Functionalization at the Double Bond Region of Jojoba Oil. 6. Production of Amines *via* Azides

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The apolar and hydrophobic jojoba molecule was made more hydrophilic by the incorporation of primary amino groups *via* the introduction and subsequent reduction of azido groups. The azides were obtained by the substitution of bromine or a mesylate group introduced into the jojoba oil molecule; by opening of the epoxide ring in epoxy jojoba; or by the addition of bromoazide to the double bonds of jojoba.

KEY WORDS: Aminojojoba oil, azidojojoba oil, hydroxyaminojojoba oil, jojoba oil.

The hydrophobicity of jojoba oil [I] precludes its miscibility with polar solvents (1). This property can be changed significantly by the introduction of hydrophilic groups, such as OH (2) or NH_2, or their derivatives. Such modified products are likely to find commercial application as amphiphilic chemicals in cosmetics or detergents. Another important application of amine derivatives of jojoba wax is their use as starting products for the synthesis of nitrogen heterocycles. Amines and heterocycles of the jojoba series have potential uses in the chemical industry as new monomers for the production of biodegradable polyamide resins; new oil-soluble extractants for heavy metal ions; or starting materials for the synthesis of a new generation of biologically active substances for the cosmetics industry and in medicine (as substances that can penetrate through the skin and be deposited in the fatty subcutaneous tissue).

As has been described previously (2,3), the double bond regions of the liquid wax may be functionalized by the addition of two or four hydroxylic groups to increase the polarity of the wax. It is assumed that the effect of two or four amino groups or their salts would be even greater. In this paper we describe the preparation of a series of amines prepared by functionalization of the double bond of jojoba oil [I]. [Derivatives of [I] (regio- and/or stereo-isomer mixtures) will be represented as follows: $(\text{-}CH_2\text{-}\underset{\displaystyle X}{\underset{|}{C}}H\text{-}\underset{\displaystyle Y}{\underset{|}{C}}H\text{-}CH_2\text{-})_2(COO)]$

$(Z,Z)CH_3(CH_2)_7CH{=}CH(CH_2)_mCOO(CH_2)_nCH{=}CH(CH_2)_7CH_3$ [I]: m = 7 (11%), 9 (71%), 11 (14%); n = 10 (44%), 12 (45%), 14 (9%).

EXPERIMENTAL PROCEDURES

Materials. Petroleum ether (60–80°C) was dried over $CaCl_2$ and distilled. Dimethyl formamide (DMF) was mixed with toluene and distilled. Ethyl acetate was dried over P_2O_5 and distilled. Chloroform, dichloromethane, acetone, ether, methanol, ethanol, butyl acetate and xylene all were CP-grade and were used without drying. Jojoba oil with an iodine value of 80.9 was used; this corresponds to a product with 94.7% of pure diunsaturated esters. Sodium azide (CP-grade) was activated by trituration with hydrazine hydrate, followed by dissolution in water and reprecipitation with acetone (4). Tributyl octadecyl phosphonium bromide (Merck, Darmstadt, Germany) was used as a phase-transfer catalyst (PTC).

General. Crude products obtained after a particular chemical transformation were used in the subsequent step without further purification. The standard work-up of azides consisted of pouring the reaction mixture into H_2O, extracting with petroleum ether (60–80°C), washing with a saturated NaCl solution and drying over anhydrous $MgSO_4$. Amines were separated by converting them to the corresponding hydrochlorides by passing a stream of dry HCl gas through a petroleum ether solution of the bases. The standard work-up of amine salts consisted of dissolving the crude salt in a minimum of methanol, washing the methanolic solution with petroleum ether and thereafter evaporating the methanol. The remaining salt was then extracted with a mixture of dichloromethane, a saturated solution at $KHCO_3$ (2.0 eq.), K_2CO_3 (1.6 eq.) and water, followed by drying over anhydrous Na_2SO_4. Evaporation under vacuum gave the corresponding bases (5).

