

# Heavily Brominated and Highly Unsaturated Derivatives of Jojoba Oil<sup>1</sup>

Arnon Shani

Department of Chemistry, Ben-Gurion University of the Negev, Be'er-Sheva 84105, Israel

Two hexabromojojoba isomers were prepared by bromine addition to bromo-olefinic and bromoallylic derivatives, and an octabromojojoba derivative was prepared from jojobatetraene. Bis-allylic bromination of jojoba wax or monoallylic bromination of jojobatetraene, both followed by HBr elimination, yielded jojobahexaene, which has two conjugated triene units on both parts of the ester. Bromine addition to jojobahexaene yielded dodecabromojojoba, which was unstable toward hydrolysis in water-decalin mixture at 120 C. This is in contrast to the relative stability of the octabromojojoba under these conditions.

In a previous paper (1) we described bromine derivatives of jojoba wax and how the unsaturation along the ester chain can be increased. Heavily brominated products probably would have a greater density and higher melting point than the wax and thus could be used as additives in fire-retardant materials (2). On the other hand, highly unsaturated derivatives might be applied in fast-drying oil paints (3) as are linseed oil, eleostearic acid  $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH}$  or licanic acid,  $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_4\text{C}(\text{CH}_2)_2\text{COOH}$ , the latter two both being  $\text{C}_{18}$  acids. We thus undertook the study of the addition of 3, 4 and 6 moles of  $\text{Br}_2$  to jojoba wax derivatives, as well as the HBr elimination from other derivatives to introduce two conjugated triene units, one on each side of the ester chain.

## EXPERIMENTAL PROCEDURES

**General.** Crude jojoba oil was purified by mixing it with bleaching earth at 60 C for 30 min and then filtering under vacuum. The crude product after each chemical transformation was used without further purification for the next step. The usual workup consisted of pouring the reaction mixture into  $\text{H}_2\text{O}$ , extraction with petroleum ether (60–80), washing with saturated  $\text{NaCl}$  solution, and drying over anhydrous  $\text{Na}_2\text{SO}_4$ . IR and NMR spectra provided monitors for the chemical change occurring in each reaction. All NMR spectra of the ester chain gave the following data: terminal  $\text{CH}_3$  as a triplet at  $\delta$  0.92–0.94 and intense signal at 1.2–1.4 for all aliphatic hydrogens; a signal at 1.98–2.05 for allylic hydrogens, a triplet at 2.20–2.26 for  $\text{CH}_2\text{COO}$ , and a triplet at 3.96–4.00 for  $\text{CH}_2\text{OCO}$ . The NMR spectra were determined on a Varian XL 100 or Bruker WP-200 SY spectrometer in  $\text{CCl}_4$  or  $\text{CDCl}_3$  solution with chemical shifts expressed in  $\delta$ . The infrared (IR) spectra were determined with a Perkin Elmer 377 spectrophotometer, the samples being neat or in  $\text{CHCl}_3$  solution or as a KBr pellet. The ultraviolet (UV) spectra

were taken on a Bausch and Lomb Spectronic 210 spectrophotometer in cyclohexane ( $\text{C}_6\text{H}_{12}$ ) solution.

Analytical thin layer chromatography (TLC) plates ( $20 \times 20$  or  $20 \times 10$  cm and 0.1 mm thickness) were prepared with Silica Gel KGS-254. Preparative thick layer chromatography (PLC) plates ( $20 \times 20$  cm and 1 mm thickness) were prepared with silica gel. Crude samples of 70–90 mg were loaded on each of the PLC plates for purification. The eluting system was 10% of ether in petroleum ether (60–80) with recovery of 70–80%, by extracting with ether.

**Solvents and reagents.** Petroleum ether (60–80) was dried over  $\text{CaCl}_2$  and distilled. Ether was dried over  $\text{CaCl}_2$ , then over Na and distilled. Pyridine was kept over KOH prior to its use. Acetone was dried over  $\text{CaCl}_2$ . Tetrahydrofuran (THF) was kept over KOH, passed through basic alumina and dried over  $\text{CaH}_2$ . Dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), benzene, chlorobenzene, toluene,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{OH}$ , *i*-PrOH and *t*-BuOH were CP and used without drying.  $\text{LiCl}$  and  $\text{Li}_2\text{CO}_3$  (CP) were dried prior to the reaction, at 120–130 C, for two hr. For more details, please refer to previous works (1,4–7).

Microanalyses were performed in the Microanalytical Laboratory of The Institutes for Applied Research, Ben-Gurion University.

***N*-Bromosuccinimide (NBS) bromination of jojoba wax (I).** A solution of 11.8 g of jojoba wax (I) (0.02 mol) and 14.2 g NBS (0.08 mol) in the 150 ml  $\text{CCl}_4$  was refluxed for six hr. Filtration of the solid succinimide and evaporation of the solvent yielded 15.5 g of curde II. IR and NMR spectra were similar to those of the product of two equivalents bromination (1), except for the integration at the 4.40–4.80 region, which accounted for 3.6H. IR, 980 and 740  $\text{cm}^{-1}$ ; NMR 5.40–5.90 (3.8H,  $-\text{CH}=\text{CH}-$ , m); 4.40–4.80 (3.6H,  $\text{BrCHCH}=\text{CHCHBr}$ , m), 1.75–2.10 (8H,  $-\text{CH}_2\text{CH}(\text{Br})-$ , m). Calcd. for Br, 35.2%; found 35.4%.

