Pseudohalogenation of Methyl 9-Hydroxy-*cis*-12- and 12-Hydroxy-*cis*-9-Octadecenoate

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ABSTRACT: Pseudohalogenation of methyl 9-hydroxy-*cis*-12-octadecenoate (**I**) and methyl 12-hydroxy-*cis*-9-octadecenoate (**II**) has been carried out with *N,N*-dibromobenzenesulfonamide (NNDBS). Compounds **I** and **II**, on reaction with NNDBS, formed four and three products, respectively. The interesting feature of these reactions was the formation of 1,4-epoxy compounds. The structures of individual compounds were established with the help of elemental and spectral analysis.
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KEY WORDS: 1,4-Epoxy fatty esters, methyl isoricinoleate, methyl ricinoleate, NNDBS.

Advances in modification of fatty chemicals have recently been made in various directions. Much research attention is being directed toward the addition of a group of reagents, categorized as "pseudohalogens," to the double bonds of aliphatic and alicyclic compounds. A number of pseudohalogens have come into prominence (1–6), *viz.*, iodine isocyanate, *N,N*-dichlorourethane, monochlorourethane, chlorine azide, bromine azide, iodine azide, nitrosyl chloride, nitryl iodide, *N,N*-dibromoacetamide, *N,N*-dibromobenzene sulfonamide (NNDBS), etc.

Addition of pseudohalogens to an unsaturated system is important (7–9) and has been known for a long time to prepare a variety of derivatives. Foglia *et al.* (10) have investigated the addition of NNDBS to internal olefins. The major products were isomeric mixtures of β-bromosulfonamides, while dibromide and bromohydrins were found in small amounts. Ahmad *et al.* (9), Foglia *et al.* (10), and Nasirullah *et al.* (11) reported the reaction of NNDBS with 10-undecenoic, oleic, and *trans*-2-hexadecenoic acids. In continuation of our program to derivatize fatty acids for possible industrial utilization, we report here the reaction of NNDBS with methyl 9-hydroxy-*cis*-12-octadecenoate (methyl isoricinoleate, **I**) and methyl 12-hydroxy-*cis*-9-octadecenoate (methyl ricinoleate, **II**).

These reactions were performed to investigate the effect of neighboring group participation of the hydroxyl function at the β- and γ-positions relative to the unsaturation. The results of the reactions are interesting because we have been able to isolate and characterize 1,4-epoxy compounds besides other expected products.

EXPERIMENTAL PROCEDURES

Infrared (IR) spectra were obtained with a Perkin-Elmer 621 spectrophotometer (Norwalk, CT) (liquid film or 1% solution in carbon tetrachloride). Nuclear magnetic resonance (NMR) spectra were recorded in CCl_4 with a Varian A60-NMR spectrometer (Palo Alto, CA) and tetramethyl silane as internal standard. Chemical shifts were measured in ppm downfield from the internal standard ($\delta = 0$). The abbreviations "*s, d, m, br, t*" denote singlet, doublet, multiplet, broad, and triplet, respectively. Mass spectra (MS) were measured with a JEOL JMS-D300 spectrometer (Tokyo, Japan). Thin-layer chromatography (TLC) plates were coated with silica gel G (0.25 mm thickness), and a mixture of petroleum ether/diethyl ether/acetic acid (70:30:1, vol/vol/vol) was used as developing solvent. The spots were visualized by charring at 100°C after spraying with a 20% aqueous solution of perchloric acid. Petroleum ether refers to a fraction of b.p. 40–60°C.

MATERIALS AND METHODS

Extraction of isoricinoleic and ricinoleic acids. The isoricinoleic (9-hydroxy-*cis*-12-octadecenoic) and ricinoleic (12-hydroxy-*cis*-9-octadecenoic) acids were isolated from *Wrightia tinctoria* (12) and *Ricinus cummunis* (castor oil) by Gunstone's partition method (13), and the structures were established by spectral methods (14). Methyl esters (**I, II**) of the corresponding acids were prepared by using a catalytic amount of hydrochloric acid in absolute methanol (H^+/MeOH). The acids (5.0 g) were dissolved in 5% methanolic hydrogen chloride (200 mL) and refluxed for 2 h. About two-thirds of the methanol was evaporated under reduced pressure. The mixture was diluted with water (100 mL) that contained 5% sodium chloride, and the methyl ester was extracted with diethyl ether. The ether layer was washed with water until neutral to litmus and dried over anhydrous sodium

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sulfate. The solution was filtered, and the solvent was removed under reduced pressure.

