Dimorphecolic Acid—A Unique Hydroxydienoid Fatty Acid[2]

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Dimorphecolic acid, the chief constituent fatty acid of *Dimorphotheca aurantiaca* seed oil, is characterized as an optically active 9-hydroxy-*trans,trans*-10,12-octadecadienoic acid.

Screening a considerable number of previously uninvestigated species revealed unusual properties of seed oils from several members of the family Compositae. These oils were of interest in connection with a search for new industrial oilseed crops. Earle, Jones and Wolff[3] reported that the seed of *Dimorphotheca aurantiaca* yielded an oil *ca.* 48% of whose acids contained *trans,trans*-conjugated diene. Comparable concentrations of epoxy and hydroxy acids were also indicated. This paper describes the isolation and proof of structure of a new fatty acid contained in that oil.

Saponification of oil obtained by petroleum ether extraction of *Dimorphotheca aurantiaca* seed was not used when it was found that the conjugated dienoid system was inordinately sensitive to alkali under certain conditions. It was found, however, that methyl esters could be prepared by a transesterification procedure without destruction of the diene moiety. The esters were separated by countercurrent distribution, using the solvent system acetonitrile-hexane.[4] After 30 transfers, the methyl ester (I) of a new fatty acid, for which the name *dimorphecolic acid* is proposed, was obtained as a distinct peak with its maximum at tube 5 (see Fig. 1). This liquid ester, which constituted about 65% of the total, was weakly dextrorotatory in chloroform. Quantitative hydrogenation indicated that it contained two double bonds. Its ultraviolet spectrum, characterized by a maximum at 231 mμ, showed the double bonds to be conjugated. The infrared spectrum of this ester indicated that its conjugated system had the *trans,trans*-configuration; this assignment followed from the fact that there was a single peak in the 10–11 μ region, at 10.09 μ.[5] One mole of hydrogen bromide was consumed by I in the Durbetaki hydrogen bromide–acetic acid titration for oxirane oxygen.[6] Spectral evidence indicated the presence of a hydroxyl group, but no epoxy group. The products accompanying methyl dimorphecolate and concentrated in tubes 16–29 were apparently predominantly esters of fatty acids of

the common types. Of these, 11% were saturated, 45% were monoethenoid and 33% were non-conjugated diethenoid acids.[7]

To resolve the apparent conflict between infrared evidence and other data, methyl dimorphecolate (I) was refluxed for 1 hour in glacial acetic acid, following Gunstone's procedure for acetolysis of epoxy acids.[8] Somewhat surprisingly, this treatment produced a *conjugated triene* (II) which contained *no* hydroxyl group. This reaction demonstrated the absence of an epoxy group in I and suggested that the hydroxyl group was located on an α-carbon with respect to the conjugated diene. Absence of epoxide groupings was further confirmed by lithium aluminum hydride reduction of I to the crystalline diene-diol VII, which consumed 1 mole of hydrogen bromide, apparently as rapidly as I. Confirmation for presence of the system —CH=CHCH=CHCHOH— was obtained by oxidizing I to IV with chromium trioxide–pyridine; IV had an ultraviolet absorption maximum at 275 mμ, in harmony with an α,β- and γ,δ-unsaturated ketone. Dehydrated product II was hydrogenated to saturated ester III, which was identified unequivocally as methyl stearate by mixed melting point determinations and by gas chromatography. A normal C-18 carbon skeleton for dimorphecolic acid was thereby established.

Direct hydrogenation of I yielded a crystalline saturated hydroxy ester V, shown by infrared spectra and melting point comparisons to be an optically active methyl 9-hydroxyoctadecanoate. Compound V was oxidized by chromium trioxide–acetic acid to VI, which was shown by infrared comparison to be identical with methyl 9-oxoöctadecanoate.

The position of the hydroxyl in dimorphecolic acid having been settled, there remained the question of the position of the conjugated double bonds, which could be either in 5,7- or 10,12-positions. The issue was decided in favor of the 10,12-positions by ozonolysis. Ozonolysis of VII followed by reductive cleavage yielded aldehydes VIII and X, and presumably glyoxal IX as well; these were separated by solvent extraction and steam distillation and isolated as 2,4-dinitrophenylhydrazones. The derivative of VIII was rigorously identified as hexanal 2,4-dinitrophenylhydrazone by mixed melting point observations, by paper chromatography, and by X-ray diffraction.

Separation of the derivatives of the non-volatile aldehydes proved difficult, and it appeared that a rather complex mixture was obtained. One crystalline derivative obtained in small yield (XI) was

(1) This is a laboratory of the Northern Utilization Research and Development Division, Ag.icultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented before the Division of Organic Chemistry, 135th Meeting American Chemical Society, Boston, Mass., April 5–10, 1959.