Azides were separated either by column chromatography (silica gel 60, 70–230 mesh; Merck) or by thin-layer chromatography (TLC) in petroleum ether (60–80°C) with ether. Analytical TLC plates were prepared with silica gel KPF-254. DC-Karten SI F and DC-Karten AL F (for amines) (Riedel-de-Haën, Hannover, Germany) were also used. The eluent was ethyl acetate. Amines were separated by column chromatography on basic aluminum oxide in methanol with 30% ethyl acetate.

Infrared (IR) spectra and ^{1}H-nuclear magnetic resonance (NMR) spectra were used to monitor the chemical changes occurring in each reaction. IR spectra were determined with a Nicolet (Madison, WI) 5ZDX FT-IR spectrometer. The samples were run neat or in CCl_4 solution. All IR spectra gave an intense carbonyl signal at 1735–1740 cm^{-1}, a signal at 1465–1466 cm^{-1} and the broad intense signal of hydrogen–carbon bonds at 2800–3000 cm^{-1}. NMR spectra were determined on a Bruker (Karlsruhe, Germany) WP-200-SY instrument in $CDCl_3$ solution with Me_4Si as the internal reference. All NMR spectra gave a terminal CH_3 as a triplet at δ 0.92–0.94, an intense signal at 1.2–1.4 for all aliphatic hydrogens, a triplet at 2.20–2.26 for $\text{-}CH_2COO$, and a triplet at 3.96–4.00 for $\text{-}CH_2OCO$. All the other signals are described later. Integration curves were consistent with the assignment of the different hydrogens.

Microanalyses were performed by the Microanalytical Laboratory of the Institutes for Applied Research, Ben-Gurion University (Beer-Sheva, Israel).

Allylic jojoba diazide [III]. A mixture of 9.0 g (0.012 mol) of [II] (3) in 40 mL of dry DMF with 4.0 g (0.062 mol) of activated NaN_3 was stirred for 4 h at 90–94°C in an oil bath. The cooled reaction mixture was poured into 120 mL H_2O and then extracted with petroleum ether (60–80°C). The crude product (7.3 g) was refined on an SiO_2 column (eluent 30% ether in petroleum ether), and 6.05 g of [III] was obtained (yield 72%). Light yellow oil;

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n_D^{20} = 1.4774; IR, 2850–2950, 2093.6 (N_3), 1736.9 (C=O), 1466.0, 1173.8 (N_3) cm^{-1}; ^{1}H-NMR, 5.3 and 5.7 (4H, C*H*=C*H*, *m*); 3.74 (2H, CH=CHC*H*(N_3), *m*).

A mixture of 1.87 g (2.5 mmol) of [**II**] with 0.82 g (0.0126 mol) of NaN_3, 0.13 g (0.25 mmol) of PTC, 2 mL butyl acetate and 2 mL H_2O was refluxed (104–106°C in an oil bath) with vigorous stirring for 24 h. After the standard work-up, 1.61 g of [**III**] (69% purity on TLC) was obtained (yield 66%).

Vinylic jojoba diazide [**V**]. A solution of 5.83 g (6.4 mmol) of [**IV**] (3) in 25 mL of dry DMF with 1.8 g (0.028 mol) of activated NaN_3 was stirred for 6 h at 90–94°C in an oil bath. After the standard work-up, 4.1 g of crude product were obtained. The final yield of purified [**V**] was 3.15 g (73%). Light yellow oil, n_D^{20} = 1.4828; IR, 2850–2950, 2104.0 (N_3), 1738.8 (C=O), 1465.7, 1174.1 (N_3) cm^{-1}; ^{1}H-NMR, 5.60 (2H, C(N_3)=C*H*-, *t*), 2.4 (4H C*H*$_2$-C(N_3)= , *t*), 2.15 (4H, =CHC*H*$_2$, *t*).

