Synthesis, Mass Spectrometry, and Nuclear Magnetic Resonance Characterization of Di-Guerbet Esters

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ABSTRACT: Several Di-Guerbet esters (DGE) suitable for lubricant applications were synthesized from branched Guerbet alcohols and Guerbet acids. The mass spectra of DGE under electron-ionization and positive chemical-ionization (PCI) conditions were recorded. Gas chromatography–mass spectrometry, especially in PCI mode with methane as reagent gas, is an effective method for analyzing DGE. In methane positive chemical-ionization mass spectrometry, the DGE give molecular ion peaks. In both PCI and EI modes, some other characteristic ions including up to four McLafferty rearrangement products with high *m/z* are observed. Thus identification of both hydrocarbon moieties is possible. The DGE were also characterized by ^{1}H- and ^{13}C nuclear magnetic resonance.

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KEY WORDS: Di-Guerbet esters, Guerbet acids, Guerbet alcohols, electron-ionization mass spectrometry, nuclear magnetic resonance, positive chemical-ionization mass spectrometry, potential lubricants.

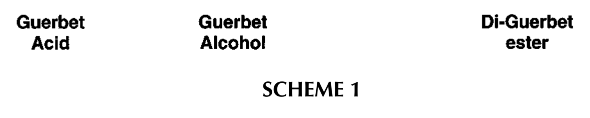
The Guerbet reaction (1)—note: apparently it was discovered prior to Guerbet by Markovnikov (2)—is summarily a dimerization of alcohols with liberation of water but actually is a modified aldol condensation with accompanying *in situ* dehydrogenation and hydrogenation steps (3). The products are alcohols branched in the 2-position containing twice the number of carbons of the starting alcohol. This mechanism, first suggested by Hückel and Naab (4), was studied in detail (5). Branched waxes were synthesized by Guerbet reaction (6) as were 5-alkyl-3-methyl cyclohexanols (7), and a cocondensation of cyclic and acyclic alcohols was conducted (8). Sulfated Guerbet alcohols were prepared (9). The influence of rhodium catalysts on the Guerbet reaction of various alcohols including methanol and secondary alcohols was studied (10,11). The excellent lubricating properties of and resulting commercial interest in Guerbet alcohols and their derivatives have caused a significant body of patent literature dealing with their synthesis and applications (12,13). They are used as components in various commercial products such as lubricants, cutting fluids, and personal-care products. For example, hydraulic oils containing Guerbet alcohols were reported (14). The esterification rate of Guerbet alcohols with stearic acid was studied (15). Esters of dicarboxylic acids with Guerbet alcohols were reported (16). Esters of Guerbet alcohols with the unsaturated fatty acids of meadowfoam oil were acceptable in personal-care applications (17) as were esters of Guerbet acids with alcohols (18,19). More recently, materials termed "Di-Guerbet esters" were obtained by reacting branched Guerbet acids (from oxidation of Guerbet alcohols) with Guerbet alcohols in the presence of stannous oxylate at temperatures of 180–200°C (20). Both hydrocarbon moieties in DGE are branched. DGE have excellent lubrication and viscosity index-modifying properties (20) as well as potential in personal-care products (21).

Despite the abundance of literature pertaining to various Guerbet compounds, to our knowledge no spectroscopic characterization of any kind of Guerbet compound was reported. Due to the commercial significance of Guerbet compounds, we investigated some DGE (Scheme 1) by electron-ionization (EI) and positive chemical-ionization (PCI) gas chromatography–mass spectrometry (GC–MS). We also reported their ^{1}H- and ^{13}C nuclear magnetic resonance (NMR) spectra.

For sake of brevity, the following acronym will be used when referring to a specific Di-Guerbet ester: DGE R_1-R_2-R_3-R_4, with R_1, R_2, R_3, and R_4 being the number of carbon atoms in the *n*-alkyl branches. Thus, a Di-Guerbet ester with $R_1 = 8$, $R_2 = 6$, $R_3 = 6$, $R_4 = 4$ (see entries 3 and 4 in Table 1) will be DGE 8-6-6-4.

EXPERIMENTAL PROCEDURES

All GC–MS runs were conducted on a Hewlett-Packard (Palo Alto, CA) 5890 Series II Plus gas chromatograph (column: 30 m × 0.25 mm HP-5MS; Hewlett-Packard Co.) coupled with a Hewlett-Packard 5989B mass spectrometer. EI was performed at 70 eV and PCI with methane as reagent gas at



SCHEME 1

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[1] Deceased.

