Preparation of ω-Hydroxynonanoic Acid and Its Ester Derivatives

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ABSTRACT: Methyl ricinoleate was ozonized in methanol or in acetic acid and the intermediate hydroperoxides were reduced electrochemically on Pb-cathode to give 9-hydroxynonanoic acid **1** in high yields. The acid **1** was also prepared by direct castor oil ozonolysis in methanol followed by sodium borohydride reduction of the intermediate hydroperoxides. The cost of the electricity for the electroreduction was at least 30 times lower as compared with sodium borohydride consumption. 9-Hydroxynonanoic acid was then transformed to alkyl 9-acetoxynonanoates **3a**–**3d**, for which ^{1}H nuclear magnetic reasonance, mass, and infrared spectra are given. Esterification of the hydroxy acid **1** with boric acid and pyrolysis of the resultant orthoborates produced 8-nonenoic acid **4** in a 45% yield. Reaction of **4** with lower aliphatic alcohols in presence of Amberlyst 15 produced alkyl 8-noneates **5a**–**5d** along with some amounts of a *cis/trans* mixture of alkyl 7-noneates.

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KEY WORDS: Castor oil, electrochemical reduction of hydroperoxides, esters, 9-hydroxynonanoic acid, 8-nonenoic acid, ozonolysis, sodium borohydride reduction.

ω-Hydroxyalkanoic acids and their esters have value as intermediates in both laboratory and industrial use. 9-Hydroxynonanoic acid is an intermediate in the synthesis of phospholipids used as membrane model systems for investigating biochemical interactions that occur within the biological milieu (1). On the other hand, some esters of the acid are employed for the preparation of synthetic antigens (2,3). Moreover, 9-hydroxynonanoic acid can be considered as a natural product owing to its presence in royal jelly of the honey bee (4,5) and in some phospholipid and lipopolysaccharide fractions of agricultural soil (6). It is also a building block for the naturally occurring antibiotic pseudomonic acid A, which has high antimicrobial activity (7,8).

Aliphatic acids or esters with an alkenic bond at the end of the chain remote from the carbonyl group, which can be considered as the ω-hydroxyalkanoic acid derivatives, are important strategic compounds in the synthesis of polyunsaturated fatty acids since they can readily be converted to the corresponding alkynic compounds (9). 8-Nonenoic acid is a starting material for a plant growth inhibitor synthesis (10) and is an intermediate in the synthesis of "royal jelly acid" of the honey bee (11).

9-Hydroxynonanoic acid can be manufactured by ozonolysis of C9–C10 unsaturated fatty acids such as oleic, linoleic, or ricinoleic acid followed by the reduction of the intermediate ozonides (12,13), or by the reduction of 9-oxo-nonanoic acid with sodium borohydride (1).

Some time ago we reported short syntheses of (*E*)-2-nonenal (14) and enantiomerically pure (*R*)-(+)-γ-decalactone (15) from castor oil. The aim of the present study was to economically synthesize 9-hydroxynonanoic acid from methyl ricinoleate or directly from commercial castor oil, to prepare some diesters of the hydroxy acid, and to transform ω-hydroxynonanoic acid into 8-nonenoic acid and its esters.

EXPERIMENTAL PROCEDURES

Commercial castor oil [$n^{20}_D = 1.475$, $[\alpha]^{20}_D = +5.5°$ (neat)] was used as starting material. Methyl ricinoleate [92% pure, gas chromatography (GC) analysis] was prepared from castor oil as described (16). The crude crystalline 9-hydroxynonanoic acid was employed for further transformation. Amberlyst 15 was purchased from Fluka Co. (Buchs, Switzerland). GC determination of all products was performed with Carlo Erba instrument (Milano, Italy) model MEGA 5300 with a flame-ionization detector using a 30 m × 0.32 mm DB-17 capillary column. The temperature was programmed from 60 to 300°C at 6°C/min. Nuclear magnetic resonance (NMR) spectra were obtained with Bruker AC spectrometer (Karlsruhe, Germany) operating at 250 MHz. All spectra were recorded in $CDCl_3$ solvent, and chemical shifts were reported as ppm (δ) from tetramethylsilane (TMS). GC-mass spectra (MS) were obtained with a Carlo Erba GC 8000 coupled to MD 800 Fisons Instruments (Poole, United Kingdom). The apparatus was equipped with the same column as for GC analysis. Helium was used as carrier gas; electron ionization 70 eV. Infrared (IR) spectra were recorded with a Specord 71 spectrophotometer (Carl Zeiss, Jena, Germany) in film. Electroreduction of intermediate hydroperoxides was carried out in a three-electrode electrolyzer (Scheme

