LITERATURE CITED

1. Ya. S. Meerov, A. N. Katyuzhanskaya, and N. F. Dyuban'kova, Khim. Prirodn. Soedin., 481 (1974).
2. A. N. Katyuzhanskaya, N. F. Dyuban'kova, A. V. Pekhov, A. N. Fyugel', and L. I. Bokareva, Rast. Res., 12, No. 2, 296 (1976).
3. U. I. Salzer, Fette, Seifen, Anstrichmittel, 77, No. 11, 446 (1975).
4. I. G. Mokhnachev and M. P. Kuz'min, The Volatile Substances of Food Products [in Russian], Moscow (1966), p. 36.
5. I. Goryaev and M. Pliva, Methods of Investigating Essential Oils [in Russian], Alma-Ata (1962), p. 634.
6. L. A. Kogan, Quantitative Gas Chromatography [in Russian], Moscow (1975).
7. R. Oberdieck, Alkohol-Industrie, 88, No. 16, 380; No. 17, 397 (1975).
8. U. I. Salzer, International Flavours and Food Additives, 6, No. 4, 206 (1975).
9. M. Porthault, M. Gronnet, and M. Rocca, Labopharma Probl. et Techn., 24, 1253, 379 (1976).
10. L. G. Astakhova, Author's Abstract of Candidate's Dissertation, Krasnodar (1972).

THE STRUCTURES OF THE BROMOHYDROXYOCTADECANOATES FORMED IN THE REACTIONS OF THE DIASTEREOMERIC METHYL ESTERS OF DIEPOXYOCTADECANOIC ACIDS WITH HYDROGEN BROMIDE

I. L. Kuranova, S. L. Gordienko, and G. N. Korskaya

UDC 547.396+547.710

In view of the fact that a report has recently appeared in the literature on dibromo- and tetrabromooctadecanoic acids isolated from the oil of the seeds of *Eremostachys moluccelloides* [1], it is a matter of undoubted interest to investigate the structure of the corresponding synthetic bromine-containing analogs that are formed by the reaction of diepoxyoctadecanoic acids with hydrogen bromide. This reaction forms the basis of a method for determining epoxide oxygen that is widely used in the chemical, foodstuffs, and oils and fats industries [2]. But in the case of the methyl ethers of threo- and erythro-cis-9,10:cis-12,13-diepoxyoctadecanoic acids (I and II, respectively) (diastereomeric diepoxides of methyl linoleate) [3], this method leads to a rather low percentage of epoxide oxygen, particularly for the erythro isomer (II). Thus, for the threo isomer the percentage of epoxide oxygen comes to 9.52 and for the erythro isomer 9.04 (the calculated value being 9.80). A similar anomaly has been pointed out in the literature [4]. A lowering of the results of the determination of epoxide oxygen has also been observed for diepoxides of terpenes [5], but the cause of this phenomenon has not so far been explained.

The present paper gives the results of a study of a number of bromohydroxy compounds obtained by the reaction of the diastereomeric methyl esters (ME's) of cis-9,10:cis-12,13-diepoxyoctadecanoic acids with hydrogen bromide. The investigation of the reaction products, performed under various conditions, has shown that in all cases identical compounds are formed: together with the isomeric open-chain products of addition of two molecules of the reagent — dibromodihydroxyoctadecanoates — cyclic derivatives — substituted tetrahydrofurans and tetrahydropyrans — are formed as the result of the addition of one molecule of HBr (Table 1).

The reaction of the threo isomer (I) with hydrogen bromide gave a complex mixture of substances (Scheme 1) from which by preparative chromatography on silica gel we isolated: the ME of threo-10-bromo-9-hydroxy-(threo-10-bromo-12-bromo)-threo-12-bromo-13-hydroxyoctadecanoic acid (III) (yield 4-9%, R_f 0.52, mp 45-46°C from hexane containing ether); the ME of threo-9-bromo-10-hydroxy-(threo-10-hydroxy-12-hydroxy)-threo-13-bromo-12-hydroxyoctadecanoic acid (IV) (yield 44-52%, R_f 0.68, mp 92-92.5°C from ethanol); fraction A (yield 20-25%, R_f 0.57, mp 30-32°C (from hexane) — a mixture of the ME's of threo-9-bromo-10-hydroxy-(erythro-12-bromo-10-hydroxy)-threo-12-bromo-13-hydroxy- and threo-10-bromo-9-hydroxy-(erythro-10-bromo-

