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The Characterization of the Active Components in Commercial β-Diketone-Type Extractants LIX 54 and MX 80 A

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Abstract

The commercially available β-diketone-type extractants LIX 54 and MX 80 A were studied by GC-MS and NMR spectroscopy in comparison with synthesized reference samples. The active components were characterized as 1-phenyl-3-isoheptyl-1,3-propanediones.

INTRODUCTION

For the extraction of metal ions, certain β-diketones are proposed beside derivatives of *o*-hydroxy oximes and 8-quinolinols. Commercially available extractants of the β-diketone type are LIX 54 (Henkel Corp.) and MX 80 A (SIGMA-Innovation AB Sweden), whereas Hostarex DK-16 (Hoechst AG) is no longer produced. These extractants can be used especially to recover copper from ammoniacal solutions. Many applications of LIX 54 are reported in the literature (*1–6*), but until now the nature of the active component seems not to be clear. According to Melling (*7*), Kunigita et al. (*5*) suppose the existence of α-acetyl-*m*-dodecylacetophenone, whereas Ramesh et al. (*3*) characterize the compound as phenyl-alkyl-β-diketone.

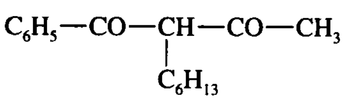
Six different components such as 1-hexylphenyl-1,3-butanedione or *n*-octylphenyl-1,3-butanedione are appointed to LIX 54 by Babcock et al. (*8*). Tavlarides et al. (*9*) denote the active compound as a dodecyl-substituted phenylbutanedione. From a systematic study, Zapatero et al. (*10*) conclude the existence of 1-phenyl-1,3-decanedione whereas Nakamura et al. (*6*) suppose benzoyl-isooctanoyl-methane. Hostarex DK-16 was thought to be hexylbenzoylacetone (*11*). Studies on MX 80 A are not reported in the literature. The purpose of this paper, therefore, was to clarify the nature of active components in commercially available extractants of the β-diketone type. For the analysis, gas chromatographic or high pressure chromatographic separation coupled to a mass spectrometer was chosen. Pure synthetic compounds which were also characterized by NMR spectroscopy were compared with the commercial components.

EXPERIMENTAL

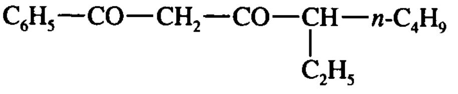
Materials

LIX 54 and MX 80 A are commercial products. They were studied as obtained and after distilling off the solvent. As reference samples, 1-phenyl-1,3-decandedione (1), 1-phenyl-2-hexyl-1,3-butane dione (2), 1-phenyl-4-ethyl-1,3-octanedione (3), and 1-heptylphenyl-1,3-butanedione (4) were synthesized by using known methods (*12*, *13*). Compounds (2) and (3) are colorless oils, whereas Compounds (1) and (4) form low melting white crystals (mp 31 and 27°C, respectively).

$$C_6H_5\text{—CO—CH}_2\text{—CO—}n\text{-}C_7H_{15} \qquad (1)$$



$$C_6H_5\text{—CO—}\underset{\displaystyle C_6H_{13}}{\underset{|}{\text{CH}}}\text{—CO—CH}_3 \qquad (2)$$



$$C_6H_5\text{—CO—CH}_2\text{—CO—}\underset{\displaystyle C_2H_5}{\underset{|}{\text{CH}}}\text{—}n\text{-}C_4H_9 \qquad (3)$$

$$n\text{-}C_7H_{15}\text{—}C_6H_4\text{—CH}_2\text{—CO—CH}_2\text{—CO—CH}_3 \qquad (4)$$

Analytical Methods

The analyses of the extractants were performed with a Nermag Automass GC-MS system (with a Delsi-Nemag gaschromatograph) using fused silica CC 25 m, BP5 0.25 mm inner diameter (Scientific Glass Engineering, Australia), a temperature program 60–250°C (10°C/min), and electron ionization by 70 eV. ^{1}H and ^{13}C-NMR spectra were measured by a Bruker-AM 300 spectrometer (^{1}H-NMR 300, 13 MHz; ^{13}C-NMR 75, 47 MHz).

