Chemistry and Physics of Lipids, 25 (1979) 191–201

ISOMERISATION AND SATURATION OF DOUBLE BONDS IN CYCLOPENTENYL FATTY ACID ESTERS DURING CATALYTIC HYDROGENATION

INGOLF RICHTER and GOLLAMUDI LAKSHMINARAYANA*

Federal Center for Lipid Research, Piusallee, D-4400 Münster (F.R.G.)

Received January 2nd, 1979 accepted March 28th, 1979

Methyl 13-(2-cyclopentenyl)tridecanoate (chaulmoograte) and methyl 13-(2-cyclopentenyl)-*cis*-6-tridecenoate (gorlate) were hydrogenated using palladium on barium sulfate in hexane. Products obtained by partial hydrogenations were fractionated by argentation thin-layer chromatography, and the components characterised and quantitatively analysed by gas-liquid chromatography, nuclear magnetic resonance spectroscopy, infrared spectroscopy, and reductive ozonolysis. The double bond in position 2 of the cyclopentene ring was found to shift to both positions 1 and 3, but the double bond in position 1 was saturated slower than that either in position 2 or 3. Isomerisation of the ring double bond was faster than its saturation. In methyl gorlate *trans*-double bonds in the chain accumulated due to their faster formation and slower hydrogenation than *cis*-double bonds. Saturation of the ring double bond was faster than that of the chain double bond.

Introduction

Seed oils containing cyclopentenyl fatty acids, such as chaulmoogric and gorlic acids, have been used for centuries in the treatment of leprosy, but presently there is little use for such oils [1]. Selective hydrogenation of these oils and their component fatty acids could perhaps yield useful derivatives. However, only a few investigations have been carried out in this direction. Kamath and Kane [2] observed that on hydrogenation with nickel catalyst *Hydnocarpus wightiana* seed oil loses its optical activity before it is completely saturated. The optically-inactive product of methyl chaulmoograte, obtained by partial hydrogenation with palladium on barium sulfate, has yielded on oxidation a keto-dibasic acid (D. Rebello, pers. comm.).

It is of interest to investigate the isomerisation and saturation of the double bond in the cyclopentene ring of methyl chaulmoograte (*I*, Fig. 1) and methyl gorate (*II*) at different stages of hydrogenation and also to compare the isomerisation and saturation of the ring double bond with that in the chain, since the double bond in a cyclopentene ring is shown to exhibit greater polarity than that in a

* *Present address*: Regional Research Laboratory (CSIR), Hyderabad 500 009, India.

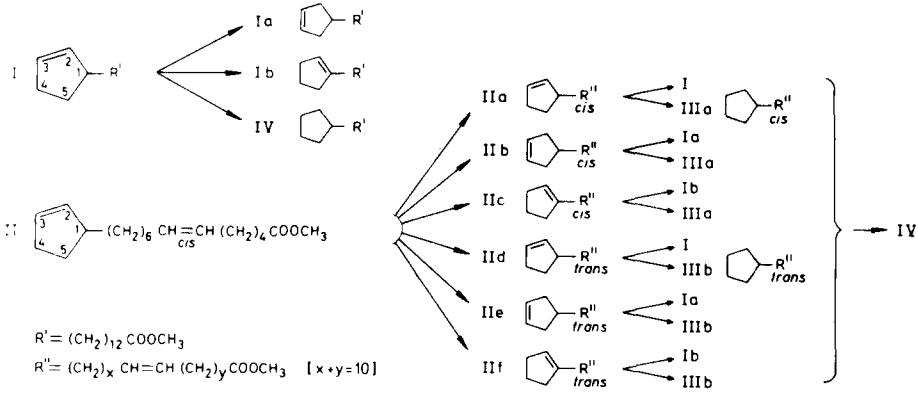

Fig. 1. Products of partial hydrogenation of methyl chaulmoograte (*I*) and methyl gorlate (*II*).

chain both in gas-liquid chromatography (GLC) [3] and argentation thin-layer chromatography (TLC) [4,5]. In the present study, *I* as well as *II* were hydrogenated to different degrees using palladium on barium sulfate and the products were identified and analysed quantitatively by combined techniques of argentation TLC, GLC, infrared spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and reductive ozonolysis. Differences were found in the extent of isomerisation and saturation of ring and chain double bonds.