**Jojobahexaene (III).** A suspension of 1.5 g of bis-allylic tetrabromojojoba (II) (1.6 mmol), 1.3 g  $\text{LiCl}$  (0.03 mol) and 1.5 g  $\text{Li}_2\text{CO}_3$  (0.02 mol) in 10 ml chlorobenzene was stirred vigorously and refluxed for 24 hr to yield 0.9 g of crude III. A sample of 100 mg was separated

on PLC to yield 59 mg of pure III.  $\text{C}_6\text{H}_{12}$  UV $\lambda_{\text{max}}$  314 ( $\epsilon$  5,300) 301 (8,100), 278 (76,100), 268 (81,400) and 257 (75,100). IR, 1720, 1685, 1665, 1645, 980, 950, 820  $\text{cm}^{-1}$ ; NMR 5.20–6.20 (12H,  $-\text{CH}=\text{CH}-$ , with two regions: at 5.90 major peak and broader one at 5.40), 1.80–2.20 (10H,  $\text{CH}_2\text{COO}-$  and allylic H,m). Analysis of the crude product showed that less than 5% of bromine was left in it.

**Hydrolysis of jojobahexaene to its acid (IV) and alcohol (V).** Hydrolysis of 0.6 g of III (1 mmol) in 5% KOH in 10 ml 80% aqueous isopropanol at room temperature for 48 hr yielded the organic phase, containing 0.15 g of alcohol (V) and the aqueous phase, from which 0.18 g of the acid (IV) was isolated after acidification and extraction with  $\text{CHCl}_3$ . The acid

<sup>1</sup>This paper is the fifth in a series on functionalization at the double bond region of jojoba oil.

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exhibited typical IR spectrum, 3500–2700, 1710  $\text{cm}^{-1}$ ,  $\text{UV}\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  279 (30,000), 269 (32,300), 258 (29,000). NMR 5.20–6.10 (6H,  $-\text{CH}=\text{CH}-$ , m). The alcohol, IR, 3300–3400  $\text{cm}^{-1}$ ,  $\text{UV}\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  280 (29,500), 270 (31,900), 259 (30,000), NMR 5.20–6.10 (6H,  $-\text{CH}=\text{CH}-$ , m).

**NBS bromination of jojobatetraene (VI).** A solution of three g of jojobatetraene (VI) (5 mmol) and 1.8 g NBS (0.01 mol) in 30 ml  $\text{CCl}_4$  was refluxed for five hr to yield 4.1 g of crude VII. IR, 990, 970, 740  $\text{cm}^{-1}$ ; NMR 5.20–6.20 (7H,  $-\text{CH}=\text{CH}-$ , m, exhibiting the feature of (E,E)- and (Z,E)-conjugated diene), 4.40 (2H,  $-(\text{Br})\text{CHCH}=\text{CH}-$ , dt,  $J=7$  and 2 cps), 1.80–2.30 (10H,  $\text{CH}_2\text{COO}$  and allylic H, bm). Calcd. for Br, 21.3%; found 22.2%.

**Jojobahexaene from VII.** The same procedure as above (from II to III) on 4.3 g of VII yielded 3.1 g of crude III, which upon purification on PLC and hydrolysis afforded IVa and Va, which are either identical to IV and V, or their positional isomers.

**Self-condensation of jojobahexaene (III).** A solution of 0.1 g of III in five ml xylene and a crystal of iodine was stirred for 50 hr at room temperature, or heated in  $\text{CCl}_4$  for four hr under  $\text{N}_2$  to yield 80 mg of crude product mixture, containing material with structures such as VIII and IX. NMR 6.50–6.70 (4–5 H,m), 5.25 (2H,m), 1.90–2.20 (4H, allylic H, broad).


**Bismaleic anhydride adduct (X).** A solution of 0.5 g jojobahexaene (III) (0.8 mmol) and 0.16 g maleic anhydride (1.6 mmol) in 20 ml toluene was refluxed for 26 hr to yield 0.6 g of crude X. IR 1760, 1740, 1710  $\text{cm}^{-1}$ . For NMR see Table 1.

**Bis N-methylmaleimide adduct (XI).** A mixture of 0.5 g jojobahexaene (III), (0.8 mmol) and 1.8 g maleimide (1.6 mmol) in 10 ml toluene was refluxed for four hr to yield 0.4 g of crude XI. For NMR see Table 1.

A sample of 100 mg was purified on PLC to yield 20 mg of XI. Calcd. for N, 3.45%; found 4.5%.