RESULTS AND DISCUSSION

By fractionated vacuum distillation, the commercial extractants were separated into two fractions containing the solvent and the active components, respectively.

The solvent had a boiling range of 70–140°C/10 torr and consists of a mixture of different hydrocarbons containing between 7 and 12 main components of strongly branched alkanes.

Analysis of the Active Components

NMR Studies

The ^{13}C-NMR spectra of the extractant which was obtained by the distillation of LIX 54 as well as those of synthesized reference samples are given in Fig. 1. In spite of a large number of resonance signals in the region up to 50 ppm, characteristic groups can be identified by comparison with reference samples. Good agreement is found for the C-1 signal of the aromatics at δ = 132 ppm as well as for the C-1 and C-3 resonance signals of the keto groups at δ = 199 and 184 ppm, respectively. This fact points to a similar chemical environment. Similarly, the C-2 signal is scarcely influenced by structural differences in the substituent, but significant differences are expected for the C-4 signal if a substituent is attached at this position. Indeed, this signal is shifted to a lower field by 10 ppm in the case of 1-phenyl-4-ethyl-1,3-octanedione. Good agreement between the experimentally observed shift (δ = 50.99 ppm) and the calculated value (δ = 52.2 ppm) (*14*) exists for the C-4 signal. Therefore, the differences for LIX 54 and the reference sample demonstrate that 1-phenyl-4-ethyl-1,3-octanedione is not present in the commercial product.

The ^{13}C-NMR spectra of LIX 54 for C-1 and C-3 show additional signals than in the case of 1-phenyl-1,3-decanedione and 1-phenyl-4-ethyl-octanedione, respectively, It is supposed that these signals are the result of the presence of isomeric β-diketones but are not caused by keto–enol tautomerism.

The signals of the aromatic C atoms clearly show that there are no additional substituents in any case.

GC-MS Studies

The gas chromatograms of the active components of LIX 54 and MX 80 A are shown in Fig. 2. It can be seen that the active substance of LIX 54