Materials and methods

Methyl chaulmoograte and gorlate concentrates (66% and 92% pure as determined by GLC) were prepared from *H. wightiana* seed oil by conventional techniques [1,4] and enriched by argentation TLC as described later to yield 72% and 99% pure esters, respectively. Methyl chaulmoograte was further purified by reversed-phase TLC [4] and TLC on silica gel using 90% aqueous methanol. Dichlorofluorescein, used for location of zones in argentation TLC, was removed by passing diethyl ether extracts of scraped-off zones through a small column of silicic acid and anhydrous sodium sulfate. Acetic acid and iodine used in reversed-phase TLC were removed by washing with sodium bicarbonate and sodium thiosulfate solutions. The purity of chaulmoograte was 93%, the impurity being hydnocarpate, a homologue two methylene groups shorter than chaulmoograte, as shown by GLC.

Palladium chloride on barium sulfate containing 10% palladium, lithium aluminium hydride (LAH), methyl hepadecanoate (E. Merck AG, D-6100 Darmstadt, Germany), triphenyl phosphine (TPP) (Supelco Inc., Bellefonte, PA

16823, U.S.A.), 10% EGSS-X on Gas-Chrom P, 100–120 mesh and 10% OV-101 on Gas-Chrom Q, 100–120 mesh (Applied Science Laboratories Inc., State College, PA 16801, U.S.A.) were purchased. All the other reagents and solvents were of analytical grade. Solvents were dried and distilled before use.

Hydrogenation. Methyl esters (approx. 25 mg) were hydrogenated in 2.5 ml hexane using 5 mg palladium chloride/barium sulfate for different durations as described elsewhere [6,7].

Argentation TLC. Products of partial hydrogenation of methyl chaulmoograte and gorlate were fractionated on 20 cm X 20 cm plates coated with a 0.25 mm thick layer of Silica Gel G (E. Merck AG, D-6100 Darmstadt, Germany) containing 25% silver nitrate by developing twice with hexane/diethyl ether (85 : 15). The separated zones were scraped off and the methyl esters eluted with water-saturated diethyl ether after adding 17 : 0 methyl ester as internal standard [8] . .

GLC. GLC analysis was carried out using a Perkin-Elmer gas chromatograph F-22 with a flame ionisation detector coupled to a Spectra-Physics Autolab System IV b Chromatography Data Analyser. Methyl esters were analysed on a glass column (1.8 m X 3 mm) packed with 10% EGSS-X at 190°C. The flow rate of nitrogen was 40 ml/min. Preparative GLC was done under the same conditions using helium (40 ml/min) and a thermal conductivity detector. Aldehyde and aldester fragments were analysed on a glass column (1.8 m X 3 mm) packed with 10% OV-101. Initially the temperature was kept at 80°C for 4 min and then programmed from 80°–260°C at a rate of 4°C per min. Response factors were determined to correct for lack of response in the flame ionisation detector by carboxyl and carbonyl carbon atoms [9]. Triols, obtained by LAH reduction of ozonides, were separated on the OV-101 column at 230°C. Peaks were identified using compounds of known structure and purity.

Infrared spectroscopy. Infrared spectra were taken on 1% solutions in carbon tetrachloride in a Perkin-Elmer infrared spectrophotometer 397.

NMR spectroscopy. NMR spectra were taken on 3% solutions in deuterated chloroform in a Varian NMR Spectrometer HA-100 using tetramethylsilane as internal standard.

Ozonolysis. Reductive ozonolysis using TPP was carried out as described elsewhere [6,7]. The esters of cyclopentenyl fatty acids carrying a saturated chain (*I, Ia* and *Ib*) could not be analysed by GLC by this method due to interference from TPP. Hence, ozonides were reduced to triols with LAH [10]. An ethereal solution of LAH was added to the ozonides at room temperature. After acidification and washing off the acid, the ether layer was dried with anhydrous sodium sulfate and analysed on the OV-101 column.

Results and discussion

The structures of components that could be present in the products of partial hydrogenation of methyl chaulmoograte (*I*) and methyl gorlate (*II*) are shown in Fig. 1.