TABLE 1
Substrates Used and Yield of Di-Guerbet Esters Prepared in This Study

			Di-Guerbet ester product			
	Substrates[a]		DGE components	Carbon number		Yield
Entry	Alcohol[b]	Acid[c]	R_1-R_2-R_3-R_4	Total[d]	Range[e]	(%)[f]
1	Jarcol I-12	Jaric 24	12-10-6-4	36	36	93.4
2	Jarcol I-20	Jaric 24	12-10-10-8	44	44	96.0
3	Jarcol I-12	Jaric 18T	8-6-6-4; 8-8-6-4; 10-8-6-4	30	28–32	95.8
4	Jarcol I-14	Jaric 18T	8-6-6-4; 8-8-6-4; 8-8-6-6; 10-8-6-4; 8-8-6-6; 8-6-8-6; 10-8-6-6; 8-8-8-6; 10-8-8-6	32	28–36	95.1
5	Jarcol I-16	Jaric 18T	8-6-8-6; 8-8-8-6; 10-8-8-6	34	32–36	95.9
6	Jarcol I-18	Jaric 18T	8-6-8-6; 8-8-8-6; 8-6-8-8; 10-8-8-6; 8-8-8-8; 8-6-10-8; 10-8-8-8; 8-8-10-8; 10-8-10-8	36	32–40	93.5
7	Jarcol I-20	Jaric 18T	8-6-10-8; 8-8-10-8; 10-8-10-8	38	36–40	96.0
8	Jarcol I-24	Jaric 18T	8-6-12-10; 8-8-12-10; 10-8-12-10	42	40–44	93.6
9	Jarcol I-18T	Jaric 12	6-4-8-6; 6-4-8-8; 6-4-10-8	30	28–32	91.1[g]
10	Jarcol I-18T	Jaric 16	8-6-8-6; 8-6-8-8; 8-6-10-6	34	32–36	90.7[g]

[a] Trade names, Jarchem Industries, Inc. (Newark, NJ).

[b] Jarcol I-12: $R_3 = 6$, $R_4 = 4$; Jarcol I-14 (three components): $R_3 = 6$, $R_4 = 4$ (22%)/$R_3 = 6$, $R_4 = 6$ (50%)/$R_3 = 8$, $R_4 = 6$ (28%); Jarcol I-16: $R_3 = 8$, $R_4 = 6$; Jarcol I-18T (three components): $R_3 = 8$, $R_4 = 6$ (15–20%)/$R_3 = 8$, $R_4 = 8$ (46–54%)/$R_3 = 10$, $R_4 = 8$ (27–33%); Jarcol I-20: $R_3 = 10$, $R_4 = 8$; Jarcol I-24: $R_3 = 12$, $R_4 = 10$.

[c] Jaric 12: $R_1 = 6$, $R_2 = 4$; Jaric 16: $R_1 = 8$, $R_2 = 6$; Jaric 18T (three components): $R_1 = 8$, $R_2 = 6$ (16%)/$R_1 = 8$, $R_2 = 8$ (52%)/$R_1 = 10$, $R_2 = 8$ (32%); Jaric 24: $R_1 = 12$, $R_2 = 10$.

[d] Sums of carbons for major alcohol + major acid.

[e] According to compositions in Table 1.

[f] After workup by alkali refining.

[g] After alumina column chromatographic refining.

230 eV. PCI spectra were background-subtracted. Prior to GC–MS analyses, all products were screened by short-column GC analyses using an HP 5890A GC fitted with a 2.5 m × 0.32 mm GB-1 silica capillary column. ^{1}H- (400 MHz) and ^{13}C NMR (100 MHz) spectra ($CDCl_3$ solutions) were obtained on a Bruker (Rheinstetten, Germany) ARX-400 spectrometer.

Synthesis of DGE. α-Branched acids and alcohols were obtained from Jarchem Industries, Inc. [Newark, NJ). Tradenames for these materials are Jaric-I*n* (acids) and Jarcol-I*n* (alcohols), where *n* = total number of carbons]. Their general structures and compositions are defined in Scheme 1 and footnotes *b* and *c* in Table 1. Synthesis of DGE was achieved by heating acid–alcohol mixtures under vacuum in the presence of *p*-toluenesulfonic acid (*p*-TsOH) until the reaction was largely completed. Specific reactions with their products and yields are listed in Table 1. The following are experimental examples illustrating two scales of preparation.