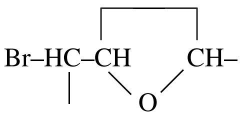
Preparation of NNDBS. Benzenesulfonamide (62.5 g), sodium bicarbonate (80.0 g), and water (300 mL) were placed in a 1-L three-necked flask. Then, bromine (127.5 g) was added with vigorous stirring. The resulting precipitate of NNDBS was filtered, washed with water, and dried. A yellow solid was obtained (122.5 g) that melted at 114°C (lit., 115°C) (15).

Pseudohalogenation of **Ib** *with NNDBS.* Pseudohalogenation of methyl isoricinoleate (**I**) with NNDBS was carried out according to the procedure of Foglia *et al.* (10). Compound **I** (4.99 g, 0.016 mol) was added dropwise to an ice-cooled solution of NNDBS (5.9 g, 0.016 mol) in CCl_4 (35.0 mL) while maintaining the reaction temperature at 15–20°C with continuous stirring. After adding all of the methyl isoricinoleate, stirring was continued further until a clear solution was obtained.

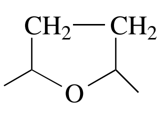
The reaction was monitored by TLC, and the reaction took about 24 h to complete. A 20% solution (25 mL) of sodium bisulfite was added to the reaction mixture at room temperature. After shaking well, the organic layer was extracted with CCl_4 three times and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure yielded a dark-brown viscous oil (7.0 g), which revealed four distinct spots on TLC. The crude mixture (4.8 g) was resolved on a silica gel (120 g) column, prepared in petroleum ether, and eluted with petroleum ether/diethyl ether (96:4, vol/vol). The TLC-monitored eluates were combined to give **III** (0.96 g, 20%). Elution with petroleum ether/diethyl ether (90:10, vol/vol) gave **IV** (0.29 g, 6%). Subsequent elution with petroleum ether/diethyl ether (80:20, 65:35, vol/vol) furnished **V** (0.19 g, 4%) and **VI** (3.12 g, 65%), respectively. Each component gave a positive Beilstein test.

*Methyl 9,12-epoxy-13-bromooctadecanoate (***III***).* Analysis: calc. for $C_{19}H_{35}O_3Br$: C, 58.31; H, 9.01% Found: C, 58.50; H, 9.03%. IR (neat): 1735 (*CO*OCH$_3$), 1110 (1,4-epoxide), 1180, 1155, 1060, 1020 (C–O), and 685 cm^{-1} (C–Br). NMR (CCl_4): 4.0 *m*(3H, **A**; 3.62 *s* (3H, COOC*H*$_3$); 2.22 *m* (2H, C*H*$_2$–COOCH$_3$); 1.8 *m* (4H, **B**) 1.4 *br, s* (chain-C*H*$_2$–), and 0.9 *t* (terminal C*H*$_3$), where

A =



and **B** =



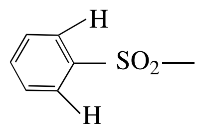
MS: M$^{+\cdot}$ (molecular ion peak) at *m/z* 390/392, followed by other important peaks at *m/z* 359/361 (M – OCH$_3$), 311 (M – Br), 293(311-18), 279(311-32), 263/265, 257, 241, 227, 209, 195, 177, 163/165 and 159.