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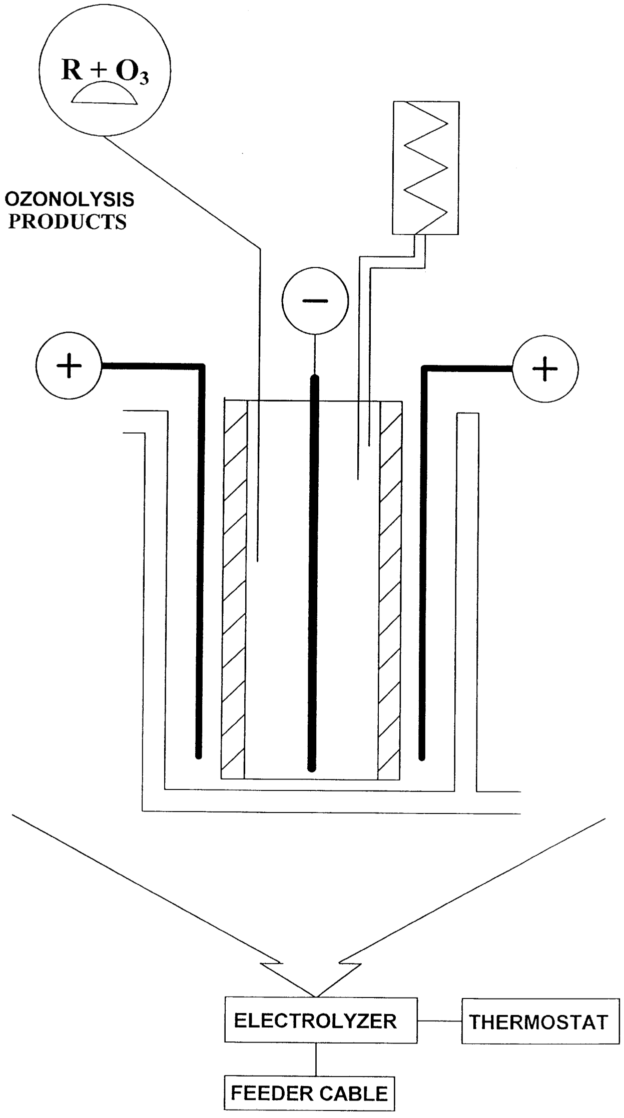


SCHEME 1

1). The cathode cell (200 × 50 × 30 mm) was made of ceramic plate and placed in a thermostatic glass container of 1 L capacity. The cathode (175 × 40 × 1 mm) was sheet lead. Each anode (150 × 45 × 1 mm) was sheet acid-proof steel. The cathode was placed centrally between two anodes at a distance of 30 mm. Prior to use, the electrodes were cleaned mechanically and the Pb-cathode was additionally etched for 3 min with a 10% aqueous solution of HNO_3 and rinsed with distilled water. Anolytes were prepared from a 10% aqueous/organic solution of NaOH (67.1 g NaOH in 375 mL of water and 375 mL of methanol) for electroreduction in methanol, and from a solution of 82.03 g (1.0 mole) of sodium acetate in 60.05 g (1.0 mole) acetic acid and 1000 mL of water for electroreduction in acetic acid.

Methyl ricinoleate ozonolysis in methanol. A solution of 20 g (0.059 mole) of methyl ricinoleate in methanol (100 mL) was cooled to −10°C, and oxygen containing 4.7 vol% of ozone was bubbled through until a positive test with potassium iodide was reached. A solution of 6.0 g (0.071 mole) sodium bicarbonate in 100 mL of water was added and the mixture was then purged with nitrogen and transferred to the cathode cell. The electrolysis was carried out at 16–20°C until 8 F/mole had been delivered (current density 1.43 A/dm^2). Some 80 mL of methanol was evaporated in vacuum, and the residue was extracted with ether (4 × 80 mL). The aqueous solution was cooled to 0°C and made acidic with concentrated hydrochloric acid (pH < 2). The liberated 9-hydroxynonanoic acid was extracted with ether (4 × 50 mL) and the combined extracts were washed with water until neutrality was achieved and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation to give 9.4 g (92%) of crystalline product, which was then recrystallized from ether to yield 9-hydroxynonanoic acid **1** of 98% purity, m.p. 51–52°C [literature value (1), 53°C].

Methyl ricinoleate ozonolysis in acetic acid. A solution of 20 g (0.059 mole) of ricinoleic acid in acetic acid (200 mL) was cooled to 7°C and oxygen containing 4.7 vol% of ozone was bubbled through until a positive test with potassium iodide was reached. Then, a solution of 11.2 g (0.14 mole) of sodium acetate in water (35 mL) and acetic acid (100 mL) were added, and the whole was placed in the cathode cell. The electrolysis was conducted at 19–26°C until 8 F/mole had been delivered (current density 1.43 A/dm^2). Excess of acetic acid (*ca.* 180 mL) was evaporated in vacuum, and 120 mL of water was added. The mixture was extracted with ethyl acetate (3 × 100 mL). The combined extracts were washed to neutrality with brine and dried over anhydrous Na_2SO_4. After solvent evaporation the slurry (29 g) was treated with a solution of sodium hydroxide (4.8 g, 0.12 mole) in water (30 mL) and ethanol (100 mL), and refluxed for 5 h. Ethanol was evaporated under reduced pressure, and the residue was extracted with ether (3 × 50 mL). The inorganic layer was cooled to 0°C, treated with concentrated hydrochloric acid (pH < 2) and extracted with ether (3 × 80 mL). The combined extracts were washed to neutrality with water, dried over anhydrous Na_2SO_4, and the solvent was evaporated. The crystalline residue (8.9 g, 87%) was recrystallized from ether to give 9-hydroxynonanoic acid **1** of 98% purity, m.p. 51–53°C.