---

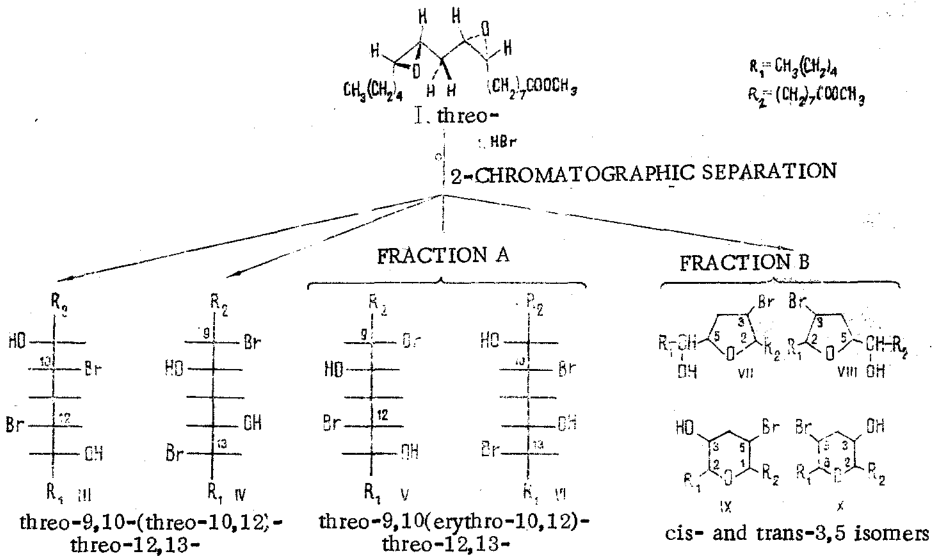
A. A. Zhdanov Leningrad State University. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 767-776, November-December, 1977. Original article submitted June 23, 1977.

0009-3130/77/1306-0646$07.50

TABLE 1. Conditions for the Reactions of the Diastereomeric Diepoxy Acids with HBr and Yields of Open-Chain and Cyclic Compounds

Initial diepoxy acid, g	Reagent	Solvent, V, ml	Ratio of diepoxy acid to HBr (mole)	Yield of reaction product, g	Yield, %, of	
					open-chain compounds	cyclic compounds
I, 0,61	Dry HBr	Hexane 10	1 : 2	0,82	80	14
I, 0,44	"	CCl_4, 7	"	0,63	80	15
I, 0,42	"	Acetone 7	"	0,57	74	8
I, 0,31	"	CH_2Cl_2, 5	"	0,36	82	14
I, 1,56	"	Ether 25	"	2,04	86	9
I, 0,30	"	CH_3COOH, 5	"	0,44	76	12
I, 0,16	HBr/CH_3COOH	CH_3COOH, 10	"	0,22	77	15
I, 0,16	HBr/ether	Ether 3	1 : 7	0,21	93	6
I, 0,16	"	Ether 3	1 : 15	0,22	94	4
I, 0,16	"	Ether 3	1 : 60	0,23	96	3
II, 3,20	Dry HBr	Ether 60	1 : 2	4,60	72	24
II, 1,24	"	CH_3COOH, 20	1 : 2	1,85	61	18

12-hydroxy)-threo-13-bromo-12-hydroxyoctadecanoic acids (V and VI); and fraction B (yield 8-15%, R_f 0.78, n_D^{20} 1.4832) — a mixture of 3-bromo-5-(1-hydroxyhexyl)-2-(7-methoxycarbonylheptyl)tetrahydrofuran (VII), 3-bromo-5-(1-hydroxy-8-methoxycarbonyloctyl)-2-pentyltetrahydrofuran (VIII), 5-bromo-3-hydroxy-6-(7-methoxycarbonylheptyl)-2-pentyltetrahydropyran (IX), and 5-bromo-3-hydroxy-2-(7-methoxycarbonlyheptyl)-6-pentyltetrahydrofuran (X).*



Scheme 1. Interaction of methyl threo-cis-9,10:cis-12,13-diepoxyoctadecanoic acid with HBr.

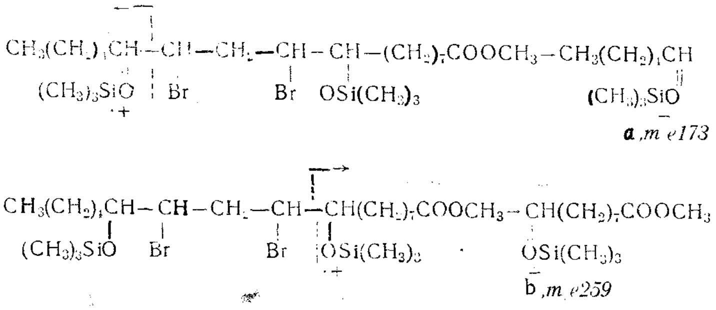
The structures of the compounds isolated were determined on the bases of the characteristics of the mass spectra of their trimethylsilyl (TMS) derivatives and were confirmed by their PMR and IR spectra. The conclusion concerning the configurations of the open-chain bromohydroxy derivatives were made on the basis of the fact that the opening of the epoxide ring under the action of HBr takes place with the inversion of the configuration and stereospecifically, as has been shown previously by one of us [6].