*Methyl 12,13-dibromo-9-hydroxyoctadecanoate (***IV***).* Analysis: calc. for $C_{19}H_{36}O_3Br_2$: C, 48.32; H, 7.68%. Found: C, 48.51; H, 7.71%. IR (neat): 3450 (OH), 1735 (*CO*OCH$_3$), 1195, 1160, 1110, 1010 (C–O), and 690 cm^{-1} (C–Br), NMR (CCl_4): 4.3 *m* (1H, O*H*, D$_2$O exchangeable); 4.15 *m* (2H, Br–CH(–)CH(–)–Br); 3.9 *m* (1H, –C*H*–OH, in parts merged with signals at 4.15); 3.68 *s* (3H, COOC*H*$_3$), 2.2 *m* (2H, C*H*$_2$–COO CH$_3$), 1.32 *br, s* (chain-C*H*$_2$–) and 0.9 *t* (terminal-C*H*$_3$). MS: M$^{+\cdot}$ at *m/z* 470/472/474 were absent, but the highest ion peaks appeared at *m/z* 399/401/403 (m-71), followed by other important peaks at *m/z* 385/387/389 (399/401/403-14), 369/371/373 (M-101) and 355/357/359 (369/371/373-14).

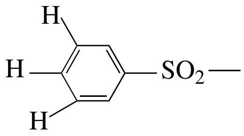
*Methyl 13(12)-bromo-9,12(13)-dihydroxy-octadecanoate (***V***).* Analysis: calc. for $C_{19}H_{37}O_4Br$: C, 55.74; H, 9.11%. Found: C, 55.87; H, 9.12%, IR (neat): 3420 (OH), 1735 (*CO*OCH$_3$), 1090, 1060, 1030 (C-O) and 690 cm^{-1} (C–Br). NMR (CCl_4): 4.13 *m*(1H, C*H*–Br); 3.9 *m* (2H, 2 × C*H*–OH); 3.62 *s* (3H, COOC*H*$_3$); 2.32 *m* (2H, 2 × CH–O*H*, D$_2$O-exchangeable); 2.22 *m* (2H, C*H*$_2$–COOCH$_3$); 1.3 *br, s* (chain-C*H*$_2$); and 0.9 *t* (terminal C*H*$_3$). MS: M$^{+\cdot}$ at *m/z* 408/410 were absent, but the highest molecular ion peak appeared at *m/z* 390/392 (M-18), followed by other important peaks at *m/z* 359/361 (390/392-31), 280 (359/361-Br), 279 (359/361-HBr), 215 [M–CH$_3$–(CH$_2$)$_4$-CH(OH)–CH(Br)–], 205/207, 193/195, 185, 171(185-14), 163/165, 157(171-14) and 101 (locates the position of OH group at C^{13}).

*Methyl 9-hydroxy-12(13)-bromo-13(12)-benzene-sulfonamidooctadecanoate (***VI***) (major product 65%).* Analysis: calc. for $C_{25}H_{42}O_5BrNS$: C, 54.75; H, 7.72%. Found: C, 56.1; H, 7.8%. IR (neat): 2440 (OH), 3260 (N–H), 3050 (C=C–H), aromatic system, 1740 (COOCH$_3$), 1560 (C=C), aromatic, 1335, 1160 (SO$_2$N), 1110, 1090, 1065, 1030 (C–O) 755 and 720 cm^{-1} (C–Br). NMR (CCl_4): 7.9 *m* (2H, **C**); 7.6 *m* (3H, **D**), 7.1 distorted *m* (1H, N–*H*, D$_2$O-exchangeable); 4.2 *m* (1H, C*H*–Br), 3.95 *m* (1H; C*H*–OH); 3.65 *s* 3H, COOC*H*$_3$); 3.45 *m* (C*H*–NH); 3.19 *m* (1H, CH–O*H*, D$_2$O-exchangeable); 2.32 *m* (2H, C*H*$_2$–COOCH$_3$); 1.3 *br, s* (chain-C*H*$_2$–); and 0.9 *t* (3H, terminal C*H*$_3$), where

C =



and **D** =

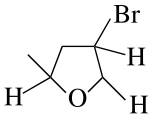


MS: M$^{+\cdot}$ at *m/z* 547/549 were absent, but the highest ion peaks appeared at *m/z* 404/406 (M – (CH$_2$)$_6$ – COOCH$_3$), followed by other important peaks at *m/z* 402/404 (M – C$_8$H$_{17}$O$_2$), 390/392 (404/406-14), 388/390 (402/404-14) 374/376 (390/392-16), 372/374 (390/392-18), 358/360(374/376-16 or 390/392-32), 346/348 [M – CH$_2$·CHOH·(CH$_2$)$_7$·COOCH$_3$], 332/334(346/348-14), 310/312, 308(388-HBr), 294, 279, 255/257(332/334-77), 252(332/334-HBr), 240, 227, 226, 221/223, 213, 195, 187, 170(187-17) 163/165, 155 (187-32), 141, 125, and 77 (base peak).

