Ethanol from the reaction mixture was removed under vacuum. The residue was diluted with water and was extracted with ether. The acid salt was treated with dilute acid, and liberated fatty acid was extracted with ether. Fatty acids thus obtained were converted to methyl esters by the usual procedure. The esters then were subjected to GLC (column: 3.04 m long, 2 mm inside diameter, packed with Chromosorb W [60-80 mesh], coated with 20% diethylene glycol succinate; temperature programed from 180-210 C at 2 C/min; chart speed: 12 in./hr; detector: flame ionization).

Wax Alcohols

Fractions 19-23 were combined and crystallized with acetone. An IR spectrum showed the product to be alcoholic in nature with 3310 cm^{-1} (OH stretching); 1055 cm^{-1} (C-O stretching for alcohol); and 730, 720 cm^{-1} (alkane chain). This combined and recrystallized material was analyzed by GLC (column: stainless steel 3 ft x 1/8 in., packed with Chromosorb W, [100-120 mesh] on 15% SE 30; carrier gas: N_2 with a flow rate 24 ml/min; chart speed: 30 in./hr; detector: flame ionization).

RESULTS

Straight chain hydrocarbons, fatty acids, and fatty alcohols of *C. pluricaulis* (Chois) were separated by column chromatography on alumina using various combinations of petroleum ether (40-60 C), benzene, and chloroform, and compounds were identified by GLC (Table II). *C. pluricaulis* (Chois) was found to contain C_{22}-C_{33} hydrocarbons, C_{27}, C_{31}, and C_{33} as the major components. Fatty acids were mainly of even number carbon atoms ranging from C_{14}-C_{28}. Palmitic, myristic, and linoleic acids were the major components. The wax-alcohol fraction was found to consist of even number carbon atoms ranging from C_{24}-C_{32}. In relative concentration, C_{26}, iso-C_{28}, iso-C_{30}, and C_{32} were found to predominate.

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TABLE II

Distribution of Wax Hydrocarbons, Fatty Acids, and Fatty Alcohols by Gas Liquid Chromatography

Carbon chain length	Percent Composition		
	Hydrocarbon	Acid	Alcohol
14	-	25.3	-
15	-	Traces	-
16	-	58.7	-
17	-	-	-
18	-	Traces	-
18:1	-	Traces	-
18:2	-	3.5	-
20	-	1.2	-
21	-	Traces	-
22	Traces	1.5	-
24	-	Traces	-
24	-	2.0	1.6
25	Traces	Traces	-
Iso-26	-	Traces	2.7
26	Traces	Traces	50.2
27	15.8	-	-
Iso-28	-	-	4.0
28	-	Traces	-
29	1.7	-	-
Iso-30	-	-	15.8
30	Traces	-	-
31	61.2	-	-
Iso-32	-	-	-
32	-	-	3.1
33	10.5	-	-
Iso-34	-	-	-

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The Stereochemistry of Linoleic Acid Tetrabromides

ABSTRACT

The NMR spectrum of the crystalline tetrabromide obtained from bromination of linoleic acid exhibited an AA′XX′ splitting pattern for the C-11 hydrogens, indicative of a racemic structure rather than a meso for the brominated part of the molecule. Thus, the crystalline isomer is a racemic mixture of 9 R, 10 R, 12 R, 13 R-tetrabromooctadecanoic acid and 9 S, 10 S, 12 S, 13 S-tetrabromooctadecanoic acid. The C-11 methylene spectrum of the liquid tetrabromide was treated as an ABX_2 pattern; thus, this isomer is a mixture of 9 R, 10 R, 12 S, 13 S-tetrabromooctadecanoic acid and 9 S, 10 S, 12 R, 13 R-tetrabromooctadecanoic acid.

INTRODUCTION

The bromination of linoleic acid produces two tetrabromides, a crystalline isomer and a liquid isomer. The crystalline isomer is an important intermediate in the preparation of pure linoleic acid (1) and in the preparation of labeled linoleic acid (2). *Trans* addition of bromine to a *cis* alkene gives the threo dibromide, hence addition of two moles bromine to *cis, cis*-octadecadienoic acid (linoleic acid) would be expected to give two different threo, threo racemic mixtures (3). These two pairs of enantiomers are diastereomeric and differ in the relationship of the 9, 10 chirality to the 12, 13 chirality (Fig. 1). The enantiomeric 9 S, 10 S, 12 R, 13 R-tetrabromooctadecanoic acid (I) and 9 R, 10 R, 12 S, 13 S-tetrabromooctadecanoic acid (II) have a pseudoplane of symmetry through C-11 (opposite chirality at C-10 and 12), whereas the other enantiomeric pair (III and IV) have a pseudoinversion plane through C-11 (same chirality at C-10 and 12). The question is which pair is the crystalline tetrabromide and which is the liquid.