The presence in the mass spectrum of the TMS derivative of compound (III) of the molecular ion M^+, m/e 630/632/634 (0.5:1:0.5) and of the ions $(M - 15)^+$, m/e 615, 617, 619 (1:2:1)

---

*Compounds (VII-X) were present in the mixture in the form of the cis- and trans-3,5 isomers.

and $(M-31)^+$, m/e 599, 601, 603 (1.3:2.5:1.2),* formed in the ejection from the molecular ion of methyl and methoxy groups, respectively, confirms the elementary composition $C_{19}H_{36}Br_2 \cdot O_4$ of compound (III). The main peaks in the mass spectrum are those of ions *a*, m/e 173 (96), and b, m/e 259 (100), which are formed from the molecular ion on the ionization of the oxygen atom of one of the $OSi(CH_3)_3$ (OTMS) groups. These ions, arising as the result of the homolytic cleavage of the bond adjacent to the OTMS group, possess great stability because of the stabilization of the + charge on oxygen [8, 9]:



The absence from the spectrum under consideration of ions characteristic for other possible isomeric ME's of dibromodihydroxyoctadecanoic acids confirms the individuality of the compound (III) isolated.

The PMR spectra of compound (III) and its TMS derivative also confirm this structure (Table 2). The signals in the δ 2.33 ppm region in the spectrum of substance (III) must be assigned to the protons of two OH groups, since this signal disappears in the spectrum of the TMS derivative, giving a strong signal of the 18 protons of two TMS groups at δ 0.12 ppm.†

TABLE 2. Characteristics of the PMR Spectra of the Open-Chain and Cyclic Compounds and Their TMS Derivatives (δ, ppm, 100 MHz, benzene)

Compound or fraction	CH_3- (3H, t)	$-(CH_2)_n-$	$-CH-CH_2-CH-$ (2H, m)	$CO-CH_2$ (2H, t)	OCH_3 (3H, s)	OH	$-OSi(CH_3)_3$ (s)	$-\overset{\vert}{\underset{\vert}{C}}-H$ (m)
III	0,91	1,22	2,49	2,15	3,40	2,33(2H)	—	3,32(2H, CHOH); 4,48 (2H, CHBr)
TMS–III	0,88	1,20	2,44	2,13	3,40	—	0,12(18H)	3,83 (2H, CHOSi $(CH_3)_3$; 4,53(2H, CHBr)
IV	0,88	1,21	2,30	2,15	3,41	2,42(2H)	—	3,91 (2H, CHOH; 2H, CHBr)
TMS–IV	0,86	1,20	2,20	2,12	3,41	—	0,16(18H)	4,06 (2H, CHOSi $(CH_3)_3$; (2H, CHBr)
A	0,90	1,22	2,32	2,14	3,40	2,82(2H)	—	3,50 (1H, CHOH); 3,90 (1H, CHOH; 1H, CHBr); 4,20 (1H, CHBr)
TMS–A	0,87	1,20	2,63	2,13	3,42	—	0,14(18H)	3,77 (1H, CHOSi$(CH_3)_3$); 4,10 (1H, CHOSi$(CH_3)_3$; 2H, CHBr)
B	0,90	1,18	2,16	2,13	3,40	2,55(1H)	—	3,16 (1H, CHOH); 3,58 (2H, CHR); 4,00 (1H, CHBr)
TMS–B	0,90	1,20	2,16	2,13	3,41	—	0,20–0,30(9H)	3,26 (1H, CHOSi $(CH_3)_3$); 3,60 (2H, CHR); 4,14 (1H, CHBr)
TMS–D	—	—	—	—	—	—	0,24(9H)	—

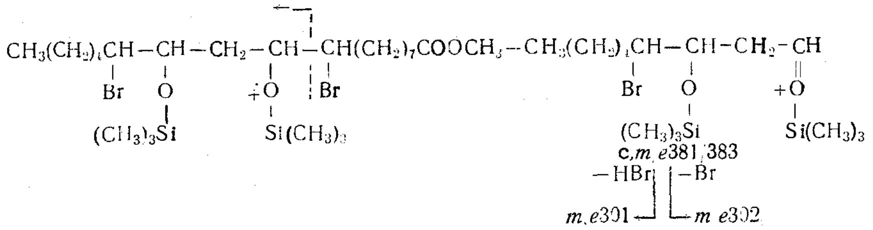
---

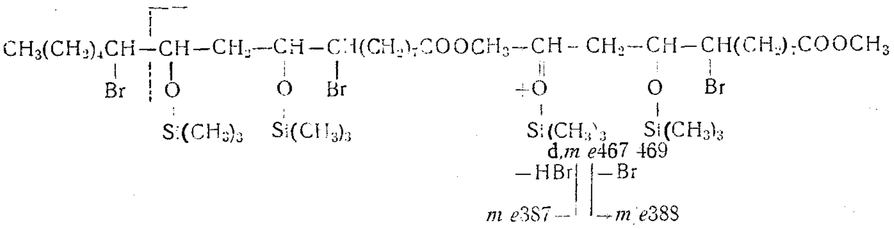
*The relative intensities of the peaks of the ions in percentages are given in parentheses. The peaks of the ions containing two bromine atoms have an intensity ratio of 1:2:1 and of those containing one bromine atom of ratio of 1:1, in correspondence with the isotopic distribution of bromine [7].

†Here and below, the number of protons is given according to the integral curve.