Entry 5 in Table 2 (50-g scale). In a 250-mL single-necked round-bottom flask was added 23.38 g (92.1 mmole) of Jarcol-I16 Guerbet alcohol, 28.60 g (99.3 mmole) of Jaric-18T Guerbet acid, and 998.6 mg (5.2 mmole) of *p*-TsOH monohydrate. The flask was placed on a rotary evaporator under vacuum at 80–83°C and 200 rpm for 24 h. Aliquots of the reaction mixture were taken at certain times for GC analyses. Crude product, 51.02 g (100%), was taken up in petroleum ether (PE) and repeatedly washed with water to remove the *p*-TsOH. To the PE layer was added alkali (209 mg NaOH/10 mL water), and the mixture was placed on a rotary evaporator (no vacuum, no heat) for 45 min. The PE layer was separated, washed with water until neutral, filtered, and the PE was removed on a rotary evaporator. Yield of very pale yellow liquid was 48.93 g (95.9% yield). GC analysis showed small amounts of original alcohol and acids (<5%) and 95% of a mixture of three Guerbet esters (19% C_{32}, 53% C_{34}, 28% C_{36}) in *ca.* the same ratio as the starting Jaric-18T acids (Table 1). The other seven products (of the first eight entries) in Table 1 were similarly prepared in yields >93%.

Entry 9 in Table 2 (500-g scale). To a 2-L single-necked round-bottom flask was added 341.36 g (1.2413 moles) of Jarcol-I18T Guerbet alcohol, 249.51 g (1.2476 moles) of Jaric-12 Guerbet acid, and 10.18 g (59.1 mmole) of *p*-TsOH monohydrate. The flask was placed on a rotary evaporator under vacuum at 125 rpm and 24˚C. The bath temperature was gradually raised to 80˚C over 4 h; no exotherm was observed. Heating under these conditions was continued for 28 h, with aliquots removed at certain times for GC analyses. The crude product was washed repeatedly until neutral with 75-mL portions of water to remove *p*-TsOH, followed by drying on a rotary evaporator under vacuum. Crude product (560.02 g, 98.7% yield) was refined by alumina open-column chromatography (activated, neutral Brockmann I standard grade, 150 mesh; Aldrich Chemical Co., Milwaukee, WI) with hexane as eluent. The product eluted in the first fractions. Total yield of refined esters was 519.26 g (91.1%). GC analysis showed 99% Guerbet esters (*ca.* 21% C_{28}, 51% C_{30}, 28% C_{32}) in *ca.* the same ratio as the starting Jarcol-18T alcohols (Table 1). No residual Guerbet acid was observed, and only *ca.* 1% residual Guerbet alcohol contaminated the product. With similar results and purity, entry 10 in Table 1 was prepared (537.52 g, 90.7% yield; *ca.* 23% C_{32}, 49% C_{34}, 28% C_{36}).

RESULTS AND DISCUSSION

DGE as depicted in Scheme 1 and corresponding to data in Table 1 were synthesized with *p*-TsOH as catalyst in high yields. With several starting materials being mixtures of Guerbet acids or alcohols, most reactions yielded mixtures of DGE (Table 1).

MS. GC–MS runs were conducted with the mass spectrometer in both EI and PCI modes. Methane was selected as ionization gas in PCI mode. While other gases such as *iso*-butane and ammonia were studied in the MS of fatty compounds (22), they do not offer any advantages in terms of additional insights through fragments not observed by the other techniques.

The EI mass spectra of straight-chain and branched (in the acid moiety) fatty esters were discussed in early fundamental work by Ryhage and Stenhagen (23–26). Studies were conducted on fatty compounds with PCI–MS (22) but little fragmentation was observed for fatty acid methyl esters, and structure determination of unsaturated compounds was complex. On the other hand, for fatty compounds with functional groups attached to the chain, PCI–MS yielded useful structural information (22,27,28).