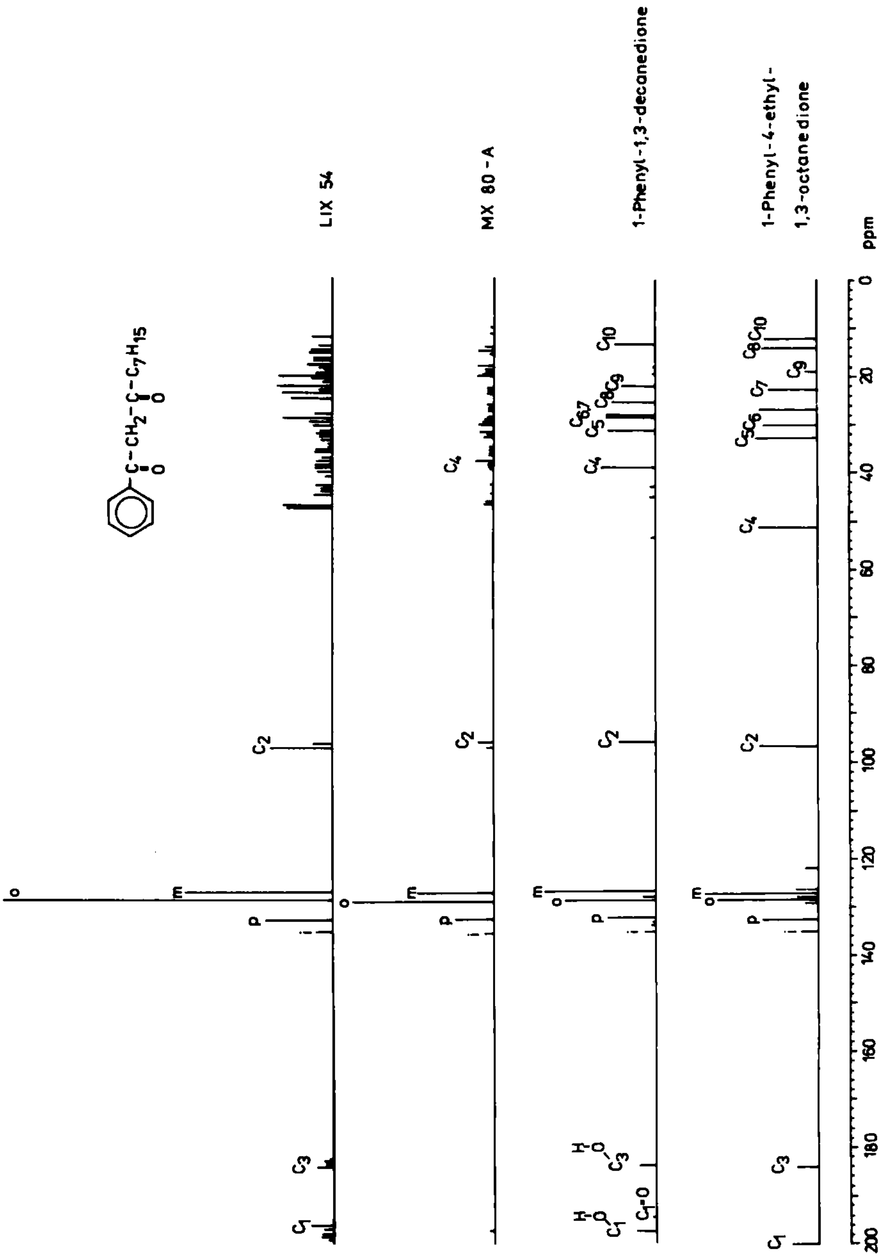


FIG. 1. ^{13}C-NMR spectra of β-diketone-type extractants.

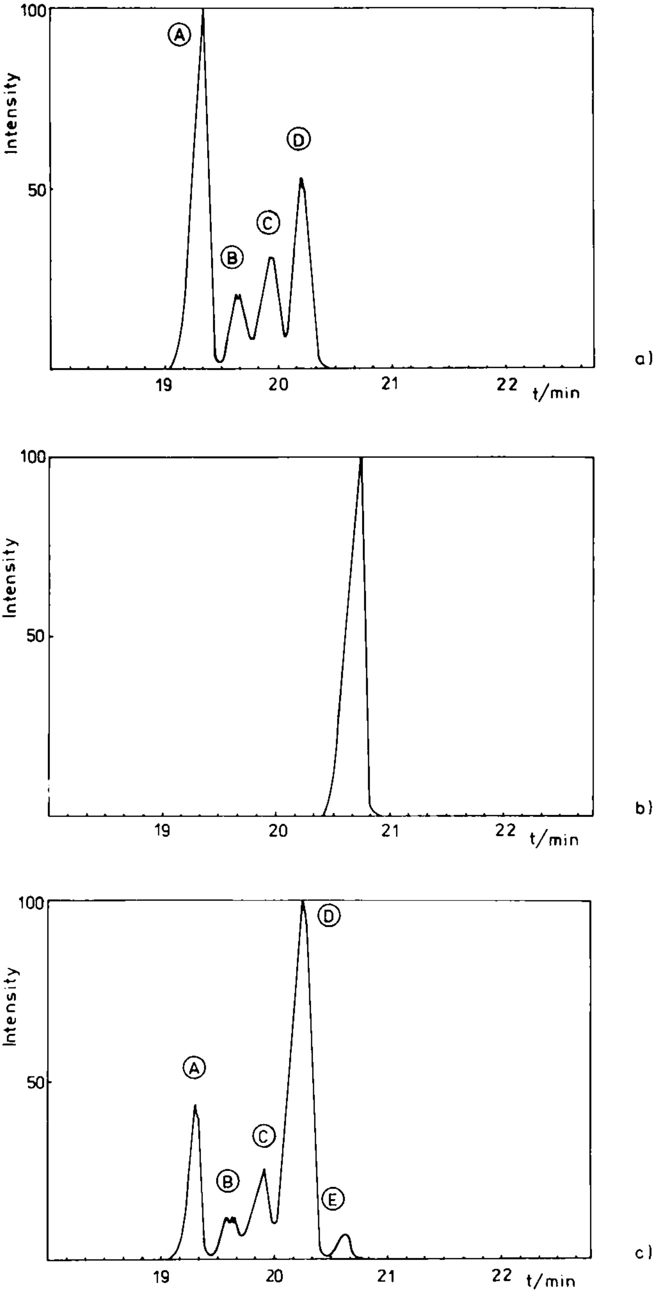


FIG. 2. Gas chromatograms of LIX 54 (Fig. 2a), MX 80 A (Fig. 2c), and 1-phenyl-1,3-decanedione (Fig. 2b).