The two multiplets in the spectrum of compound (III) at δ 3.32 and 4.48 ppm belong to the signals of the methine protons of two C̲HOH and two CHBr groups, respectively [10]. In the spectrum of the TMS derivative of substance (III) these signals shift downfield. Such a distribution of the chemical shifts of the methine protons in the spectrum is due to the symmetrical distribution of the bromine atoms and OH groups in the molecule, namely: the bromine atoms at C-10 and C-12 and the OH groups at C-9 and C-13. This conclusion concerning the structure of substance (III) agrees well with the mass-spectral results.

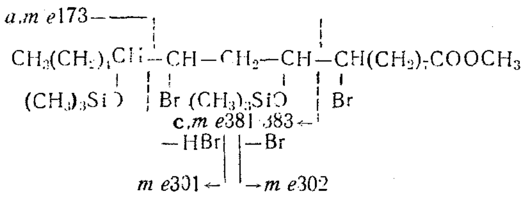
The mass spectrum of the TMS derivative of compound (IV) contains the peaks of the ions $(M - 15)^+$ (0.5:1:0.5) and $(M - 31)^+$ (1:2:1), confirming the elementary composition of $C_{19}H_{36}\cdot Br_2O_4$. Characteristic fragments for this compound are the ion c, m/e 381/383 (30:31), which is then converted into ions with m/e 301 (5) and 302 (1), and also ion d, m/e 467/469 (37:38), then giving ions with m/e 387 (5) and 388 (1). These ions are formed from the molecular ion that arises from the ionization of the oxygen atom of one of the OTMS groups, as can be illustrated by the following schemes:

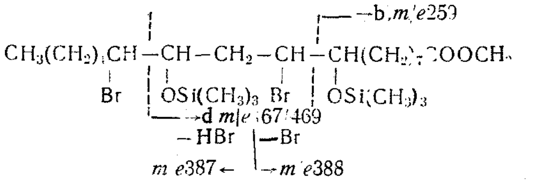




In the PMR spectrum of substance (IV) at δ 3.91 ppm there is the unresolved signal of four methine protons, which are shifted downfield to δ 4.06 ppm in the spectrum of the TMS derivative. Such a pattern can apparently be explained by an averaging of the chemical shifts of the methine protons of the compound (IV).

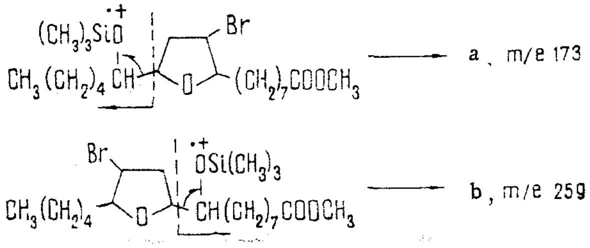
According to the mass spectrum, fraction A consists of a mixture of two other possible isomers of the ME's of the dibromodihydroxyoctadecanoic acids (V) and (VI) with the composition $C_{19}H_{16}Br_2O_4$. The mass spectrum of the TMS derivatives of the substances of fraction A contains, in addition to the peaks $(M - 15)^+$ (1:2:1) and $(M - 31)^+$ (1.5:3:1.5) the ions *a* (55) and b (100), which, together with the ions c (5:5), (c − HBr) (24), (c − Br) (7), d (3:4), (d − HBr) (22), and (d − Br) (4) permit the conclusion that two compounds are present in the mixture:



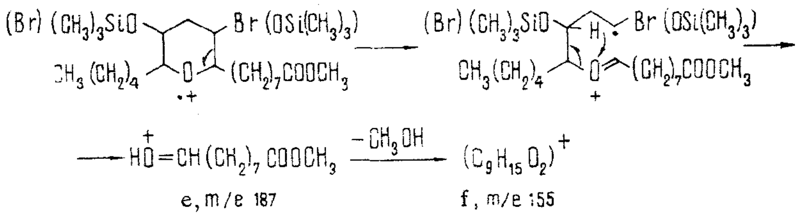


The PMR spectra of the substances of fraction A and of their TMS derivatives are given in Table 2. In spite of the fact that fraction A consists of a mixture of substances (V) and (VI), from the stereochemical point of view these compounds are similar in relation to the environments of the OH and Br groups, respectively, undergo identical descreening, and, in all probability, the PMR spectra of compound (V) and (VI) are identical. The characteristics of these spectra confirm the erythro configuration in the 10,12 position.