Bis(α-hydroxy-azido)jojoba [**VII**]. A mixture of 1.92 g (3.1 mmol) of the epoxide [**VI**] (2), 4.2 g (0.064 mol) of activated NaN_3, 0.9 g (0.017 mol) of NH_4Cl and 2 drops of dry pyridine in 12 mL of dry DMF was stirred for 50 h at 90–94°C in an oil bath. The cooled mixture was poured into 100 mL H_2O and extracted with ethyl acetate. After drying over anhydrous $MgSO_4$ and evaporation under vacuum, 1.91 g of crude and 1.44 g of purified [**VII**] (69%) were obtained. Light yellow oil; n_D^{20} = 1.4784; IR, 3350–3500, 2850–2950, 2105.3 (N_3), 1736.6 (C=O), 1466.0, 1178.1 (N_3) cm^{-1}; ^{1}H NMR, 2.90–3.60 (4H, -C*H*(N_3)-C*H*(OH), *m*).

Bis*(α-hydroxy-azido)jojoba di*(p-*nitrobenzoate)* [**VIII**]. A mixture of 0.71 g (0.001 mol) of [**VII**], 2.5 mL of dry ethyl acetate, 0.47 g (0.046 mol) of NEt_3 and 0.4 g (2.2 mmol) of *p*-nitrobenzoyl chloride was allowed to react at room temperature for two days. The mixture was then poured into 20 mL saturated NaCl solution and extracted three times, each time with 10 mL petroleum ether. The extract was washed with 10 mL methanol. After drying over anhydrous $MgSO_4$ and evaporation under vacuum, 0.58 g of the crude product (about 70% purity) was obtained. After TLC in 30% ether in petroleum ether, the yield was 0.4 g of purified [**VIII**]. Orange oil; n_D^{20} = 1.4831; IR, 2850–2950, 2108.6 (N_3), 1736.6 (C=O), 1609.4, 1532.0, 1103.1, 1178.1 (N_3) cm^{-1}; ^{1}H NMR, 8.22–8.34 (8H, aromatic, *m*), 5.22–5.30 (2H, -C*H*(OCOC$_6$H$_4$NO$_2$), *m*), 3.19–3.56 (2H, -C*H*(N_3) *m*).

Bis*(α-bromo-azido)jojoba* [**X**]. The bromoazide [**IX**] was prepared as follows. To a vigorously stirred and cooled (to <0°C) suspension of 12.7 g (0.195 mol), NaN_3 in 30 mL CH_2Cl_2, 9.75 mL of conc. HCl was added. A solution of 1 mL Br_2 (3.2 g, 0.04 mol) in 9 mL CH_2Cl_2 was added immediately thereafter. The mixture was stirred for 45 min at <0°C and for 15 min at room temperature. The orange solution of BrN_3 was decanted into a dropping funnel for subsequent use. The BrN_3 solution was cooled to <20°C and dropped into a solution of 4.75 g (9.7 mmol) of jojoba oil [**I**] in 20 mL CH_2Cl_2 cooled in an ice bath. The reaction mixture was washed with H_2O. After drying over anhydrous $MgSO_4$ and evaporation under vacuum, 6.67 g of crude [**X**] and finally 6.34 g of purified [**X**] (94%) were obtained. Light yellow oil, n_D^{20} = 1.4950; IR, 2850–2950, 2103.2 (N_3), 1735.8 (C=O), 1465.8, 1258.4, 1174.6 cm^{-1} (N_3); ^{1}H NMR, 4.01–4.09 (4H, -C*H*Br + -C*H*$_2$OCO-, *m*), 3.30–3.40 (2H, -C*H*(N_3)-), *m*). Calculated for Br: 19.17%; found: 19.5%.

Tetraazidojojoba [**XI**]. To a solution of 1.78 g (2.5 mmol) of [**VII**] and 1 g (0.01 mol) of Et_3N in 10 mL of dry ethyl acetate, cooling in an ice bath, 1.15 g (0.01 mol) of CH_3SO_2Cl was added. After the mixture had been allowed to stand overnight, it was poured into 20 mL H_2O and extracted three times, each time with 20 mL ether. The crude dimesylate of [**VII**] (2.1 g) was obtained. IR, 2103.9 (N_3), 1734.2 (C=O), 1346.8, 1352.9 and 1176.7 (SO_3), 1169.4 (N_3), 910.6 cm^{-1}; ^{1}H NMR, 4.64 (2H, -C*H*(OSO$_2$CH$_3$) *m*), 3.35 (2H, -C*H*(N_3), *m*).