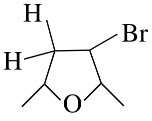
Pseudohalogenation of **IIb** *with NNDBS.* Pseudohalogenation of methyl ricinoleate (**II**) with NNDBS was carried out in the same manner as that of methyl isoricinoleate (**I**), described earlier. Direct TLC of the resulting oily product revealed three distinct spots. The product mixture (4.6 g) was chromatographed over a silica gel (120 g) column. Elution with mixtures of petroleum ether/diethyl ether, 92:8, 80:20 and 65:35 (vol/vol), gave **VII** (0.87 g, 19%), **VIII** (0.23 g, 5%), and **IX** (3.22 g, 70%), respectively. Each fraction showed a positive test for halogen.

Methyl 9,12-epoxy-10-bromooctadecanoate (**VII**). Analysis: calc. for $C_{19}H_{35}O_3Br$: C, 58.31; H, 9.01%. Found: C, 58.5; H, 9.05%. IR (neat): 1735 ($COOCH_3$), 1170, 1080, 1040, 1020 (C–O) and 730 cm^{-1} (C–Br). NMR (CCl_4): 4.5–3.9 *br, m* (3H, **E**), 3.65 *s* (3H, $COOCH_3$); 2.25 *m* CH_2–$COOCH_3$); 1.65 (2H, **F**); 1.35 *br, s* (chain-CH_2–); and 0.88 *t* (3H, terminal CH_3), where

E =



and **F** =



Methyl 9,10-dibromo-12-hydroxyoctadecanoate (**VIII**). Analysis: calc. for $C_{19}H_{35}O_3Br_2$: C, 48.32; H, 7.68% Found: C, 48.6, H, 7.7%. IR (neat): 3500 (OH), 1735 ($COOCH_3$), 1170, 1080, 1020 (C–O) and 720 cm^{-1} (C–Br). NMR (CCl_4): 4.2 *m* (2H, Br–CH(–)–CH(–)–Br); 4.0 *m* (1H, –CH–OH); 3.65 *s* (3H, $COOCH_3$); 2.85 *br, s* (1H, CH–OH, D_2O-exchangeable); 2.32 *m* (2H, CH_2–$COOCH_3$) 1.35 *br, s* (chain-CH_2–) and 0.92 *t* (3H, terminal CH_3).

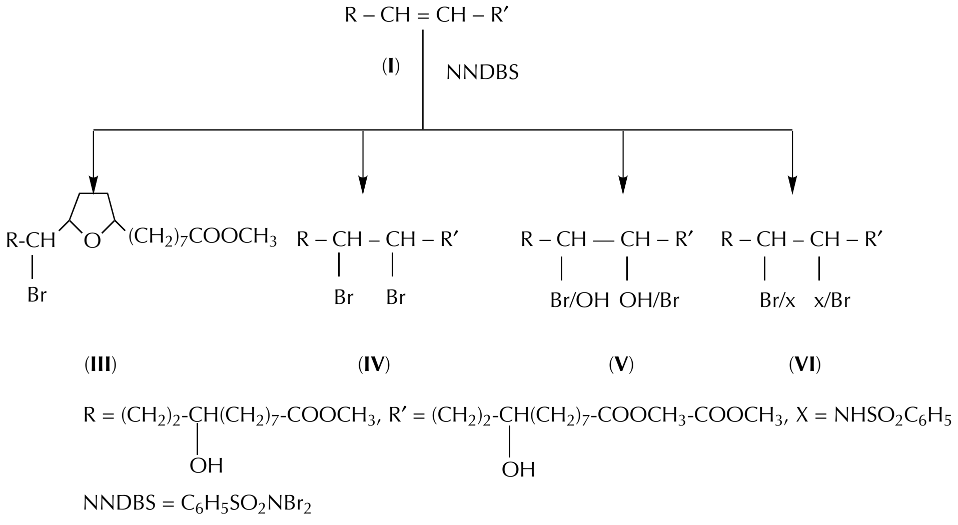
Methyl 12-hydroxy-9(10-bromo-10(9)-benzenesulfonamidoctadecanoate (**IX**). Analysis: calc. for $C_{25}H_{42}O_5BrNS$: C, 54.74; H, 7.72; N, 2.55%. Found: 54.91; H, 7.81; N, 2.45%. IR (neat): 3470 (OH), 3275 (N–H), 3075 (C=C–H, aromatic system), 1735 ($COOCH_3$), 1501 (C=C, aromatic) 1335, 1160 ($C–SO_2N$), 1110, 1090, 1055, 1030 (C–O), 770 and 710 cm^{-1} (C–Br). NMR (CCl_4); 7.85 *m* (2H, **C**), 7.55 *m* (3H, **D**), 7.1 distorted *m* (1H, N–H, D_2O-exchangeable), 4.25 *m* (1H, CH–Br), 3.95 *m* (1H, CH–OH), 3.72 *s* (3H, $COOCH_3$), 3.51 *m* (1H, CH–OH, D_2O-exchangeable) 2.35 *m* (2H, CH_2–$COOCH_3$), 1.35 *br, s* (chain-CH_2), and 0.9 *t* (3H, terminal CH_3), where **C** and **D** are explanined above.

