Brassidic Acid: Preparation from Erucic Acid and Mechanism of Elaidinization

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ABSTRACT

Brassidic acid was prepared by elaidinization of 95% erucic acid with 4 mole % nitrous acid at 70 C for 30 min, followed by crystallization from 95% ethanol. Yield was 70%, and purity was 96-97% by gas liquid chromatography and thin layer chromatography. The isomerization reaction was monitored by IR *trans* absorption for optimal reaction rate and yield. There was no migration of the double bond. The NMR spectrum of the *trans* protons was wide and complex with a chemical shift of 5.34 δ. The nitrous acid elaidinization, generally explained as a free radical process, is believed to be induced initially by the nitrogen dioxide anion (nitrite) and followed immediately by complex formation between the excited triplet anion and the olefin. The complex rotates to the opposite geometric configuration driven by a spin-orbital coupling process.

INTRODUCTION

Brassidic (*trans*-13-docosenoic) acid was first prepared from erucic (*cis*-13-docosenoic) acid more than a century ago (1), but not until large quantities of erucic acid became available could its use become a reality. In continuing studies on the uses of crambe (2) and other high-erucic oils, allyl esters of erucic and derived acids were prepared for evaluation as industrial monomers, homopolymers or copolymers (S.P. Chang, T.K. Miwa, W.H. Tallent and I.A. Wolff, unpublished). Brassidic was selected as one of the acids to be evaluated, even though earlier reports showed the formation of undesirable byproducts (3-6) during the elaidinization of erucic acid.

Unlike earlier workers who used only melting points and iodine values for analysis (7,8), we monitored the isomerization reaction with an IR spectrophotometer and optimized experimental conditions for the best reaction rate coupled with a good yield. Byproducts from catalyst addition were minimized and removed readily, while double bond migration was completely suppressed. Purity of the recrystallized product was determined by thin layer chromatography (TLC) and gas liquid chromatography (GLC). Recently Emken (9) reported an analytical procedure for *cis* and *trans* fatty esters by GLC. However the method requires conversion of the ethylenic bond to *cis* or *trans* epoxide.

The lack of any detailed mechanism for *cis,trans* isomerization of monoenoic fatty acids catalyzed by NO_2 or nitrous acid led us to evaluate available information critically and to perform several experiments that elucidated the mechanism of elaidinization. The anion-induced free radical mechanism we propose is compatible with all observations reported by other workers.

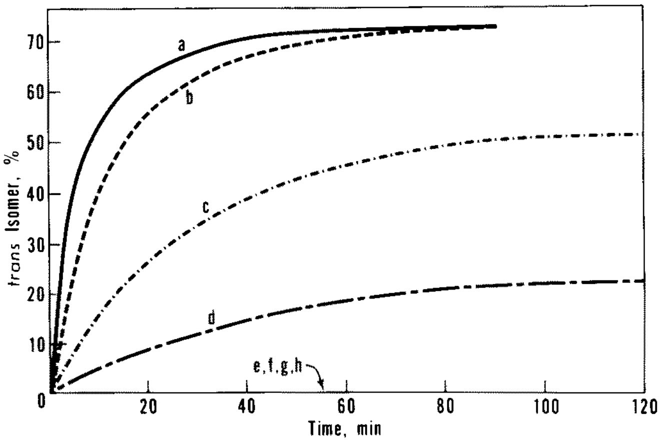

FIG. 1. Elaidinization of erucic to brassidic acid: (a) 4 mole % HNO_2 at 70 C; (b) 7 mole % HNO_2 at 70 C; (c) 4 mole % HNO_2 at 50 C; (d) 1 mole % HNO_2 at 50 C; (e) 4 mole % HNO_2 and 8 mole % hydroquinone at 70 C; (f), (g) and (h) 4 mole % benzoyl peroxide, azobisisobutyronitrile and tertiary-butyl perbenzoate at 70 C. Each reaction analyzed at 10 min intervals by IR on thin-film samples.