(3) F. R. Earle, Q. Jones and I. A. Wolff, presented before the 32nd Fall Meeting, American Oil Chemists' Society, Chicago, Ill., October 20–22, 1958.
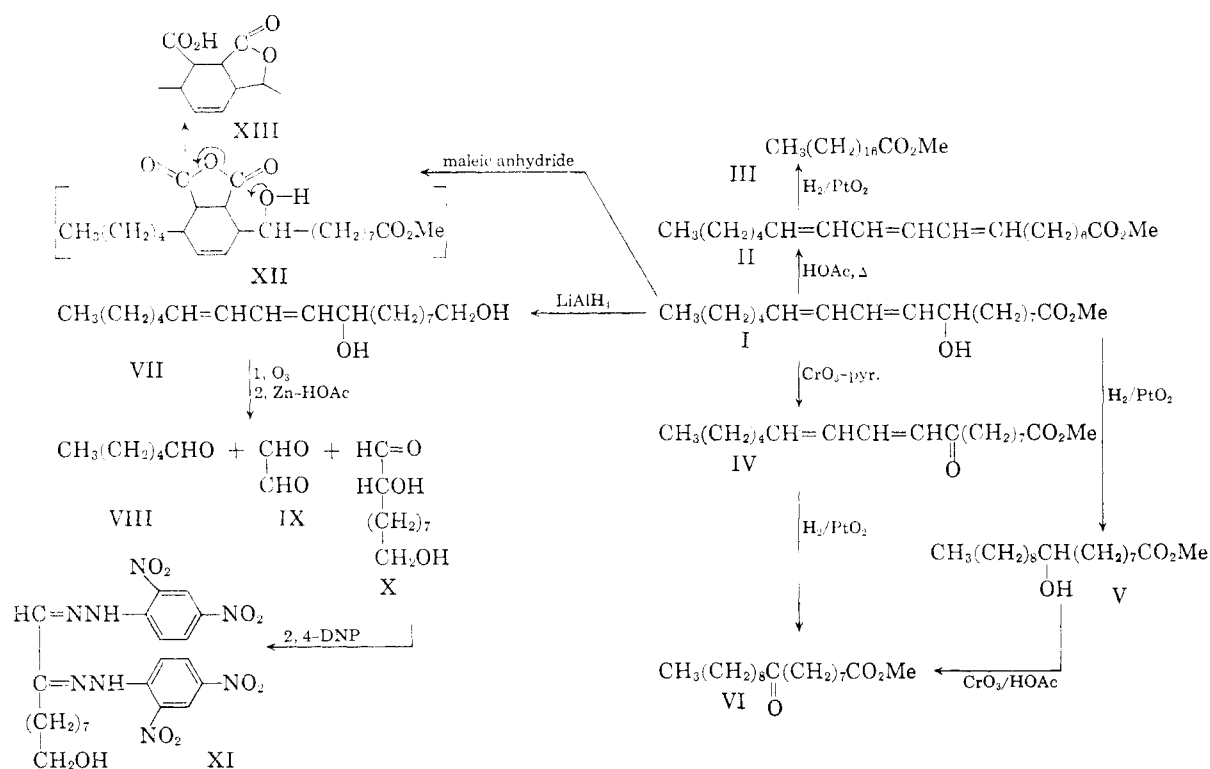
(4) C. R. Scholfield, J. Nowakowska and H. J. Dutton, Presentation before the 50th Spring Meeting, American Oil Chemists' Society, New Orleans, La., April 20–22, 1959.

(5) J. E. Jackson, R. F. Paschke, W. Tolberg, H. M. Boyd and D. H. Wheeler, *J. Am. Oil Chemists' Soc.*, **29**, 229 (1952); N. H. E. Ahlers, R. A. Brett and N. G. McTaggart, *J. Appl. Chem. (London)*, **3**, 433 (1953); D. H. Wheeler in "Progress in the Chemistry of Fats and Other Lipids," Vol. 2, ed. by R. T. Holman, *et al.*, Pergamon Press, London, 1954, p. 268.

(6) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

(7) M. C. Burnett, unpublished data; for analytical methods used, *cf.* "Official and Tentative Methods of the American Oil Chemists' Society," Cd 7–48, revised April, 1956.

(8) F. D. Gunstone, *J. Chem. Soc.*, 1611 (1954).