RESULTS AND DISCUSSION

The reaction of NNDBS with methyl 9-hydroxy-*cis*-12-octadecenoate (**I**, methyl isoricinoleate) and methyl 12-hydroxy-*cis*-9-octadecenoate (**II**, methyl ricinoleate) was carried out by following the method of Foglia *et al.* (10). Compound **I** on reaction with NNDBS gave four products (**III–VI**), which responded positively toward the Beilstein test (Scheme 1). The IR spectrum of **III** revealed no band for an OH group in the region 3650–3200 cm^{-1}, indicating the absence of a free OH group. This suggested that neighboring group participation has taken place. Other bands were observed at 1735 ($COOCH_3$), 1110 (1,4-epoxide), 1180, 1155, 1060, 1020(C–O) and 685 cm^{-1} (C–Br). The PMR spectrum of **III** exhibited structure-revealing signals at δ 4.0 *m* (3H, **A**) and 1.8 *m* (4H, **B**), along with the characteristic signals of fatty esters at 3.62 *s* (3H, $COOCH_3$), 2.22 *m* (2H, CH_2–$COOCH_3$), 1.4 *br, s* (chain-CH_2) and 0.9 *t* (3H, terminal CH_3), where **A** and **B** are as given above. The mass spectrum of **III** provided further support to its structure. Mass spectrum **III** gave molecular ion peaks at *m/z* 390/392 with other significant peaks at *m/z* 359/361 (M – OCH_3); 311 (M – Br); 293 (311-18); 279 (311-32); 263/265; 257; 241; 209; 195; 177; 163/165 and 159. Thus, in light of the above spectra data and mass fragmentation pattern, the structure of **III** was established as methyl 13-bromo-9,12-epoxyoctadecanoate.

The IR spectrum of **IV** showed bands at 3450 (OH), 1735 ($COOCH_3$), 1195, 1160, 1110, 1010(C-O) and 690 cm^{-1} (C–Br). The PMR spectrum of this compound gave important signals at δ 4.3 *m* (1H, OH, D_2O-exchangeable), 4.15 *m*, (2H, Br–CH(–)–CH(–)–Br), 3.9 *m* (1H, CH, OH in part merged with signals at δ 4.15), along with the usual signals for fatty esters. This suggests that the addition of bromine to the double bond of the ester has taken place.

Further support to the structure of dibromo ester was pro-



SCHEME 1

vided by its mass-spectral studies. The mass spectrum of **IV** showed absence of molecular ion peaks at *m/z* 470/472/474, and the highest molecular ion peaks were observed at *m/z* 399/401/403 (M – 14), followed by other important peaks at *m/z* 385/387/389 (399/401/403-14), 369/371/373 (M-101), 355/357/359 (369/371/373-14). Thus, on the basis of above evidence, compound **IV** was characterized as methyl 12,13-dibromo-9-hydroxyoctadecanoate.