EXPERIMENTAL PROCEDURES

Preparation of Brassidic Acid

To a 500 ml three-necked flask, fitted with a thermometer and a mechanical stirrer, 200 g of 95% erucic acid was added and heated to 70 C under a blanket of nitrogen. With vigorous stirring, 7.2 ml of 6.0 M HNO_3 and 10.6 ml of 2.0 M $NaNO_2$ (4 mole % HNO_2) were added. After 30 min the reaction mixture was cooled and dissolved in 1 liter of ethyl ether. The solution was washed with water, dried with anhydrous magnesium sulfate and filtered. Ether was removed and the product was recrystallized from 2 liters of 95% ethanol at 5 C. In a typical reaction the yield was 134.8 g, or 71% conversion of erucic acid to purified brassidic acid. Average yield from seven preparation was 70%.

Determination of *trans* Isomers

Quantitation of fatty acids was performed on their methyl ester derivatives. The esters were prepared by treating the acids with an ethyl ether solution of freshly generated diazomethane.

IR spectrophotometry: A Perkin-Elmer Model 337 IR spectrophotometer was used with a pair of 0.20-mm sodium chloride cells. Solutions of methyl esters in carbon disulfide were adjusted to 0.14 mmole/ml, i.e., 50.0 mg of brassidate or 42.0 mg of elaidate-oleate mixture in 1.00 ml CS_2 solution. Instead of the extremely strong carbonyl band at 5.75 μm, the medium intensity ester C-O-C absorption band at 8.6 μm ($A_{8.6}$) was selected as the internal reference, against which the absorbance of the *trans* double bond at 10.4 μm ($A_{10.4}$) was compared. $A_{8.6}$ remained relatively constant (absorbance = 0.5), whereas $A_{10.4}$ varied according to the abundance of the *trans* double bond. By adjusting $A_{8.6}$ to 0.500, a standard curve was readily prepared for the brassidate-erucate mixtures. Molar absorptivities were $\epsilon_{8.6} = 1.8 \times 10^2$ and $\epsilon_{10.4} = 1.5 \times 10^2$. The elaidate-oleate mixtures yielded an identical standard curve. Allen (10) reported a similar IR procedure. The content of *trans* isomers in elaidinization products was calculated by the derived equation: $\% \, trans = 2.35 \, (A_{10.4} - 0.047) \times 10^2$. The value 2.35 is the reciprocal of the difference in absorbances at 10.4 μm for 100% and 0% methyl brassidate.

Alternatively the esters were analyzed as thin films on sodium chloride plates and the percentage of *trans* isomer

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[1] N. Market. Nutr. Res. Div., ARS, USDA.

TABLE I

Composition and Physico-Chemical Properties of Brassidic Acid

Composition, gas liquid chromatography area %[a]	
Nonadecanoic	0.1
Eicosanoic	0.8
trans-11-Eicosenoic	0.1
Docosanoic	2.4
trans-13-Docosenoic	96.3
Tetracosanoic	0.1
trans-15-Tetracosenoic	0.2
Melting point, deg C	58-59
Reported[b]	61.5
Refractive index, n_D^{64}	1.4458
Reported[b]	1.4472
Iodine value, mg KOH/g	72
Calculated for brassidic	75
Neutralization equivalent, mg/meq	337
Calculated for brassidic	339
Elemental analysis, %	
Carbon, calculated	78.04
Found	78.83
Hydrogen, calculated	12.51
Found	12.88
Nitrogen (Dumas), found	0.0 ± 0.2

[a] Identification by equivalent chain lengths (11) of methyl esters.
[b] Reference 21.

was calculated from the $A_{10.4}/A_{8.6}$ ratio. The instrument was adjusted to zero absorbance at 11.0 μm, and $A_{10.4}$ and $A_{8.6}$ were measured at the 24 min scanning speed ($\Delta\nu = 39$ wave numbers per min). The ratio $A_{10.4}/A_{8.6}$ was 0.784 for pure methyl brassidate. $A_{10.4}$ for pure erucate was 0.015. Relative precision from 10 measurements was 1.8%. The *trans* content of isomerization products was calculated by the equation: $\%\ trans = 1.28\ ([A_{10.4} - 0.015]\ /\ A_{8.6}) \times 10^2$.