Castor oil ozonolysis. A solution of 60 g castor oil (containing *ca.* 0.16 mole of ricinoleic acid) in methanol (220 mL) was cooled to −15°C and oxygen containing 4.7 vol% of ozone was bubbled through until a positive test with potassium iodide was reached. The mixture was then purged with nitrogen, and 6.9 g (0.18 mole) sodium borohydride was added portionwise, with agitation at a rate that kept the temperature of the reaction mixture at −10 to 5°C (4 h). The stirring was continued for another 2 h at room temperature. A solution of 6.5 g (0.17 mole) sodium hydroxide in water (20 mL), was added and the mixture was refluxed for 2 h. Methanol (*ca.* 190 mL) was removed by vacuum distillation, and 120 mL water was added. 1,3-Nonandiol and other nonacidic components were extracted with ether (3 × 120 mL), and the aqueous solution was cooled to 0°C and made acidic (pH < 2) with concentrated hydrochloric acid at a rate that kept the temperature below 5°C. The liberated 9-hydroxynonanoic acid was extracted with ether (4 × 150 mL) and the combined organic layers were then washed with water (3 × 40 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation, and the crude solid (21 g, 75%) was recrystallized from ether to give 9-hydroxynonanoic acid **1** of over 97% purity (m.p. 50–52°C).

*Alkyl 9-acetoxynonanoates **3a–3d***. To a solution of 0.02 mole of alkyl 9-hydroxynonanoate **2** (prepared by direct esterification, see references 1,12,13) in freshly distilled acetic anhydride (0.04 mole), 0.5 g anhydrous sodium acetate was added. The mixture was stirred at 120°C for 2 h, and then 10 mL of water was added and stirring was continued for another 30 min at 50–60°C. The aqueous layer was extracted with ether (3 × 30 mL). The combined organic layers were then washed with a concentrated sodium bicarbonate solution (5 × 20 mL) and water, and dried over anhydrous $MgSO_4$. After solvent evaporation the crude diesters **3** were purified by distillation under reduced pressure to yield product of 94–99% purity (Table 1).

*8-Nonenoic acid (**4**)*. A mixture of 13.5 g (0.077 mole) 9-hydroxynonanoic acid **1**, 1.7 g (0.027 mole) boric acid, and 150 mL of chloroform was refluxed under azeotropic conditions until *ca.* 1.4 mL water was collected. The solvent was removed by vacuum evaporation and the residue, 13.8 g [^{1}H NMR: 9.2–8.0 (*br. s*, 1H), 3.75 (*t*, *J* = 6.5 Hz, 2H), 2.35 (*t*, *J* = 7.0 Hz, 2H), 1.66–1.54 (*m*, 4H), 1.32 (*m*, 8H)] was heated, under argon, up to 290–450°C to yield 8.8 g of crude product (b.p. 95–215°C). This material was fractionally distilled under argon to give 5.5 g (45%) 8-nonenoic acid **4** of 95% purity (GC), b.p 98–101°C/0.5 mm Hg. Analysis: Found C 69.00, H 10.33%; Calc. for $C_9H_{16}0_2$ (156.22) C 69.19, H 10.32%. IR: 3300–2700, 1720, 1660, 1040 cm^{-1}. ^{1}H NMR: 5.8 (*ddt*, *J* = 16.9, 10.2, 6.5 Hz, 1H), 4.99 (*dm*, *J* = 17.0, 1.5 Hz, 1H), 4.93 (*dm*, *J* = 10.2, 1.5 Hz, 1H), 2.35 (*t*, *J* = 7.5 Hz, 2H), 2.04 (*m*, 2H), 1.64 (*m*, 2H), 1.34 (*m*, 6H). MS (*m/z*): 55 (100), 41 (69), 69 (51), 60 (44), 96 (40), 68 (38), 73 (31), 138 (28), 67 (22), 82 (20).

*Alkyl 8-nonenoates **5a–5d***. To a solution of 8-nonenoic acid **4** (0.02 mole) in toluene (10 mL), 0.5 mole of the appropriate alcohol and 0.2 g Amberlyst 15 were added, and the mixture was refluxed for 5 h. Thereafter, the catalyst was filtered off, and the solution was washed twice with sodium bicarbonate solution and water and concentrated to give crude esters **5**. Vacuum distillation of the residue furnished unsaturated esters **5** of 77–96% purity (Table 2).

RESULTS AND DISCUSSION

A few ozonolytic methods for the synthesis of 9-hydroxynonanoic acid are known from the literature (12,13). However, they employ for the reduction of the intermediate ozonides a relatively costly reducing agent, and the catalytic reduction of ozonides with hydrogen also has disadvantages. We suggest a new approach to the preparation of ω-hydroxynonanoic acid **1** which involves an electrochemical reduction of the intermediate hydroperoxides of the methyl ricinoleate (Schemes 1 and 2).

