L. Cohen, F. Soto and M. S. Luna, Algeciras, Spain, D. W. Roberts, C. D. Saul, K. Lee and E. Williams, Port Sunlight, United Kingdom, J. E. Bravo, San Roque, Spain

Derivatization, GC-MS, LSIMS and NMR Analysis of Sulfoxylated Methyl Esters

Derivatization of Φ-Methyl ester sulfonic acids with trimethylorthoacetate (TMOA) in a one step reaction gave derivatized sulfonic esters. These resulting methyl esters have been analysed by GC, GC-MS, LSIMS, LSIMS-tandem MS and HNMR techniques so that for the first time, isomers and even minor components such as polysulfonates are shown.

Derivatisierung, GC-MS-, LSIMS- und NMR-Analyse sulfoxylierter Methylester. Durch Derivatisierung von Φ-Methylestersulfonsäuren mit Orthoessigsäuretrimethylester wurden in einer Einstufenreaktion Sulfonsäureesterderivate erhalten. Diese Ester wurden mittels GC, GC-MS, LSIMS und LSIMS-Tandem MS und NMR analysiert, so dass erstmalig Isomere und Nebenprodukte wie z. B. Polysulfonate nachgewiesen werden konnten.

1 Introduction

Sulfoxydation of fatty acid methyl esters with SO_2, O_2, and ultraviolet light of 257.3 nm wavelength, has led to sodium methyl ester sulfonates known as Φ-MES as described in [1].

According to most recent works on the subject [2, 3], Φ-methyl esters sulfoxylates exhibit good surfactant properties, presumably owing to the mechanism of their synthesis *via radical*, which may allow the introduction of the SO_3 group in a random position along the hydrophobic chain. Although in a recent publication [4] paraffin sulfonate (SAS) isomers were identified by GC-MS, the random position hypothesis that has never before been confirmed for Φ-MES, is the object of the present work. Different analytical techniques and methods were combined to reach the goal.

The sulfoxydation reaction mechanisms proposed by different authors have been summarised and are shown in Scheme 1. Accordingly, the reaction seems to proceed by two mechanisms: an irradiated reaction, where the persulfonic acid molecule disappears through its action as an electron donor, and a dark reaction, where the persulfonic molecule disappears by thermal decomposition. Therefore, the main step is the radical production, contrary to α-MES traditional sulfonation that proceeds through an electrophilic substitution.

In this investigation GC-MS, NMR, LSIMS and tandem MS analytical techniques have been used.

2 Experimental part

2.1 Derivatization of Φ-MES C_{16}

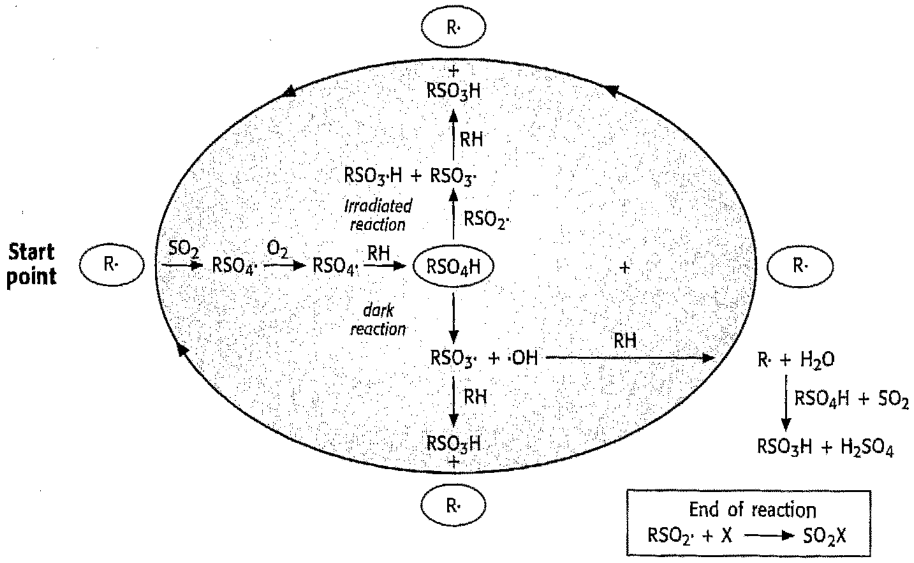
According to the method developed by Unilever Research [5], a sulfonic acid methyl ester sample was methylated using an excess of trimethylorthoacetate (TMOA) to obtain the dimethylester sulfonate. By this way the non-volatile sulfonic acid can be analysed by different techniques.