TLC and GLC: Purity of brassidic acid preparation was determined by TLC and GLC of the methyl esters. Because our GLC columns could not separate brassidic from erucic, the absence of *cis* compounds was established with TLC plates of 20% silver nitrate-impregnated silica gel. A slurry of 27 g of Silica Gel G (EM Reagents, Brinkmann Instruments, Inc.) in 60 ml of 11.2% silver nitrate solution was spread over a 20 x 20 cm glass plate; the spotted plate was developed with ascending benzene at 23 C; and the color was developed with chromic acid at 160 C. The *trans* ester moved faster than the silver-complexed *cis* ester; R_f values were 0.78 and 0.71, respectively. A detailed evaluation disclosed the minimum detection level for *cis*, as a contaminant in the *trans* product, as 2.5 μg; and the minimum detectable percentage of *cis*, at which resolution is not affected, as 0.5% (T.K. Miwa and S.P. Chang, unpublished). When the sample was spotted with an amount less than the minimum level of detection, even a large *cis* contamination (10%) was not detectable.

Composition of the brassidic acid preparation was determined by GLC of the methyl esters as follows: (a) Apiezon L. Five per cent on Chromosorb W, acid-washed, silylated, 60-80 mesh; stainless steel column, 0.2 cm ID., 0.3 cm OD, 300 cm long; helium carrier gas, 100 ml/min, 50 psig; injection port 250 C, on-column, column oven 245 C; flame ionization detector oven 325; F&M 5750 gas chromatograph. (b) Resoflex 446. Five per cent on Chromosorb W, acid-washed, silylated, 60-80 mesh; glass-coiled column, 0.6 cm OD., 366 cm long; helium carrier gas 50 ml/min, 30 psig; injection port 250 C, on-column, column oven 190 C; flame ionization detector oven 275 C; Packard 7401 gas chromatograph.

A relatively large amount (0.1 μl) of sample was injected for easier detection of trace impurities. Peaks in the chromatograms were identified by their equivalent chain lengths (ECL) (11), and the area under each peak was electronically integrated by the Infotronics CRS-40 system.

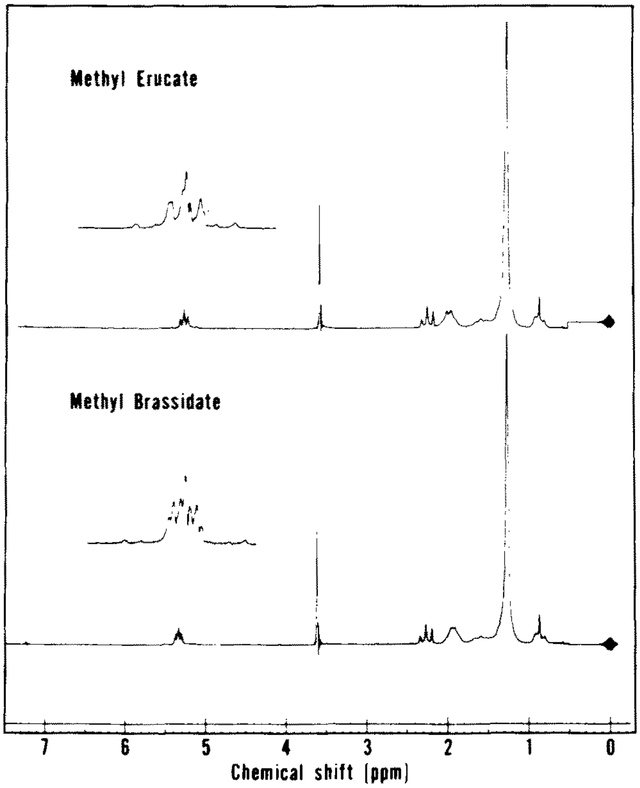

FIG. 2. NMR spectra of methyl erucate and methyl brassidate. Amplified spectra for double bond protons expanded 4 times (sweep width changed from 1000 to 250 MHz). Deuterochloroform used as solvent with tetramethylsilane as reference.