Both ozonolysis and electrochemical reduction of the intermediate products can be conveniently carried out in a methanol or in an acetic acid solution (17). During the electroreduction process in the presence of sodium bicarbonate (1.2 equiv) as a support electrolyte, the ester group is hydrolyzed to give sodium ω-hydroxynonanoate. This has an additional advantage from the preparative point of view because, after methanol evaporation, the enantiomerically pure (*R*)-1,3-nonanediol, the by-product, can be isolated by extraction with ether. The diol is the major component of the male rectal glandular secretion of *Dacus tau* (18). It can also be employed to the two-step synthesis of the sensorially important (*R*)-γ-decalactone (15). On the other hand, by treatment of the aqueous solution with hydrochloric acid (pH < 2), the 9-hydroxynonanoic acid could be extracted with ether and purified by recrystallization from ether to give white crystals, m.p. 51–52°C.

Another method which we have tried for the preparation of 9-hydroxynonanoic acid was castor oil ozonolysis in methanol followed by sodium borohydride reduction of the intermediate hydroperoxides (Scheme 2). Although the method is known, commercial castor oil was employed to that purpose for the first time in the ozonolysis process. Use of commercial castor oil was possible because of the high content of ricinoleic acid in castor oil (up to 90%) and, contrary to other oils, the castor oil is solu-

TABLE 1
Boiling Points and Specral Data of Diesters 3a–3d

Compound[a]	B.p. (°C/mm Hg)	Yield (%)	^{1}H NMR	GC–MS (*m/z*)	IR (cm^{-1})
3a	116–118/0.8	55	4.05 (*t*, *J* = 7.5 Hz), 3.67 (*s*), 2.31 (*t*, *J* = 6.5 Hz), 2.05 (*s*), 1.64–1.59 (*m*), 1.35–1.29 (*m*)	43 (100), 55 (70), 74 (64), 97 (42), 41 (31), 69 (28), 87 (25), 96 (23), 59 (21), 138 (17)	1760–1720, 1440, 1240, 1170, 1035, 760
3b	146–149/1.5	50	4.12 (*q*, *J* = 7.5 Hz), 4.05 (*t*, *J* = 7 Hz), 2.30 (*t*, *J* = 7.5 Hz), 2.05 (*s*), 1.61 (*m*), 1.23 (*m*)	43 (100), 55 (73), 97 (48), 88 (44), 69 (34), 41 (31), 61 (27), 96 (20), 70 (19), 101 (18)	1760–1725, 1470, 1235, 1180, 1040, 760
3c	120–121/03	79	4.05 (*m*), 2.30 (*t*, *J* = 7.5 Hz), 2.04 (*s*), 1.62 (*m*), 1.31 (*m*), 0.94 (*t*, *J* = 7.5 Hz)	43 (100), 55 (96), 61 (75), 97 (69), 69 (60), 41 (53), 157 (46), 60 (36), 84 (26), 96 (26)	1760–1725, 1470, 1230, 1170, 1040, 760
3d	125–128/0.3	71	4.05 (*m*), 2.29 (*t*, *J* = 7.5 Hz), 2.04 (*s*), 1.63 (*m*), 1.31 (*m*), 0.93 (*t*, *J* = 7 Hz)	43 (100), 55 (77), 56 (70), 97 (49), 41 (48), 69 (47), 157 (40), 57 (32), 139 (20), 84 (18)	1750–1730, 1465, 1230, 1175, 1040, 760

[a] (**3a**) methyl 9-acetoxynononoate, (**3b**) ethyl 9-acetxynonanoate, (**3c**) *n*-propyl 9-acetxynonanoate, (**3d**) *n*-butyl 9-acetxynonanoate. Abbreviations: NMR, nuclear magnetic resonance; GC–MS, gas chromatography–mass spectroscopy; IR, infrared.

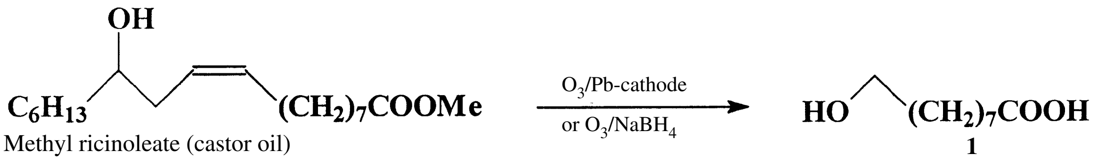
TABLE 2
Boiling Points, Purities, and Spectral Data of Unsaturated Esters 5a–5d