**$\alpha,\alpha,\beta,\beta,\alpha',\beta'$ -Hexabromojojoba (XIV).** A solution of 0.43 g bromine (2.7 mmol) in 10 ml  $\text{CCl}_4$  was added drop by drop to a solution of one g of bromo-olefin XIII (1.35 mmol) in 10 ml  $\text{CCl}_4$  at 5 C to yield 1.4 g of

crude XIV. IR, 1250, 770, 750  $\text{cm}^{-1}$ ; NMR 3.90–4.20 (4H,  $\text{CH}_2\text{OCO}$ ,  $-\text{CHBr}-$ , m), 2.00–2.60 (10H,  $\text{CH}_2\text{COO}$ ,  $\text{CH}_2\text{CHBr}$ ,  $-\text{CH}_2\text{CBr}_2-$ , m). Calcd. for Br, 44.8%; found 42.5%.

**Partial HBr elimination from XIV to yield XV and XVI.** A mixture of 1.6 g of XIV (1.5 mmol) and 0.420 g t-BuOK (3.7 mmol) in 10 ml dimethylsulfoxide (DMSO) was refluxed for five hr to yield 0.9 g of crude mixture of XV (major) and XVI (minor). IR, 1250, 720  $\text{cm}^{-1}$ ; NMR 5.50 (0.5H,  $\text{CH}_2\text{CH}=\text{C}-$ , t,  $J=7$  cps), 3.90–4.0  
  
 (2.5H,  $-\text{CH}_2\text{OCO}$ ,  $-\text{CH}(\text{Br})-$ , m), 1.90–2.70 (10H,  $-\text{CH}_2\text{COO}$ , allylic H,  $-\text{CH}_2\text{CHBr}$ ,  $-\text{CH}_2\text{C}(\text{Br})=\text{C}(\text{Br})\text{CH}_2-$ ). Calcd. for Br 35.2%; found 29.4%.

**NBS bromination of XIII to yield XVII.** A solution of one g of XIII (1.35 mmol) and 0.480 g of NBS (2.7 mmol) in 15 ml  $\text{CCl}_4$  was refluxed for 20 hr to yield 1.4 g crude XVII. IR, 1200, 770  $\text{cm}^{-1}$ ; NMR 6.05 (0.1H, olefinic H, m) 5.8 (1.2H,  $\text{BrCHCH}=\text{C}(\text{Br})-$ (vi), d,  $J=10$  cps), 5.6 (0.5H,  $\text{CH}=\text{C}(\text{Br})\text{CH}(\text{Br})$ , (vii) t,  $J=7$  cps), 5.3 (0.2H, olefinic H, t,  $J=7$  cps), 4.76 (1.2H,  $-\text{CH}(\text{Br})\text{CH}=\text{C}(\text{Br})-$ (vi), dt,  $J=10$  and 7 cps), 4.50 (0.5 H,  $\text{CH}=\text{C}(\text{Br})-\text{CH}(\text{Br})-$ (vii), t,  $J=7$  cps), 4.20 (0.6H,  $\text{BrCH}-\text{CHBr}$ , bd), 1.80–2.70 (10H,  $-\text{CH}_2\text{COO}$ ,  $-\text{CH}_2\text{CHBr}$ , allylic H, m). Calcd. for Br, 35.2%; found 31.3%.

**Dibromojojobatetraene (XVIII).** A suspension of 0.9 g of XVII (1 mmol), 2.1 g of LiCl (0.05 mol) and 2.2 g  $\text{Li}_2\text{CO}_3$  (0.03 mmol) in 10 ml chlorobenzene was re-

fluxed for 30 hr to yield 0.6 g crude XVIII,  $\text{UV}\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  238 ( $\epsilon$  22,700). IR, 1170  $\text{cm}^{-1}$ ; NMR 5.60–6.20 (4H,  $-\text{CH}=\text{CH}-\text{C}(\text{Br})=\text{CH}-$ ,  $-\text{CH}=\text{CH}-\text{CH}=\text{C}(\text{Br})-$ , m), 5.3–5.6 (1H) and 4.20–4.80 (1H) peaks of starting material, 1.90–2.50 (10H,  $-\text{CH}_2\text{COO}$ , allylic H). Calcd. for Br, 21.8%; found 25.2%.

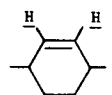
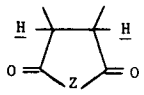
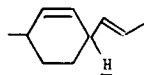
**Bis-(vicinal tribromo)jojoba [ $\alpha,\beta,\gamma,\alpha',\beta',\gamma'$ -hexabromojojoba (XX)].** A solution of 0.96 g bromine (6 mmol) in 10 ml  $\text{CCl}_4$  was added drop by drop to a solution of 2.2 g XIX (1) (3 mmol) in 10 ml  $\text{CCl}_4$  at 0 C to yield 2.9 g of crude XX. IR, 785, 760, 590  $\text{cm}^{-1}$ , NMR 4.65 (1H,  $-(\text{Br})\text{CHCH}(\text{Br})\text{CH}(\text{Br})-$ , m), 4.25–4.45 (3H,  $-(\text{Br})\text{CHCH}(\text{Br})-$ , m), 3.95–4.10 (4H,  $(\text{Br})\text{CHCH}(\text{Br})-$ ,  $\text{CH}_2\text{OCO}$ , m), 1.80–2.30 (8H,  $-\text{CH}_2\text{CH}(\text{Br})-$ ). Calcd. for Br, 44.8%; found 42.6%.