Figure 1 depicts the mass spectra of some DGE in both EI and PCI (methane) modes. The mass spectra in both ionization modes of DGE 8-6-6-4 are shown in Figures 1*a* and 1*b*. While the fragmentation pattern is similar, PCI with methane offers several distinct advantages. The molecular ion is clearly established, and the abundances of some key fragments (cleavages and some fragments depicted in Fig. 2) are improved compared to EI. The EI spectrum contains strong but nondistinctive hydrocarbon fragments of lower *m/z*. Therefore, the following discussion focuses mainly on characterization of the DGE by PCI with methane as reagent gas. Characteristic fragment ions shift by 28 amu from spectrum to spectrum because of the two additional CH_2 units in the chains (Fig. 1B–1D). Shifts of *m/z* 56 shown in that figure occur because of four additional CH_2 units in the compounds whose spectra are depicted; different peaks shift depending on the addition of the CH_2 units in either the acid or alcohol moiety of the DGE. The PCI mass spectra also show some smaller fragment ions at high *m/z*, such as [M – 15], [M – 29], and so on, resulting from loss of hydrocarbon moieties.

In straight-chain fatty methyl esters, $[M + H]^+$ is the most abundant ion in PCI mass spectra, but ions corresponding to $[M - H]^+$ (which may be $[M + H]^+$-H_2) are also found (22). In the branched DGE studied here by PCI GC–MS, $[M - H]^+$ is more abundant than $[M + H]^+$. The most abundant peak is the protonated acid from cleavage C (Fig. 2A). Peaks of greater abundance than the molecular ion were reported for other fatty compounds with functional groups (27,28).

In Figure 1B, for DGE 8-6-6-4, *m/z* 257 is the most abundant ion. This corresponds to cleavage C, fragment I, in Figure 2A, with protonation of the resulting acid. For higher fatty esters, the protonated carboxylic acid residue results from loss of the alkyl group of the alcohol and rearrangement of two protons (22,23). This holds for PCI mode also. The deprotonated acid at *m/z* 255 resulting from cleavage C (Fig. 2A), however, is the second most abundant peak. Figure 1A also shows *m/z* 257 for EI mode of DGE 8-6-6-4, but, as discussed above, at significantly decreased abundance.

The methane PCI spectrum of DGE 8-6-6-4 shows a relatively strong fragment at *m/z* 285 which is absent in the corresponding EI mass spectrum (see Fig. 1A–1B). In the methane PCI mass spectra of DGE 8-8-6-4 and DGE 10-8-6-4, this ion shifts to *m/z* 313 and 341 (see Fig. 1C for the spectrum of DGE 10-8-6-4), respectively. It is caused by adduct formation of the acid moiety formed by cleavage C (Fig. 2A) with $C_2H_5^+$. Such adduct formations are common with methane as reagent gas (22) because of its low proton affinity.

McLafferty rearrangement fragments (22,23) are often the most abundant peaks in the mass spectra of fatty esters, especially in the EI mass spectra of saturated methyl and ethyl esters (23) but usually decrease in abundance with increasing size of the alcohol moiety (24). These fragments are observed at $m/z_{\text{McLafferty}} = 60 + 14n$, with *n* being the number of CH_2 units resulting from the alcohol moiety (acids $n = 0$). Higher *m/z* values result from either the alcohol moiety of the ester possessing more CH_2 units or by branching of the acid moiety at C2. (However, a proton at C4 is necessary for the McLafferty rearrangement to be operable; see Ref. 22.) Thus, Ryhage and Stenhagen (25) found *m/z* 88 in the EI mass spectra of ethyl 9-methyl and 10-methyloctadecanoate and of methyl 2-methylhexacosanoate. Odham (29) reported *m/z* 88 in the EI mass spectra of methyl 2,4,6,8-tetramethyldecanoate and methyl 2,4,6,8-tetramethylundecanoate. With an alkyl substituent ethyl or larger in the 2-position of a fatty acid, the rearrangement could occur in two different ways (26). Thus, in methyl 2-ethylhexadecanoate, two ions were found at *m/z* 102 and 270, while methyl 2-*n*-hexyldecanoate exhibited *m/z* 158 and 186. Similar observations were made in the present work. However, up to four even-numbered rearrangement ions satisfying the McLafferty *m/z* requirements were observed for DGE in both EI and methane PCI modes. In DGE 8-6-6-4 (see Fig. 1A, 1B), the peaks at *m/z* 312 and 340, although of low abundance, are characteristic. They likely correspond to McLafferty fragments 1 (Fig. 2B) from cleavage of either *n*-alkyl chain of the acid moiety. Other even-numbered fragments 2, *m/z* 144 and 172, are present (Fig. 1B). These McLafferty fragments arise from fragment I of cleavage C (Fig. 2A), followed by cleavage of one of the chains in the acid moiety