Compound[a]	B.p. (°C/mm Hg)	Yield (%)	Purity (%)	^{1}H NMR	GC–MS (*m/z*)	IR (cm^{-1})[a]
5a	96/14	61	95	5.80 (*ddt, J* = 16.9, 10.2, 6.5 Hz), 5.0 (*dm, J* = 17 Hz), 4.91 (*dm, J* = 10.2 Hz), 3.66 (*s*), 2.3 (*t, J* = 7.5 Hz), 2.05 (*m*), 1.64 (*m*), 1.3 (*m*)	88 (100), 55 (85), 69 (60), 41 (59), 96 (55), 138 (45), 101 (36), 60 (34), 61 (28), 84 (21)	3100, 1755, 1655, 1210, 1180, 920
5b	88/1	74	96	5.7 (*ddt, J* = 16.7, 10.3, 7.5 Hz), 4.92 (*dm, J* = 16.8), 4.86 (*dm, J* = 10.3 Hz), 4.05 (*q, J* = 7.5 Hz), 2.3 (*m*), 1.96 (*m*), 1.55 (*m*), 125 (*m*), 1.18 (*t, J* = 7 Hz)	88 (100), 55 (88), 41 (85), 69 (70), 138 (51), 96 (49), 60 (43), 101 (40), 61 (37), 72 (31)	3100, 1740, 1645, 1255, 1170, 910, 735
5c	77–81/0.3	60	82	5.79 (*ddt, J* = 16.7, 10.3, 6.5 Hz), 4.98 (*dm, J* = 16.7 Hz), 4.93 (*dm, J* = 10.3 Hz), 4.07 (*t, J* = 7 Hz), 2.29 (*t, J* = 7.5 Hz), 2.03 (*m*), 1.63 (*m*), 1.35 (*m*), 0.93 (*t, J* = 7.5 Hz)	55 (100), 41 (92), 69 (88), 43 (82), 61 (76), 96 (73), 60 (62), 73 (43), 121 (42), 97 (33)	3100, 1735, 1645, 1250, 1170, 910, 760
5d	78–82/0.1	56	77	5.8 (*ddt, J* =16.9, 10.4, 6.2 Hz), 5.02 (*dm, J* = 17 Hz), 4.92 (*dm, J* = 10.4 Hz), 4.03 (*t, J* = 7 Hz), 2.33 (*m*), 2.03 (*m*), 1.65 (*m*), 1.36 (*m*), 0.92 (*t, J* = 7.5 Hz)	55 (100), 41 (98), 56 (84), 69 (66), 57 (60), 96 (57), 60 (33), 73 (30), 121 (29), 97 (28)	3100, 1730, 1645, 1465, 1250, 1170, 1000, 970, 910

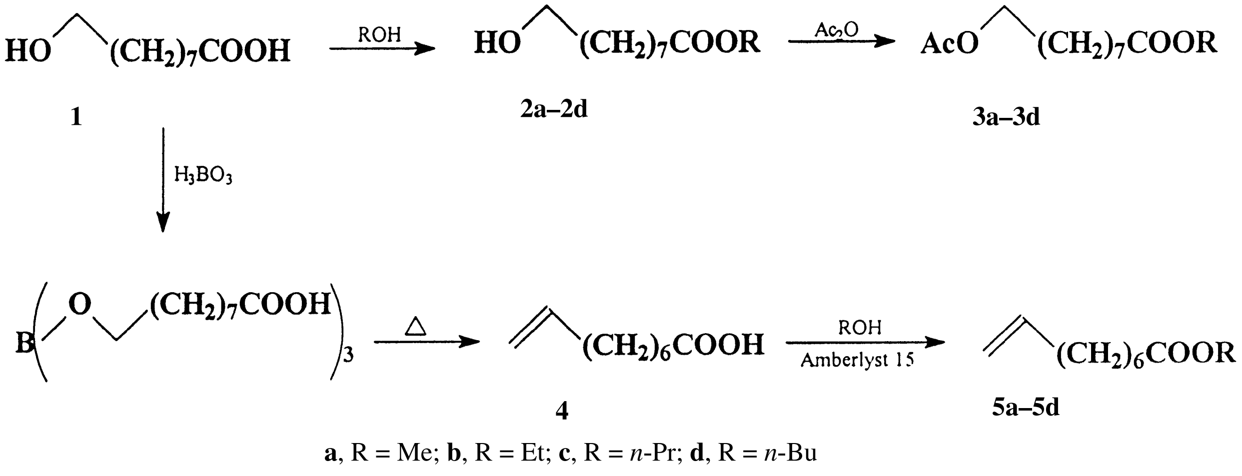
[a](**5a**) Methyl 8-nonenoate, (**5b**) ethyl 8-nonenoate, (**5c**) *n*-propyl 8-nonenoate, (**5d**) *n*-butyl 8-nonenoate. For abbreviations see Table 1.

ble in methanol even at low temperature, e.g., at –15°C. Methyl ricinolate is also soluble in methanol, and is easily available by the chemical or enzymatic transesterification of castor oil. This is why castor oil is an excellent starting material in ozonolysis processes. As can be seen from the Experimental Procedures section, both methods give satisfactory results as far as the yield and purity of the hydroxy acid are concerned. However, an electrochemical reduction of the intermediate is undoubtedly more convenient and has economic and environmental advantages. Electroreduction must be carried out until 8 F/mole is delivered because, if not, some aldehydic compounds still remain in the reaction product. The cost of the electricity for the electroreduction was at least 30 times lower as compared with sodium borohydride consumption.

