



# Carbonaceous aerosol characterization in the Amazon basin, Brazil: novel dicarboxylic acids and related compounds

Alena Kubátová<sup>a</sup>, Reinhilde Vermeylen<sup>a</sup>, Magda Claeys<sup>a,\*</sup>, Jan Cafmeyer<sup>b</sup>,  
Willy Maenhaut<sup>b</sup>, Greg Roberts<sup>c</sup>, Paulo Artaxo<sup>d</sup>

<sup>a</sup>Department of Pharmaceutical Sciences, University of Antwerp (UIA), Universiteitsplein 1, B-2610 Antwerp, Belgium

<sup>b</sup>Institute for Nuclear Sciences, University of Gent, Proeftuinstraat 86, B-9000 Gent, Belgium

<sup>c</sup>Biogeochemistry Department, Max Planck Institute for Chemistry, P.O. Box 3060, D-55122 Mainz, Germany

<sup>d</sup>Institute of Physics, University of Sao Paulo, P.O. Box 66318, CEP 05315-970 Sao Paulo, SP, Brazil

Received 13 December 1999; received in revised form 28 April 2000; accepted 13 June 2000

## Abstract

High-resolution capillary gas chromatography (GC) and GC/mass spectrometry (MS) were employed for the quantitative determination of dichloromethane-extractable organic compounds in total and size-fractionated aerosol samples which were collected in the Amazon basin, Brazil, during the wet season, as part of the LBA–CLAIRE-98 experiment. Special emphasis was placed on the characterization and identification of several novel unknown dicarboxylic acids and related oxidative degradation products. This class of acidic products was enriched in the fine size fraction, suggesting that they were secondary organic aerosol products formed by gas-to-particle conversion. Some of the unknowns contributed more to the class of dicarboxylic acids than the major known compound, nonadioic acid (azelaic acid). The same unknowns were also observed in urban aerosol samples collected on hot summer days in Gent, Belgium. For the characterization and structure elucidation of the unknowns, various types of derivatizations and fractionation by solid-phase extraction were employed in combination with GC/MS. Four unknowns were identified. The most abundant were two derivatives of glutaric acid, 3-isopropyl pentanedioic acid and 3-acetyl pentanedioic acid. The other two identified unknowns were another oxo homologue, 3-acetyl hexanedioic acid, and, interestingly, 3-carboxy heptanedioic acid. To our knowledge, the occurrence of these four compounds in atmospheric aerosols has not yet been reported. The biogenic precursors of the novel identified compounds could not be pinpointed, but most likely include monoterpenes and fatty acids. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Aerosols; Carbonaceous; Secondary organic aerosol; Dicarboxylic acids; Amazon basin

## 1. Introduction

Dicarboxylic acids containing two to nine carbon atoms are ubiquitous organic aerosol constituents in the atmosphere. Their origin can be attributed to formation by photochemical oxidation of anthropogenic hydrocarbons and biogenic compounds, to direct emission from combustion engines, or to biomass combustion (Gros-

jean et al., 1978; Simoneit, 1986; Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993; Rogge et al., 1993a, 1998; Kawamura et al., 1996; Limbeck and Puxbaum, 1999). It has been demonstrated that they accumulate in aerosols and account for 1–15% of the total aerosol carbon (Kawamura and Ikushima, 1993; Kawamura et al., 1996), and exhibit their highest concentrations during periods of increased solar radiation (Kawamura et al., 1995). In addition to  $\omega$ -dicarboxylic acids, keto mono- and dicarboxylic acids and  $\alpha$ -dicarbonyls have also been reported to be atmospheric oxidation products (Kawamura, 1993; Kawamura et al., 1996). For example, the major oxidation products of the

\* Corresponding author. Tel.: + 32-23-820-2707; fax: + 32-23-820-2734.