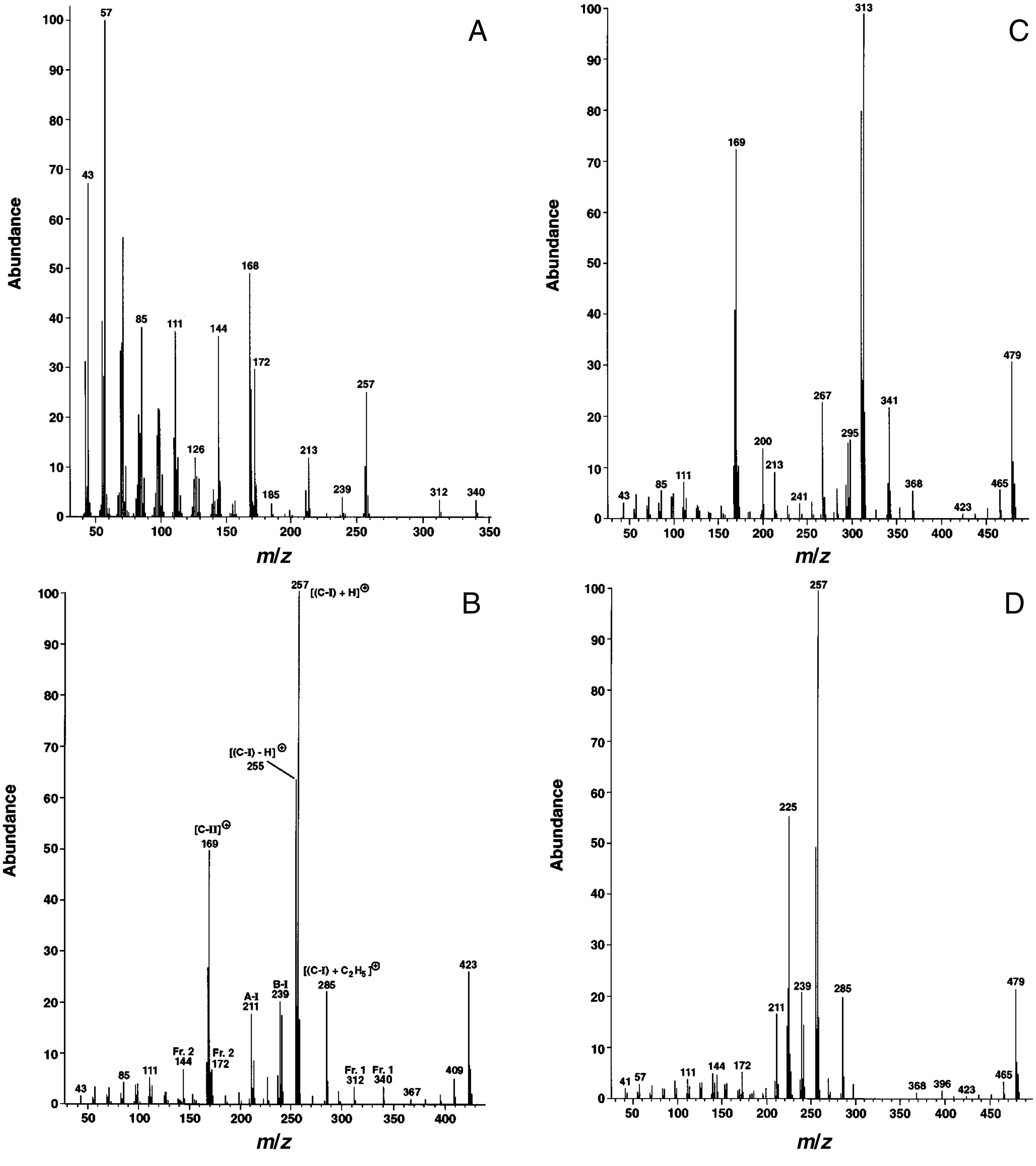

FIG. 1. Mass spectra of Di-Guerbet esters (DGE). (A) Electron ionization mass spectrum of DGE with $R_1 = 8$, $R_2 = 6$, $R_3 = 6$, $R_4 = 4$. (B) Positive chemical-ionization (PCI) (methane) mass spectrum of DGE with $R_1 = 8$, $R_2 = 6$, $R_3 = 6$, $R_4 = 4$. Assignments of key peaks are given here. The acronyms refer to the cleavage pattern in Figure 2 (Fragment 1 = fragment in Fig. 2*b*, etc.). (C) PCI (methane) mass spectrum of DGE with $R_1 = 10$, $R_2 = 8$, $R_3 = 6$, $R_4 = 4$. (D) PCI (methane) mass spectrum of DGE with $R_1 = 8$, $R_2 = 6$, $R_3 = 6$, $R_4 = 8$.

(or reverse cleavage order). While four McLafferty fragments are identified in DGE with $R_1 \neq R_2$, only two McLafferty ions are found when $R_1 = R_2$. The McLafferty fragments are distinctive for the structure of the acid moiety of the DGE by yielding direct information on the length of the alkyl chains in the acid moiety. Ryhage and Stenhagen (24) listed a McLafferty ion with accompanying cleavage C to form *m/z* 60 in butyl octadecanoate besides the ion at *m/z* 116.

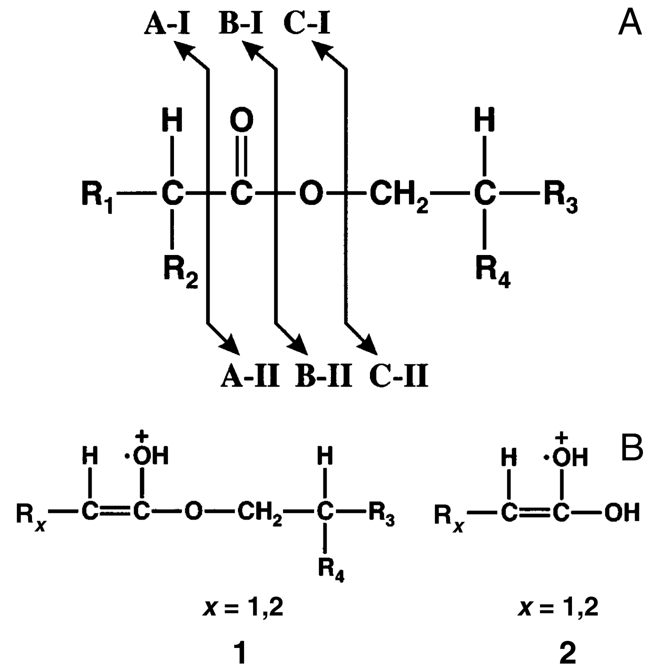

FIG. 2. (A) Cleavages leading to significant fragments in the mass spectra of DGE. (B) McLafferty rearrangement ions in the mass spectra of DGE. See Figure 1 for abbreviation.