$$R\text{–}SO_3H + CH_3C\,(OCH_3)_3 \rightarrow R\text{–}SO_3\text{–}CH_3 + CH_3CO_2CH_3 + CH_3\text{–}OH$$

Dimethyl ester
sulfonate

2.2 Gas chromatography conditions

A TRB-1 capillary column from Tracer (30 m×0,25 mm I.D, 0,25 µm film thickness) was used.



Scheme 1 Sulfoxidation reaction mechanisms without the addition of water [1]

Temperature Program: 70 °C (4 min), 3 °C/min to 270 °C, hold 10 min at 270 °C. Injector temperature: 250 °C. Detector type: Flame ionisation, temperature: 280 °C.

2.3 Mass Spectrometry

Detector	HP-5970
Multiplier	2000 V
Solvent Delay	10 minutes
Run Time	60 Minutes
Low Mass	50 amu
High Mass	500 amu
Scan/second	1.1

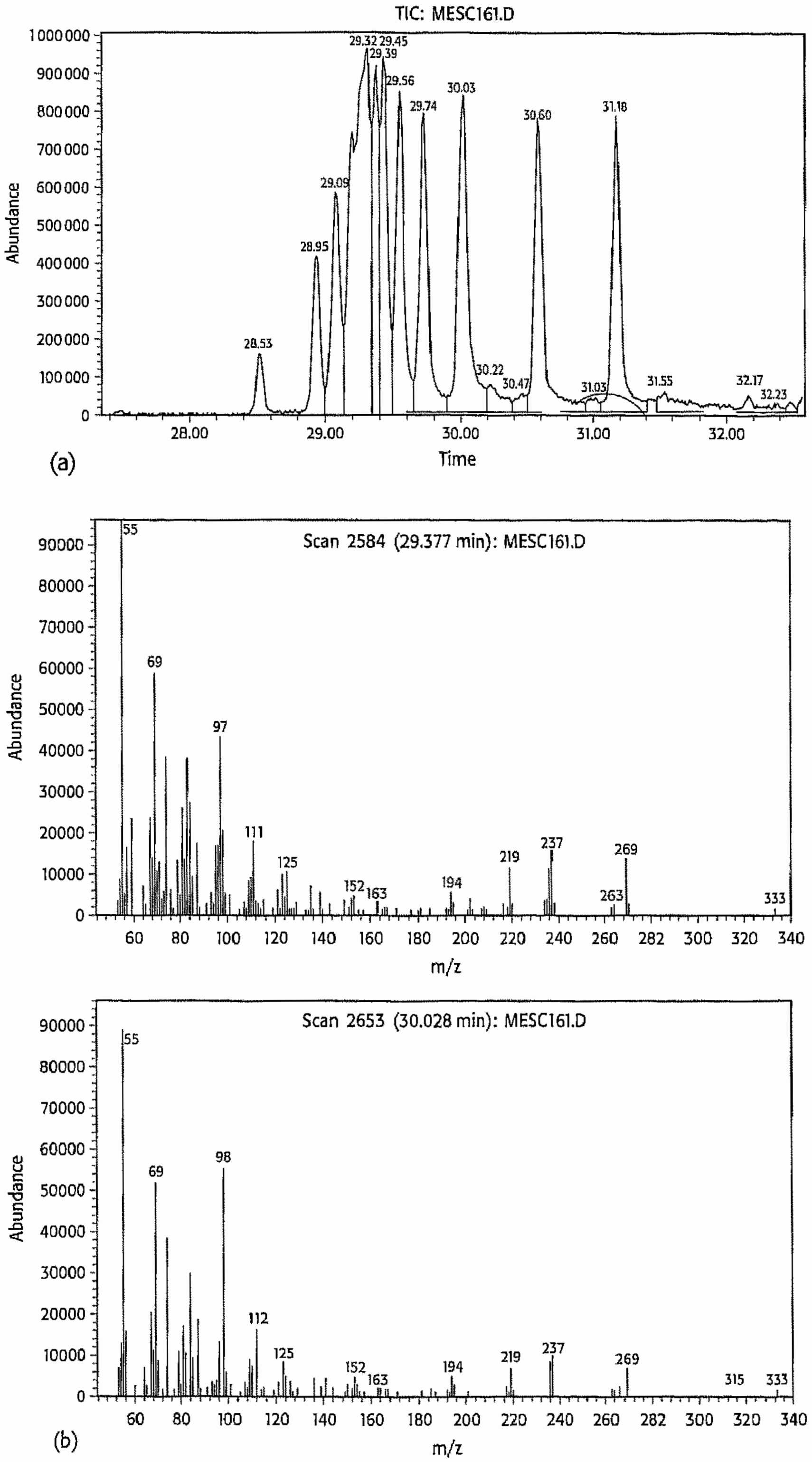


Figure 1 (a) TIC Chromatogram of Φ-MESC$_{16}$, (b) Mass fragmentation spectrums of selected peaks at 29.377 and 30.028

2.4 LSIMS

LSIMS (Liquid Secondary Ionisation Mass Spectrometry) is a soft ionisation technique, i. e. one which produces little fragmentation. It is suitable for the analysis of (amongst others) polar or ionic species. It therefore covers a range of non-volatile analytes which are not amenable to EI or GC-MS.

All LSIMS and LSIMS-tandem MS experiments were carried out on the Micromass ZABSpec Ultima – OA TOF at Unilever Research Port Sunlight. This is a sector-Time Of Flight hybrid instrument capable of both accurate mass measurement and tandem MS experiments.

LSIMS experiments were carried out in a glycerol matrix. The primary ion beam was provided using a Cs ion gun operating at 25 KV.

The instrument was operated at an accelerating voltage of 8 KV. For accurate mass measurement a resolution of 5000 was used. For nominal mass measurement, calibration was carried out using glycerol peaks; for accurate mass measurement, calibration was carried out using a polyethylene glycol standard appropriate to the mass range.

2.5 Tandem MS

In tandem MS experiments a precursor ion, selected using the magnetic sector, is collided with an inert gas in a collision cell situated between the magnetic sector and the TOF analyser. The mass spectrum of the fragments formed (product ions) is then recorded using the TOF.