Fig. 1.—Weight distribution obtained in countercurrent distribution of mixed methyl esters, using hexane–acetonitrile.

an orange-red compound, m.p. 144–147°, tentatively formulated as a **dinitrophenylosazone** on the basis of elementary analyses and visible spectrum.
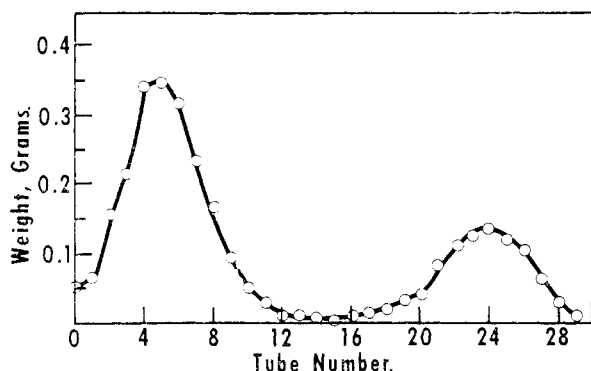
Methyl dimorphecolate (I) on treatment with maleic anhydride readily formed a Diels–Alder adduct which was not obtained crystalline. Infrared spectra of the adduct showed maxima at 5.59 (γ-lactone), 5.73 (ester) and 5.82 μ (acid), but none ascribable to an anhydride. It is therefore suggested that the formally expected adduct may have rearranged to lactone XIII. Precedents for such a rearrangement are known. Heilbron and co-workers[9] found that the maleic anhydride adducts of 3,5-hexadiene-2-ol and some related dienols were isolated as lactonic acids analogous to XIII.

On the basis of the evidence available, dimorphecolic acid can be assigned the structure I, that of 9-hydroxy-*trans,trans*-10,12-octadecadienoic acid.

(9) I. M. Heilbron, E. R. H. Jones, J. T. McCombie and B. C. L. Weedon, *J. Chem. Soc.*, 84 (1945).

The reasons for the high reactivity of I toward hydrogen bromide remain obscure. Spectral evidence suggests that hydrogen bromide reacts with I under the conditions of the oxirane oxygen determination[6] by displacement of hydroxyl accompanied by some elimination. This allylic hydroxyl would be expected to be highly reactive, but further work will be required to elucidate fully the mechanism of this reaction. It is noteworthy in this connection that Bergström and Hansson[10] treated methyl linoleate with N-bromosuccinimide and obtained initially a *conjugated dienoid* bromide. This product tended to eliminate hydrogen bromide to form a conjugated triene, but the elimination reaction *did not* go to completion.

Dimorphecolic acid appears to be unique in being the first naturally occurring fatty acid having more than 12 carbon atoms which is a conjugated diene.[11] It increases by one the list of previously known long-chain hydroxy acids of lipid origin.[12] It is apparent from the formulas of known C-18 fatty acids that dimorphecolic acid falls into a widespread biogenetic pattern, since the carbon atoms involved in centers of unsaturation or oxygenation are most frequently carbons 9 to 13. It differs
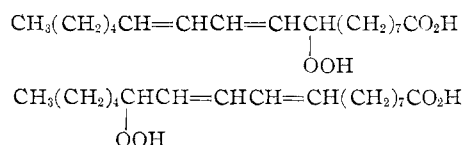
(10) S. Bergström and G. Hansson, *Acta Chem. Scand.*, **4**, 435 (1950).

(11) With the possible exception of 9,14-dihydroxy-10,12-octadecadienoic acid, which Davis, Conroy and Shakespeare (*cf.* THIS JOURNAL, **72**, 124 (1950)) isolated from tung oil, but considered to be an artifact. The longest chain conjugated dienoid fatty acid previously known to occur naturally is 2,4-dodecadienoic acid, isolated from *Sebastiana lingustrina* seed oil by Holman and Hanks (*cf. J. Am. Oil Chemists' Soc.*, **32**, 356 (1955)).

(12) For reviews of this subject, see (a) T. P. Hilditch, "Chemical Constitution of Natural Fats," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 517; (b) F. D. Gunstone in "Progress in Organic Chemistry," Vol. IV, ed. by J. W. Cook, Academic Press, Inc., New York, N. Y., 1958, p. 14.

from 9-hydroxy-12-octadecenoic acid[13] only in having an additional double bond in the 10-position. The structure of dimorphecolic acid is somewhat analogous to that of ximenynolic acid (8-hydroxyoctadec-9-yn-11-enoic acid), a constituent of *Ximenia caffra* oil.[14] It is also of interest to note that dehydration product II should have double bonds in the same positions as the 8,10,12-octadecatrienoic acids isolated from *Calendula officinalis* oil by McLean and Clark.[15]