Let us return to a consideration of the unusual reaction products of the threo isomer (I) with hydrogen bromide. According to the results of elementary analysis, substances (VII-X) forming fraction B had the composition $C_{19}H_{35}BrO_4$, which was confirmed by mass spectroscopy and, consequently, consisted of products of the addition of one molecule of HBr to the diepoxy acid molecule. The absence of an α-epoxide ring from the substances of this fraction was confirmed by titration with HBr in acetic acid [2]. In addition, there was no adsorption at ν 830-850 cm^{-1} in the IR spectrum of the substances of fraction B, and in the PMR spectrum there was no signal at δ 2.70-3.00 ppm, these features being characteristic for the cis-epoxy acids [11]. The probable isomerization of the α-epoxide ring into a carbonyl group was not confirmed by spectroscopic results, either. The PMR spectrum of the substances of fraction B had signals at δ 2.55 ppm (OH), 3.16 (CHOH), and 4.00 ppm (CHBr), each corresponding to one proton. In the PMR spectrum of the TMS derivatives of the substances of the same fraction, the signal of the proton of an OH group had disappeared, but the signal of a TMS group had appeared. In the mass spectrum of the TMS derivatives of the substances of fraction B there was no peak of the molecular ion but there were the peaks of $(M - 15)^+$, m/e 463/465 (2:2), and $(M - 31)^+$, m/e 447/449 (2:2). An analysis of the mass spectrum showed that there was no ionization of the oxygen of the OTMS group and the ions with the greatest intensity in the spectrum were *a* (100) and b (86), the formation of which for substances with structures (VII) and (VIII) can be represented in the following way [3, 8, 12]:



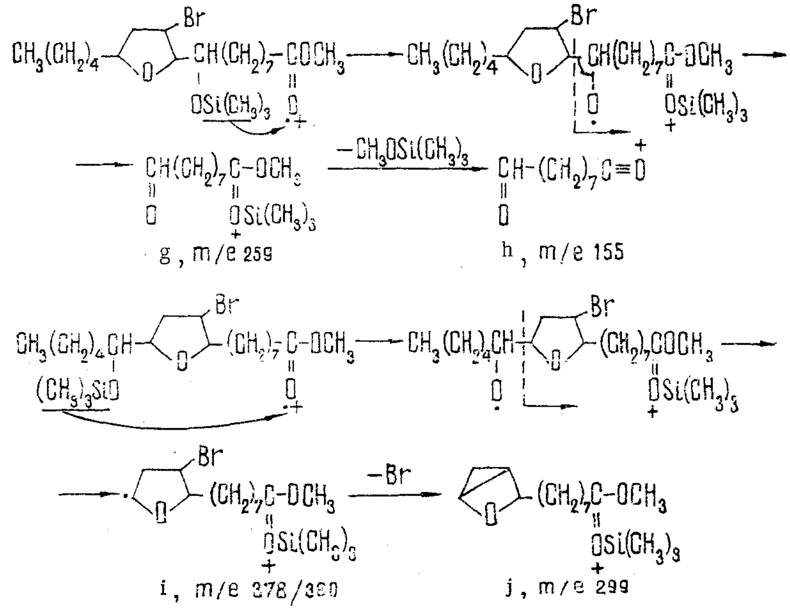
The presence of the ions e, m/e 187 (60), and f, m/e 155 (62) with considerable intensities permits the assumption that fraction B also contains substances (IX) and (X) with tetrahydropyran structures [3, 13]:



The fragmentations of the molecular ion that have been considered are not the only possible ones and can also take place on the ionization of the carbonyl oxygen of the ester group with the subsequent migration of the TMS group to it [9] (see below).

The fact that in the tetrahydrofuran derivatives of fraction B [compounds (VII) and (VIII)] the nitrogen atom is present in the ring and the hydroxy group in the alkyl or methoxycarbonyl alkyl side chain is confirmed by the IR spectra of the substances of this fraction taken with dilution. In the IR spectrum of a dilute solution with a concentration c of $4.8 \cdot 10^{-4}$ M, at which intermolecular interactions are excluded, there are the absorption bands of a hydroxyl in an unassociated molecule at ν 3580 and 3605 cm^{-1}, which must be assigned to the absorption of OH in a side chain connected by an intramolecular hydrogen bond with the O atom of the heterocycle [3, 14].

Since we have previously [3] established that the cis derivatives of tetrahydrofuran wit a hydroxyl in the side chain and the cis-tetrahydropyrans formed from the threo isomer of the diepoxide derivative of methyl linoleate have absorption in the ν 3565-3575 cm^{-1} region, while for trans-tetrahydrofurans and tetrahydropyrans absorption is included in the range of 3585-3597 cm^{-1}, we assume that the absorption band at ν 3580 cm^{-1} is due to the cis isomers and that at ν 3605 cm^{-1} to the trans isomers of substituted tetrahydropyrans and tetrahydrofurans present in fraction B. The inhomogeneity of the signals of the protons of the TMS group in the high-field region of the PMR spectrum of the TMS derivatives of the substances of fraction B also shows the stereochemical nonequivalence of these groups.