Most of the tandem MS experiments were carried out in xenon as the collision gas, the typical collision cell pressure was $2 \cdot 10^{-6}$ Torr. Measurements on dimethyl Φ-MESC$_{16}$ were also repeated using both helium and Xenon, each at a pressure of $8 \cdot 10^{-7}$ Torr. The resulting spectra showed good qualitative agreement over the range of collisional regimes.

To perform the tandem MS experiments the TOF was calibrated using CsI peaks. A two point calibration is used over the m/e range 200 to 0.

2.6 ^{1}HNMR

A couple of drops of the neat sample were dissolved in deutero-chloroform ($CDCl_3$) and filtered into a 5 mm NMR tube. The sample was examined on a Bruker DRX 500FTNMR Spectrometer using the following parameters:

Nucleus: ^{1}H
Sweep width = 10330.579 Hz
Pulse width = 30 degree
Number of scans = 16
Relaxation Delay = 3 seconds
Probe temperature = 300 K
Offset (O1) = 3088.51 Hz
Time domain size = 65536 points
Real Spectrum size = 32768 points
Line Broadening = 0.3 Hz

3 Results and discussion

3.1 GC-MS results

In Fig. 1 a, a TLC-chromatogram of Φ-MES C_{16} dimethylester is shown. According to their distribution pattern these peaks are expected to be dimethylester sulfonate isomers with the SO_3 group located along the alkyl chain. Nevertheless further investigations are necessary to characterize all the peaks, that is to identify exactly where the SO_3 group is located with respect to the ester group. Typical mass fragmentation spectrums of two selected isomers are shown in Fig. 1 b. As can be seen, no significant differences appear. The molecular ion at m/z 364 amu does not appear due to the loss of O–CH_3 group, but other diagnostic peaks are observed, like

m/z	**Assignment**
333	364 minus CH_3O–
269	364 minus –SO_3CH_3
237	364 minus –C_9H_{19}
55,69,83	corresponding to the loss of water molecule (18 amu) in esters. As an example, –CH_2–C(O)–O–CH_3 gives 73 minus 18 = 55.