Although dimorphecolic acid apparently has not been reported as a naturally occurring constituent of a seed oil or other plant material, this acid and its methyl ester have been prepared, in combination with isomeric materials, by reduction of linoleate hydroperoxides. Bergström[16] demonstrated that metal-catalyzed autoxidation of sodium linoleate, or oxidation with lipoxidase, produced conjugated dienoid hydroperoxides. The product was shown to be a mixture of 9- and 13-hydroperoxides

$$CH_3(CH_2)_4CH=CHCH=CHCH(CH_2)_7CO_2H$$
$$\underset{OOH}{|}$$

$$CH_3(CH_2)_4CHCH=CHCH=CH(CH_2)_7CO_2H$$
$$\underset{OOH}{|}$$

These hydroperoxides were reduced to the corresponding hydroxy compounds and subsequently converted to saturated methyl esters, which were separated chromatographically. In one of the more recent extensions of this work, Sephton and Sutton[17] obtained from linoleate hydroperoxides mixed methyl hydroxyoctadecadienoates which gave correct carbon and hydrogen analyses. These mixed esters were also separated into concentrates of *cis,trans*- and *trans,trans*-conjugated isomers having infrared maxima which were different from each other and which had the same maxima in the 10–11 μ region expected for the corresponding conjugated diene having no hydroxyl substituent. Similar observations were made earlier by Privett and co-workers[18] in their work with linoleate hydroperoxides. These results show that α-hydroxyl or hydroperoxido substituents cause no anomalies which prevent ready identification of the different geometric isomers of conjugated dienes in the fatty acid series, and thus substantiate our assignment of a *trans,trans*-configuration to the dienoid system of dimorphecolic acid.

In view of the fact that linoleic acid can be converted to dimorphecolic acid in a two-step reaction *in vitro*, it seems not unlikely that linoleic acid may be a biogenetic precursor of dimorphecolic acid. If it were, however, it would seem possible that dimorphecolic acid might be accompanied by the analogous 13-hydroxy-9,11-octadecadienoic acid. No evidence for the occurrence of a 13-hydroxy acid in *Dimorphotheca* oil has been found by the authors of this paper.

The unique α-hydroxydiene structure of dimorphecolic acid suggests that it may have considerable industrial utility if proper cultural practices for growing *Dimorphotheca aurantiaca* seed can be developed.

Experimental[19]

Isolation of Methyl Dimorphecolate (I).—Dehulled, coarsely ground seeds of *Dimorphotheca aurantiaca* were extracted overnight in a Soxhlet apparatus with 30–60° petroleum ether. The bulk of the solvent was evaporated on a steam-bath under a nitrogen atmosphere, and the remainder was removed *in vacuo* with a rotating evaporator.

A 27.9-g. portion of oil was refluxed for 2 hours in 200 ml. of methanolic sodium methoxide (4.0 g. Na/l. MeOH). The mixture was acidified by dropwise addition of acetic acid, then diluted with 400 ml. of water and extracted with ether. The combined ether extracts, dried with sodium sulfate, yielded on evaporation 22.5 g. of mixed methyl esters.

A 3.36-g. portion of mixed methyl esters was subjected to a 30-tube countercurrent distribution in a Craig–Post apparatus. The solvent system chosen was acetonitrile–hexane (1:1)[4]; 40 ml. of each solvent per tube was used. The weight distribution curve obtained is shown in Fig. 1. This procedure was repeated several times on a larger scale, using separatory funnels and pooling material in "tubes" 11–30. The material obtained from tubes 3 to 12 consisted chiefly of methyl dimorphecolate. Tubes 0–2 contained mainly an acidic material, apparently dimorphecolic acid. The ultraviolet spectrum of the oily ester showed λ_{max} 231 mμ (ϵ 27,900); infrared maxima at 2.94 (OH), 5.72 (ester); one at 10.09 but none at 10.55 μ (*trans,trans*-conjugated diene[5,17,18]); $[\alpha^{26}]D + 5°$ (c 5.0, CHCl₃).

Anal. Calcd. for $C_{19}H_{34}O_3$: neut. equiv., 310. Found: neut. equiv. 305; absorbs 1.8 moles hydrogen per mole.