The crude dimesylate was stirred intensively together with a mixture of 2 mL butyl acetate, 2 mL H_2O, 0.82 g (12.6 mmol) NaN_3 and 0.13 g (0.25 mmol) of the PTC at 88–92°C (in an oil bath) for 22 h. After the standard work-up for azides, 1.73 g of crude product (63% purity on TLC) and then 1.1 g of pure [**XI**] (60%) were obtained. IR, 2850–2950, 2102.5 (N_3), 1728.1 (C=O), 1460.6, 1264.5, 1169.4 cm^{-1}; light yellow oil; n_D^{20} = 1.4788; ^{1}H NMR, 3.32 (4H, -C*H*(N_3) *bs*).

Diaminojojoba [**XII**]. A mixture of 8.8 g (10.6 mmol) of [**X**] in 150 mL ethanol with 1.0 g of 10% Pd/C (Fluka AG, Bush SG, Switzerland) was hydrogenated with H_2 for 24 h at room temperature (and a pressure of 63 psi). The catalyst was filtered off, and the solvent was evaporated off under vacuum to give 8.26 g of crude dihydrobromide of [**XII**]. The yield of pure product was 7.23 g (87%). Calculated for N: 3.56%; found 3.8%. Calculated for Br: 20.3%: found 26.0%. The base [**XII**] was obtained from the dihydrobromide by the standard work-up. A white wax, melting at 40–45°C (MeOH), was obtained. Yield 5.27 g (80%). Calculated for N: 4.49%; found 4.7%. IR (in CCl_4), 3000–3500 (slight broad signal -NH_2), 1736.8 (C=O), 1466.9, 1179.2 cm^{-1}; ^{1}H NMR, 2.6–2.7 (2H, -C*H*NH_2, *bs*).

Bis*(α-hydroxyamino)jojoba* [**XIII**]. The hydroxyamine [**XIII**] was obtained by hydrogenation, as described previously, of 6.6 g (9.3 mmol) of *bis*(α-hydroxy-azido)jojoba [**VII**]. After the standard work-up, 5.69 g of crude and 5.28 g (77%) of the pure dihydrochloride of [**XIII**] were obtained. Calculated for N: 3.83%; found 3.0%. Calculated for Cl: 10.8%; found 9.8%. The base [**XIII**] was obtained from the dihydrochloride by the standard work-up. Yield 4.35 g (71%). White wax melting at 40–48°C. Calculated for N: 4.28%; found 3.4%. IR, 3348, 3150-3518 (-OH, -NH_2) broad intense signal, 1743.3 (C=O), 1600.5, 1505.4, 1464.6, 1369.4, 1281.0, 1172.2, 1063.4 and 716.7 cm^{-1}. ^{1}H NMR, 3.67 (2H, -C*H*OH, *bs*), 2.53 (2H, -C*H*NH_2, *bs*).

Bis*[α-(p-aminobenzoyloxy)amino]jojoba* [**XIV**]. The azido benzoate [**VIII**] (0.68 mmol) was hydrogenated as described previously. After the standard work-up, 0.57 g of the tetrahydrochloride of [**XIV**] (81%) was obtained. Calculated for N: 5.39%; found 4.9%. Calculated for Cl: 14.1%: found 11.6%. Base [**XIV**]: 0.34 g (56%). IR (in CCl_4), 3000–3500 (slight broad signal -NH_2), 1736.8 (C=O). Oxalate [**XIV**]: m.p. 55–60°C (MeOH); ^{1}H NMR, 7.83–7.87, 7.60–7.64, 7.10–7.16 and 6.62–6.66 (8H, aromatics, 4*m*), 4.21 (2H, -C*H*OCO-, *m*), 3.67 (2H-C*H*NH_3^+, *m*).