3.2 ^{1}H-NMR Results

The sample gave a complex NMR spectrum (Fig. 2) that indicates the presence of the following groups:

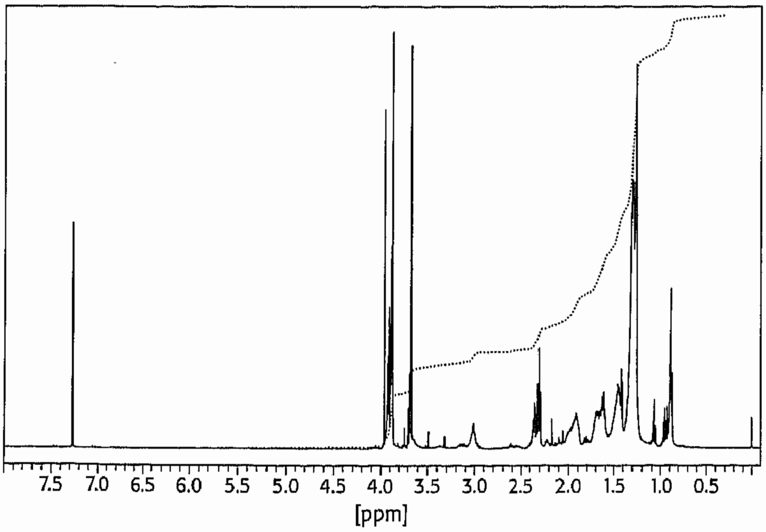
- Alkyl chain seen 0.8 to 1.76 ppm
- Bands 1.76 to 2.1 ppm that could be due to CH_2 of $CH_2CH(CO_2)SO_3$ or $CH(SO_3)(CH_2)_nCO_2$ or $C(SO_3)_2CH_2$ where n = 1 or 2
- Bands 2.27 to 2.46 ppm assigned to $RCH(SO_3Me)(CH_2)mCH_2CO_2Me/H$ where m is > 4
- Bands 2.47 to 2.75 ppm assigned to $RCH(SO_3Me)(CH_2)_mCH_2CO_2Me/H$ where m is < 4
- *The NMR indicates that a range of positional isomers is present although nothing is known about all possible isomers.*
- Bands 2.9 to 3.2 ppm assigned to CH–SO_3 (many CH–SO_3 bonds present)
- Bands 3.57 to 3.73 ppm assigned to CO_2**Me** and $MeOSO_3$ – (if present) and (if present) $CH(SO_3H)CO_2H$
- Bands 3.8 to 4.0 ppm assigned to SO_3**Me** of product and $CH(CO_2Me)SO_3$**Me**/$CH(CO_2$**Me**$)SO_3H$ (if present).

Integration of the spectrum gave the following results:

Group	Integral/H	Mole Ratio
Terminal Methyls (total)	76/H	1
CH_2CO_2Me/H (total)	74/H	0.97
CH–SO_3	79/H	1.04
CO_2**Me**	58/H	0.76
SO_3**Me**	122.67/H	1.6
$CH(SO_3)CH_2CH_2CO_2$ or $CH_2C(SO_3)_2CH_2$	69/H if 2 H	0.91

From the mole ratios it can be seen that:

- The difference between the CO_2**Me** figure and the CH_2CO_2 figure, 0.97 and 0.76 respectively, could indicate that there are non-methylated acid groups in the products as well as the required dimethyl ester.
- The major species present contains one CH–SO_3 and one CH_2CO_2 group.



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O1          :  3088.51 Hz
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PULPROG     : zg30
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Figure 2 NMR spectrum of dimethyl Φ-MESC$_{16}$

3.3 LSIMS, LSIMS – tandem MS results

3.3.1 Standard pure dimethyl α-MESC$_{16}$

Positive ion LSIMS using a glycerol matrix gave ions as shown in Figure 3. Tandem MS on the 365 ion in this sample gave the fragment ions that are shown in Figure 4. Note that the ion at m/e = 181, $CH_2{=}C(SO_3CH_3)CO_2CH_3H^+$ which indicates substitution at the alpha position has a reasonable intensity, similar to that of the ion at 219. Beta sulphonated ester may also be expected to give an ion of mass 181, structure $CHSO_3Me{=}CHCO_2Me + H^+$.