is composed of at least four, isomeric compounds, each of them with the molar mass 246. In the case of MX 80 A, an additional fifth compound was found. Both extractants have a very similar quantitative composition and they differ only by the relative concentration ratio of the active components. For comparison, the gas chromatogram of 1-phenyl-1,3-decanedione is also given. In the mass spectra of the isomers A, B, C, D, and E, the following fragments of high intensity are observed in each case:

$C_6H_5—CO—CH—C(OH)=CH_2^+$	m/z = 162 (base peak)
$C_6H_5—CO—CH_2—CO^+$	m/z = 147
$C_6H_5—C(OH)=CH_2^+$	m/z = 120
$C_6H_5—CO^+$	m/z = 105
$C_6H_5^+$	m/z = 77
$C_5H_9^+$	m/z = 69

All compounds exhibit a weak molecular ion peak (m/z = 246). Because of the agreement in their mass spectrometric behavior, A, B, C, D, and E can be regarded as isomeric alkyl analogues of 1-phenyl-1,3-butanedione. As a common fragment of the enol forms, m/z = 228 (M − H_2O) was found.

Different fragmentation occurs in the region above m/z = 162. The interesting parts of the mass spectra of compounds A, B, C, and D are shown by Fig. 3. For comparison, mass spectrometric data for reference substances are given in Table 1.

First of all, the presence of alkyl-substituted phenyl groups in any of the isomers is excluded by the appearance of the fragments m/z = 105 and 147. Likewise, no evidence is found for the meso-substituted β-diketone 1-phenyl-2-hexylbutane-1,3-dione because a characteristic fragment M − $CH_2=CO$ (m/z = 204) was only found in the case of the Reference Compound (2). To check for the presence of the n-C_7H_{15} group, 1-phenyl-1,3-decanedione was studied as a reference sample. By comparison of the chromatographic behavior and of the mass spectrometric fragmentation (Fig. 4), it was found that isomer E is identical with unbranched 1-phenyl-1,3-decanedione. In this case fragments such as M − C_2H_5, M − C_3H_7, M − C_4H_9, and M − C_5H_{11} resulting from the successive splitting of the unbranched alkyl chain are observed. Contrarily, the isomers A, B, C, and D should contain branched heptyl groups, but branching of the heptyl group adjacent to the carbonyl group is excluded according to the NMR data. Some more information gave the different fragmentation pathways of A, B, C, and D. In the case of A, C, and D, a selected fragmentation at the heptyl group is observed. Typical fragments of A are M − C_4H_9

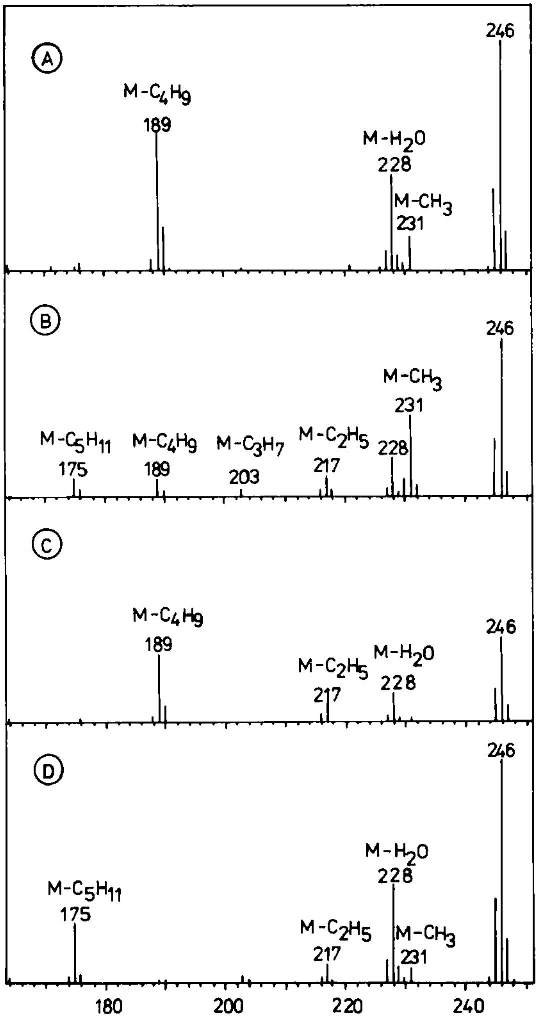


FIG. 3. Mass spectrometric fragmentation of the active components of LIX 54.