Allylic jojoba diamine [**XV**]. To a solution of 3.1 g (0.022 mol) of hexamethylene tetraamine in 10 mL $CHCl_3$, 7.5 g (0.01mol) dibromojojoba [**II**] were added, and the solution was stirred at room temperature for 24 h. After diluting the mixture with 20 mL $CHCl_3$ and filtering off the white crystals (hexamine hydrobromide), the solution was evaporated under vacuum. To the residue (12.7 g of

caramel), 30 mL EtOH and 12 mL (0.12 mol) of conc. HCl were added. The mixture was left to stand overnight and was then evaporated. The residue was stirred with 8.4 g (0.06 mol) K_2CO_3, 50 mL of saturated $KHCO_3$ solution and 40 mL ether at room temperature for 2 h. The resulting mixture was separated, and the aqueous phase was extracted twice with 20 mL ether each time. After drying over anhydrous Na_2SO_4, the ether solution was evaporated off under vacuum. Two hundred mL (0.02 mol) of 0.1 N ethanolic HCl were added to the residue, and the solution was evaporated under vacuum. After the standard work-up, 6.76 g of crude and 4.66 g of pure dihydrochloride [**XV**] were obtained (yield 67%). Calculated for N: 4.04%; found 3.9%. Calculated for Cl: 10.25%: found 12.9%. Base [**XV**]: 2.48 g (62%), yellow oil, n_D^{20} = 1.4862. Calculated for N: 4.52%; found 3.9%. IR, 3320 (slight broad signal at 3000–3500 cm^{-1}, $-NH_2$), 1742.7 cm^{-1} (C=O), 1665.5, 1595.4, 1462.1, 1370.9, 1174.5, 1104.4, 964.1, 725.6 cm^{-1}; ^1H NMR, 5.3 and 5.5 (4H, C*H*=C*H*, *m*), 3.6 (2H, -C*H*NH_2, *bs*).

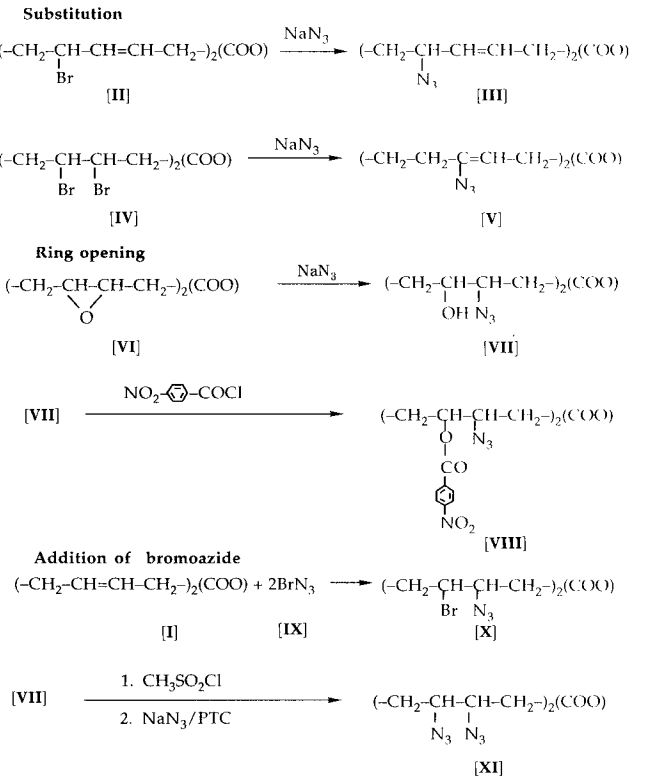
Small portions of Zn powder (to a total of 0.66 g; 0.02 mol) were added with heating (55–60°C in an oil bath) over a period of 4 h to a mixture of 3.36 g (5 mmol) of [**III**], 5 mL pyridine and 5 mL AcOH. After the Zn had dissolved, the reaction mixture was poured into 80 mL of conc. NH_4OH, and 1.35 g of a brown oil was obtained. To the crude substance, 76 mL of 0.1 N ethanolic HCl solution were added, and the mixture was evaporated under vacuum. After the standard work-up, 2.8 g of crude and 1.18 g pure hydrochloride [**XV**] were obtained. Base [**XV**]: 1.07 g (34%).