**Bis-(vicinal tetrabromo)jojoba [ $\alpha,\beta,\gamma,\delta,\alpha',\beta',\gamma',\delta'$ -octabromojojoba (XXII)].** This synthesis comprised a two-step addition of bromine to VI: A solution of 1.6 g bromine (0.01 mol) in 15 ml  $\text{CCl}_4$  was added drop by drop to a solution of three g jojobatetraene (VI) (0.005 mol) in 20 ml  $\text{CCl}_4$  at 5 C to yield XXI, IR, 955  $\text{cm}^{-1}$ . NMR 5.00–6.00 (4H,  $\text{BrCHCH}=\text{CHCHBr}$ ,  $-\text{CH}=\text{CHCH}(\text{Br})$ , with a main peak at 5.75 for 2H), 4.38 (3H,  $(\text{Br})\text{CHCH}=\text{CH}$ , m) 3.95–4.05 (3H,  $-\text{CH}(\text{Br})-$ ,  $\text{CH}_2\text{OCO}$ , m), 1.80–2.30 (10H,  $-\text{CH}_2\text{COO}-$ , allylic and  $-\text{CH}_2\text{CH}(\text{Br})-$ ). Calcd. for Br 35.1%; found 39.3%. Further addition of 0.01 mol bromine was much slower and continued for 10 hr at room temperature to yield XXII. Calcd. for Br 51.8%; found 48.7%.

When the reaction was repeated with jojobatetraene derived from all-*trans*-jojoba (9), no olefin protons were found in XXII,  $\text{UV}\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  209 (5100), IR, 725, 590

TABLE 1

Chemical Shifts (in  $\delta$ ) of Specific Hydrogens in Diels-Alder Adducts X and XI

Hydrogens		
Assigned	Adduct X	Adduct XI
	5.80 (4H) major peak	5.60 (3H)
	6.10, 5.35 (3H) 2 small peaks	6.10–5.40 (3H)
	Z = O	Z = $\text{NCH}_3$
	3.25 (3H)	3.35 (3H)
	2.85 (1.4H)	3.00–2.80 (6H) (including 2 $\text{CH}_3\text{N}$ )

cm<sup>-1</sup>; NMR 4.05–4.80 (8H,  $-\underline{\text{CH}}(\text{Br})-$ , m), 1.70–2.25 (10H,  $\underline{\text{CH}}_2\text{CH}(\text{Br})$ ,  $-\underline{\text{CH}}_2\text{COO}-$ ). Calcd. for Br, 51.8%; found 50.7%. Basically, the IR and NMR spectra of this product and those received from VI were identical.

*Bis-(vicinal hexabromo)jojoba* [ $\alpha, \beta, \gamma, \delta, \epsilon, \xi-\alpha', \beta', \gamma', \delta', \epsilon', \xi'$ -dodecabromojojoba (XXV)]. The procedure consisted of a three-step addition of bromine to (III): A solution of 0.32 g bromine (0.002 mol) in 10 ml  $\text{CCl}_4$  was added drop by drop to a solution of 0.6 g jojobaheptaene (III) (0.001 mol) in 20 ml  $\text{CCl}_4$  at 5 C to

yield XXIII,  $\text{UV}\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  254 (53,300). NMR 5.75–6.35 (8H,  $(\text{Br})\text{CHCH}=\underline{\text{CH}}-\text{CH}=\text{CHCH}(\text{Br})$ , m, two regions at 5.85 and 6.15), 4.6 (4H,  $\text{BrCHCH}=\text{CHCH}(\text{Br})$ , q(dt),  $J=10$  cps), 4.12(2H,  $\underline{\text{CH}}_2\text{OCO}$ , t). The second addition of 0.32 g  $\text{Br}_2$  yielded XXIV, NMR 5.75–6.20 (4H, olef, m), 4.10–4.90 (8H,  $(\text{Br})\underline{\text{CH}}$ , m), 4.10 (2H,  $\underline{\text{CH}}_2\text{OCO}$ , t). The addition of the third portion of  $\text{Br}_2$  was much slower, and stirring was conducted at room temperature for 12 hr to yield 1.5 g XXV; UV, end absorption. IR 1710, 965, 790, 765  $\text{cm}^{-1}$ , NMR 4.25–5.50 (12H,  $(\text{Br})\underline{\text{CH}}$ , m), 4.12 (2H,  $\underline{\text{CH}}_2\text{OCO}$ , t), 1.80–2.60 (10H,  $\underline{\text{CH}}_2\text{CH}(\text{Br})$ ,  $\underline{\text{CH}}_2\text{COO}$ , m). Calcd. for Br 61.8%; found 58%.