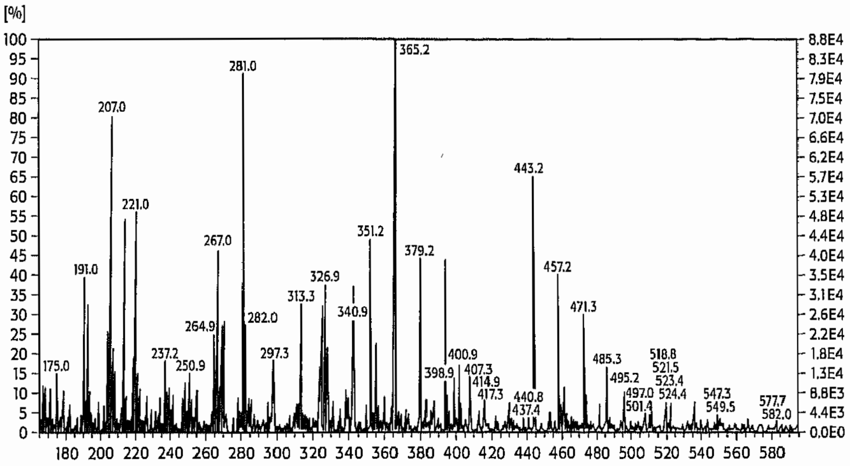

Figure 3 LSIMS spectrum of α-dimethyl MESC$_{16}$

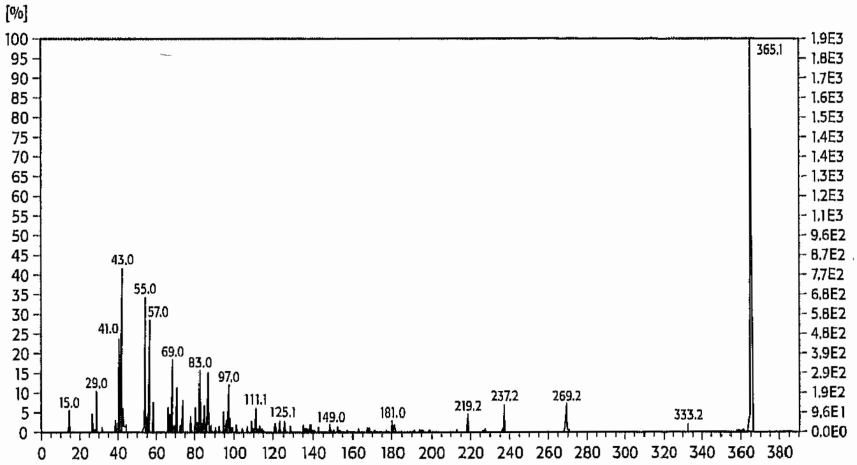

Figure 4 MS/MS spectrum of ion 365 of standard pure dimethyl α-MESC$_{16}$

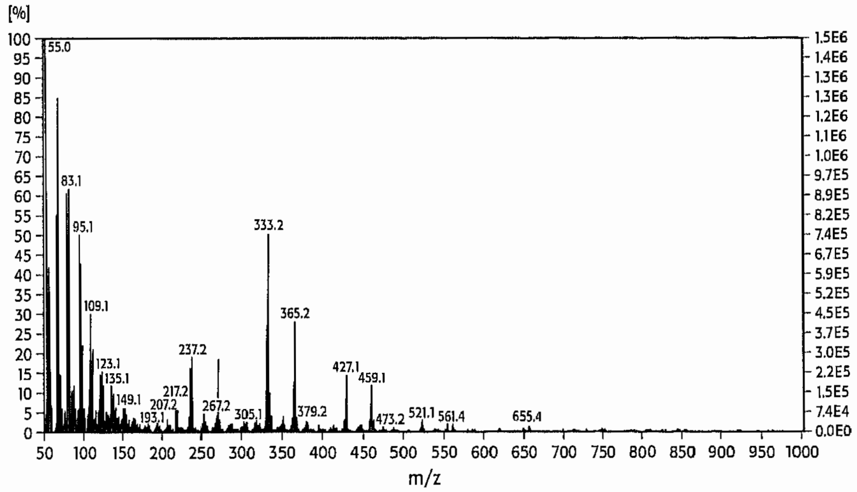

Figure 5 LSIMS/MS spectrum of dimethyl Φ-MESC$_{16}$

3.3.2 Dimethyl Φ-MESC$_{16}$

The positive ion LSIMS spectrum of this sample (Figure 5) gave ions at the m/e values listed below:

m/e 365

This corresponds to the main species observed in the case of the dimethyl α-MESC$_{16}$ standard.