Saponification of *Dimorphotheca aurantiaca* **Oil.**—A 0.28-g. portion of *Dimorphotheca* oil was heated under reflux 1 hour with 1.2 ml. of 0.8 N ethanolic potassium hydroxide. After cooling, the mixture was diluted with water, then extracted four times with ether. From these ether extracts was obtained 0.07 g. of unsaponifiable matter. The alkaline liquor was acidified with sulfuric acid and free acids were isolated in the usual way; 0.22 g. of free acid was obtained. About three-fourths of the dienoid absorption of the original oil (231 mμ) had disappeared, but it was not replaced with trienoid absorption. The intensity of the hydroxyl peak in the infrared spectrum was substantially undiminished.

Saponification was also carried out with the same concentrations of oil and potassium hydroxide, except that the mixture was allowed to stand overnight at 0°. This treatment resulted in destruction of about half the dienoid absorption.

Dehydration of Methyl Dimorphecolate (I).—Compound I (0.22 g.) was dissolved in 3 ml. of glacial acetic acid and refluxed 5 hours. The acetic acid was then removed by vacuum distillation. The ultraviolet spectrum of the dehydration product II showed λ_{max} 259 mμ, 268 mμ (ϵ 32,400), and 279 mμ; its infrared spectrum showed no hydroxyl; II was not further characterized.

Hydrogenation of Conjugated Triene II.—A 0.19-g. portion of II dissolved in 3 ml. of glacial acetic acid was hydrogenated 1 hour at room temperature with platinum oxide catalyst. The catalyst was removed by filtration. A crude product (III) of 0.19 g., m.p. 28–33°, was obtained. Two recrystallizations from methanol and careful drying produced a specimen having m.p. 37–38°; no depression of melting point was observed on admixture with authentic methyl stearate. Gas chromatographic analysis confirmed the identity of III with methyl stearate.

Anal. Calcd. for $C_{19}H_{38}O_2$: C, 76.4; H, 12.8; OMe, 10.4. Found: C, 76.0; H, 12.5; OMe, 10.6.

Hydrogenation of Methyl Dimorphecolate (I).—Methyl dimorphecolate (0.419 g.) was dissolved in 25 ml. of absolute ethanol and hydrogenated 1 hour at room temperature and 1

(13) F. D. Gunstone, *J. Chem. Soc.*, 1274 (1952).

(14) S. P. Lightelm, *Chemistry & Industry*, 249 (1954).

(15) J. McLean and A. H. Clark, *J. Chem. Soc.*, 777 (1956).

(16) S. Bergström, *Arkiv Kemi, Mineral. Geol.*, **21A**(15), 1 (1945).

(17) H. H. Sephton and D. A. Sutton, *J. Am. Oil Chemists' Soc.*, **33**, 263 (1956).

(18) O. S. Privett, W. O. Lundberg, N. A. Khan, W. E. Tolberg and D. S. Wheeler, *ibid.*, **30**, 61 (1953).

atmosphere with platinum oxide catalyst. The catalyst was removed by filtration and the solvent evaporated, yielding 0.319 g. of white solid (V), m.p. 43–48°. Two recrystallizations from hexane yielded 0.071 g. of V, m.p. 49–51°, whose infrared spectrum was very similar to that of ($\pm$)-methyl-9-hydroxyoctadecanoate, but markedly different from those of isomeric hydroxyoctadecanoates. This preparation was not readily reproducible, owing to the fact that compound I tended to suffer loss of hydroxyl. Yields were variable and generally very low. The preferred route for conversion of I to VI is through intermediate IV.

Anal. Calcd. for $C_{19}H_{38}O_3$: C, 72.6; H, 12.2; OMe, 9.8; C–Me, 1.0. Found: C, 72.3; H, 12.0; OMe, 9.8; C–Me, 0.9.

Oxidation of Methyl Dimorphecolate (I).—Compound (1.89 g.) in 10 ml. of dry pyridine was added to a solution of 2.0 g. of chromium trioxide in 20 ml. of dry pyridine.[20] The mixture was allowed to react 24 hours at room temperature with continuous stirring. The mixture then was diluted with water and extracted four times with ether. The combined ether extracts were washed with 5% hydrochloric acid, then with water, dried over sodium sulfate and evaporated. The yield was 1.42 g. of dark reddish oil, which was purified by chromatography on neutral alumina; 1.09 g. of purified IV, m.p. 26–28°, was obtained by benzene elution. A 0.169-g. portion of the eluate recrystallized from hexane yielded 0.039 g. having m.p. 28–30°. The ultraviolet spectrum showed λ_{max} 275 mμ (ϵ 16,700); infrared maxima included 5.72 (ester), 5.90 (conjugated dienone[21]), 5.98 and 9.95 μ (conjugated dienone).

Anal. Calcd. for $C_{19}H_{32}O_3$: C, 74.0; H, 10.5. Found: C, 73.8; H, 10.4.