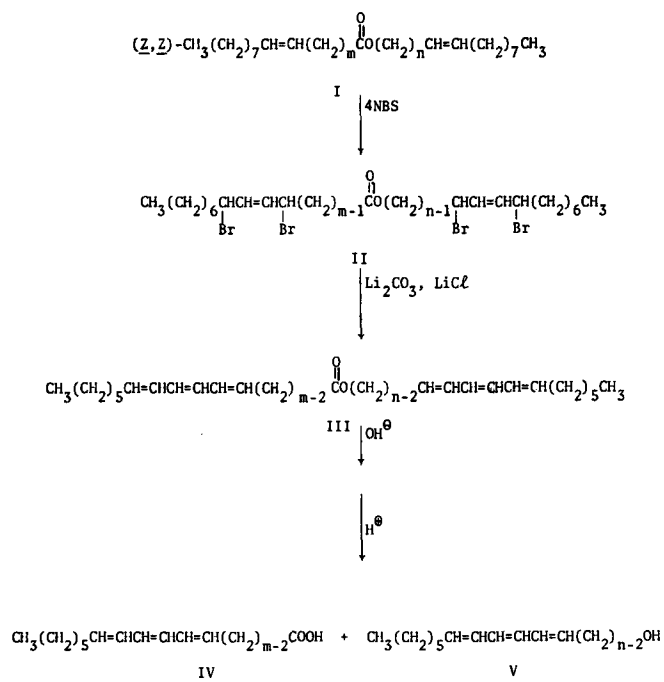
*Heating of XXII and XXV in H<sub>2</sub>O and decalin.* A mixture of five g of XXII in 70 ml  $\text{H}_2\text{O}$  and 20 ml decalin was heated to 120 C and stirred vigorously for 200 hr. Samples were withdrawn for Br analysis every 24 hr. The last analysis for XXII showed 47.3% bromine content in the wax, no new peaks were detected in NMR spectrum, and integration was similar to that of pure XXII.

A mixture of two g of XXV in 20 ml  $\text{H}_2\text{O}$  and five ml decalin was heated as above. Samples were withdrawn for Br analysis after 50, 100 and 200 hr. All three analyses showed 49–51% bromine content. New peak at 3.45 (t,  $J=7$  cps) appeared after 50 hr of heating, while integration of  $-\underline{\text{CH}}(\text{Br})-$  dropped by 10% as compared to starting XXV.

## RESULTS AND DISCUSSION

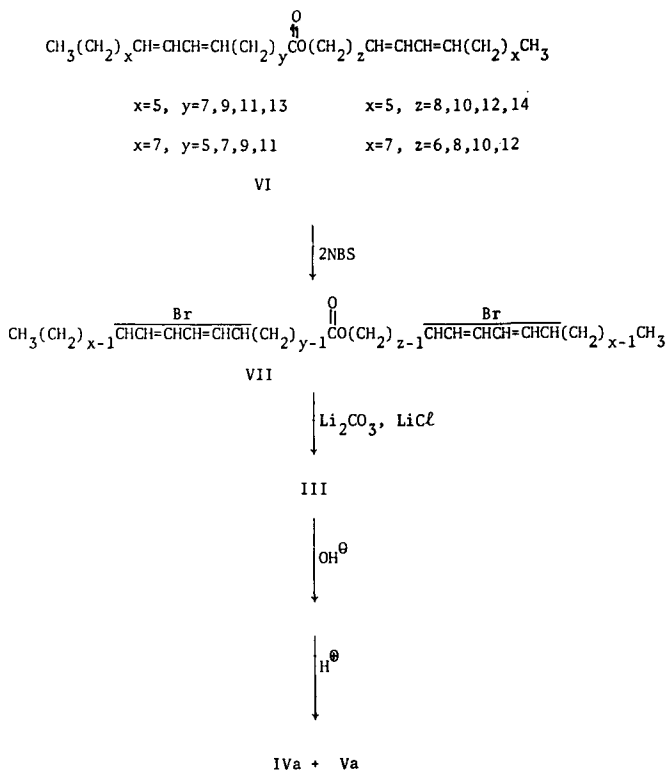
The preparation of jojobaheptaene (III) (Scheme 1) was based on allylic bromination of either jojoba wax (I) with four equivalents of NBS, or of jojobatetraene (VI) (1,8) with two equivalents of NBS, followed by HBr elimination. Both approaches went smoothly to yield, first, the corresponding brominated products II (Scheme 1) and VII (Scheme 2). We cannot exclude double bromination on one side of the ester in the reaction of VI, to yield a structure such as (i),  $-\text{CH}_2\text{CH}_2\text{CHCH}=\text{CHCH}=\text{CHCHCH}_2\text{CH}_2-$  (i), which might produce a

tetraene unit such as (ii),  $-\text{CH}_2\text{CH}=\text{CHCH}=\text{CHCH}=\text{CHCH}=\text{CHCH}_2-$  (ii). And, in fact, we could attribute the two small absorption bands at 301 and 314 nm, which we found in the UV spectrum of III (see Experimental Procedure) to the two major peaks of a tetraene unit (9). We also detected some of the same UV absorption in the product III, derived from II, which might arise from in situ HBr elimination during the NBS