E-mail address: claeys@uia.ua.ac.be (M. Claeys).

unsaturated fatty acid, oleic acid, which is sensitive to atmospheric oxidation, include nonadioic acid (azelaic acid) and 9-oxononanoic acid (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993).

In this study, we have focused on the structural characterization, using mass spectral approaches, of unknown dicarboxylic acids and related compounds of similar polarity, which were present at elevated levels in tropical aerosols collected in the Amazon basin, Brazil, during the wet season and which were also important in urban aerosols collected during summer in Gent, Belgium. These compounds, denoted here as “oxidative degradation products”, have, to our knowledge, not been reported before in atmospheric aerosols. As these compounds were enriched in the fine size fraction ( $< 2 \mu\text{m}$ ) of the tropical aerosol, suggesting that they were secondary organic aerosol constituents (i.e., formed by gas-to-particle conversion processes) and were also substantially enhanced in the urban aerosol during a period of increased ozone concentrations, they may have significance as markers for atmospheric oxidation processes. It is unlikely that the novel characterized oxidative degradation products in the aerosol samples from Brazil originate from biomass combustion or other combustion processes. The collections in Brazil took place during the wet (non-biomass-burning) season, and the atmospheric concentrations of typical pyrogenic indicators such as submicrometer-sized potassium and black carbon were generally very low (Maenhaut et al., 1998, and unpublished results). For the chemical characterization of the compounds, use was made of gas chromatography/mass spectrometry (GC/MS). In order to facilitate the structural characterization, different volatile derivatives were prepared, including methyl esters, trimethylsilyl (TMS) esters, and methyl ester, methoxime derivatives. Derivatization of methyl esters into methoxime derivatives was especially useful to reveal the presence of keto groups. However, as the structural characterization of most of the unknown compounds was solely based on the interpretation of the mass spectral data obtained for the different derivatives, their identification should be regarded as tentative.

## 2. Experimental

### 2.1. Aerosol collections and analyses

As part of the LBA–CLAIRE-98 experiment (CLAIRE = Cooperative LBA Airborne Regional Experiment; LBA = Large Scale Biosphere–Atmosphere Experiment in Amazonia), atmospheric aerosols were collected in Balbina ( $1^{\circ}55'S$ ,  $59^{\circ}24'W$ ), 130 km north of Manaus, Brazil, during the wet season. The collection devices included a total filter sampler, a Hi-Vol dichotomous sampler, several Gent PM10 stacked filter

unit (SFU) samplers, and different types of cascade impactors. The collection time per sample varied from 12 h to 2 d, and samples were taken from 23 March until 15 April 1998. As part of a different study (Claeys et al., 1999; Kubátová et al., 1999), daily aerosol samples were also taken with a total filter sampler and with Gent PM10 SFU samplers in Gent, Belgium, during winter and summer campaigns in 1998. The total filter samplers used in Balbina and Gent were of the same design. The open-faced samplers used a 47-mm diameter Whatman QM-A quartz fiber filter. They were equipped with a cylindrical intake tube facing downward, and were operated at a flow rate of  $150 \text{ l min}^{-1}$ . The Hi-Vol dichotomous sampler used was designed by Solomon et al. (1983). It separates the aerosol into two size fractions, coarse and fine, with the separation between the two fractions at about  $2\text{--}3 \mu\text{m}$  equivalent aerodynamic diameter (EAD). Pallflex quartz fiber filters were used to collect both size fractions. The Gent PM10 SFU sampler (Maenhaut et al., 1994) operates at a flow rate of  $171 \text{ l min}^{-1}$  and provides two size fractions, coarse ( $2\text{--}10 \mu\text{m}$  EAD) and fine ( $< 2 \mu\text{m}$  EAD). The coarse filter is a 47 mm diameter,  $8 \mu\text{m}$  pore size, Apiezon-coated Nuclepore polycarbonate filter, whereas virtually any type of 47 mm diameter filter with high collection efficiency can be used as fine filter. In some of the Gent PM10 SFU samplers, a Whatman QM-A quartz fiber filter was used to collect the fine size fraction.