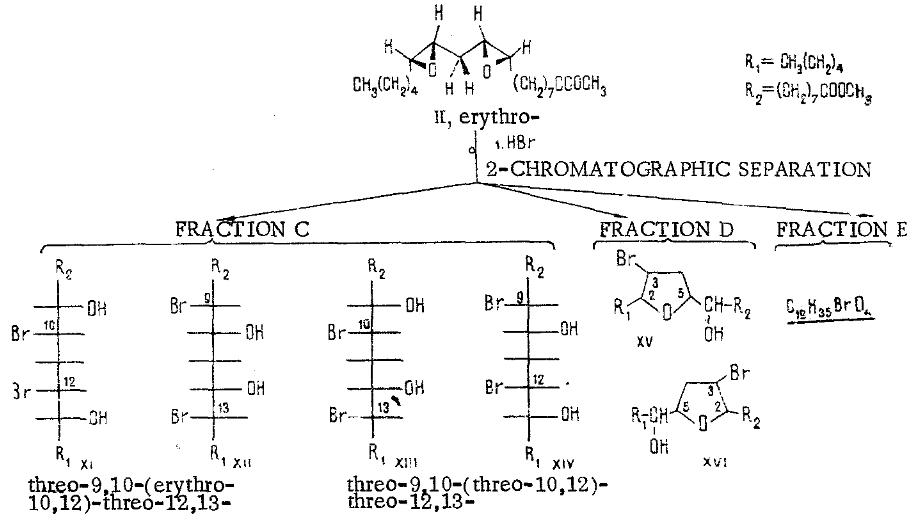


The reaction of the erythro isomer (II) of the diepoxide from methyl linoleate with HBr also led to the formation of a complex mixture of substances (Scheme 2) from which by preparative chromatography on silica gel we isolated open-chain compounds — fraction C (yield 61-72%, R_f 0.63, n_D^{20} 1.5011); tetrahydrofuran derivatives — fraction D (yield 10-14%, R_f 0.81); and fraction E (yield 8-10%, R_f 0.49, n_D^{20} 1.4871) (see Table 1).

In the mass spectrum of the TMS derivatives of the substances of fraction B, the presence of the ions $(M-15)^+$, m/e 615/617/619 (1:2:1) and $(M-31)^+$, m/e 599/601/603 (0.5:1:0.5) confirmed the composition of the substances of fraction C, $C_{19}H_{36}Br_2O_4$. The simultaneous presence in the spectrum of the ions *a* (32), b (100), c (2:2), (c — HBr) (35), (c — Br) (12), d (3:3), (d — HBr) (20), and (d — Br) (5) permits the conclusion that fraction C consists of a mixture of the ME's of all the possible isomeric dibromodihydroxyoctadecanoic acids, namely threo-10-bromo-9-hydroxy-(erythro-10-bromo-12-bromo)-threo-12-bromo-13-hydroxyoctadecanoic acid (XI), threo-9-bromo-10-hydroxy-(erythro-10-hydroxy-12-hydroxy)-threo-13-bromo-12-hydroxyoctadecanoic acid (XII), threo-10-bromo-9-hydroxy-(threo-10-bromo-12-hydroxy)-threo-13-bromo-12-hydroxyoctadecanoic acid (XIII), and threo-9-bromo-10-hydroxy-(threo-12-bromo-10-hydroxy)-threo-12-bromo-13-hydroxyoctadecanoic acid (XIV). These compounds are diastereomeric in relation to substances (III-VI) since they are formed similarly in the opening of the epoxide rings of the diastereomeric diepoxide (II) with the inversion of the configuration, the vicinal threo derivatives being formed from the cis-monoepoxy acids [6].

According to the results of elementary analysis, the substances of fractions D and E had the composition $C_{19}H_{35}BrO_4$, and this was confirmed mass-spectrometrically for the TMS derivatives of fraction D by the presence of the ions M^+, m/e 478/480 (0.5:0.5), $(M-15)^+$, m/e 463/465 (1.5:1.5), and $(M-31)^+$, m/e 447/449 (1:1). A chemical and spectroscopic investigation excluded the incomplete opening or isomerization of the α-epoxide rings. The presence of one hydroxy group in the substances of fraction D was established with the aid of the PMR spectrum of their TMS derivatives, which, in the strong-field region, contained a singlet at δ 0.24 ppm corresponding to the nine protons of a TMS group.

In the mass spectrum of the TMS derivatives of the substances of fraction D, the main ions were *a* (100), b and g (85), e (8), f and h (15), i (6:6), and j (13), the formation of which has already been discussed, which shows that fraction D consisted of 3-bromo-5-(8-methoxycarbonyl-1-hydroxyoctyl)-2-pentyltetrahydrofuran (XV) and 3-bromo-5-(1-hydroxyhexyl)-2-(7-methoxycarbonylheptyl)tetrahydrofuran (XVI).

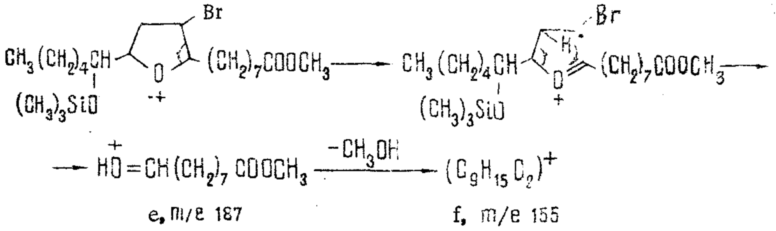


Scheme 2. Interaction of methyl erythro-cis-9,10:cis-12,13-diepoxyoctadecanoic acid with HBr.