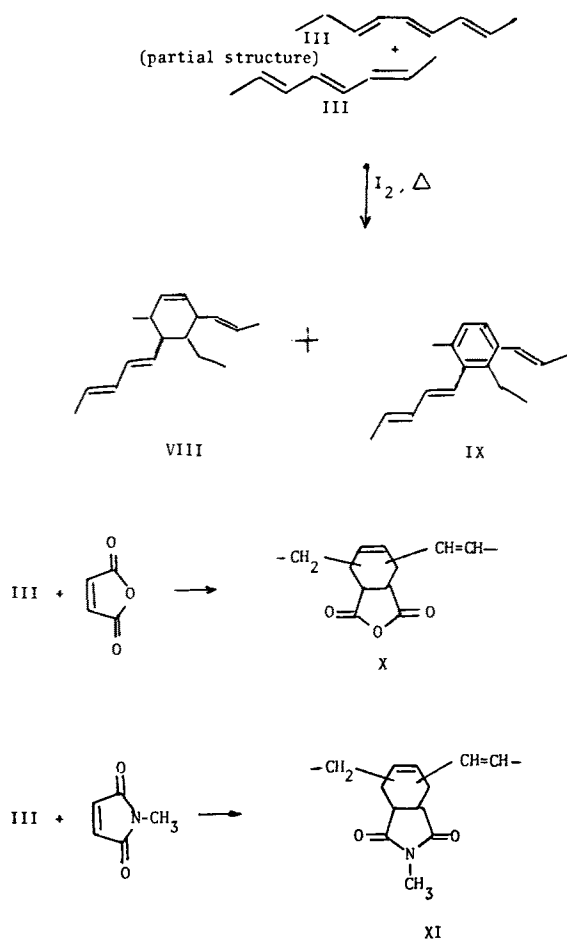
$$m = 7, 9, 11, 13; n = 8, 10, 12, 14$$

SCHEME 1.



SCHEME 2.

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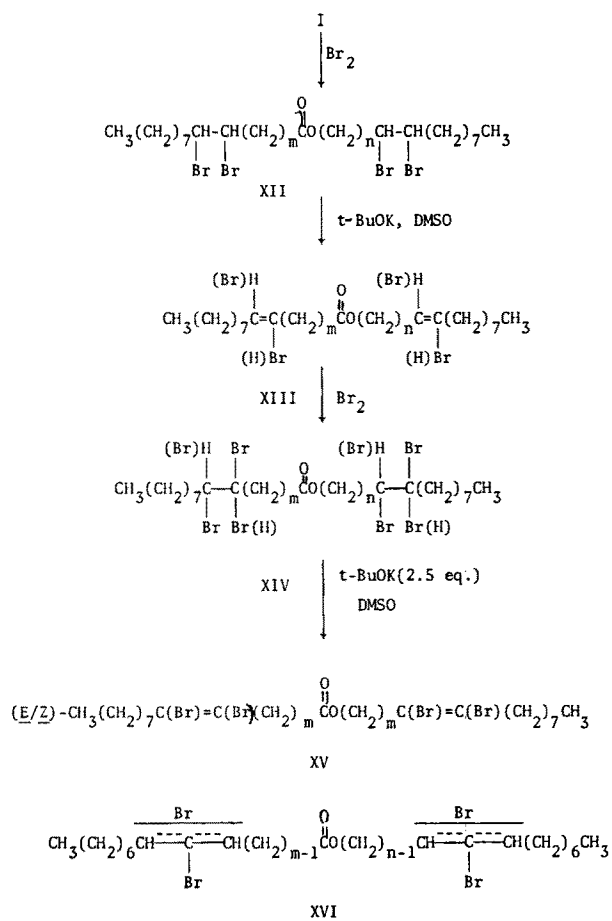


SCHEME 3.

reaction, to introduce one more equivalent of allylic bromine along the reacting chain. The HBr elimination by the  $Li_2CO_3/LiCl$  system proved to be efficient enough to produce III in relatively high yield ( $\sim 90\%$  crude,  $\sim 60\%$  of purified product). The typical UV absorption of a hexaene unit is exhibited by the product, and the intensity is doubled as compared to a triene unit (9). Two low-intensity bands at 301 and 314 nm appear in the spectrum, which might arise from a tetraene unit. The hydrolysis of III from both syntheses yielded the same triene acid IV and alcohol V.

The "Diels-Alder activity" of the hexaene is demonstrated both in its self-cycloaddition of III to form structures such as VIII and IX (Scheme 3) and in the formation of bis adducts with maleic anhydride (X) and N-methylmaleimide (XI). The large number of possible isomers excludes any attempt to separate the crude mixtures, except for cleaning from other products and impurities. In Scheme 3 only partial possible structures are shown without any effort to establish specific structure. The relative instability of III in air or in light (forming rubber-like viscous material) demonstrates the reactivity of the triene units, as expected.