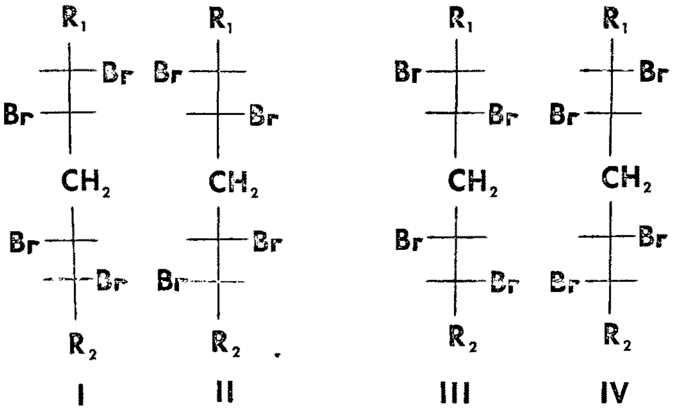

FIG. 1. Structures of 9 S, 10 S, 12 R, 13 R-tetrabromooctadecanoic acid (I); 9 R, 10 R, 12 S, 13 S-tetrabromooctadecanoic acid (II); 9 R, 10 R, 12 R, 13 R-tetrabromooctadecanoic acid (III); 9 S, 10 S, 12 S, 13 S-tetrabromooctadecanoic acid (IV). R_2 = $CH_3(CH_2)_4$-; R_1 = $HO_2C(CH_2)_7$-.

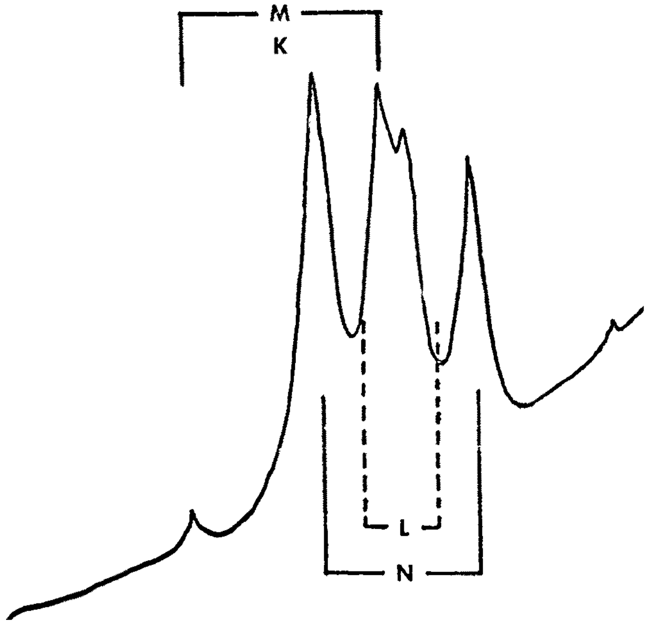

FIG. 2. A60A NMR spectrum of C-11 hydrogens of crystalline tetrabromooctadecanoic acid with shift reagent, $Pr(fod)_3$. M = K = 16 Hz; N = 12.7 Hz; and L = 8.3 Hz.

A similar case of diastereomeric products was studied in the peracid oxidation of linoleic acid, where a solid and liquid diepoxide were obtained (4). Since a solid diepoxide with a significant rotation and a liquid diepoxide with a very small rotation were isolated from epoxidation of vernolic acid, the liquid must have been the isomer with the pseudoplane of symmetry (opposite chirality at C-10 and 12), and the solid must have been the isomer with the same chirality at C-10 and 12. Since the tetrabromide has never been resolved, this method is not applicable.

METHOD

The NMR spectrum of the C-10, 11, 12 portion of the isomers with the pseudoplane of symmetry, I and II, would be predicted to exhibit a splitting pattern of the type XABX, since the C-10 and 12 hydrogens are magnetically equivalent in this system because of the symmetry and since the two C-11 hydrogens are not isochronous. None of the conformations have equivalent C-11 hydrogens, and there are no equi-energy pairs in which the magnetic environments are exchanged (5,6). An XAA'X' splitting pattern should be observed for the other racemic isomers, III and IV, since the C-11 hydrogens are isochronous, because of the pseudoplane of inversion through C-11, but not magnetically equivalent, because of different coupling constants to the hydrogens on adjacent carbons. This system is, thus, not like that in 2,3-dibromobutane where both the racemic and the meso forms can exhibit $X_3AA'X_3$ spectra, because the meso form in that case has one conformation where the C-2 and C-3 hydrogens are equivalent and two others which are equi-energy and in which the magnetic environments are exchanged (7,8).

