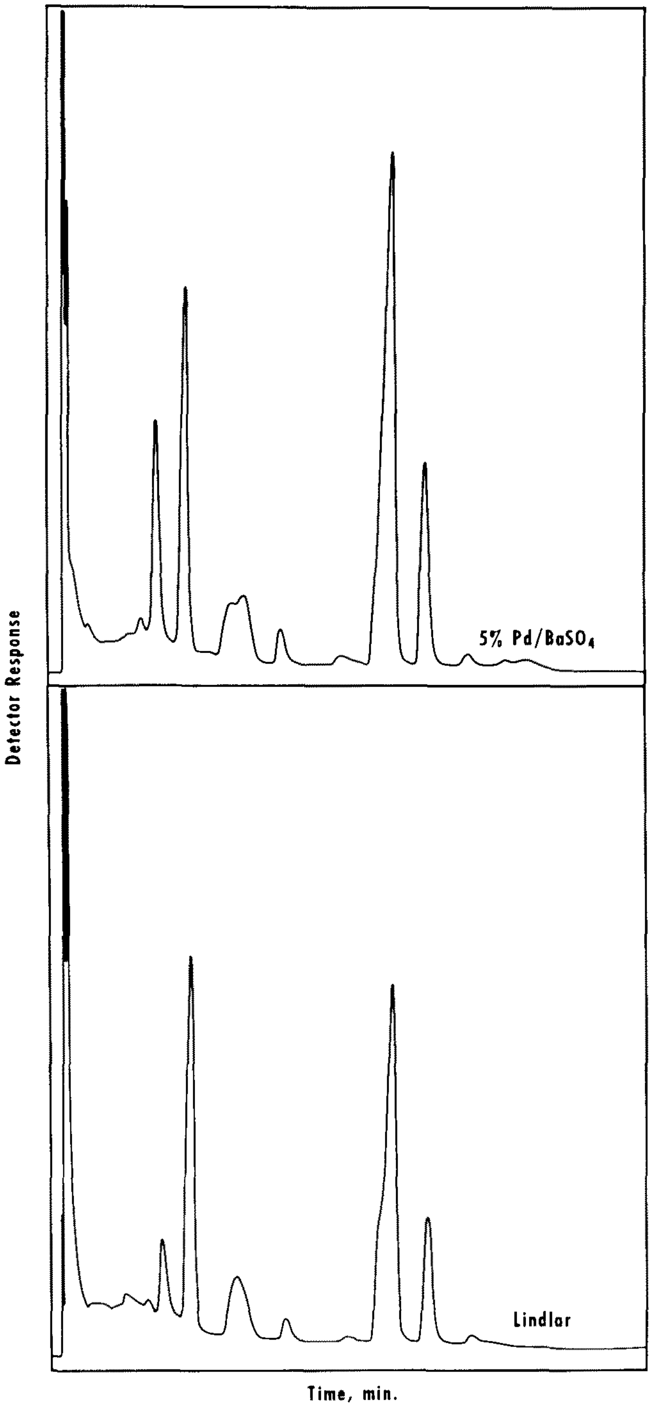

FIG. 1. Analysis by GLC of acetals from the reduction of the ozonolysis product by [A] 5% Pd/$BaSO_4$ or [B] Lindlar catalysts. The main peaks are: a) caproaldehyde dimethyl acetal, b) malonaldehyde tetramethyl acetals, c) methyl azelaaldehydate dimethyl acetals, and d) methyl azelate.

with ozone at 0C, and the product reduced by stirring with Lindlar catalyst (0.5 g) under an atmosphere of hydrogen at 0C. Methanol (600 ml) was added and the acetals were formed as above. The methanol was removed and the resulting oil distilled.

The total wt of volatile material collected, bp 40–95C/20 mm, was 20.91 g (81% of a crude mixture of malonaldehyde and caproaldehyde methyl acetals).

The volatile material was heated for 3 hr on a steam bath with propylene glycol (50 ml) and H_2SO_4 (0.2 ml). After the cooled solution was diluted with ether, it was washed with saturated sodium bicarbonate solution, and then ether was removed. The resulting oil (16.57 g) was distilled.

Fraction 1, bp 37–40C/0.1 mm, 0.787 g; fraction 2, bp 41–45C/0.1 mm, 1.94 g; fraction 3, bp 48–49C/0.1 mm, 9.44 g. Fraction 2 contained 50% malonaldehyde dipropylene glycol acetal and fraction 3, 90% by GLC analysis. The total yield was 40%.

The residue from the initial distillation was dissolved in 10% sodium methoxide in methanol (200 ml), and the solution was refluxed for 3 hr. The cooled solution was diluted with ether and washed well with water. After drying, the ether was removed and the resulting oil was distilled to give methyl azelaaldehydate dimethyl acetal (115–120C/0.3 mm, 11.97 g, 54%).

Ozonolysis of Methyl Linoleate. Methyl linoleate (50 g) was ozonized in methanol (350 ml) as described, and the product reduced with hydrogen and Lindlar catalyst (1 g). The methyl acetals were prepared as before and distilled in a 2-in. Vigreaux column to give fraction 1, bp <50C/0.2 mm, 39.23 g (a mixture of 60% malonaldehyde tetramethyl acetal and 40% caproaldehyde dimethyl acetal) and fraction 2, bp 115–120C/0.2 mm, 42.01 g (a 91% yield of crude methyl azelaaldehydate dimethyl acetal).

