Hydrogenation of Unsaturated Fatty Acid Methyl Esters Using Decalin for Hydrogen Transfer

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A laboratory procedure was developed for hydrogenation of methyl esters of unsaturated fatty acids using decalin as a hydrogen-transfer agent and 10% Pd/C as catalyst. The esters of 10-undecenoic, oleic, elaidic, stearolic, linoleic, cycloaliphatic C_{21} di-, C_{22} tri- and C_{36} dicarboxylic acids, and a mixture of hydnocarpic, chaulmoogric and gorlic acids were hydrogenated. Chromatographic and spectral analyses showed complete saturation. This procedure is simple, requiring no external source of hydrogen.

Catalytic hydrogen-transfer reduction has attracted considerable attention in organic and biological chemistry. Various hydrogen transfer agents have been used for reduction of olefins and olefinic acids and other functional groups (1,2). The conversion of oleic acid to stearic acid was reported to be 40% with cyclohexene as the hydrogen donor and Pd-black as the catalyst (3), and 100% with α-phellandrene-Pd/C system (4). Linoleic acid was hydrogenated fully in α-phellandrene in the presence of Pd/C (4). Hydrogenation of methyl linoleate using cyclohexene as the hydrogen donor and Pd/C as the catalyst gave stearate (48%) and monoenoate (40%) containing *trans* unsaturation (5). Methyl linoleate on hydrogenation in a methanolic solution of $PtCl_2(Ph_3As)_2$ and $SnCl_2$ yielded 51.6% monoenes, 23.6% conjugated dienes and no stearate, but the product contained 61.6% *trans* unsaturation (6). Selective reduction of methyl linoleate to *cis*-monoene was achieved using $PdBr_2$-indoline, $PdBr_2$-isopropanol and $RuCl_2(PPh_3)_3$-isopropanol (7). The migration of the double bond in these hydrogenations was, however, not ascertained. We have examined decalin as the hydrogen donor in the presence of Pd/C for hydrogenation of a variety of unsaturated fatty acid methyl esters, and the results are reported here.

MATERIALS AND METHODS

Methyl oleate, elaidic acid, methyl linoleate and silica gel G were obtained from ACME Synthetic Chemicals, Bombay, India. 10-Undecenoic acid was obtained from M/s. Jayant Oil Mills, Bombay, India. Decalin was obtained from Fluka Laboratory, Germany.

Stearolic acid. Stearolic acid (8) was prepared by adding bromine (9.46 g) to methyl oleate (17.5 g) in a round-bottom flask (500 ml) while keeping the temperature below 50 C. n-Amyl alcohol (25 ml) and potassium hydroxide pellets (20 g) were added and refluxed for four hr in an oil-bath at 150 C. Amyl alcohol was distilled off, and the ice-cooled mixture was neutralized with conc. hydrochloric acid. Water (100 ml) was added, and the mixture was allowed to come to room temperature. Addition of concentrated hydrochloric acid and subsequent cooling resulted in solidification of the organic layer into a waxy material. The acidic water solution was decanted, and the wax-like material was dissolved in 95% ethanol (50 ml). The solution was cooled in an ice-bath, and the resulting semisolid mass was filtered. This was recrystallized three times from an alcohol-water mixture and finally dried in a vacuum desiccator yielding stearolic acid (32%), m.p. 46 C (lit. 46-46.5 C).

Cyclopentene fatty acid methyl esters. A mixture of hydnocarpic, chaulmoogric and gorlic acids was prepared by saponification of the oil extracted with hexane from the seeds of *Hydnocarpus wightiana* and subsequent acidification. The mixed fatty acids were subjected to urea adduct separation (fatty acids:urea:methanol, 1:1.3:8, w/w/w) and the filtrate was again subjected to urea adduction (1:2.6:10, w/w/w) (9). The fatty acids isolated from the second filtrate were esterified with methanol containing 2% sulfuric acid. The esters were worked up and distilled at 2.5 mm Hg pressure and the fraction distilling from 170 to 175 C was collected. GLC analysis showed the fraction to contain hydnocarpate (59.7%), chaulmoograte (30.1%) and gorlate (10.2%).

Cycloaliphatic C_{21} di- and C_{22} tricarboxylic acids. C_{21} Di- and C_{22} tricarboxylic acids were prepared by Diels-Alder reaction of dehydrated castor oil (DCO) fatty acids with acrylic and fumaric acids, respectively.