Preparation of Methyl 9-Oxoöctadecanoate (VI). A. By Oxidation of V.—A 0.220-g. portion of V was dissolved in 10 ml. of glacial acetic acid. To this was added, dropwise and with continuous stirring, 0.70 g. of chromium trioxide dissolved in 0.5 ml. of water and 8 ml. of acetic acid. The mixture was heated at 50° for 15 minutes, then cooled, diluted with water and extracted four times with ether. The combined ether extracts were washed with dilute sodium hydroxide, then with water and dried over sodium sulfate. Upon evaporation, 0.128 g. of VI was obtained, m.p. 44–45°. This was recrystallized from methanol, but without increase in melting point.

B. By Hydrogenation of IV.—A 0.276-g. portion of IV was hydrogenated in 30 ml. of absolute ethanol with 0.013 g. of platinum oxide catalyst for 30 minutes at 1 atmosphere and room temperature. A crude product, 0.267 g. of VI having m.p. 40–42°, was obtained. After two recrystallizations from hexane, 0.090 g. was obtained, m.p. 44–45° (lit.[22] m.p. 47.5–48°). There was no depression of melting point on admixture of specimens prepared by methods A and B. The infrared spectrum of VI was identical with that of synthetic methyl 9-oxoöctadecanoate, but different from those of isomeric oxoöctadecanoates.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.0; H, 11.6. Found: C, 72.7; H, 11.5.

Lithium Aluminum Hydride Reduction of I.—Lithium aluminum hydride (2.22 g.), suspended in dry ether, was reated dropwise with 2.08-g. of I, dissolved in dry ether. Spontaneous refluxing was at first maintained by controlling the rate of addition of I. Sufficient heat was applied to maintain reflux for 2.5 hours. Sufficient ethyl acetate was then added to decompose the excess lithium aluminum hydride. The mixture was extracted with 10% sodium hydroxide to remove inorganic matter. The remaining ethereal solution, after being dried with sodium sulfate and evaporated, yielded 1.57 g. of crude VII, m.p. 44–46°. This was recrystallized from hexane; 1.34 g., m.p. 46–47°, was obtained.[23] The ultraviolet spectrum of VII showed λ_{max} 231 mμ (ϵ 19,360); infrared maxima included: 2.95 (hydroxyl, very strong), 10.12μ (conjugated diene[5,17,18]).

Anal. Calcd. for $C_{18}H_{34}O_2$: C, 76.5; H, 12.1. Found: C, 76.7; H, 11.9.

Ozonolysis of VII.—A 1.01-g. portion of VII (7.12 mmoles) was dissolved in 20 ml. of absolute methanol and ozonized at −35° with *ca.* 8.5 mmoles of ozone. The measured uptake of ozone was 7.28 mmoles. Ozonides were decomposed reductively by heating the mixture with 2 ml. of glacial acetic acid, followed by adding 1 g. of zinc dust in portions until a negative peroxide test was obtained. Zinc was then removed by filtration; the filtrate was diluted somewhat with water and extracted several times with petroleum ether.

The combined petroleum ether extracts were distilled cautiously to remove most of the solvent. The residue was steam distilled. A volatile aldehyde (VIII) was isolated from the steam distillate by ether extraction. The 2,4-dinitrophenylhydrazone of VIII was prepared by the method of Shriner, Fuson and Curtin.[24] This derivative had m.p. 94–97°; no depression of melting point was apparent on admixture with an authentic specimen of the 2,4-dinitrophenylhydrazone of hexanal. The identity of this derivative was confirmed by its X-ray diffraction pattern and by paper chromatography, using the solvent system heptane–methanol[25]. The observed R_f value was 0.78 for both the 2,4-dinitrophenylhydrazone of VIII and authentic hexanal 2,4-dinitrophenylhydrazone; for heptanal 2,4-dinitrophenylhydrazone run simultaneously, the observed R_f was 0.82.

Anal. Calcd. for $C_{12}H_{16}N_4O_4$: C, 51.4; H, 5.8; N, 20.0. Found: C, 50.8; H, 5.8; N, 19.8.