9-Hydroxynonanoic acid as a bifunctional compound may be of some interest for the preparation of diesters that, as such, are



SCHEME 2



a, R = Me; **b**, R = Et; **c**, R = *n*-Pr; **d**, R = *n*-Bu

SCHEME 3

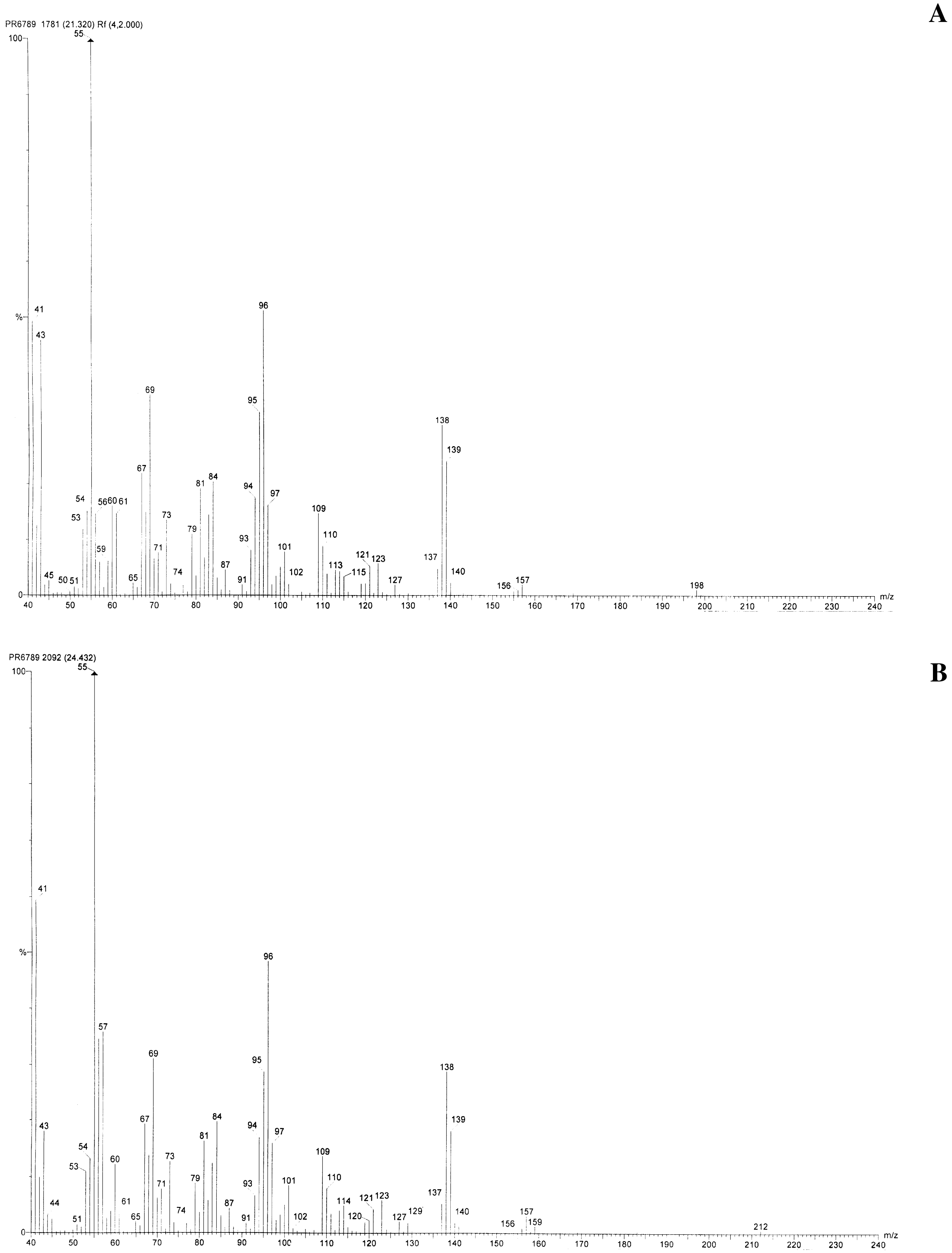


FIG. 1. Mass spectra of propyl-nonenoate (A) and butyl-nonenoate (B).

applied in cosmetics (19) or sometimes exhibit flavor properties (20). Generally there is no literature concerning synthesis, spectral characteristics, and olfactory properties of ω-acetoxynonanoic acid esters. Now we show a series of diesters **3a–3d** that were prepared from readily available starting material using the standard reaction sequence (Scheme 3). The substrate monoesters (methyl, ethyl, *n*-propyl, and *n*-butyl) of the 9-hydroxynonanoic acid (**2a–2d**) were prepared by direct esterification of the hydroxy acid with the corresponding alcohols. Their physical and spectral data coincided with those reported in the literature (1,12,13).