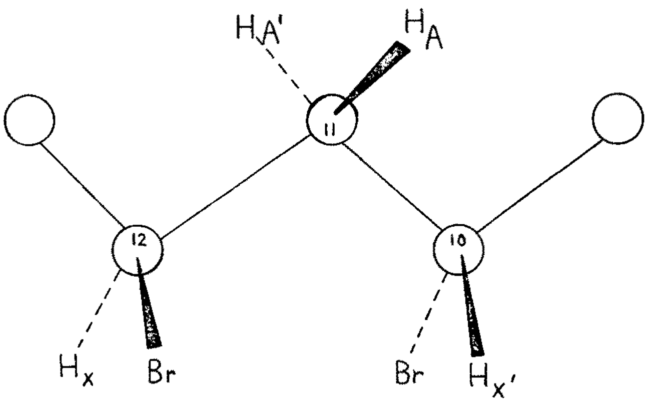

FIG. 3. Crystalline 9 R, 10 R, 12 R, 13 R-tetrabromooctadecanoic acid in $_9ap^{12}$ – $_{10}ap^{13}$ conformation.

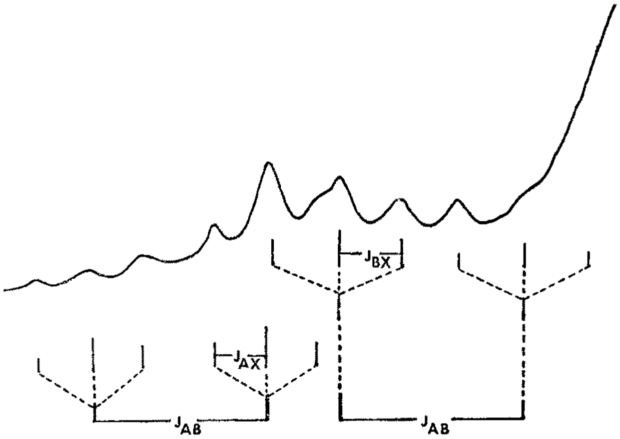

FIG. 4. A60A NMR spectrum of C-11 hydrogens of the liquid tetrabromooctadecanoic acid with $Pr(fod)_3$. J_{AB} = -22 Hz; J_{AX} = 6 Hz; J_{BX} = 8 Hz.

The NMR spectra of the tetrabromides are complicated by the overlap of the peaks of the C-11 methylene hydrogens with the triplet of the methylene adjacent to the carboxy group. When the shift reagent, tris-(1,1,1,2,2,3,3-heptafluoror-7,7-dimethyl-4,6-octanedionato) - praseodymium–$Pr(fod)_3$–was used, the interfering C-2 methylene triplet was shifted upfield. The liquid tetrabromide was purified by silicic acid chromatography.

RESULTS AND DISCUSSION

The spectrum of the C-11 methylene hydrogens of the crystalline tetrabromide was resolved clearly into an XAA'X' splitting pattern expected for the 9 R, 10 R, 12 R, 13 R-tetrabromooctadecanoic acid (III) and its enantiomer (IV). The C-11 hydrogen spectrum closely resembled that of racemic 2,4-dibromopentane (5) Fig. 2).

Since $J_{XX'}$ is a four bond coupling, it is very small and the spectrum analysis is simplified. The geminal coupling constant $|J_{AA'}|$ thus equals M or K, since the antisymmetric and symmetric subspectrum quartets are superimposed (5). The small peak on the left represents the c and g peaks of the superimposed subspectrum quartets, thus $J_{AA'} = -16$ Hz.

The J_{AX} and $J_{AX'}$ coupling constants obtained from N and L, the subspectrum shift differences, were found to be 10.5 Hz and 2.2 Hz, respectively. These values are consistent with the assumption that the molecule exists mainly in a preferred conformation, presumably that in which the carbon chain is antiperiplanar on both sides of C-11 or $_9ap^{12} - {}_{10}ap^{13}$ (*trans-trans*) (6) (Fig. 3).

The C-11 hydrogen spectrum of the liquid tetrabromide was consistent with an XABX system with $J_{AB} = -22$ Hz, $J_{AX} = 6$ Hz, and $J_{BX} = 8$ Hz. Thus, the liquid tetrabromide is composed of I and II, the isomers with the pseudoplane of symmettry. The far right triplet was obscured by the C-8, C-14, and shifted C-2 methylenes. The J_{AX} and J_{BX} values are consistent with high populations of the conformers of II with the chain conformation $_9ap^{12} - {}_{10}M^{13}$ (G^-T) and $_9P^{12} - {}_{10}ap^{13}$ (TG^+), (5) which result in coupling constants between synclinal and antiperiplanar values (Fig. 4).

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