All filters, except those from the Hi-Vol, were weighed before and after sampling to determine the particulate mass (PM). The weighings were done at  $20^{\circ}\text{C}$  and 50% relative humidity and the filters were pre-equilibrated at these conditions for at least 24 h before the actual weighings. Furthermore, all quartz filters were subjected to analysis for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission technique (Birch and Cary, 1996). This technique delivers OC and EC results in  $\mu\text{g(C)} \text{ m}^{-3}$ . To convert the measured OC value to organic aerosol mass one needs to account for the other atoms in the OC molecules and multiplying factors ranging from 1.2 to 1.8 are used to do so (Seinfeld and Pandis, 1997). For both Balbina and Gent, the  $\text{PM}_{\text{tot}}$  aerosol data derived from the total filter samples agreed well with the PM10 levels from SFU samples taken in parallel, indicating that there was either relatively little aerosol mass in the size fraction above  $10 \mu\text{m}$  EAD or that this size fraction was not efficiently collected by our “total” aerosol sampler.

### 2.2. Detailed analyses for organic compounds

Selected total and Hi-Vol filter samples (and field blanks) from Balbina were subjected to detailed analyses for organic compounds. Similar analyses were also done on total filter samples from the 1998 study on the Gent aerosol (Claeys et al., 1999; Kubátová et al., 1999). The

detailed measurements for organic compounds involved quantitative analyses by means of capillary gas chromatography (GC)-flame ionization detection (FID) and qualitative analyses by GC/MS, using a modification of the method originally described by Mazurek et al. (1987, 1989). The filter samples were extracted in 25 ml Pyrex glass flasks with Teflon-lined stoppers (Mazurek et al., 1987). All glassware was deactivated with diazomethane prior to use. Before extraction, a mixture of three perdeuterated recovery standards (isoquinoline, tetradecanoate, dotriacontane) was added to correct for losses during sample work-up. The volume of recovery standard (RS) mixture added was related to the amount of OC in the sample, in order to keep the heights of the RS peaks of the same intensity as those of the sample peaks in the chromatograms. The samples were extracted three times, each time for 30 min with 20 ml of dichloromethane under ultrasonic agitation (Simoneit and Mazurek, 1982; Abas and Simoneit, 1996). This procedure was applied to three total filter samples and to the fine and coarse filters of two Hi-Vol samples from Balbina. For the total filters, the percentage of extractable and elutable organic compounds (EEOC), relative to OC determined with the TOT technique, was limited to 6%, whereas EEOC yields of around 20% were typical for total filter samples from Gent (Kubátová et al., 1999). It was therefore decided to use acidification prior to extraction for two additional total filters and for the fine and coarse filters of two additional Hi-Vol samples from Balbina. The acidification was the same as used by Stephanou and Stratigakis (1993) and was intended to release acids present in the salt form. This procedure resulted in an increased EEOC yield of 16% for the total filter samples. The extraction efficiency was tested for azelaic acid, was found to be higher than 95%, and was assumed to be similar for tricarboxylic acids because extraction was performed after acidification.

For each filter, the combined dichloromethane extracts were concentrated employing a rotary evaporator (533 hPa, 27°C) to about 1 ml. Subsequently, the concentrated extract was filtered through a Teflon syringe filter (0.45 µm pore size) and completely dried under a stream of nitrogen. Finally, the dried sample was redissolved in dichloromethane/cyclohexane (30 µl; 1:1, v/v). Part of the solution was directly analyzed by GC with co-injection of an internal standard (1-phenyldodecane) to correct for retention time shifts. The remainder of the solution was methylated with diazomethane, and the internal standard was added.