The aqueous alcoholic residue left after petroleum ether extraction was saturated with sodium chloride, then extracted several times with ether. The combined, dried ether extracts were concentrated to 19 ml. and heated with a solution of 1.2 g. of 2,4-dinitrophenylhydrazine, 6 ml. of concd. sulfuric acid, 9 ml. of water and 20 ml. of ethanol.[24] An intractable mixture of 2,4-dinitrophenylhydrazones was obtained. By a combination of fractional crystallization and column chromatography (neutral alumina), two main fractions were obtained. One, a poorly crystalline orange substance, m.p. 144–147°, sparingly soluble in ethanol, was formulated tentatively as the dinitrophenylphenylosazone of 2,10-dihydroxydecanal (X); λ_{max} 399 (ϵ 39,900) and 433 mμ (ϵ 40,600).[26]

The other solid derivative, a brown substance, m.p. 280–320°, insoluble in chloroform and ethanol and moderately soluble in dioxane, was presumed to be the bis-dinitrophenylhydrazone of glyoxal.[27] It was not obtained in pure or well-crystallized form.

Maleic Anhydride Adduct of I.—A 0.314-g. portion of I (1.02 mmoles) and 0.110 g. of maleic anhydride were dissolved in 3 ml. of benzene and refluxed 3 hours. The benzene was evaporated and the residue dissolved in ether. The ether solution was extracted twice with water, then dried over sodium sulfate and evaporated, yielding 0.381 g. of clear oil. This adduct was not obtained crystalline. Its infrared spectrum was in agreement with a carboxylactone formulation (XIII) rather than an anhydride (XII); maxima were at 5.59 (γ-lactone), 5.73 (ester) and 5.82 μ (acid); it was transparent in the 231 mμ region of the ultraviolet spectrum.

Reaction of I and VII with Hydrogen Bromide.—Under conditions of Durbetaki's method for determining oxirane oxygen,[6] compound I consumed 1.0 mole of hydrogen bromide; I (0.184 g., 5.72 mmoles) was dissolved in 10 ml. of benzene, then 10 ml. of hydrogen bromide–acetic acid reagent (5.72 mmoles) was added dropwise. The solvents were removed *in vacuo*. The infrared spectrum of the product showed practically no hydroxyl peak (2.94 μ); ultraviolet absorption spectra indicated disappearance of about half the absorbance of I at 231 mμ (conjugated diene) with appearance of a corresponding amount of triene (max. at 260, 268 and 279 mμ). Compound VII consumed 1.1 moles of

(20) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

(21) R. N. Jones, D. A. Ramsay, D. S. Kier and K. Dobriner, *ibid.*, **74**, 80 (1952).

(22) S. Bergström, G. Aulin-Erdtman, B. Rolander, E. Stenhagen and S. Östling, *Acta Chem. Scand.*, **6**, 1157 (1952).

(23) This 10,12-octadecadiene-1,9-diol should be analogous to, and isomeric with the diene-diol, m.p. 62.3–63°, obtained by lithium aluminum hydride reduction of ximenynolic acid (*cf.* ref. 13).

(24) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 219.

(25) D. F. Meigh, *Nature*, **170**, 579 (1952).

(26) Glucose 2,4-dinitrophenylosazone has $\lambda_{max}^{dioxane}$ 445 mμ (*cf.* A. L. Lehninger, *J. Biol. Chem.*, **149**, 43 (1943)).

(27) Literature m.p. 328° (*cf.* Shriner, Fuson and Curtin, ref. 24, p. 283).

hydrogen bromide per mole under conditions of the analytical method.[6]

Methylation of Acidic Material in Tubes 0-2, Countercurrent Distribution.—The material obtained in tubes 0–2 of the countercurrent distribution was a semi-solid. Its infrared spectrum was similar to that of methyl dimorphecolate (I), except that it had the characteristics of an acid rather than an ester. A 3.4-g. portion of this acidic material was dissolved in dry ether and added dropwise to a solution of 0.63 g. of diazomethane in 75 ml. of ether at room temperature. The excess diazomethane was removed by warming gently; on evaporation of solvent, an oily substance was obtained whose infrared spectrum was that of I.
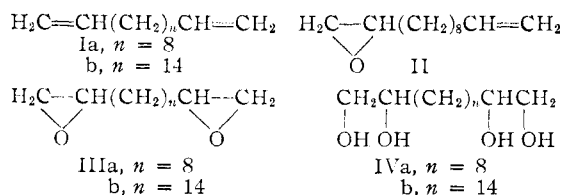

The Preparation and Properties of Some Oxidation Products of 1,11-Dodecadiene and 1,17-Octadecadiene[1]

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1,11-Dodecadiene, 1,2-epoxy-11-dodecene, 1,2,11,12-diepoxydodecane, 1,2,11,12-tetrahydroxydodecane, 1,17-octadecadiene, 1,2,17,18-diepoxyoctadecane and 1,2,17,18-tetrahydroxyoctadecane have been prepared for testing as possible intermediates in the oxidation of dodecane and octadecane by microörganisms. The epoxidation of both olefins with perbenzoic acid proceeded stepwise. The reaction of 1,2,11,12-diepoxydodecane with sodium p-bromophenoxide gave 1,2-epoxy-11-hydroxy-12-p-bromophenoxydodecane and bis-1,12-p-bromophenoxy-2,11-dihydroxydodecane. Tests with yeast *Candida lipolytica* indicate that the various derivatives of dodecane are oxidized more slowly than oxidation products involving one end of the hydrocarbon.