Partial hydrogenation of methyl chaulmoograte

Identification of the products. The analytical data obtained on the products of *I*, hydrogenated for 15, 30 and 60 s, are given in Table I. Argentation TLC gave 4 zones. Zone 4 had the highest relative R_F value (RR_F), almost the same as that of 17 : 0 ester and the lowest relative retention time (RRT) on EGSS-X compared to the other zones. The component in zone 4 showed no double bond proton signal at δ = 5.70 (ppm) [11]. The data obtained on zone 4 are in conformity with those on fully hydrogenated ester showing that it contained only *IV*. Similarly the data obtained on the substance in zone 1 agreed with those of *I* indicating the presence of *I*. For chaulmoogric acid two double bond protons were reported by NMR at δ = 5.70 (ppm) [11]. The NMR spectra of the compounds in zone 1 as well as of *I* showed a resonance for two double bond protons at δ = 5.68 (ppm), thus confirming the presence of *I* only in zone 1.

TABLE I

PARTIAL HYDROGENATION PRODUCTS OF METHYL CHAULMOOGRATE [a]

TLC zone	RR_F [b]	RRT [b]	RRT of triols derived from ozonides [c]	δ value (ppm) of double bond protons in NMR [d]	Components [e]	Composition (%)		
						15 s	30 s	60 s
1	0.54	2.67	5.58	5.68 (2)	*I*	21	3	2
2	0.62	2.70	5.57	5.68 (2)	*Ia*	9	6	trace
3	0.81	2.85	5.26	5.30 (1)	*Ib*	40	33	34
4	0.99	2.26	–	–	*IV*	30	58	64

[a] R_F value in argentation TLC and retention time on EGSS-X relative to 17 : 0 ester are 0.56 and 2.67 respectively.

[b] R_F value and retention time are relative to 17 : 0 ester. R_F value in argentation TLC and retention time on EGSS-X of 17 : 0 ester are 0.89 and 283 s respectively.

[c] Retention time is relative to 17 : 0 alcohol on OV-101. Retention time of 17 : 0 alcohol is 319 s. Retention time of triol obtained from methyl chaulmoograte (*I*) ozonide relative to 17 : 0 alcohol is 5.57.

[d] Figures in parenthesis denote number of protons (after 15 s of partial hydrogenation). δ value of double bond protons of ring in methyl chaulmoograte (*I*) is 5.68 (2) (ppm).

[e] See Fig. 1.

No significant differences were observed between the infrared spectra of *I* and of the compounds in the 4 zones.

Apart from the starting compound (*I*) and the fully saturated compound (*IV*) two other compounds are possible due to shifting of the double bond to either side. The triol obtained from *Ib* by reduction of ozonide with LAH will have two primary hydroxyls and one secondary hydroxyl, whereas the triol from *Ia* and *I* will have three primary hydroxyl groups; the former from *Ib* could be expected to have lower RRT than the latter two compounds from *Ia* and *I*. The triol obtained from the component in zone 3 thus appears to be *Ib* and that from zone 2, either *Ia* or *I*. The components in zones 1 and 2 each gave a sharp NMR signal for two double bond protons at δ = 5.68 (ppm), whereas the component in zone 3 gave a broad resonance at higher field due to only one double bond proton at δ = 5.30 (ppm), thus conclusively proving the presence of *Ib* only in zone 3. The NMR data also show that zone 2 contained *I* or *Ia*.

Zone 3 (*Ib*) had a RR_F nearer to that of zone 4 (*IV*) than to that of zone 2 (*Ia* or *I*) and the RR_F value of zone 2 is higher than that of zone 1. This is not surprising since the R_F value in argentation TLC depends on the strength of π complex, which appears to be in the order of $I > Ia > Ib$ possibly due to differences in the degree of steric hindrance. Thus *Ib* behaves like a straight chain *trans*-monoene ester, as was demonstrated by argentation TLC of methyl elaidate alone or admixed with the component in zone 3. Compounds in zone 1 (*I*) and zone 2 (*Ia*) had therefore close RRTs in GLC on EGSS-X but differing RR_F values in argentation TLC and the compound in zone 3 (*Ib*) had entirely different RR_F and RRT values.