Another type of product is based on partial HBr elimination from tetrabromojojoba (XII), as shown in Scheme 4. The dibromoester XIII (1) added bromine to yield  $\alpha, \alpha, \beta, \alpha', \beta', \alpha'$ -hexabromojojoba (XIV), which upon partial HBr elimination yielded mainly the tetrab-

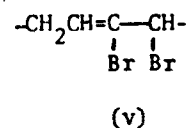


SCHEME 4.

romo olefinic ester XV [probably as a mixture of *cis*- and *trans*- olefins (iii) and (iv)] together with another

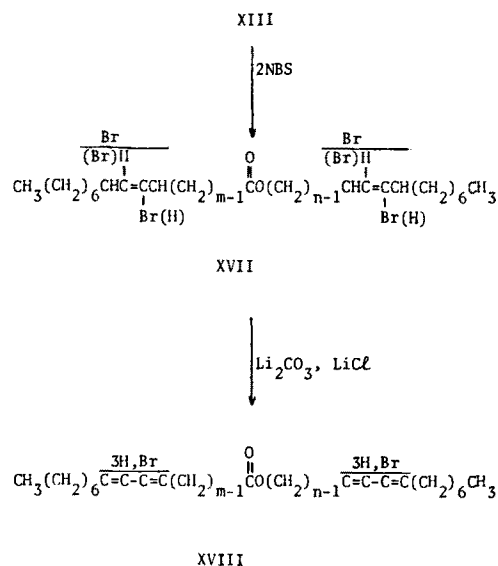


isomer XVI (Scheme 4), which probably has partial structure such as (v).



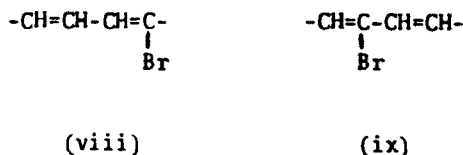
It is interesting to note that the same procedure on all-*trans* (*E, E*)-jojoba (10) yielded pure XV, without the other isomer XVI. When the dibromoester XIII underwent allylic bromination with two equivalents of NBS, a mixture of isomers such as XVII was obtained, with structure vi predominating, and structure vii as a minor component (Scheme 5). HBr elimination





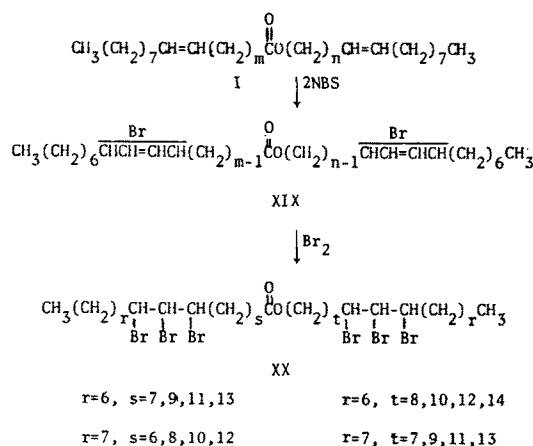
SCHEME 5.

from this isomer mixture yielded a bisbromodiene (or dibromotetraene) system, with gross structure of XVIII and partial structure viii (from vi) predominating, and probably smaller amounts of structure, ix, arising from vii. The two conjugated diene units exhibit typical



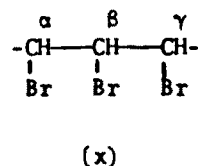
UV absorption at  $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  238 ( $\epsilon$  22,700), which is a red shift (longer wavelengths) from the jojobatetraene (VI),  $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  230 ( $\epsilon \sim 22,000$ ). This bathochromic effect of the bromine atom is well documented (11).

Another hexabromo-isomer ( $\alpha, \beta, \gamma, \alpha', \beta', \gamma'$ ) could be obtained from the previously known allylic dibromojjoba XIX (1) (Scheme 6) by bromine addition to



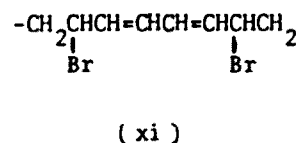
SCHEME 6.

yield XX. The NMR spectra clearly show the difference between the two hexabromo isomers XIV and XX, as described in the experimental section. The separated peak at  $\delta$  4.65 is of the H on  $\text{C}^\beta$ , center of the partial structure (x). The two bands at 4.25–4.45 (3H)



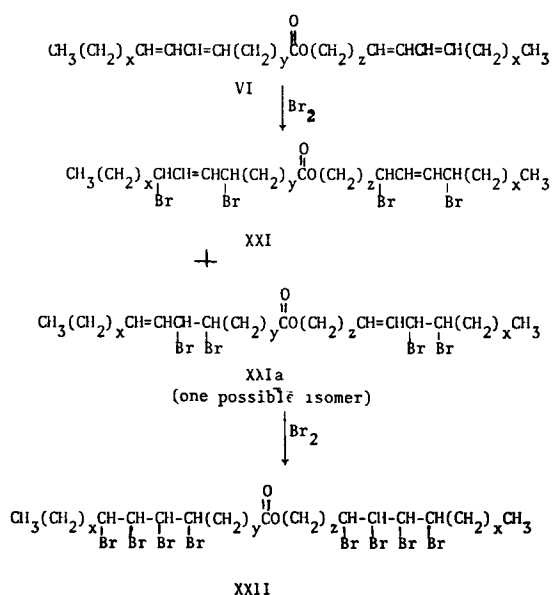
and at 4.10 (2H) are attributed to the d, l and meso stereoisomers, respectively (12).