Tetraaminojojoba [**XVI**]. The crude tetraazide [**XI**] (3.6 g, 4.7 mmol) was hydrogenated as described earlier, and 3.25 g of crude and 3.08 g of pure tetrahydrochloride [**XVI**] were obtained (yield 81%). Calculated for N: 7.00%; found 5.2%. Calculated for Cl: 17.72%: found 18.9%. Base [**XVI**]: 2.48 g (80%), brown viscous wax melting at 50–55°C. IR, 3270 ($-NH_2$), 1732 (C=O), 1590, 1464, 1380, 1250, 1172, 810, 720 cm^{-1}. ^1H NMR, 2.62 and 2.31(4H, $-CHNH_2$, *m*).

RESULTS AND DISCUSSION

Amino derivatives of jojoba were synthesized in two steps: Step one: synthesis of azido derivatives (Scheme 1): (i) by a substitution reaction—displacement of the bromine atom or mesylate group already on the jojoba molecule by an azide ion; (ii) by a ring-opening reaction of the epoxide with the azide ion; or (iii) by direct addition of bromoazide to C=C double bonds. Step two: hydrogenation of the azides to aminojojoba.

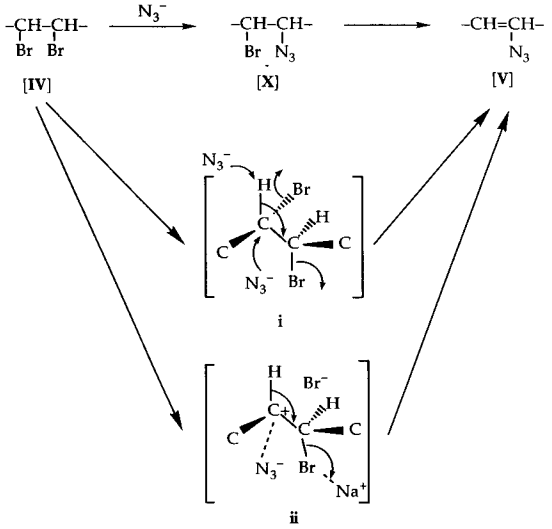
Substitution reactions. The allylic dibromojojoba [**II**] was obtained earlier (3) from jojoba oil and N-bromosuccinimide with good yield. The nucleophilic substitution reaction of the bromine in the dibromojojoba molecule proceeds with difficulty (3), probably owing to stearic hindrance and bulky lipophilic encirclement; the elimination reaction of HBr is the predominant reaction. Thus, all our attempts to displace the bromine in allylic dibromojojoba [**II**] with aniline or other amines were unsuccessful because of the dominant elimination reaction. After prolonged exposure of [**II**] to N-methylaniline in dimethyl sulfoxide at room temperature (34 d), only traces of allylic *bis*(N-methylanilino) jojoba were obtained; even under these mild conditions, jojobatetraene was again the main