Isomerisation and saturation of the double bond in methyl chaulmoograte. The compositions of the 4 zones, obtained by argentation TLC, from the products of hydrogenation of methyl chaulmoograte after 15, 30 and 60 s are given in Table I. The data show that the double bond appears to shift from position 2 (*I*) to position 1 (*Ib*) to a greater extent than to position 3 (*Ia*). But, this may not be the actual situation since faster saturation of the double bond in position 3 rather than in position 1 could lead to accumulation of the latter (*Ib*), even if the migration of the double bond to position 3 is equal or faster than to position 1. This is expected because the double bond in position 1 is sterically hindered and more stable due to a greater number of alkyl substituents compared to the double bonds in positions 3 and 2. Indeed, the data show that the double bond in position 1 was hydrogenated slower than in the other two positions resulting in accumulation of *Ib*. The data in Table I also show that, in the earlier stages of hydrogenation, isomerisation of the double bond was faster than saturation. However, saturation was faster than isomerisation in the later stages in spite of the fact that the double bond in position 1 was hydrogenated slower than that in position 2 or 3; this suggests that the double bond in position 3 was hydrogenated faster than that in position 1. The data in Table I also show that the double bond in position 3 was hydrogenated faster than that in position 2.

Partial hydrogenation products of methyl gorlate

Identification of the products. The analytical data on the methyl esters in the 6 zones, obtained by argentation TLC, from the products of *II* after hydrogenation for 2, 4 and 8 min are given in Table II. The RR_F and RRT values of the component in zone 6 were the same as those of zone 4 obtained from *I* (Table I), thus identifying it as *IV*. Moreover, the component in zone 6 did not show resonances of double bond protons in NMR [11].

In zone 5 there were two components with slightly differing RR_F values (0.80, 0.84) which were not separated in preparative TLC. However, these were separated in GLC (RRT: 2.84 and 2.57) and isolated by preparative GLC. The triol, obtained from the fraction having the RR_F value 0.80 and RRT 2.84 (almost the same as those of zone 3, Table I) by LAH reduction of the ozonide, had the same RRT (5.26) as that of the zone 3 from *I* (Table I). These data as well as the NMR resonance at δ = 5.31 (ppm), due to a single double bond proton, prove that the fraction of higher RRT (2.84) in zone 5 is *Ib*.

TABLE II

PARTIAL HYDROGENATION PRODUCTS OF METHYL GORLATE [a]

TLC zone	RR_F [b]	RRT [b]	RRT of triols derived from ozonides [c]	δ value (ppm) of double bond protons in NMR [d]		Components [e]	Composition (%)		
				Ring	Chain		2 min	4 min	8 min
1	0.04	3.25	f	5.68 (<1), 5.31 (<1)	5.38 (≪1), 5.34 (≪2)	*IIa, IIb, IIc, IId, IIe*	37	10	5
2	0.16	3.31	f	5.31 (1)	5.38 (2)	*IIf*	16	17	9
3	0.33	3.26	f	5.31 (1)	5.38 (2)	*IIf*	4	8	4
	0.52	2.67	5.58	5.68 (2)	–	*I, Ia*	3	7	1
4	0.58	2.64	f	–	5.34 (2)	*IIIa*	17	19	11
5	0.80	2.84	5.26	5.31 (1)	–	*Ib*	6	10	21
	0.84	2.57	f	–	5.38 (2)	*IIIb*	7	13	22
6	0.99	2.25	–	–	–	*IV*	10	16	27

[a] R_F value in argentation TLC and retention time on EGSS-X relative to 17 : 0 ester are 0.03 and 3.25 respectively.

[b] R_F value and retention time are relative to 17 : 0 ester. R_F value in argentation TLC and retention time on EGSS-X of 17 : 0 ester are 0.89 and 283 s respectively.

[c] Ozonides were obtained from fractions isolated by preparative GLC on EGSS-X. Retention times on triols of OV-101 are relative to 17 : 0 alcohol (319 s). Relative retention time of the triol from methyl chaulmoograte is 5.57.

[d] Figures in parenthesis denote number of protons (after 8 min of partial hydrogenation). δ values of double bond protons of ring and chain in methyl gorlate (*II*) are 5.68 (2) and 5.34 (2), respectively.