The boiling points and spectral data of the acetoxy esters **3**, supporting their structures, are shown in Table 1.

Neither the hydroxyesters nor the acetoxyesters had an interesting odor. They are probably odorless when pure.

When 9-hydroxynonanoic acid was purified by distillation under reduced pressure, a small quantity of a lower boiling fraction could sometimes be collected. We were intrigued by the substance and, after ^{1}H NMR analysis, it appeared that the material was mainly composed of 8-nonenoic acid **4**. The mechanism of the unsaturated acid formation is likely of a dimer (polymer) pyrolysis origin. Pyrolysis of esters is a known method for the production of unsaturated compounds (21). On the other hand, hydroxy acids tend to dimerize (polymerize) under elevated temperature (22). Thus, the thought of combining the two reactions in a one-step process is attractive. However, to make the process more effective high-temperature pyrolysis was necessary. This could be easily reached by distilling 9-hydroxynonanoic acid under atmospheric pressure in the presence of argon. Under conditions we tried, the yield of the pure (92%, GC) 8-nonanoic acid amounted to 28%, and the pyrolysis reaction was difficult to control.

A number of widely different methods have been described for the preparation of terminal unsaturated carboxylic acids including ω-chloro- and ω-acetoxy-carboxylic acids as starting materials, but the yields of the unsaturated acids were rather low (21). We prepared 8-nonenoic acid **4** in a two-step conversion of 9-hydroxynonanoic acid **1** (Scheme 3). In the first step hydroxy acid **1** was reacted with boric acid to give quantitatively orthoborate ester which in the next step, underwent pyrolysis under atmospheric pressure. In this way 8-nonenoic acid **4** could be obtained in 45% overall yield from 9-hydroxynonanoic acid. It was 95% pure and its structure was confirmed by infrared, ^{1}H NMR, mass spectra, and elemental analysis. Thus, the olefinic proton at C-8 in the NMR spectrum of the unsaturated acid **4** appeared at 5.80 ppm as *ddt* with J = 16.9, 10.2 and 6.5 Hz owing to *trans* and *cis* coupling with C-9 olefinic protons. The olefinic protons at C-9 at 4.99 and 4.93 ppm showed as a double doublet with *J* = 17.0, 1.5, and 10.2, 1.5 Hz, respectively, clearly indicating the terminal position of the double bond. It should be noted that the NMR spectrum contained also a small, strange triplet (J=6.5 Hz) at 0.88 ppm and a multiplet at 5.2 ppm disclosing at the same time the nature of the impurity as isomeric nonenoic acid(s) with the double bond inside the chain (*vide infra*).

The unsaturated acid was then converted to alkyl esters **5a–5d** to produce lower homologs of undecylenic acid esters known from their attractive sensory properties (20). Spectral data and purities (GC) of the unsaturated esters are shown in Table 2. The esterification was carried out in the presence of Amberlyst 15 as catalyst because the reaction catalyzed by concentrated sulfuric acid resulted in formation of products in a yield of 42–60% containing scarcely 60–82% of the expected esters. The structure of the esters **5a–5d** was confirmed by spectral data. ^{1}H NMR spectra of all the esters gave an H-H olefinic coupling pattern that matched that characteristic for 8-nonenoic acid. However, as can be seen from Table 2, the propyl and the butyl esters were only 82 and 77% pure, respectively. GC analysis indicated that both products contained (13 and 18%) two additional compounds in a 2:1 ratio. The other two esters, **5a** and **5b**, contained only a negligible amount of such an impurity and were not identified.

GC–MS spectra of the accompanying compounds (Fig. 1A, 1B) show molecular peaks at 198 and 212 corresponding to propyl and butyl nonenoate. The spectrum in Figure 1A contains a large signal *m/z* = 43 that is characteristic for the propyl fragment, and Figure 1B possesses a peak m/z = 57 characteristic for the butyl fragment. A strong peak *m/z* = 138 present in both spectra is a result of propanol and butanol elimination from the ester molecule. The major signal *m/z* = 55 is assumed to originate from a stable allylic cation, $CH_3CH{=}CHCH_2^+$, which can readily form from the unsaturated moiety of the ester. Interestingly, the fragmentation pathways of the considered compounds coincide with the MS data for *cis* and *trans* methyl 7-noneate (23). We concluded therefore that the mass spectra in Figures 1A and 1B were of propyl and butyl 7-nonenoate, respectively. Apparently, the activity of the catalyst was sufficient to cause the double bond migration at an elevated temperature. All the unsaturated esters **5a–5d** were found to have olfactory activity. For instance, ethyl 8-nonenoate demonstrated a very strong and clean pineapple aroma.