C_{21} Dicarboxylic acid. In a typical experiment, a 0.5-l stainless steel autoclave was charged with DCO fatty acids (190 g), acrylic acid (48.86 g) and iodine (0.19 g, 0.1% based on DCO fatty acids). The contents were flushed with nitrogen and heated to 225 C in about 40 min. The reaction was carried out at this temperature for one hr, after which the reaction bomb was taken out and cooled. The product was washed free of acrylic acid with water, the catalyst was removed by washing with an aqueous solution of potassium iodide and sodium thiosulfate acidified with acetic acid, and the total product was partitioned between aqueous methanol and hexane to obtain C_{21} dicarboxylic acid in the methanol layer (yield: 71%; saponification value:315).

C_{22} Tricarboxylic acid. DCO fatty acids (190 g), fumaric acid (78.71 g) and iodine (0.19 g; 0.1% based on DCO fatty acids) were charged in a 0.5-l stainless steel autoclave. The contents were flushed with nitrogen and heated to 200 C in one hr. At this temperature the reaction was carried out for three hr, after which the reaction bomb was taken out and cooled. The unconverted fumaric acid was precipitated from benzene, and C_{22} tricarboxylic acid was isolated free of iodine and unconverted DCO fatty acids as described above (yield: 80%; saponification value: 402).

Cycloaliphatic C_{36} dicarboxylic acid was prepared from castor oil fatty acids by thermal dimerization in an autoclave and purified by silica gel TLC. The acids were esterified with diazomethane in methanol. Palladium on carbon (10% Pd/C) was prepared in the laboratory (10).

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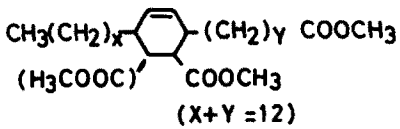
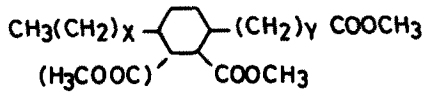
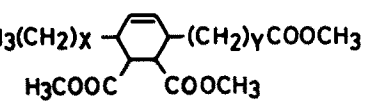
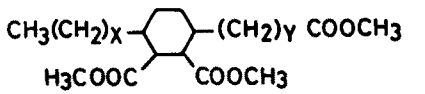
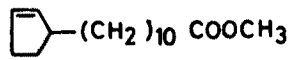
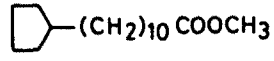
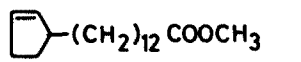
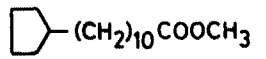
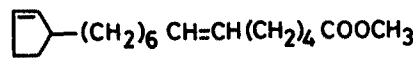
TABLE 1

Hydrogenation of Unsaturated Fatty Acid Methyl Esters with 10% Pd/C and Decalin

Unsaturated ester			Hydrogenated product		
Name	Structure	Purity (%)	Name	Structure	Purity (%)
10-Undecenoate	$CH_2=CH(CH_2)_8COOCH_3$	98.5[a]	Undecanoate	$CH_3(CH_2)_9COOCH_3$	98.5[a]
Oleate	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	99.5[a]	Stearate	$CH_3(CH_2)_{16}COOCH_3$	99.5[a]
Elaidate	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	99.0[a]	Stearate	$CH_3(CH_2)_{16}COOCH_3$	99.0[a]
Stearolate	$CH_3(CH_2)_7C\equiv C(CH_2)_7COOCH_3$	99.0[a]	Stearate	$CH_3(CH_2)_{16}COOCH_3$	99.0[a]
Linoleate	$CH_3(CH_2)_4CH=CH-CH_2-CH=CH(CH_2)_7COOCH_3$	100.0[a]	Stearate	$CH_3(CH_2)_{16}COOCH_3$	99.2[a]
C_{21}-Dicarboxylate	 (X+Y =12)	100.0[b]	C_{21}- Hydrogenated dicarboxylate		100.0[b,c]
C_{22}-Tricarboxylate	 (X+Y = 12)	100.0[b]	C_{22} Hydrogenated tricarboxylate		100.0[b,c]
C_{36}-Dimerate[d]	———	100.0[b]	C_{36}- Hydrogenated dimerate[e]	———	100.0[b,c]
Mixture of hydnocarpate,		59.7[a]	Mixture of dihydrohydnocarpate,		58.4[a]
chaulmoograte		30.1[a]	dihydrochaulmoograte		38.9[a]
and gorlate		10.2[a]	and unknown	———	2.7[a]

[a] By GLC; [b] TLC-pure; [c] Absence of olefinic protons by ^{1}H-NMR; [d] mixture of mainly substituted cyclohexenes; [e] mixture of mainly substituted cyclohexanes