The tandem MS spectrum of this ion (Figure 6) gives a series of ions similar to those for the m/e = 365 ion in the dimethyl α-MESC$_{16}$ standard, but with a much reduced intensity for the 181 ion. Though a range of MS/MS conditions (different collision gases and gas pressures) had been tested, the intensity of the 181 ion has never exceeded 1/3 of the intensity of the ion at 219. This indicates that there is very little alpha or beta substitution.

In general, the intensity of the ion at m/e = 333 was greater than that for the corresponding ion in the tandem spectrum of the dimethyl α-MESC$_{16}$. This again suggests that the alpha substituted MES is not a major isomer in this sample (the increased intensity of the 333 ion may be due to the greater ease of loss of CH_3OH in the case where there is no alpha substitution).

This result is in agreement with the fact that radical formation is easier when the CH_2 group is farther from $C(O){-}OCH_3$, owing to the inductive effect of the latter

m/e 333

This is the most intense ion in the spectrum. This ion is absent in the LSIMS/MS spectrum of the dimethyl α-MESC$_{16}$ standard (but an ion at m/e = 333 does appear in the tandem MS spectrum of the standard) suggesting that this may be a real chemical species. Alternatively, it may be that the ion at m/e = 333 is a fragment produced by loss of CH_3OH in the LSIMS source. The presence of this ion in the spectrum of this sample, and its absence from the spectrum of pure dimethyl α-MESC$_{16}$, may be explained by arguments similar to those presented above for the intensity of the 333 fragment ion in the tandem spectra of these materials. That means fragmentation by loss of CH_3OH is easier in the absence of substitution at the alpha position. It should also be noted that there may be more than one isomeric species contributing to this ion.

The accurate mass measurement for this ion is consistent with $C_{17}H_{33}SO_4^+$.

Ions in the Tandem spectrum of the m/e = 333 ion include an ion series common to the tandem spectrum of the 365 ion, i. e. ions at m/e = 269, 237, 219. There is also a fragment at m/e = 253.

m/e 331

The accurate mass measurement for this ion is consistent with the formula $C_{17}H_{31}SO_4^+$ i. e. 333 – 2 H's.

m/e 269

The accurate mass value for this ion is consistent with the formula $C_{17}H_{33}O_2$, i. e. the species $CH_3C_{14}H_{26}CO_2CH_3H^+$.

3.4 Evidence of disulphonation

m/e 459

The accurate mass value for this ion is consistent with the formula $C_{19}H_{39}S_2O_8^+$, i. e. the disulphonated species $CH_3C_{14}H_{26}(SO_3CH_3)_2CO_2CH_3H^+$.

The tandem spectrum of this ion shows the following ions:

m/e	Assignment
427	459 minus CH_3OH
363	459 minus HSO_3CH_3
331	427 minus HSO_3CH_3
267	363 minus HSO_3CH_3 – i. e. confirms that the 459 ion contains two SO_3CH_3 groups
235	331 minus HSO_3CH_3 – i. e. confirms that the 459 ion contains OCH_3 as well as two SO_3CH_3 groups

No 181 ion is seen in the tandem spectrum of 459, indicating that this ion does not contain significant amounts of alpha substituted species, it may also indicate that there is little beta substitution. Similarly, the tandem spectrum does not contain any ion at 275, suggesting that there is no disubstitution at the alpha or beta positions.

The tandem spectrum of this ion (Figure 7) does, however, contain an ion at m/e = 217. This mass is consistent with $C_2H_2(SO_3CH_3)_2H^+$, indicating the presence of either geminal or viscinal substitution. Further studies on standards of known substitution would be needed to confirm this.