[e] See Fig. 1.

[f] See Table III for double bond distribution by reductive ozonolysis.

TABLE III

DOUBLE BOND DISTRIBUTION IN THE PARTIAL HYDROGENATION PRODUCTS OF METHYL GORLATE

Sample	Distribution of double bonds														Components [a]
	Position in the chain (Δ) (%)											Position in the ring (%)			
	3	4	5	6	7	8	9	10	11	12	13	2	1	3	
Methyl gorlate [b]	–	–	–	99	–	–	<1	–	–	–	–	100	–	–	*II*
TLC zone [c]															
1 [b]	tr	2	12	64	13	4	2	<1	<1	tr	tr	5	(95)		*IIa, IIb, IIc, IId, IIe*
2 [b]	–	tr	3	56	29	8	2	1	<1	tr	tr	–	100	–	*IIf*
3 (RRT 3.26) [b,d]	<1	11	63	19	3	1	2	tr	–	–	–	–	100	–	*IIf*
2 [b] + 3 (RRT 3.26) [b,d]	tr	4	21	44	21	6	2	<1	tr	tr	tr	–	100	–	*IIf*
3 (RRT 2.67) [d,e]	–	–	–	–	–	–	–	–	–	–	–	100	–	–	*I*
4 [f]	tr	2	11	72	10	2	1	<1	tr	<1	tr	–	–	–	*IIIa*
5 (RRT 2.84) [d,e]	–	–	–	–	–	–	–	–	–	–	–	–	100	–	*Ib*
5 (RRT 2.57) [d,f]	tr	5	21	45	19	5	2	1	<1	<1	tr	–	–	–	*IIIb*

[a] See Fig. 1.
[b] Composition was based on aldester and either trialdehyde or dialdehydeketo fragments obtained from ozonides.
[c] Argentation TLC of partial hydrogenation products (8 min, see Table II).
[d] Ozonides were obtained from fractions isolated by preparative GLC on EGSS-X. RRT of fractions, see Table II.
[e] Composition was based on triols obtained from ozonides.
[f] Composition was based on aldester and aldehyde fragments obtained from ozonides.
tr: trace.

The analysis of the aldehyde and aldester fragments (Table III) obtained from the other fraction of zone 5 (RRT: 2.57, Table II) by TPP reduction of the ozonides showed a wide distribution of double bonds in the chain, typical for *trans*-isomers. The infrared spectrum showed an absorption maximum at 968 cm^{-1} proving the presence of *trans*-double bonds [12]. The *trans*-double bond protons of the components in zone 5 were responsible for a multiplet at δ = 5.38 (ppm) in the NMR spectrum, while the absorptions of the *cis*-double bond protons of the chain in methyl gorlate (*II*) appeared at δ = 5.34 (ppm) with a coupling constant of J = 10.5 Hz, which are characteristic for isolated *cis*-bonds [13,14]. Analogous differences in chemical shifts of olefinic protons of isolated *cis*- and *trans*-double bonds are documented in the literature [13,14]. The ozonolysis data also showed the absence of a double bond in the ring, thus identifying it as *IIIb*. Being a monounsaturated *trans*-isomer, it is not surprising that *IIIb* had almost the same RR_F as *Ib*, as discussed earlier.

The corresponding ozonolysis data on zone 4 indicated the absence of a double bond in the ring and a narrow distribution of the double bonds in the chain, typical for *cis*-isomers. The infrared spectrum also showed no absorption for *trans*-double bonds. The multiplet at δ = 5.34 (ppm) in the NMR spectrum was due to two *cis*-double bond protons of the chain only (Table II). These findings show the presence of *IIIa*.

In zone 3, there were two components (RR_F: 0.33, 0.52) which were not well-demarcated in preparative TLC. However, two peaks were obtained in GLC on EGSS-X (RRT: 3.26 and 2.67). These two fractions were isolated by preparative GLC. The triol, obtained from the fraction (RR_F 0.52, RRT 2.67) by LAH reduction of the ozonide, had the same RRT (5.58) as that of zone 1 obtained from *I* (Table I). The sharp NMR signal for two double bond protons at δ = 5.68 (ppm) confirmed the presence of a double bond in position 2 or 3 of the ring, thus identifying the component (RR_F 0.52, RRT 2.67) as either *I* or *Ia*. However, it is mentioned earlier that the double bond in position 3 was hydrogenated faster than that in position 2, thus showing that this fraction essentially consisted of *I* in the later stages of hydrogenation.