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded in $CDCl_3$ solution using a JEOL FX 90 Q Fourier Transform NMR spectrometer with tetramethylsilane as an internal standard. Infrared (IR) spectra were recorded in CCl_4 or CS_2 solution using a Perkin-Elmer Model 283 B spectrophotometer. Mass spectra were recorded in a V.G. Micromass 7070 H mass spectrometer. Gas liquid chromatography (GLC) was carried out using a Hewlett-Packard 5840 A unit equipped with a flame ionization detector (FID), a data processor and a stainless steel column (1.8 m × 6 mm) packed with 10% Silar 10 C/Chromosorb W HP (100–120 mesh). The column temperature was maintained at 150 C for analysis of the reduction product of methyl undecenoate and at 210 C for other products. Injection port and detector block were kept at 250 C and 300 C, respectively. The flow rate of nitrogen was 30 ml/min.

The typical reduction procedure consisted of refluxing decalin (25 ml) containing methyl oleate (150 mg; 0.51 mmol) and 10% Pd/C (50 mg) for four hr in a round-bottom flask equipped with a water condenser and an inlet tube for introducing nitrogen. At the end of the reaction time, the contents were allowed to cool to room temperature and filtered. The solvent was recovered in a rotary vacuum evaporator. Reaction conditions were first standardized on 150-mg and 2-g samples of methyl oleate and subsequently were used for other esters.

The course of hydrogenation was followed either by GLC or ^{1}H-NMR analysis. The hydrogenated products were purified by silica gel G TLC. Petroleum ether (60–80 C) was used for purification of the hydrogenated methyl undecenoate. Benzene was used for purification of the hydrogenated C_{36} ester. Mixtures of n-hexane-diethyl ether (80:20, 70:30, 90:10, v/v, respectively) were used for purification of the hydrogenated products of C_{21} dicarboxylic, C_{22} tricarboxylic and the other unsaturated esters.

RESULTS AND DISCUSSION

The compositions of the starting fatty acid esters and the reaction products are given in Table 1. The GLC analysis of the reduction products of 10-undecenoate, oleate, elaidate, stearolate and linoleate showed that the conversion to the respective saturated product was quantitative. Analysis by GLC and IR spectroscopy of methyl oleate partly hydrogenated for 0.5 hr showed formation of methyl stearate (47.8%), *trans*-monoenoate (35%) and *cis*-monoenoate (17.2%). Thus, the hydrogenation is not stereospecific. The partly hydrogenated methyl oleate was separated into saturated, *trans*-monoenoate and *cis*-monoenoate fractions by silver ion TLC. The monoenoate fractions were subjected to periodate-permanganate oxidation. The GLC examination of the resulting products after esterification with diazomethane in methanol showed migration of double bond to the carbons between C_6 and C_{17} in the *cis*-monoenoates and between C_6 and C_{16} in *trans*-monoenoates, the migration being predominantly toward the terminal CH_3 group. The GLC of hydrogenated *H. wightiana* fatty acid esters showed that C_{16} and C_{18} cyclopentene esters were reduced to an extent of ca. 97% to their respective saturated analogues. The ^{1}H-NMR spectrum did not show any evidence for chain methyl group protons, and the mass spectrum showed molecular ion peaks $(M)^+$ at 268 and 296 for hydrogenated hydnocarpic and chaulmoogric fatty acid methyl esters, respectively.

The course of hydrogenation of C_{21} di-, C_{22} tri- and C_{36} dicarboxylic acid methyl esters was followed by ^{1}H-NMR analysis which showed that the esters were saturated completely in four hr. The mass spectra of hydrogenated C_{21} di- and C_{22} tricarboxylic acid esters showed molecular ion peaks (M)+ at 382 and 440, respectively. The retro Diels-Alder fragment at m/e = 294 that arises from unhydrogenated materials was absent, indicating complete saturation of the double bond. The IR spectra of the hydrogenated di- and tricarboxylic acid esters did not show any band at 655 cm^{-1} characteristic for *cis*-disubstituted cyclohexene derivatives (11). The signal at δ 5.65 (2 H) characteristic of protons attached to the double bond in the cyclohexane moiety (12) and signals at δ 2.45 and δ 2.65 (2 H) for methine protons allylic to the double bond present in the unhydrogenated di- and tricarboxylic acid methyl esters, respectively, were absent in the hydrogenated products indicating full saturation.

The hydrogenated C_{36} dicarboxylic acid ester did not show any signals at δ5.3 to 5.65 for protons attached to acyclic and cyclic double bonds and at δ2.1 for protons alpha to the double bonds, indicating complete hydrogenation of both the double bonds.

The present procedure provides a mild laboratory method of hydrogenation requiring no elaborate apparatus or external source of hydrogen.

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