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REFERENCES

1. Kallury, R.K., U. Krull, and M. Thompson, Synthesis of Phospholipids Suitable for Covalent Binding to Surfaces, *J. Org. Chem. 52*:5478–5480 (1987).
2. Kinzy, W., and A. Loew, Carbohydrate Building Blocks for Tumor Associated Antigens. Synthesis of Lewis Y Determinants, *Carbohydr. Res. 245*:193–218 (1993).
3. Dean, B., S. Oguchi, S. Cai, E. Otsuji, K. Tashiro, S. Hakomori, and T. Toyokuni, Synthesis of Multivalent β-Lactosyl Clusters as Potential Tumor Metastasis Inhibitors, *Ibid. 245*:175–192 (1993).
4. Lercker, G.L., S. Conte, F. Ruini, G. Giordani, and P. Capella, Compound of Royal Jelly. II. The Lipid Fraction, Hydrocarbons and Sterols, *J. Apic. Res. 21*:178–184 (1982).
5. Serra Bonvehi, J., Organic Acid in Royal Jelly, *Agroquim. Tech-*

nol. Aliment. 31:236–250 (1991).

6. Zelles, L., and Q.Y. Bai, Fractionation of Fatty Acids by Solid Face Extraction and Their Quantitative Analysis by GC–MS, *Soil Biol. Biochem. 25*:495–507 (1993).
7. Clayton, J.P., K. Luk, and N.H. Rogers, The Chemistry of Pseudomonic Acid. Part 2. The Conversion of Pseudomonic Acid A into Monic Acid A and Its Esters, *J. Chem. Soc. Perkin Trans. 1*:308–313 (1979).
8. Chain, E.B., and G. Mellows, Pseudomonic Acid. Part 1. The Structure of Pseudomonic Acid A, a Novel Antibiotic Produced by *Pseudomonas fluorescens, Ibid.* 294–309 (1977).
9. Osbond, J.M., Progress in the Chemistry of Fats and Other Lipids IX, part 1, Pergamon Press, Oxford, 1966, pp. 121, 135.
10. Chan, T.H., and D. Stoessel, Chemistry of 1,3,5-Tris(trimethylsiloxy)-1-methoxyhexa-1,3,5-triene, a β-Tricarbonyl Trianion Equivalent, *J. Org. Chem. 51*:2423–2428 (1986).
11. Sisido, K., M. Kawanisi, K. Kondo, T. Morimoto, A. Saito, and N. Hukue, Syntheses of 9-Keto- and 10-Hydroxy-*trans*-2-decenoic Acids and Related Compounds, *Ibid. 27*:4073–4076 (1962).
12. Pryde, E.H., C.M. Thierfelder, and J.C. Cowan, Alcohols from Ozonolysis Products of Unsaturated Fatty Esters, *J. Am. Oil Chem. Soc. 53*:90–93 (1976).
13. Diaper, D.G.M., and D.L. Mitchell, An Improved Preparation of ω-Hydroxy Aliphatic Acids and Their Esters, *Can. J. Chem. 38*:1976–1982 (1960).
14. Kula, J., M. Sikora, and R. Dabrowski, Further Study on the One-Pot Synthesis of (*E*)-2-Nonenal from Castor Oil, *J. Am. Oil Chem. Soc. 71*:545–546 (1994).
15. Kula, J., M. Sikora, H. Sadowska, and J. Piwowarski, Short Synthetic Route to the Enantiomerically Pure (*R*)-(+)-γ-Decalactone, *Tetrahedron 52*:11321–11324 (1996).
16. Ranganathan, D., S. Ranganathan, and M. Mehrotra, The Synthesis of $PGF_{1\alpha}$ by Re-structuring Castor Oil, *Ibid. 36*:1869–1875 (1980).
17. Gora, J., S. Smigielski, and J. Kula, A New Method for the Preparation of Keto-Alcohols from α-Alkylcycloalkenes *via* Ozonization and Electrochemical Reduction, *Synthesis*:310–311 (1982).
18. Perkins, M.V., W. Kitching, R.A.I. Drew, and K.J. Moore, Chemistry of Fruit Flies: Composition of the Male Rectal Gland Secretions of some Species of South-East Asian Dacinae. Reexamination of *Dacus cucurbitae* (Melon Fly), *J. Chem. Soc. Perkin Trans. 1*:1111–1115 (1990).
19. Balsam, M.S., and E. Sagarin, *Cosmetics Science and Technology*, 2nd edn., John Wiley & Sons, Inc., New York, 1972, Vol. 1, pp. 371–375; Vol. 2, pp. 635–657.
20. Arctander, S., *Perfume and Flavor Chemicals*, Montclair, NJ, 1969, published by the author (Steffen Arctander, publisher, P.O. Box 114, Elisabeth, New Jersey).
21. Cardinale, G., J.A.M. Laan,. and J.P. Ward, Preparation of Terminal Alkenic Esters by an Oxidative Radical Reaction, *Tetrahedron 41*:2899–2902 (1985).
22. Spanagel, E.W., and W.H. Carothers, Preparation of Macrocyclic Lactones by Depolymerization, *J. Am. Chem. Soc. 58*: 654–656 (1936).
23. Rubottom, G.M., E.C. Beedle, C.-V. Kim, and R.C. Mott, Stereochemistry of the Lead (IV) Acetate Fragmentation of 1-(trimethylsiloxy)Bicyclo[n.1.0]alkanes, *Ibid. 107*:4230–4233 (1985).