Double bond position in the fatty acids was determined by the tandem reductive microozonolysis-GLC method (12). Special conditions were set for the analysis to detect minor unsaturated constituents down to 0.5% of the total unsaturated fatty acids.

RESULTS

Selection of Elaidinization Conditions

Small scale (10 g) kinetic experiments were performed before brassidic acid was prepared on a large scale (200 g). Concentration of catalyst (4 mole % HNO_2), temperature (70 C) and time (30 min) of reaction were selected from the results plotted in Figure 1. No explanation can be given for the lowered initial rate in curve b. Each sample was analyzed at 10 min intervals by IR as water-washed, dried thin films. Because the inhibitor hydroquinone completely suppressed the elaidinization reaction, as expected for free radical-induced geometric isomerism, benzoyl peroxide, azobisisobutyronitrile (AIBN) and tertiary-butyl perbenzoate were tested as free radical catalysts. With all three catalyst, no *trans* isomer was detected by IR even after 120 min at 70 C.

Absence of Double Bond Migration

According to reductive microozonolysis-GLC analysis (12), no migration of double bonds occurred during elaidinization. The compositons of the ozonolysis products from both the starting erucic acid and the total mixture of reaction products were identical. The recrystallized brassidic acid yielded no bifunctional derivative other than the expected C-13 aldehyde-ester.

Properties of Brassidic Acid

Composition of the accumulated 1 kg of brassidic acid, as determined by GLC, is given in Table I. Apiezon L and Resoflex 446 analyses were identical. IR analysis gave

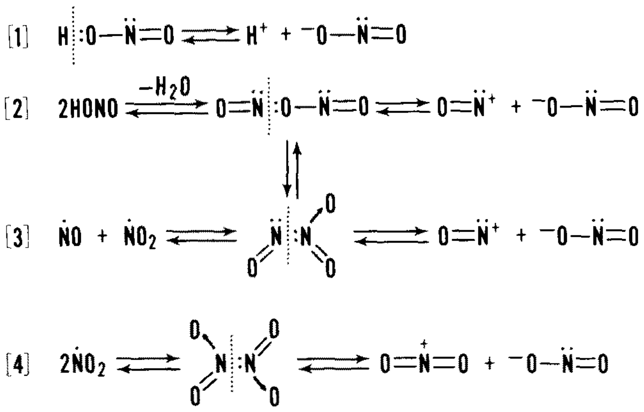

FIG. 3. Formation of nitrite ion from nitrous acid and oxides of nitrogen.

96.8% *trans*, expressed as brassidate, which left 3.2% as either erucate or as the saturated behenate. However TLC indicated no erucate in the preparation, even though enough sample was spotted on the plates to show the *cis* isomer whenever present in concentrations 0.5% or greater. IR analysis showed absence of nitro derivates (6.43 μm), whereas the mother liquor from crystallization showed some contamination (quantity undetermined). Other physico-chemical constants and the elemental analysis of brassidic acid are also listed in Table I.

The *cis* and *trans* double bonds in erucic and brassidic acids were identified by NMR as applied previously to monoenoic fatty acids (13,14). Spectra of the methyl esters (Fig. 2) were recorded on a Varian HA-100 at 100 MHz. The *trans* protons in methyl brassidate had a chemical shift of 5.34 δ, whereas the *cis* protons in erucate had a shift of 5.25 δ. The spectrum for the *trans* protons was more complex and wider than that for *cis* protons (theoretically 33 lines vs. 15 lines and coupling ranges 20% greater for *trans* than for *cis*). These spectra were in good agreement with the theoretically constructed spectra for *trans* protons (5.33 δ) in elaidic acid and for *cis* protons (5.27 δ) in oleic acid, published earlier by Schuamburg and Bernstein (13).