The analysis of the aldehyde and aldester fragments (Table III) obtained from the other fraction of zone 3 (RR_F 0.33, RRT 3.26) by TPP reduction of ozonides showed the presence of a double bond in the ring either in position 1 or 3 as well as in the chain. It is mentioned earlier that the double bond in position 3 was hydrogenated faster than in position 1. The components in this fraction showed a wide distribution of double bonds and infrared absorption for *trans*-double bonds. The NMR data (Table II) gave evidence for a double bond in position 1 of the ring and confirmed the presence of a *trans*-double bond in the chain. Thus the component of the zone 3 having the lower RR_F and higher RRT was *IIf*.

The NMR spectrum of methyl esters in zone 2 indicated the presence of a double bond in position 1 of the ring and of a *trans*-double bond in the chain. The double bonds of the components in zone 2 showed a characteristic *trans* absorption in infrared spectrum and were widely distributed as shown by ozonolysis data,

confirming that this zone also contained *IIf*. However, the distribution of positional isomers of *IIf* from zone 2 differed from that of zone 3. Nevertheless, recombination of these two groups of *IIf* according to their proportions in the two zones (Table II and III) gave a distribution pattern of positional isomers in the chain, typical for *trans*-isomers. The effect of distance of a double bond from the carboxyl group on the R_F values of monoenes is a well established fact [15].

The analytical data, namely, NMR resonances of double bond protons, RR_F in argentation TLC, RRT in GLC (Table II), infrared spectrum and double bond distribution as determined by reductive ozonolysis (Table III) on the components in zone 1 indicate that these consisted of *IIa, IIb, IIc, IId* and *IIe*. In the later stage of partial hydrogenation (8 min) the content of components with a ring double bond in position 2 (*IIa* plus *IId*) was 5% of the mixture in zone 1, as shown by reductive ozonolysis. The multiplet at δ = 5.34 (ppm) in the NMR spectrum corresponded to almost two *cis*-double bond protons in the chain, while the multiplet at δ = 5.38 (ppm) was due to only a minor portion of *trans*-double bond protons, indicating also a low level of *IId* plus *IIe* in zone 1. The number of double bond protons represented by the singlet at δ = 5.68 (ppm) showed, that total of components with a double bond in position 2 or 3 of the ring (*IIa, IIb, IId* and *IIe*) contributed to the composition of the mixture to an extent of less than 50%. The NMR resonances at δ = 5.31 and δ = 5.34 (ppm) for almost one or two protons, respectively, demonstrated that *IIc*, with one double bond in position 1 of the ring and one *cis*-double bond in the chain, predominated over all other compounds in zone 1, after 8 min of partial hydrogenation.

Isomerisation and saturation of the double bond in the ring. The compositions of the 6 zones, separated by argentation TLC, from the products of hydrogenation of methyl gorlate after 2, 4 and 8 min are given in Table II. The compounds (Table II) having a saturated chain and a double bond in position 1 of the ring (*Ib*–6, 10 and 21% after 2, 4 and 8 min) predominated over those having a saturated chain and a double bond in position 2 or 3 of the ring (*I* and *Ia*–3, 7 and 1% after 2, 4 and 8 min). In particular, the interpretation of NMR resonances revealed that the dienes containing a double bond in position 1 of the ring (*IIc* and *IIf*) also predominated over those having a double bond in position 2 or 3 (*IIa, IIb, IId* and *IIe*) in the later stages of hydrogenation. The data are thus in accordance with the data on the hydrogenation of methyl chaulmoograte (Table I), showing that extensive isomerisation and preferential saturation of the double bonds at positions 2 and 3 over that in position 1 occurred in partial hydrogenation of methyl gorlate.