It must be mentioned that in the mass spectrum of the TMS derivatives of fraction D there are weak peaks of ions with m/e 187 and 155. It has been established [3] that these are the maximum ions in the spectra of the tetrahydropyran derivatives. On the other hand, for tetrahydrofuran derivatives containing no substituent in the methoxycarbonyl alkyl side chain fragmentation with the cleavage of the ring is possible, like the fragmentation of tetrahydropyran derivatives [3, 13] (see below).

Since in the mass spectra of the TMS derivatives of fraction D the intensities of the ions with m/e 187 and 155 are low (8 and 15%) in comparison with the spectrum of the TMS derivatives of fraction B (60 and 62%) and do not exceed the intensities of the same ions in the spectrum for the individual derivatives of tetrahydrofurans [3], we consider that no compounds with a tetrahydropyran structure are formed in the reaction of the erythro isomer of the diepoxide from methyl linoleate (II) with HBr. The IR spectrum of the substances of fraction D taken with dilution is similar to the IR spectrum of the substances of fraction B. The structures of the substances of fraction E have not been determined.

As can be seen from what has been said above, the reaction of the threo isomer and of the erythro isomer of the diepoxy acids with HBr forms tetrahydrofuran derivatives with a bromine atom in the ring and an OH group in the side chain — (VII) and (XVI), and (VIII) and (XV).



It follows from a consideration of this transformation of the diastereomeric diepoxy acids with Dreiding and "Eugon" models that these substances are diastereomeric in relation to one another, differing by the configuration of the C atom of the side chain to which OH is attached and at C-5 of the tetrahydrofuran ring [3].

Thus, an investigation of the reaction of diastereomeric diepoxides from methyl linoleate with hydrogen bromide under various conditions has shown that cyclic compounds stable under the reaction conditions are always formed. This is the reason for the low values of the percentage of epoxide oxygen obtained in determinations by titration with a solution of HBr in glacial acetic acid. It follows from the figures given (Table 2) that the determination of epoxide oxygen must be performed in the presence of an excess of HBr, i.e., "back-titration" must be used in order to decrease the error of the determination.

EXPERIMENTAL

The instruments, the conditions for recording the spectra, the preparation of the dilute solutions, and the method of obtaining the trimethylsilyl derivatives have been described previously [3]. The PMR spectra were taken on a Varian-HA-100 D/15 instrument (100 MHz) for 20% solutions in benzene. TMS was used as the internal standard.

For preparative chromatography we used LSL_{254}, 5-40 μ, silica gel with the solvent system chloroform–acetone (100:5), and the distribution of the substances was observed in the UV light of a "Khromatoskop" lamp. For analytical TLC we used Woelm silica gel and the above-mentioned solvent system. Detection was performed with $(NH_4)_2SO_4/NH_4HSO_4$ solution followed by heating [15].

The conditions for performing the reactions and the yields of compounds formed are given in Table 1.

The reaction of the isomeric diepoxy acids with HBr were performed by passing dry hydrogen bromide freed from bromine into a reaction vessel containing the dissolved diepoxy acid with stirring at 20°C. The course of the reaction was followed by TLC. After the disappearance of the diepoxy acid from the reaction mixture, the latter was diluted with ether 10-fold, washed with water to neutrality, and dried with calcined sodium sulfate, and then the solvent was distilled off in vacuum and the reaction product was subjected to chromatographic separation.

To obtain the solutions, dry and bromine-free HBr was passed into a reaction vessel containing the solvent with stirring. The concentration was determined by titrating a weighed sample with calcined sodium carbonate in the presence of Crystal Violet.

The reaction of the threo isomer with HBr solution in acetic acid was performed under titration conditions [2]. A weighed sample of the diepoxy acid was dissolved in 5 ml of glacial acetic acid. On titration with a solution of HBr in the presence of Crystal Violet, after a persistent yellow coloration had been obtained the solution was diluted 10-fold with ether and was then worked up as described above.

The reaction of the threo isomer (I) with a large excess of hydrogen bromide solution in ether was performed by adding a solution of the diepoxy acid to a known excess of the reagent with stirring, and the reaction mixture was then worked up by the method described above.

The analyses of all the compounds obtained corresponded to the calculated figures.

LITERATURE CITED

1. S. D. Gusakova and A. U. Umarov, Khim. Prirodn. Soedin., 717 (1976).
2. A. I. Durbetaki, Anal. Chem., 28, 2000 (1956).
3. I. L. Kuranova, S. D. Gordienko, G. N. Korskaya, and E. B. Filonova, Zh. Org. Khim., 12, 1699 (1976).
4. G. Maerker, E. T. Haeberer, and S. F. Herb, J. Am. Oil Chemicsts' Soc., 43, 505 (1966); J. F. Rusling, G. R. Riser, M. F. Snook, and W. E. Scott, J. Am. Oil Chemists' Soc., 45, 760 (1968).
5. S. A. Kozhin and E. I. Sorochinskaya, Zh. Anal. Khim., 29, 166 (1974).
6. I. L. Kuranova and L. V. Balykina, Zh. Org. Khim., 11, 720 (1975).
7. J. Beynon, Mass Spectrometry and Its Application to Organic Chemistry, Elsevier, Amsterdam (1960).
8. P. Capella, C. Galli, and R. Fumagalli, Lipids, 3, 431 (1958).
9. P. Capella and C. M. Zorzut, Anal. Chem., 40, 1458 (1968); A. Zeman and H. Scharmann, Fette, Seifen, Anstr., 75, 32 (1973).
10. I. L. Kuranova and L. V. Balykina, Zh. Org. Khim., 9, 260 (1973).
11. A. Strocchi and G. Bonaga, Riv. Ital. Sost. Grasse, 52, 84 (1975); A. Strocchi, G. Bonaga, and P. N. Capitani, Riv. Ital. Sost. Grasse, 58, 40 (1976).