The above mentioned hexabromo isomers contain up to 42–43% Br and thus have a high density of 1.24 g/ml. We succeeded in preparing even more heavily brominated products, namely octabromojjoba (XXII) and dodecabromojjoba (XXV). They were synthesized from jojobatetraene (VI) in two steps (Scheme 7) and jojobahexaene (III) in three steps by gradual addition of bromine (Scheme 8). The first intermediate in the preparation of XXII was the tetrabromo derivative XXI, which is the major isomer as the result of 1,4-addition, together with the minor isomer XXIa, the result of 1,2-addition. Further addition of bromine yielded XXII, no olefinic hydrogens were observed in the NMR spectrum and Br analysis showed 50.7%. This compound appears as a semi-solid material, and its density is 1.43 g/ml. The addition of bromine to the hexaene derivative (III) proceeded in three steps. The first one, with two equivalents of bromine, resulted mainly in 1,6-addition to give tetrabromotetraene (partial structure xi), which exhibited a (E,E)-conjugated diene system in the NMR spectrum (see Experimental). The UV spectrum showed the conjugated diene

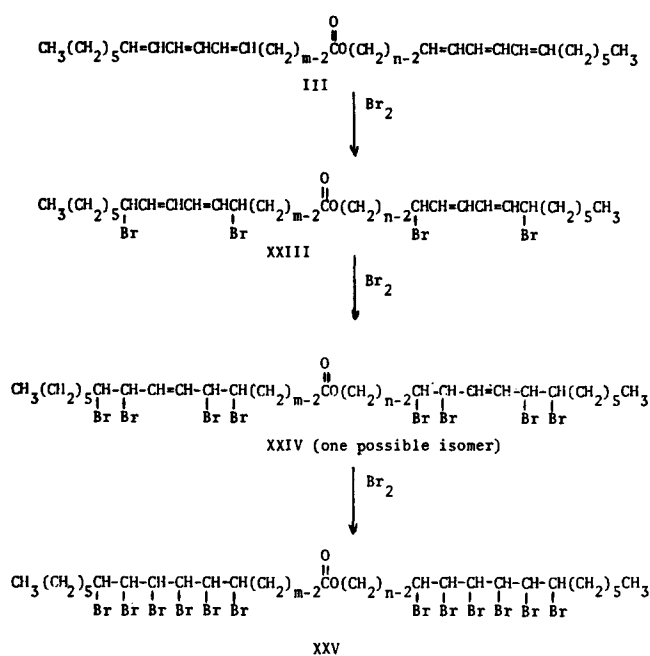


unit with the expected intensity at 254 nm, demonstrating the bathochromic effect of the Br atoms. The second portion of two equivalents of  $\text{Br}_2$  gave the octabromodiolefinic product, which, in a slow addition of the last portion of bromine (2 more equivalents), yielded dodecabromojjoba XXV as very viscous material, with a density of 1.54 g/ml. The stability toward hydrolysis and/or HBr elimination in  $\text{H}_2\text{O}$ /decalin mixture at 120 C seemed to be acceptable for 200 hr for the octabromojjoba (XXII), but not as good for the dodecabromojjoba (XXV). In the first case loss of Br was negligible, and NMR showed the original structure. Neither  $\alpha$  to oxygen nor olefinic hydrogens could be detected in the NMR spectrum. On the other hand, XXV lost up to 13% of its original bromine content, probably through hydrolysis, as OH absorption band appeared in the IR spectrum. These results demonstrate that six bromine atoms in an aliphatic chain on six adjacent carbon atoms are not as stable as those on four adjacent atoms. This is probably the result of the steric hindrance caused by several adjacent large

## BROMINATED AND UNSATURATED JOJOBA OIL DERIVATIVES



SCHEME 7.



SCHEME 8.

bromine atoms, and some repulsive parallel and anti-parallel dipolar interactions of the C-Br bonds. This hindrance, which is more severe in XXV than in XXII, probably forces one or two bromine atoms to be extended outward, thus bringing them into a more favorable reaction orientation with H<sub>2</sub>O molecules to introduce a OH group, replacing a bromine atom. It is not clear whether C-Br bond breaking (thermal-radical or

ionic reaction) takes place first, or this is a classical S<sub>N</sub>2 reaction. As no olefinic hydrogens appear in the NMR spectrum after 200 hr of heating, there is no elimination product in the reaction mixture. This might hint at a S<sub>N</sub>2 reaction. A preliminary C-Br breaking might lead to either a carbon radical or carbocation intermediate, which can eliminate hydrogen atom (or proton) to form a double bond. Still, such an olefin, if formed, can add H<sub>2</sub>O molecule. The hydrolysis forms HBr, which can catalyze such additions. More studies should be done in order to understand the reaction mechanism.

The relative instability of the dodecabromojojoba should be taken into account if such heavily brominated products are used or submitted to an aqueous environment under drastic conditions.

Some preliminary experiments with the octabromojojoba in fire-retardant mixtures have been conducted. The few results obtained could not point to any advantageous application. More diversified studies should be performed before final conclusions are made.

All reactions and products discussed above demonstrate, once more, the wide versatility of jojoba wax in chemical manipulations, which facilitates synthesis of desired or promising derivatives of jojoba wax. Most of these reactions are easy to handle, even in large quantities, usually give high yields, and even though several isomers are formed in one reaction, the product is homogeneous for further reactions and hopefully for application.

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