The m/z values of the McLafferty fragments can be used to calculate the molecular weight of the DGE by utilizing Equation 1:

$$\mathrm{MW} = m/z_{\mathrm{McLafferty,\ low}} + m/z_{\mathrm{McLafferty,\ high}} - 60 \qquad [1]$$

in which MW is the molecular weight of the DGE, $m/z_{\mathrm{McLafferty,\ low}}$ and $m/z_{\mathrm{McLafferty,\ high}}$ are pairs of McLafferty ions. The pairs of McLafferty ions are corresponding high- and low-mass fragments, i.e., fragment 1 with R_1 and fragment 2 with R_2 being one pair and fragment 1 with R_2 and fragment 2 with R_1 being the other. In other words, the highest and lowest m/z McLafferty fragments are one pair as well as the smaller high-mass and larger low-mass fragments (for example, in DGE 8-6-6-4, m/z 144 and m/z 340 are one pair and m/z 172 and m/z 312 are the second pair). To our knowledge, the McLafferty ions from DGE are among the largest ever observed and this is the first time that such ions were used directly for MW determination in the absence of a molecular ion. Indeed, for DGE 12-10-10-8, the McLafferty ions at m/z 480 and 508 were present in EI mode as highest mass fragments, even though in low abundance (1–1.5%).