The IR spectrum of **V** gave bands at 3420(OH), 1735 (*COO*CH_3), 1090, 1060, 1030 (C–O) and 690 cm^{-1} (C–Br). PMR of this compound revealed important signals at δ 4.13 *m* (1H, –CH-Br), 3.9 *m* (2H, 2 × C*H*–OH), 2.32 *m* (2H, 2 × CHO*H*, D_2O-exchangeable), along with other peaks typical for fatty esters. The IR and PMR data suggested that compound **V** was a simple bromohydrin derivative of methyl isoricinoleate. The formation of bromohydrin is not unusual because it has been reported that the reaction of NNDBS with olefins results in the formation of bromohydrins as minor reaction products (16).

Compound **V** was expected to be an isomeric mixture of methyl 13-bromo-9,12-dihydroxyoctadecanoate and methyl 12-bromo-9,13-dihydroxyoctadecanoate. This was supported by mass spectrometry. The mass spectrum of **V** showed the absence of molecular ion peaks at *m/z* 408/410, and the highest molecular ion peaks appeared at *m/z* 390/392 (M – 18). Other significant peaks were noticed at *m/z* 359/361 (390/392-31); 280 (359/361-Br); 279 (359/361-HBr), 215 [M–CH_3–$(CH_2)_4$–CH(OH)–(Br)–]; 205/207 (193/195); 185; 171(185-14), 163/165; 157(171-14) and 101 (locates the position of the OH group at C_{13}).

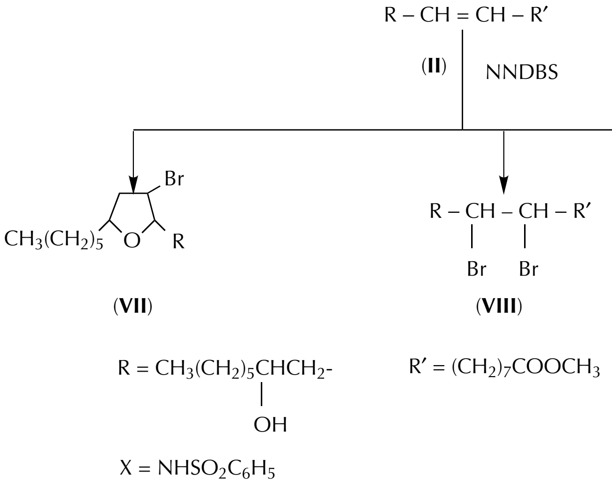
The IR spectrum of **VI** showed bands at 3440 (OH), 3260 (N-H), 3050 (C=C–H, aromatic system), 1740 (*C*OOCH_3), 1560 (C=C, aromatic), 1335; 1160 (SO_2N), 1110, 1090; 1065; 1030 (C–O), 755 and 720 cm^{-1} (C–Br). PMR of this compound revealed important signals at δ 7.9 *m* (2H, **C**) 7.6 *m* (3H, **D**); 7.1 distorted *m* (1H, N–*H*, D_2O exchangeable), 4.2 *m* (1H, C*H*–Br) and 3.95 *m* (1H, C*H*OH) along with usual signals for fatty esters. These spectral data indicated the presence of hydroxybromo and benzene sulphonamide moieties in the molecule. This could be attributed to the addition of NNDBS across the double bond. This compound was also expected to be an isomeric mixture of methyl 9-hydroxy-12-bromo-13-benzenesulfonamidooctadecanoate and methyl 9-hydroxy-13-bromo-12-benzenesulfonamidooctadecanoate.

Further confirmation of the structure of compound **VI** was obtained with the help of mass-spectral studies. The mass spectrum of the compound showed no molecular ion peaks at *m/z* 547/549, but again the highest molecular ion peaks appeared at *m/z* 404/406 [M – $(CH_2)_6$–$COOCH_3$], along with other significant peaks at *m/z* 402/404 (M – $C_8H_{17}O_2$), 390/392 (404/406-14); 388/390 (402/406-14), 374/376 (390/392-16); 373/374 (390/392-18); 358/360 (374/376-16 or 390/392-32); 346/348 [M – $CH_2CHOH(CH_2)_7COOCH_3$]; 332/334 (346/348-14); 310/312; 308 (388-HBr); 294, 297, 255/257 (332/334-77); 252 (332/334-HBr); 240; 227; 226; 221/223; 213; 195; 187; 170 (187-17); 163/165; 155 (187-32); 141; 125 and 77 (base peak, 100%).