The GC-FID analyses of the methylated samples were used to obtain quantitative data on the total extractable and elutable mass of organic compounds (EEOC). The GC-FID mass determination was based on the response of known amounts of internal standard and recovery standards (Mazurek et al., 1987). The GC-FID analyses were performed with an 8000 Top gas

chromatograph (Carlo Erba, Milan, Italy). A non-polar capillary column CP Sil 8CB (95% dimethyl, 5% phenyl polysiloxane; 0.25 µm film thickness, 0.25 mm i.d., 30 m length; Chrompack, Middelburg, The Netherlands) was employed, as this column also exists as a low-bleed version which could be used for GC/MS. Injections were performed in the splitless mode (90 s). Helium was employed as carrier at a pressure of 100 kPa. The flow rates of the detector gases were 30 ml min<sup>-1</sup> for H<sub>2</sub> and He and 300 ml min<sup>-1</sup> for air. The injector and detector temperatures were 250 and 320°C, respectively. The following temperature program was used: first 1.5 min at 60°C isothermally, then a steep gradient of 25°C min<sup>-1</sup> to 100°C, followed by 5 min at 100°C isothermally, then a gradient of 5°C min<sup>-1</sup> to 315°C, followed by 35 min at 315°C isothermally.

Qualitative analyses were performed by GC/MS, using an HP 5890 gas chromatograph (Hewlett Packard, USA) connected to a VG 70 SEQ hybrid mass spectrometer (Micromass, Manchester, UK). The gas chromatograph was equipped with a capillary column CP Sil 8CB – low bleed (95% dimethyl, 5% phenyl polysiloxane; 0.25 µm film thickness, 0.25 mm i.d., 30 m length; Chrompack, Middelburg, The Netherlands). GC/MS analyses were performed in the electron impact (EI) ionization mode with an electron energy of 70 eV and the mass range *m/z* 50–550 was scanned at 1.5 s decade<sup>-1</sup>. The analyses were performed under the same temperature program as used for GC-FID. Helium was employed as carrier gas at a pressure of 50 kPa. The temperatures of the injector and the transfer line were set at 250 and 275°C, respectively.

The identification was based on mass chromatograms obtained for major mass fragment ions of different classes of compounds. The individual components in the aerosol samples were identified using computer matches to standard reference mass spectra of the National Institute of Standards and Technology (NIST) library and the identification was confirmed by comparison to reference compounds, where available. For the identification of compounds, the a, b, c, d labeling introduced by Rogge et al. (1991) was followed. Compounds were designated: (a) *positive*, when the sample spectrum, reference compound spectrum, and NIST-library spectrum were identical and also the retention times of the authentic compound and the sample compound were comparable; (b) *probable*, same as above, except that no authentic reference compound was available, but the NIST-library spectrum agreed very well with the sample spectrum; (c) *possible*, same as above, except that the sample mass fragmentation pattern contained additional ions from other compounds having minor peak co-elution; and (d) *tentative*, when the sample spectrum revealed additional mass fragments from one or more co-eluting compounds (noise) with substantial overlap. The retention times in the GC/MS mass chromatograms used for identification

have to be related to those in the GC-FID chromatograms used to quantify the individual organic compounds. Therefore, both types of analyses were performed on the same column under similar chromatographic conditions.

### 2.3. Derivatizations and analyses for characterizing unknown compounds

In order to obtain specific structural information on unknown compounds which were present at significant levels in the Balbina samples and which had also been detected in summer aerosols from Gent, different derivatization techniques were applied. As more samples were available for Gent than for Balbina, the derivatizations and structural characterizations were performed on selected Gent samples which were collected during a hot period in August 1998 with increased ozone levels. For these samples, the redissolved dried dichloromethane extract was divided into three parts: one part was analyzed directly, the second part was methylated with diazomethane, and the third part was trimethylsilylated. Trimethylsilylation was performed by adding *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA)/pyridine (60  $\mu$ l; 1:1, v/v) and reacting for 1 h at room temperature. After analysis of the methylated part, the remainder was trimethylsilylated and re-analyzed.