For sake of completeness of study, the DGE whose mass spectra are depicted in Figure 1 were also investigated with *iso*-butane as reagent gas. The considerably simpler spectra showed mainly $[M + H]^+$ as well as the protonated acid, fragment 1, resulting from cleavage C and fragment 2 from cleavage C, (for example, m/z 169 for DGE 8-6-6-4) species in Figure 2A.

NMR spectroscopy. The ^{1}H NMR spectrum of DGE 12-10-6-4 (entry 1 in Table 2) is depicted in Figure 3. Assignments for the carbons of or near the ester linkage in ^{13}C NMR are given in Figure 4. The NMR spectra of all DGE samples are nearly identical, even if they consist of mixtures as is shown for the spectra of entry 3 in Table 1. In ^{1}H NMR, the doublet at 3.96 ppm is caused by the protons on the alcohol carbon adjacent to C=O (66.55 ppm in ^{13}C NMR), which is confirmed by two-dimensional heteronuclear correlation. The multiplet at 2.30 ppm is assigned to the methine proton in the acid moiety (R_1R_2CHCO; carbon signal at 45.9–46.0 ppm). Otherwise, the ^{1}H NMR shows expected CH_2 and CH_3 peaks. ^{13}C NMR of DGE-12-10-6-4 shows the following peaks: 176.72 , 66.55, 45.96, 37.27 (for assignment of peaks >37 ppm, see Fig. 4), 32.57, 31.87, 31.81, 31.29, 30.96, 29.64, 29.61, 29.58, 29.49, 29.31, 29.29, 28.89, 27.49, 26.65, 22.97 (CH_2CH_3), 22.63 (CH_2CH_3), 14.05 (CH_3), 14.00 (CH_3). The present assignments agree with literature values for similar compounds (30,31).

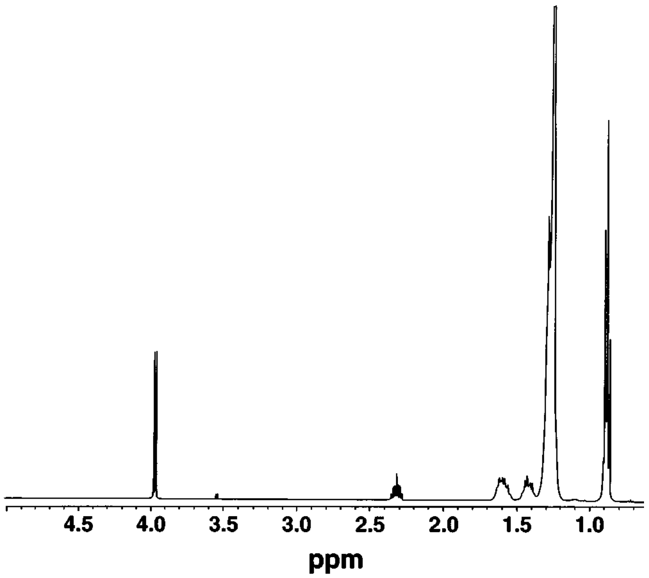

FIG. 3. ^{1}H nuclear magnetic resonance (NMR) spectrum of Di-Guerbet esters (DGE) 12-10-6-4. The ^{1}H NMR spectra of DGE of varying R_1, R_2, R_3, and R_4 are nearly indistinguishable. See Figure 1 for other abbreviation.

In conclusion, DGE were synthesized from Guerbet acids and Guerbet alcohols and characterized by MS and NMR. PCI–MS with methane as reagent gas is especially informative for the structure of the DGE. Four McLafferty rearrange-

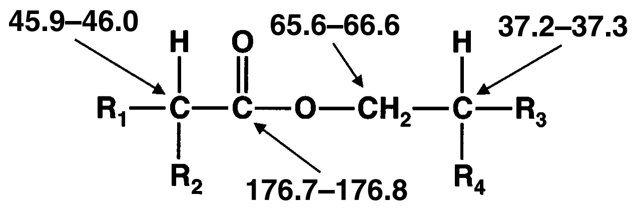

FIG. 4. Assignment of the ^{13}C NMR signals (ppm) of the carbons of or adjacent to the ester linkage in DGE. See Figures 1 and 3 for abbreviations.

ment products in the mass spectra of DGE were identified and provide structural information about the acid moiety.

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