REFERENCES

1. Blackmore, R. L., and J. W. Szatkowski (A. Boake, Roberts and Co., Ltd.), British 846,906 (1960).
2. Hattori, S. (Mitsubishi Chemical Industries Co.), Japan. 2271 (1958); CA *53*, 6090 (1959).
3. Hultquist, M. E. (American Cyanamid), U.S. 2,459,076 (1949); Gaspar, G. (Chromogen, Inc.), U.S. 2,465,586 (1949); Copenhaver, J. W. (General Aniline and Film Corp.), U.S. 2,527,533 (1950); Young, F. G. (Union Carbide and Carbon Corp.), U.S. 2,556,312 (1951); Tsukamoto, T. (Mitsubishi Chemical Industries Co.), Japan. 4773 (1953); CA *49*, 6994 (1955); Tsukamoto, T., and T. Suzucki (Mitsubishi Chemical Industries Co.), Japan. 3071 (1955); CA *51*, 16519 (1957); Tsukamoto, T., T. Suzucki, K. Heijo, S. Takebe, G. Sudo and Y. Tanaka (Mitsubishi Chemical Industries, Ltd.), U.S. 2,823,226 (1958).
4. Lindlar, H. (Hoffmann-La Roche, Inc.), U.S. 2,681,938 (1954).
5. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, J. Org. Chem. *25*, 618 (1960).
6. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, *Ibid.* *27*, 3055 (1962).
7. Pryde, E. H., D. J. Moore, H. M. Teeter and J. C. Cowan, J. Polymer Sci. *58*, 611 (1962).
8. Shiobasa, Y., and S. Ishida (Yamanouchi Pharmaceutical Co.), Japan. 17,020 (1960); CA *55*, 17578 (1961).

[Received July 21, 1964—Accepted September 15, 1964]

Vinyl Esters of Some Aldehydic Acid Acetals[1]

E. H. PRYDE, D. J. MOORE and J. C. COWAN, Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Vinylation of azelaaldehydic and brassylaldehydic acid cyclic acetals from ethylene glycol gave excellent yields of the vinyl esters. Under conditions of the vinyl exchange reaction used, acyclic acetals from monohydric alcohols cleaved to give enol-ethers as major, inseparable impurities. Radical-initiated polymerization of the pure vinyl esters of the aldehydic-acid cyclic acetals resulted in crosslinking when initiation was by either peroxide or azobis(isobutyronitrile).

Introduction

ALDEHYDIC ESTERS, readily obtained by ozonolysis of unsaturated fatty acid esters, are versatile compounds that undergo a wide variety of reactions (8–10). For example, selective alcoholyses may be carried out on the dimethyl acetal of methyl azelaaldehydate to obtain various ester-acetal derivatives of azelaaldehydic acid in good yield (12). We have described the evaluation of certain of these ester-acetal derivatives as external plasticizers for poly(vinyl chloride) (PVC) (11). Possible internal plasticizers for PVC are the vinyl esters of aldehydic acid acetals. This paper describes the preparation and preliminary studies on the polymerization of the vinyl esters of azelaaldehydic and brassylaldehydic acid acetals.

Experimental

Gas-Liquid Chromatographic Analyses. Gas-liquid chromatographic (GLC) analyses of the vinyl esters were carried out on an F&M model 500 programmed temp gas chromatography unit equipped with a ¼ in. x 4 ft copper column packed with 20% butanediol succinate on 60–80 mesh Chromosorb W. The runs were made isothermally at 185C with a flow rate of 50 cc/min.

All other GLC analyses were carried out in a ¼ in. x 4 ft stainless-steel column packed with 20% silicone rubber on 60–80 Chromosorb P. The column was programmed at a rate of 7.9°/min from 100–275C with a flow rate of 50 cc/min.

Aldehyde Esters. Methyl azelaaldehydate and methyl brassylaldehydate were obtained by ozonization in methanol of soybean methyl esters and methyl erucate, respectively, followed by reductive decomposition of the ozonolysis products either by zinc and acetic acid or by catalytic hydrogenation (2,8,9). The aldehyde esters were purified by forming the sodium bisulfite adducts, regenerating the aldehyde ester with 10% NaOH, then fractionally distilling (7). Based on the aldehyde content of the crude aldehyde esters, 75–80% recoveries of pure products were obtained by this purification procedure.

Acetal Esters. Aldehyde esters were converted to dimethyl acetals in 90–95% yields by using 2,2-dimethoxypropane as a water scavenger (8). Conversion of the dimethyl acetal of methyl azelaaldehydate to dibutyl, distearyl and ethylene glycol acetals, and of the dimethyl acetal of methyl brassylaldehydate to the ethylene glycol acetal, was carried out by selective alcoholyses in the presence of potassium acid sulfate as reported (12).

8-(1,3-Dioxolan-2-yl)octanoic Acid. The hydrolysis of methyl azelaaldehydate ethylene glycol acetal to the azelaaldehydic acid ethylene glycol acetal [8-(1,3-dioxolan-2-yl)octanoic acid] is described in detail as a representative example. Methyl 8-(1,3-dioxolan-2-yl) octanoate (87.3 g, 0.379 mole) was added to 400 ml

---

[1] Presented at the AOCS Meeting, Toronto, October 1962.
[2] A laboratory of the No. Utiliz. Res. Dev. Div., ARS, USDA.