12. R. Brandt and C. Djerassi, Helv. Chim. Acta, 51, 1750 (1968).
13. G. G. Abbot and F. D. Gunstone, Chem. Phys. Lipids, 7, 279 (1971); G. G. Abbot and F. D. Gunstone, Chem. Phys. Lipids, 7, 303 (1971).
14. S. A. Barker, J. S. Bromacombe, A. B. Foster, D. H. Whiffen, and G. Zweifel, Tetrahedron, 7, 10 (1959); A. Leboue, Bull. Soc. Chim. Fr., 3037 (1971); J. Muzart and J. P. Pete, Bull. Soc. Chim. Fr., 1373 (1973); D. Gagnaire and M. Leclercq, Bull. Soc. Chim. Fr., 721 (1963).
15. T. Ziminski and E. Borowski, J. Chromatogr., 23, 480 (1966).

PHOSPHOLIPIDS OF THE SEEDS OF KENAF OF VARIETY "UZBEKSKII-1574"

I. Tolibaev, Kh. S. Mukhamedova, and S. T. Akramov

UDC 547.953:665.37

Continuing an investigation of the phospholipids (PL's) of plants of the family Malvaceae, we have studied the seeds of kenaf (*Hibiscus cannabinus*) of the industrial variety "Uzbeksii-1574." The combined PL's were obtained, purified, and fractionated by the method described in previous papers [1, 2]. Two-dimensional chromatography in solvent systems 1 (direction I) and 2 (direction II) showed the presence in the total material of six phosphorus-containing components which were distributed qualitatively and quantitatively in the following way (R in direction II): 0.52, phosphatidylcholines (PC's; 35.6%); 0.70, phosphatidylinositols (PI's; 25.0%); 0.78, phosphatidylethanolamines (PE's; 22.2%); 0.96, N-acylphosphatidylethanolamines (N-acyl-PE's; 9.3%); 0.83, N-acyllysophosphatidylethanolamines (N-acyllyso-PE's; 5.3%); and 0.80, unidentified phospholipids (X; 2.6%).

After the distribution of the total PL's on a column of silica gel, the main and the minor components were finally purified by subfractionation in a thin layer of silica gel in systems 3 and 4. The structures of the fractions mentioned were confirmed by an investigation of the water-soluble products of acid hydrolysis and by IR spectroscopy [3, 4]. The fatty acids of the triglycerides, of the total PL's, and of the individual fractions were determined by saponifying them with alcoholic alkali. The position distributions of the fatty acids in the PC, PE, and PI molecules were determined by enzymatic hydrolysis with the aid of phospholipase A_2 from kufi venom and, after the appropriate working up [1], the fatty acids in the form of their methyl esters were analyzed by GLC (Table 1). The results of the analysis showed that the compositions of the fatty acids of the oils of the total PL's were identical qualitatively and similar quantitatively. The degrees of saturation of the molecules of the individual components of the total PL's rose in the following sequence: PE's → N-acyl-PE's → PC's → PI's → N-acyllyso-PE's. We may note that the phosphatidylcholines isolated from plant materials are almost always more unsaturated than the PE's, but in this case, conversely, the PE's were considerably more unsaturated than the PC's. It was established by means of the results of enzymatic hydrolysis that in the PC's the fatty acids are distributed more selectively between the two positions: 70.5% of saturated acids in position 1 and 91.1% of unsaturated acids in position 2. The results of the position distributions of the fatty acids enabled us to calculate the possible molecular compositions of the PC's, PE's, and PI's:

	PC's	PE's	PI's
Disaturateds	6,4	1,6	10,6
Saturated—unsaturateds	64,0	52,6	55,7
Diunsaturated	27,1	44,5	28,3
Unsaturated—saturateds	2,5	1,3	5,4

The results of the calculations show that the amount of disaturated species in the PE's is considerably smaller than in the PI's and PC's, and the amount of diunsaturated species is greater. This is explained by the comparatively higher degree of unsaturation of the PE molecules than of those of PC's and PI's. The saturated—unsaturated species were formed mainly from the 16:0 and 18:1 or 18:2 acids and the diunsaturated species from the 18.1 and 18.2 acids-

---

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, N. 6, pp. 776-780, November-December, 1977. Original article submitted June 20, 1977.

0009-3130/77/1306-0654$07.50