Additional analyses were performed on fractions of different polarity obtained from pooled methylated samples from the hot summer period in Gent. For fractionation, a 500 mg silica gel solid-phase extraction cartridge (IST, Belgium) was used, and five fractions were obtained

by eluting with 10 ml of the following solvent systems: (1) cyclohexane; (2) 5% dichloromethane in cyclohexane; (3) 60% dichloromethane in cyclohexane; (4) 10% methanol in dichloromethane; and (5) methanol. All fractions were evaporated under a stream of nitrogen, reconstituted in dichloromethane/cyclohexane (50  $\mu$ l; 1:1, v/v), and analyzed by GC/MS. The remainder of each of the five fractions was then divided: one part of each was derivatized with BSTFA and the other with methoxyamine, and both parts were again analyzed by GC/MS. Derivatization with methoxyamine was performed by the addition of a solution of methoxyamine hydrochloride in pyridine (30  $\mu$ l; 0.5%). The derivatization mixture was kept overnight, dried, and the residue was reconstituted into the original volume of solvent.

## 3. Results and discussion

### 3.1. Overview of selected aerosol parameters for Balbina

During the first week of the LBA–CLAIRE-98 campaign at Balbina, high PM<sub>10</sub> levels up to 35  $\mu$ g m<sup>-3</sup> at standard temperature and pressure (STP: 1013 hPa, 0°C) and elevated concentrations of mineral dust elements (Al, Si, Fe) were noted. During this week, mineral dust accounted for approximately 80% of the PM<sub>10</sub> aerosol mass (Maenhaut et al., 1998). Air mass trajectories indicated that the mineral dust was advected from northern Africa. After about 30 March 1998, the PM<sub>10</sub> aerosol levels remained fairly constant at around 7  $\mu$ g m<sup>-3</sup> STP, and the organic aerosol became the dominant aerosol

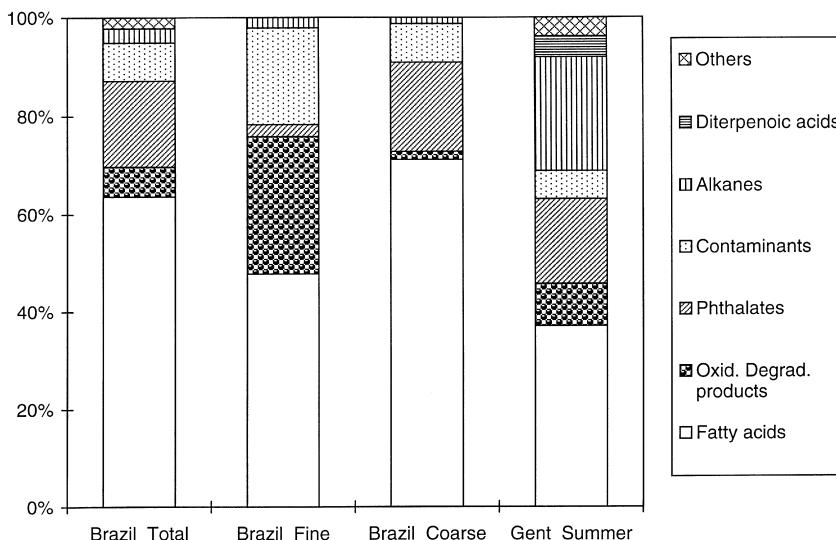


Fig. 1. Average percentage contributions of different compound classes to the identified extractable and elutable compounds (EEOC) for total filter samples and fine and coarse filters from Hi-Vol dichotomous samples collected in Balbina, Brazil. Also shown are similar average contributions for total filter samples from the 1998 hot summer period in Gent, Belgium.