Geometrical isomerisation and saturation of the double bond in the chain. The proportions of the compounds (Table II) having a saturated ring and a *trans*-double bond in the chain (*IIIb*–7, 13 and 22% after 2, 4 and 8 min) increased in the later stages of hydrogenation with simultaneous decrease in proportions of the com-

pounds having a saturated ring and a *cis*-double bond in the chain (*IIIa*–17, 19 and 11% after 2, 4 and 8 min). The dienes (Table II NMR) carrying *trans*-double bonds in the chain (*IId, IIe* and *IIf*) also predominated over those containing *cis*-double bonds (*IIa, IIb* and *IIc*) during the later stages of hydrogenation. Further, a comparison of the proportions of *IV* with either *IIIb* or *IIIa* (10, 16 and 27% versus 7, 13 and 22% or 17, 19 and 11%, respectively, after 2, 4 and 8 min) shows that the level of *trans*-isomers and saturated compound increased while that of the *cis*-isomers decreased. The data thus suggest that geometrical isomerisation of double bond in the chain was extensive during the later stages of hydrogenation, and that *trans*-isomers were more slowly hydrogenated than *cis*-isomers.

Saturation of the ring double bond versus the chain double bond. As can be seen from Table II, the saturated ring compounds (*IV, IIIa* and *IIIb*) accumulated more (totalling to 34, 48 and 60% after 2, 4 and 8 min) than the compounds carrying a saturated chain (*I, Ia, Ib* and *IV* totalling to 19, 33 and 49%), which suggests that ring saturation was faster than chain saturation.

Saturation of methyl chaulmoograte versus gorlate. Methyl gorlate was saturated slower than methyl chaulmoograte, though the former is expected to be more reactive, being more unsaturated. This is because of extensive isomerisation of the double bonds in the ring as well as in the chain and slower saturation of the isomers formed.

Conclusions

Methyl chaulmoograte and methyl gorlate appear to be suitable model compounds for studies of selective catalytic hydrogenation, since the expected products can be isolated and identified. Some of the derivatives thus obtained may be useful in biomedical investigations.

Acknowledgements

G.L. thanks the Council of Scientific and Industrial Research, Government of India and Deutscher Akademischer Austauschdienst (DAAD) for financial support under the bilateral exchange programme for visiting scientists. Thanks are also due to Dr. A.J. Pantulu, Regional Research Laboratory, Hyderabad, for help in the preparation of methyl chaulmoograte and methyl gorlate concentrates, and to Dr. F. Spener, University of Münster, for providing NMR spectra.

References

1 H. K. Mangold and F. Spener, in M. Tevini and H.K. Lichtenthaler (Eds.), Lipids and lipid polymers in higher plants, Springer-Verlag, Berlin, 1977, p. 85.

2 K.M. Kamath and J.G. Kane, J. Sci. Industr. Res. India, 20D (1961) 244.
3 I. Zeman and J. Pokorny, J. Chromatog., 10 (1963) 15.
4 V.V.S. Mani and G. Lakshminarayana, J. Chromatog., 39 (1969) 182.
5 Z.L. Bandi and H.K. Mangold, Separation Sci., 4 (1969) 83.
6 M.M. Paulose, K.D. Mukherjee and I. Richter, Chem. Phys. Lipids, 21 (1978) 187.
7 I. Richter, K.D. Mukherjee and N. Weber, Z. Naturforsch., 33 c (1978) 629.
8 W.W. Christie, R.C. Noble and J.H. Moore, Analyst, 95 (1970) 940.
9 R. Kleiman, G.F. Spencer, F.R. Earle and I.A. Wolff, Lipids, 4 (1969) 135.
10 F. Spener and H.K. Mangold, Biochemistry, 13 (1974) 2241.
11 C.Y. Hopkins, Prog. Chem. Fats Other Lipids, 8 (1965) 213.
12 D.H. Wheeler, Prog. Chem. Fats Other Lipids, 2 (1954) 268.
13 K. Schaumburg and H.J. Bernstein, Lipids, 3 (1968) 193.
14 D.J. Frost and F.D. Gunstone, Chem. Phys. Lipids, 15 (1975) 53.
15 F.D. Gunstone, I.A. Ismail and M. Lie Ken Jie, Chem. Phys. Lipids, 1 (1967) 376.