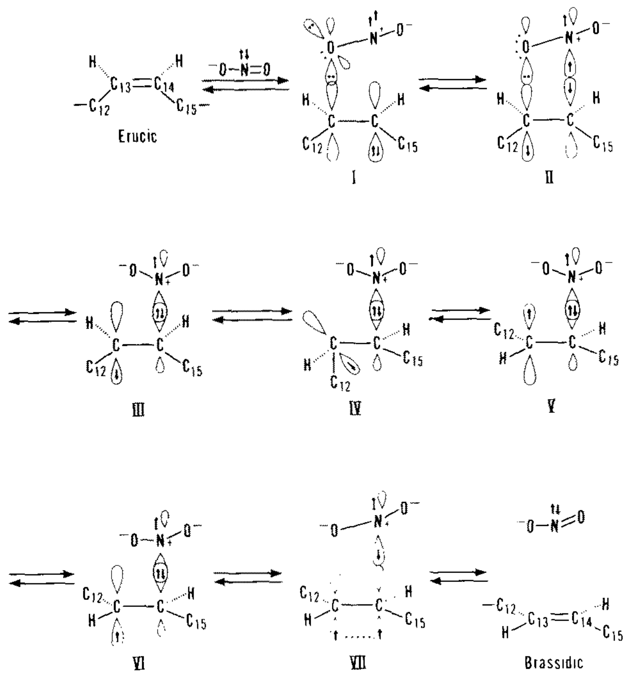

FIG. 4. Postulated mechanism of geometrical isomerism between erucic and brassidic acids.

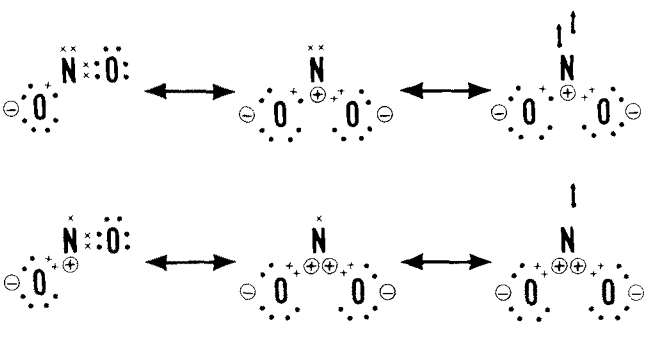

FIG. 5. Electron distribution in some canonical forms of nitrite anion (top) and nitrogen dioxide (bottom).

DISCUSSION

Ion-Induced Free Radical Elaidinization Mechanism

In our elaidinization experiments (a) hydroquinone completely suppressed isomerization; (b) benzoyl peroxide and AIBN failed to induce any isomerization; (c) nitrogen dioxide gas, bubbled directly into the *cis* (erucic) acid, did not catalyze elaidinization as rapidly and fully as nitrous acid (57% *trans* after 30 min); (d) no double bond migration was observed; and (e) high temperature (70 C) was preferred. Earlier Litchfield et al. (15) showed that nitrous acid generated in situ as a catalyst was superior to liquid NO_2 vaporized and mixed into the reaction system. Bielski and Gebicki (16) postulated an NO_2-olefin π complex based on electron paramagnetic resonance (EPR) studies, and Jonkman et al. (17) found that a mixture of NO_2 and NO enhanced intensity of the EPR spectrum 20-fold for the interaction of NO_2 with the olefinic bond. Although all three groups postulated mechanisms for dinitroderivative formation, none proposed a detailed mechanism for *cis,trans* isomerization by NO_2 or nitrous acid.

On the basis of the information developed, we noted several factors: (a) a free radical mechanism is indicated; (b) a nitrous acid related form of NO_2 is most active; (c) the active form is derivable from each of the nitrogen oxide catalysts used; and (d) the active form induces partial polarization of the double bond before interaction of free radicals. Because the isolated double bond in oleic or erucic acid does not have any net polarizing substituent on or adjacent to the olefinic carbons (a requirement in the complex formation proposed by Bielski and Gebicki), polarization of the double bond is induced by the negatively charged form of the NO_2 catalyst, which is identical to the nitrite anion in nitrous acid.

Formation of the nitrite anion from the various systems discussed is listed in Figure 3. Heterolytic cleavages of the dinitrogen oxides yield, in addition to the anion, the stable nitrosonium and nitronium cations (18).