and M − CH_3, whereas C exhibits M − C_4H_9 besides M − C_2H_5. Hence the heptyl group is probably of type 2,4-dimethyl-pentyl (A) or 2,3-dimethyl-pentyl (C). For D, M − C_5H_{11} is found as a characteristic fragment besides M − CH_3. This behavior can be explained by assuming the presence of 3,4-dimethyl-pentyl or 3-methyl-hexyl groups. In the case of isomer B, a great variety of fragments occurs as was found for unbranched heptyl compound E. Therefore, it can be supposed that the alkyl substituent is lowly branched as it is in the case for different methyl-hexyl groups.

TABLE 1
Typical Fragments in Mass Spectra of LIX 54 Type β-Diketones

Compound	*m/z*	Fragment	Relative intensity (%)
1-Phenyl-1,3-decanedione (1)	228	M − H_2O	35
	217	M − C_2H_5	10
	204	M − C_3H_6	39
	190	M − C_4H_8	15
	175	M − C_5H_{11}	10
1-Phenyl-2-hexyl-1,3-butanedione (2)	231	M − CH_3	21
	204	M − CH_2—CO	68
	189	M − C_4H_9	29
	175	M − C_5H_{11}	46
	162	Ph—CO—CH_2—CO—CH_3	33
	43	CH_3—CO^+	100
1-Phenyl-4-ethyl-1,3-octanedione (3)	190	M − C_4H_8	45
	57	C_4H_9	17

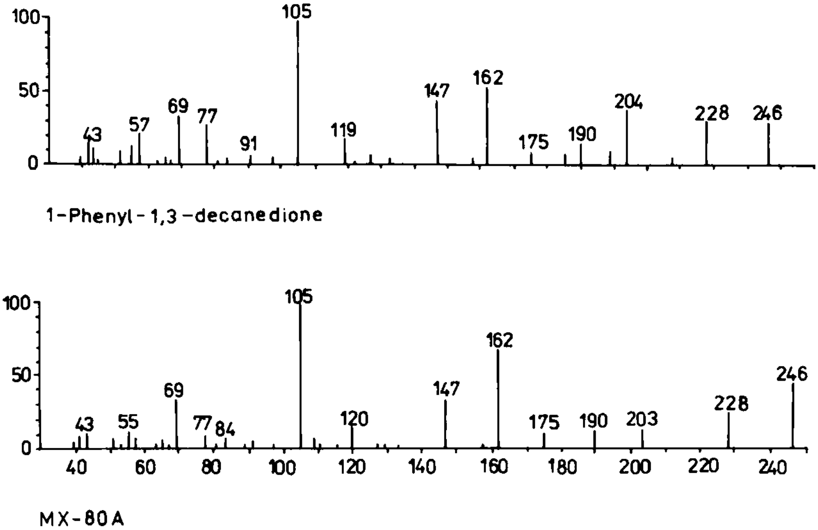


FIG. 4. Mass spectrometric fragmentation of 1-phenyl-1,3-decanedione in comparison with isomer E of MX 80 A.

Besides the isomeric 1-phenyl-3-heptyl-1,3-propanediones, a compound $m/z = 222$ was found as an impurity in the technical extractants. It is probably a self-condensation product of acetophenone resulting from the synthesis (*15*). Furthermore, the GC-MS analysis of MX 80 A shows traces of acetophenone ($m/z = 120$) and of some low-molecular β-diketones such as benzoylacetone ($m/z = 162$) and dibenzoylmethane ($m/z = 224$).

CONCLUSIONS

By GC-MS measurements, LIX 54 was found to exist as a mixture of at least four isomeric 1-phenyl-3-isoheptyl-1,3-propanediones solved in saturated alkanes. MX 80 A has a similar composition but additionally contains a small amount of 1-phenyl-3-*n*-heptyl-1,3-propanedione.

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