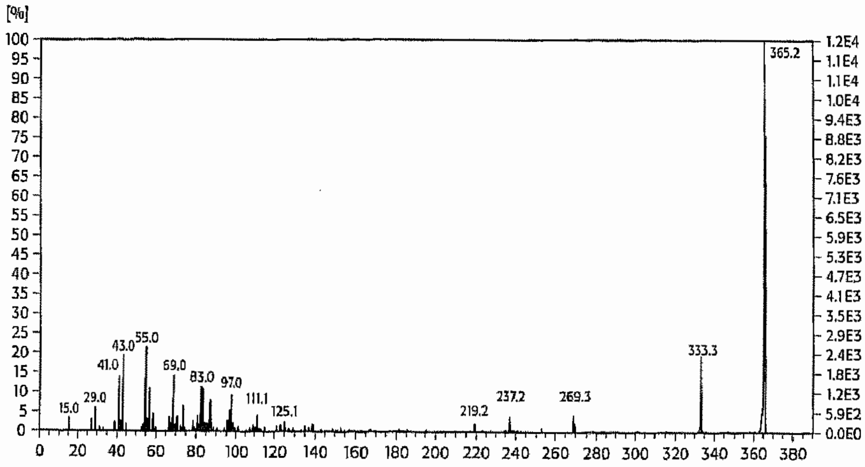

Figure 6 MS/MS spectrum of ion 365 of dimethyl Φ-MESC$_{16}$

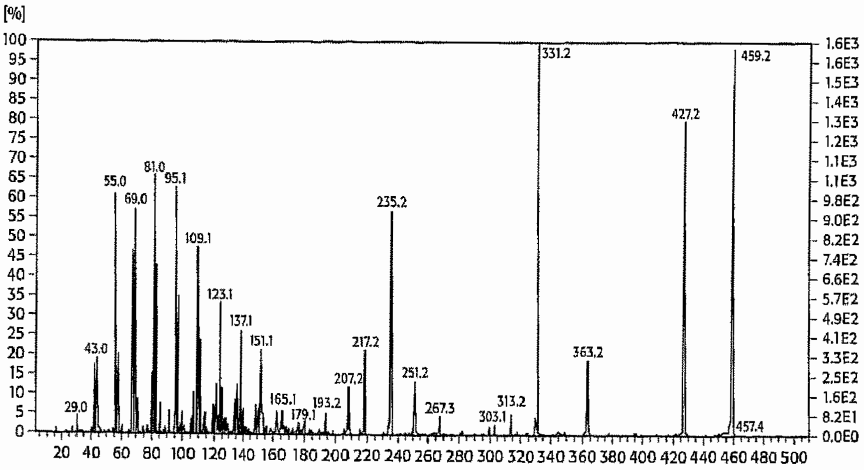

Figure 7 MS/MS spectrum of ion 459

m/e 427

The accurate mass value for this ion is consistent with the formula $C_{18}H_{35}S_2O_7^+$, i. e. the species $CH_3C_{14}H_{26}(SO_3CH_3)_2CO^+$, a disulphonated analogue to the ion at m/e = 333.

The tandem spectrum of this ion (Figure 8) shows the following ions:

m/e	Assignment
395	427 minus CH_3OH
331	427 minus HSO_3CH_3
299	331 minus CH_3OH
251	331 minus SO_3
235	331 minus HSO_3CH_3

The above ions suggest that the 427 peak consists of more than one species, as no single isomer can easily explain all the fragments of this spectrum.

4 Conclusions

- The SO_3 group in a random position has been demonstrated.
- GC-MS shows the presence of at least eleven isomers that cannot be characterised.
- ^{1}HNMR indicates that the major species present contains one CH–SO_3 and one CH_2CO_2 group, and confirms the presence of different isomers and suggests the presence of polysulfonates