In the elaidinization of erucic acid the nitrite anion, which is nonlinear but symmetrical in charge distribution (18), polarizes the ethylenic bond by the approach of its negative center (one of two oxygen atoms) toward either the 13th or 14th carbon atom in erucic acid, illustrated in Figure 4 as structure I. At elevated temperatures, one of the unshared pair of 2*s* electrons of the nitrogen atom becomes excited and will cross over (flip) to the triplet state (19) as indicated in structure I. The triplet electron shown in a *p*-orbital approaches the pair of electrons that are localized in the π orbital of C_{14} (I and II), then pairs itself with the electron of opposite spin as it forces the remaining electron that has the parallel spin over to the empty lobe of the π orbital of C_{13}. The last step releases the negatively charged oxygen from its partial overlap with the π orbital of C_{13} (structures II and III). The acid is now free to rotate along its C_{13}-C_{14} σ bond and may assume the preferred (19,20) orthogonal geometry (structure IV).

Although IV is structurally the intermediate between the *cis* and *trans* geometries, the spin of the lone electron on C_{13} would dictate the forward rearrangement toward the *trans* configuration, V, because this rearrangement leads to a spin-orbital coupling reaction (19) on the nitrogen. The coupling reaction is greatly favored over the reverse rearrangement to the *cis* configuration where the triplet electron on the nitrogen must undergo a reversed intersystem crossing and decay in a high energy environment or remain in the activated triplet state to reinitiate complex formation (structure II) with the olefin. This proposed mechanism therefore favors the full conversion to the geometrical isomer followed by reactivation of the catalyst, before any reversal to the *cis* isomer proceeds. The concentrations of *cis* and *trans* isomers at equilibrium would then depend mainly upon the rate of rotation of III to V and upon the competitive rate of rotation of corresponding structures for the *trans* to *cis* isomerization. If the rate of the former were twice that of the latter (in other words, if straightening out the molecule were twice as easy as bending it), a 67:33 equilibrium mixture would result.

During the rotation of III to V the spin of the lone electron on C_{13} is conserved without any flip, relative to the nucleus of C_{13} (19). However, when viewed from the nucleus of C_{14} or from its original paired electron, now paired instead with the triplet electron from nitrogen, the spin of the electron on C_{13} appears to have flipped; in essence the electrons in the π molecular orbital have undergone an intersystem crossing by virtue of sensitization by the triplet from nitrogen. This "flipped" electron, shown in VI after antisymmetrization, would then seek and couple with the electron of similar orbital symmetry, which is the one that originally had intervened as the triplet electron from the nitrogen atom (see structure II). The two matching electrons are shown in structure VII with the correct orbital symmetries for bond formation; the third electron is forced to leave the π orbital of C_{14} and enter a *p* atomic orbital of the departing nitrogen atom. The spin of this electron now favors its immediate spin-orbital coupling (19) with the lone electron on nitrogen. The paired electrons return to the 2*s* orbital in the singlet state. This spin-orbital coupling is a driving force that is very important in causing the intermediate structures to rotate from one geometric configuration to the other, especially for the unfavored *trans* to *cis* conversion. In the *trans* to *cis* reaction none of the intermediates have spin-orbital configurations that are identical to any of the structures shown for the *cis* to *trans* reaction in Figure 4.

The high thermal stability of erucic acid against geometric isomerization may be ascribed to the reluctance of the excited singlet states to cross over to the triplet state. A crossover facilitates breakdown of the π molecular orbitals between C_{13} and C_{14}. The extremely short-lived excited singlets need sensitization by stable triplets or by readily excitable free radicals, such as NO_2^- and NO_2. Furthermore polarization of the π orbital must be induced before sensitization becomes effective (16). This last assumption was corroborated by the total ineffectiveness of free radical catalysts, such as benzoyl peroxide and AIBN.

Conceivably nitrogen dioxide induces the same reaction as the nitrite anion without the intermediate dimerization-heterolytic cleavage steps listed in Figure 3. If this induction were to occur, the slightly lower activity of neutral nitrogen dioxide would then be ascribed to the lack of the net negative charge. Nearly identical electron distributions may be drawn for the two chemical species (Fig. 5). The canonical forms on the right represent active forms that are believed to catalyze the *cis,trans* isomerization process.

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