A similar reaction of NNDBS and methyl 12-hydroxy-*cis*-9-octadecenoate (**II**, methyl ricinoleate) afforded three products (**VII–IX**), which showed positive Beilstein tests for the presence of halogen (Scheme 2).

Compound **VII** analyzed for $C_{19}H_{35}O_3Br$, (positive Beilstein test). The IR spectrum of **VII** showed no band at 3400 cm^{-1}, indicating the absence of a free OH group. This suggested that neighboring group participation might have occurred. Other bands were observed at 1735 (*CO*OCH_3), 1170, 1080, 1040, 1020 (C–O), and 730 cm^{-1} (C–Br). The NMR spectrum of the compound (**VII**) gave structure-revealing signals at 4.5–3.9 *br, m* (3H, **E**) and 1.65 (2H, **F**), along with the usual signals of fatty esters, where **E** and **F** are explained above. Thus, on the basis of these elemental and spectral data, **VII** was characterized as methyl 9,12-epoxy-10-bromo-octadecanoate.

Microanalysis of **VIII** gave the composition $C_{19}H_{36}O_3Br_2$

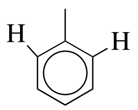


SCHEME 2

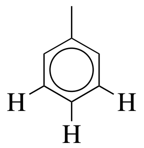
(positive Beilstein test). The composition suggested that bromination of the double bond has taken place. Its IR spectrum showed bands at 3500 (OH), 1735 (COOCH$_3$), 1170, 1080, 1020 (C–O) and 720 cm^{-1} (C–Br). The NMR of this compound gave signals at 4.2 *m* (2H, Br–CH(–)–CH(–)–Br), 4.0 *m* (1H,–C*H*(OH)–), 2.85 *br, s* (1H, –CH–O*H*, D$_2$O-exchangeable). In light of these elemental and spectral data, compound **VIII** was characterized as methyl 9,10-dibromo-12-hydroxy-octadecanoate.

Compound **IX** corresponded to formula $C_{25}H_{42}O_5BrNS$ (positive Beilstein test). Its IR spectrum revealed bands at 3470 (OH), 3275 (N–H), 3075 (C=C–H, aromatic system), 1735 (COOCH$_3$), 1501 (C=C, aromatic), 1335, 1160 (C–SO$_2$N), 1110, 1090, 1055, 1030 (C–O), 770 and 710 cm^{-1} (C–Br). NMR of **IX** showed important signals at 7.85 *m* (2H, **G**), 7.5 *m* (3H, **H**), 7.1 distorted *m* (1H, N–H, D$_2$O-exchangeable), 4.25 *m* (1H, CH–Br), 3.95 *m* (1H, C*H*–OH), 3.51 *m* (1H, CH–O*H*, D$_2$O-exchangeable), along with the usual signals of fatty esters, where

G =



and **H** =



These elemental and spectral data established the structure of **IX** as methyl 12-hydroxy-9(10)-bromo-10(9)-benzenesulfonimidooctadecanoate.

Pseudohalogenation with NNDBS appears to be in conformity with the accepted mechanism of electrophilic addition to the carbon-carbon double bond and involves a cyclic bromonium ion intermediate. The initial attack of bromine ion produces a cyclic bromonium ion intermediate. This intermediate, unlike other similar intermediates from internal olefins, offers an opportunity for preferential attack of the anionic part of the reagent (nucleophile) from an unhindered methylene side, thus, resulting in the almost exclusive formation of addition products. The formation of dibromides and bromohydrins in reactions of NNDBS with olefins has been supported by an earlier report (10). The reaction of NNDBS with 12- and 9-hydroxy-olefinic (ricinoleic and isoricinoleic) acid has been proved to be a convenient route to synthesis of tetrahydrofuran (1,4-epoxide) derivatives. The formation of the tetrahydrofuran could be rationalized by neighboring group participation of the hydroxy function.

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