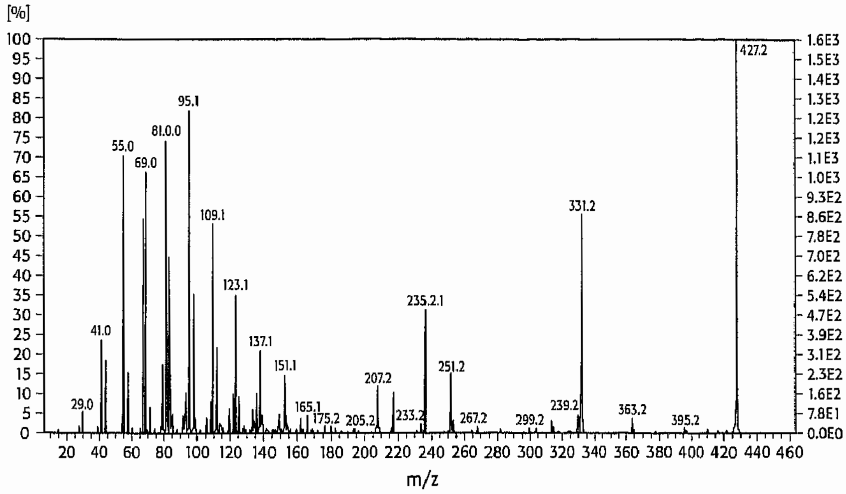

Figure 8 MS/MS spectrum of ion 427

- LSIMS and LSIMS/MS confirms: (a) The presence of $CH_3(CH_2)_mCH(SO_3Me)(CH_2)_nCH_2CO_2Me$; $Mw = 364$ where $m + n = 12$. (b) There is very little alpha or beta substitution. (c) The presence of polysulphonated species of the form: $CH_3(CH_2)_mCH(SO_3Me)(CH_2)_nCH(SO_3Me)(CH_2)_pCH_2CO_2Me$ and/or $CH_3(CH_2)_mC(SO_3Me)_2(CH_2)_nCH_2CO_2Me$
- Further research has to be implemented to characterise each isomer.

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Correspondence to

Dr. Leon Cohen
Universidad de Cadiz
Escuela Superior Politécnica
Avda Ramón Puyol s/n.
11202 Algeciras. Spain.
E-mail: leon.cohen@uca.es

The authors of this paper

Dr. *Leon Cohen* got his Ph.D. in chemistry at Sevilla University. In 1994, he earned the EURCHEM designation. He worked for Petresa from 1970 to 1996. He is currently a Professor of Chemical Engineering at the University of Cadiz, where he has lead the research group entitled "Surface Activity and Detergency", since 1994. He is author of more than 25 papers related to detergency.

Dr. *Fernando Soto* received his M.S. in chemistry at Sevilla University and his Ph.D. in Chemical Engineering in 2001 at Cadiz University. He has been a Professor of Chemical Engineering at the University of Cadiz, since 1979. He has been a member of the research group entitled "Surface Activity and Detergency" since 1994.

Mª de la Sierra Luna received her B.S. in Chemical Engineering at Cadiz University in 1998. She is a member of the above-mentioned research group.

Mr. *C. D. Saul* obtained his degree in Chemistry at the North East Wales Institute of Further Technology, and ran the High Resolution NMR facility in Unilever R&D Port Sunlight before retiring in 2001.

Dr. *David W. Roberts* graduated from the University of Manchester Institute of Science and Technology (UMIST) in 1962 and obtained his PhD from UMIST in 1965. He joined Unilever R&D Port Sunlight in 1967. His main research interests are concerned with sulphonation chemistry and structure-activity relationships in toxicology. He is the author of more than 100 publications and patents.

Dr. *Kenneth Lee*, born in 1963, obtained his BSc and PhD in Chemistry from the University of Manchester, UK. After completing his studies he joined Unilever Research in 1987, working in the Analytical Chemistry Section. Following 15 years in measurement he moved to the Unilever Laundry Global Technical Centre in 2002.

Erik Williams was born in Bangor, North Wales in 1968 and obtained an honours degree in Chemical and Pharmaceutical Sciences at Sunderland University in 1990. From early 2000 to mid 2001 he worked at Unilever R&D Port Sunlight on many different projects involving high resolution mass spectrometry using the Micromass ZabSpec OA-TOF instrument. He is currently one of the GC Technical Consultants with Phenomenex, based in Macclesfield, Cheshire.

Mr. *José E. Bravo* was graduated in Chemistry at Granada University in 1965. In 1969 he joined Petresa where is currently Chief Assistant Chemist to the Chemical Department.