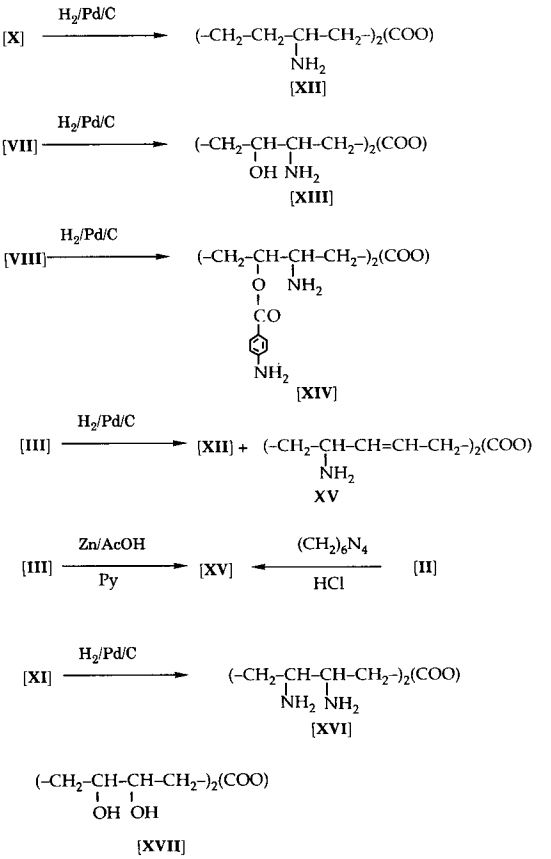
SCHEME 1

product. However, replacing bromine in [**II**] by the azide group proceeded smoothly by heating [**II**] with activated NaN_3 in DMF. The reaction yielded an allylic jojoba diazide [**III**]. Under analogous conditions, tetrabromojojoba [**IV**] yielded a product in which one of two vicinalic bromine atoms was replaced with the azide, and one bromine was removed by HBr elimination to give vinylic jojoba diazide [**V**]. This elimination reaction is unique, because the azide ion is known to act as a good nucleophile rather than a base (pKa of HN_3 is 4.8) (6), as compared to amines, which behave largely as bases in the abovementioned reactions (pKa of quaternary amines is in the range of 9–10) (7). A literature search showed that for a vicinal dibromide adjacent to an ester group, such as in 2,3-dibromoalkanoates, the azide ion behaves both as a nucleophile and a base to yield 2-azido-2-alkenoate in DMF at 60°C (5). In that case, the driving force is probably the formation of a conjugated α,β-unsaturated ester, whereas in our case the product is a simple unconjugated vinylic azide. It is possible that, in our reaction, the elimination reaction takes place because of higher acidity of the hydrogen on the carbon bearing the azide group, as is shown below for the suggested intermediate bromoazide [**X**] (Scheme 2). However, an attempt to obtain the azide [**V**] under the same conditions (excess NaN_3, DMF, 95°C, 6 h) from jojoba bromoazide [**X**] failed (compound [**X**] was recovered unchanged). This evidence contradicts the mechanism suggested above.

Another explanation could be that the high excess of azide (2 mol equivalent) could explain the attack of one azide as a base on the more acidic hydrogen at the same time as nucleophilic attack of an azide ion takes place, as



SCHEME 2



SCHEME 3

shown in (i) of Scheme 2. Still another alternative mechanism could operate through the formation of a carbo cation—S_N1 type reaction—followed by concerted nucleophilic attack by the azide ion with electrophilic assistance from Na^+ and elimination of H^+ and Br^- from the species (ii) shown in Scheme 2. Complete elimination of two molecules of HBr with formation of the corresponding acetylene or allene (3) and subsequent addition of HN_3 seems less likely.

Reactions performed under PTC conditions, such as those previously used for the transformation of *sec*-alkylbromides into azides (8), did not prove to be superior to the classic substitution reaction. Thus, reaction of [**II**] with a PTC to produce [**III**] took a longer time and gave a lower yield. Under these conditions, tetrabromide [**IV**] was recovered unchanged, even after prolonged heating. The same poor results were obtained in attempts to produce [**XI**] by means of substitution of the Br in [**X**] with the N_3 ion, both in DMF and under PTC conditions. In the former case, only the starting product [**X**] was recovered unchanged, and in the latter only 15–20% of [**XI**] was obtained. On the other hand, replacement of the mesylate group by azide in the dimesylate of [**VII**] proceeded smoothly under PTC conditions and yielded jojobatetraazide [**XI**].

Ring-opening reaction. The jojoba diepoxide [**VI**] was obtained earlier (2) from jojoba oil and *m*-chloroperbenzoic acid with good yield. Ring cleavage of epoxides by the azide ion may be accomplished regioselectively by means of Al_2O_3-supported NaN_3 (9) or with NaN_3 and $LiClO_4$ in acetonitrile (10). However, regioselectivity was not essential for jojoba, and we therefore used another "classic" method (10,11), with some modifications (DMF instead of $MeOH/H_2O$ as the solvent and more drastic temperature conditions). Ring cleavage of jojoba diepoxide [**VI**] by the azide ion was achieved when the epoxide [**VI**] was heated (90–94°C) in DMF with a tenfold excess of NaN_3 and an excess of NH_4Cl with one drop of pyridine. A hydroxy azide [**VII**] was obtained. Reaction of [**VI**] with Al_2O_3-supported NaN_3 also yielded [**VII**], but in lower yield. The *p*-nitrobenzoate [**VIII**] of the hydroxy azide was obtained as an oily product.