In the study of the oxidation of saturated hydrocarbons by certain microörganisms, oxidation products involving both ends of the hydrocarbons were required for the elucidation of the path of the oxidation. Work in this study was limited to the oxidation products of dodecane and octadecane and included the preparation of 1,11-dodecadiene (Ia), 1,17-octadecadiene (Ib), 1,2-epoxy-11-dodecene (II), 1,2,11,12-diepoxydodecane (IIIa), 1,2,17,18-diepoxyoctadecane (IIIb), 1,2,11,12-tetrahydroxydodecane (IVa) and 1,2,17,18-tetrahydroxyoctadecane (IVb).

$$H_2C{=}CH(CH_2)_nCH{=}CH_2 \quad H_2C{-}CH(CH_2)_8CH{=}CH_2$$
$$\text{Ia, } n = 8 \qquad\qquad\qquad \diagdown\!\diagup$$
$$\text{b, } n = 14 \qquad\qquad\qquad\quad O \quad II$$

$$H_2C{-}CH(CH_2)_nCH{-}CH_2 \qquad CH_2CH(CH_2)_nCHCH_2$$
$$\diagdown\!\diagup \qquad\quad \diagdown\!\diagup \qquad\qquad |\ \ | \qquad\qquad |\ \ |$$
$$O \qquad\qquad O \qquad\qquad OH\ OH \qquad\quad OH\ OH$$
$$\text{IIIa, } n = 8 \qquad\qquad\qquad \text{IVa, } n = 8$$
$$\text{b, } n = 14 \qquad\qquad\qquad \text{b, } n = 14$$

Both dienes were obtained from the action of allyl chloride on the Grignard reagent from 1,6-dichlorohexane.[4] Purification of the dienes was accomplished through the formation of the silver nitrate complexes and was necessary for 1,11-dodecadiene since this compound co-distilled with 1,6-dichlorohexane.

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(2) Abstracted in part from the M.S. thesis, February, 1957, and the Ph.D. thesis, June, 1959, of P. D. Klimstra.

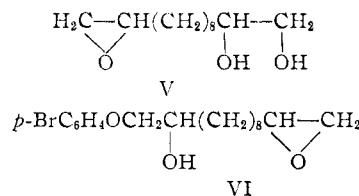(3) American Chemical Society Petroleum Research Fund Predoctoral Fellows.

(4) F. Drahowzal, *Monatsh.*, **82**, 793 (1951).

The preparation of 1,2,11,12-diepoxydodecane (IIIa) from the bis-chlorohydrin was not successful. The bis compound, which was not obtained pure, was resistant to cyclization with cold alkali.

Direct epoxidation of 1,11-dodecadiene (Ia) with peracetic acid gave 1,2,11,12-diepoxydodecane (IIIa). Better yields and less side products were obtained, however, using perbenzoic acid. The epoxidation at low temperatures was found to proceed stepwise with both reagents. Using an excess of perbenzoic acid one mole of the reagent added at 5–6° in less than two hours while the second mole required about ten hours to react (see Fig. 1).

A similar stepwise addition of perbenzoic acid occurred with 1,17-octadecadiene (Ib) and 1,5-hexadiene and is shown in Fig. 1.

By interrupting the reaction with peracetic acid and 1,11-dodecadiene before it had gone to completion it was possible to isolate both the monoepoxide II and diepoxide IIIa together with a fraction which had the composition expected for 1,2-epoxy-11,12-dihydroxydodecane (V).

$$H_2C{-}CH(CH_2)_8CH{-}CH_2$$
$$\diagdown\!\diagup \qquad\qquad\quad |\ \ \ |$$
$$O \qquad\qquad\quad OH\ OH$$
$$V$$

$$p\text{-}BrC_6H_4OCH_2CH(CH_2)_8CH{-}CH_2$$
$$| \qquad\qquad\qquad\qquad \diagdown\!\diagup$$
$$OH \qquad\qquad\qquad\qquad O$$
$$VI$$

To determine whether this stepwise addition was characteristic of other reagents, the addition of bromine was studied with both 1,11-dodecadiene (Ia) and 1,17-octadecadiene (Ib) and found to be