Addition of bromoazide to jojoba. Bromoazide adds to olefins regio- and stereospecifically either by an ionic mechanism or in a pathway mediated by free radicals, depending on the polarity of the solvent (12). Again, as these selectivities are not crucial for our modification, we chose the simplest conditions for the addition reaction. Thus, the addition of bromoazide [**IX**] in dichloromethane to jojoba led to dibromojojoba diazide [**X**] with good yields. (Bromoazide [**IX**] was prepared *in situ* from bromine and sodium azide).

Reduction of azides to primary amines. It was thought that azides of the jojoba series could be reduced with sodium borohydride, a common reducing reagent for azides (13). However, we did not succeed in reducing the azide [**III**] with sodium borohydride, either by refluxing it in isopropanol or by allowing the reaction to take place under PTC conditions. In both cases, only [**III**] was recovered. Thus, saturated azides were reduced by hydrogenation in ethanol on a 10% Pd/C catalyst (Scheme 3). In the hydrogenation of dibromojojoba diazide [**X**], debromination also occurred, and jojoba diamine [**XII**] was obtained with good yield. Hydrogenation of the hydroxy azide [**VII**] under the same conditions yielded an α-hydroxyamine [**XIII**]. Hydrogenation of the *p*-nitrobenzoate [**VIII**] gave the *p*-aminobenzoate [**XIV**]. However, hydrogenation of the allylic azide [**III**] produced only a mixture (approximately 1:1 from NMR data) of saturated

TABLE 1

Solubility of Jojoba Amines[a]

Product	Petroleum ether	Ether	Chloroform	Methanol	Water
Jojoba oil [I]	950	560	1300	Insoluble	Insoluble
Jojoba tetraol [XVII]	600	650	600	17	Insoluble
Jojoba diamine [XII]	330	200	600	30	17
Allylic jojoba diamine [XV]	330	700	1500	85	10
Dihydroxy diamino jojoba [XIII]	330	140	540	330	20
Jojoba tetraamine [XVI]	160	210	400	160	40

[a]Amount of sample (in mg) soluble in 1 mL of solvent at room temperature.

TABLE 2

R_f Values for Thin-Layer Chromatography of Amines on Al_2O_3[a]

Product	System #1	System #2	System #3	System #4
Jojoba oil [I]	0.98	Tail	0.91	0.90
Jojoba tetraol [XVII]	0.78	0.83	0.62	0.90
Jojoba diamine [XII]	0.77	0.47	0.45	0.33
Allylic jojoba diamine [XV]	0.76	0.62	0.49	0.41
Dihydroxy diamino jojoba [XIII]	0.76	0.54	0.40	0.60
Jojoba tetraamine [XVI]	0.76	0.50	0.39	0.58

[a]System #1, methanol/Et_3N (19:1) and 30% ethyl acetate; System #2, methanol with 30% ethyl acetate; System #3, methanol/ether (1:1); and System #4, methanol with 30% ether.

[XII] and unsaturated [XV] amines, which was not separated. In a further study of the reduction of [III], it was found that the azido groups could be reduced selectively with Zn powder in acetic acid and pyridine or with triethyl phosphite *via* the Staudinger reaction (8). However, we succeeded in obtaining preparatively the amine [XV] from jojobadibromide [II] and hexamethylene tetraamine *via* a Delepin reaction.

Hydrophilicity of the jojoba amines. The solubility of jojoba amines in a number of solvents was compared to that of jojoba oil and jojobatetraol [XVII] (2), as shown in Table 1. It is clear that the solubility of the amino derivatives of jojoba decreased in nonpolar solvents and increased in more polar and hydrogen-bonded solvents. It is interesting that the compound most soluble in methanol was the α-hydroxyamino derivative [XIII], while the product most soluble in water was the tetraamine [XVI] (even though only to a slight degree). The trend of polarity, demonstrated by TLC plates (Table 2), is similar to the solubility tests.

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