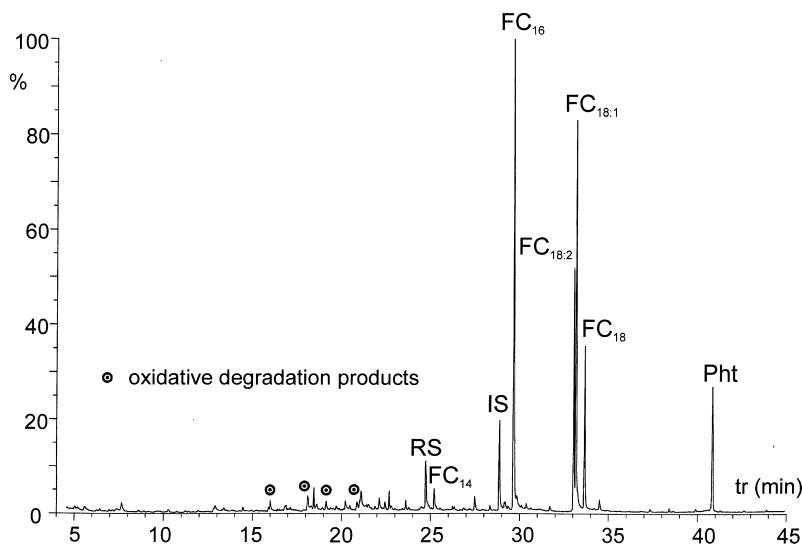


Fig. 2. GC/MS total ion chromatogram (TIC) obtained for a methylated extract of a total aerosol filter sample collected in Balbina, Brazil. Labeling:  $FC_x$ : fatty acids, where  $x$  represents the number of carbons; Pht: dioctyl phthalate; RS: recovery standard; IS: internal standard.

Table 1

Overview of known (K) oxidative degradation products found in tropical aerosols from Balbina, Brazil, and urban summer aerosols from Gent, Belgium

Systematic name (trivial name)	Label	MS ident. <sup>a</sup>	Formula	MW	Methyl esters		TMS derivatives	
					MW	$t_r$ (min)	MW	$t_r$ (min)
2-Methoxybutanedioic acid	$K_1^b$	b	$C_5H_8O_5$	148.1	176.2	8.7	292.5	16.4
3-Methoxypentanedioic acid	$K_2$	c	$C_6H_{10}O_5$	162.1	190.2	12.0	306.5	18.8
Propane-1,2,3-tricarboxylic acid	$K_3$	b	$C_6H_8O_6$	176.1	218.2	17.2	392.7	22.4
9-Oxononanoic acid	$K_4$	d	$C_9H_{19}O_3$	172.2	186.2	17.9	244.4	21.8
Nonanedioic acid (azelaic)	$K_5$	a	$C_9H_{16}O_4$	188.2	216.3	20.9	332.6	26.8
Butanedioic acid (succinic)	$KG_1^c$	a	$C_4H_6O_4$	118.1	146.1	5.6	262.5	14.1
2-Methylbutanedioic acid	$KG_2$	b	$C_5H_8O_4$	132.1	160.2	6.3	276.5	14.3
Pentanedioic acid (glutaric)	$KG_3$	b	$C_5H_8O_4$	132.1	160.2	8.4	276.5	16.9
Hexanedioic acid (adipic)	$KG_4$	b	$C_6H_{10}O_4$	146.1	174.2	11.9	290.5	19.7
4-Oxoheptanedioic acid	$KG_5$	b	$C_7H_{10}O_5$	174.2	202.2	18.9	318.5	25.2
4-Oxo-octanedioic acid	$KG_6$	b	$C_8H_{12}O_5$	188.2	216.2	21.7	332.5	27.4

<sup>a</sup>For the explanation of the codes a, b, c, and d used for identification, see Section 2.2.

<sup>b</sup> $K_x$  refers to oxidative degradation products found in both tropical and urban aerosols.

<sup>c</sup> $KG_x$  refers to products which were only found in the urban aerosol.

type. The organic aerosol in the PM<sub>10</sub> size fraction, estimated as 1.5 times OC in order to account for the other atoms in the OC molecules (Seinfeld and Pandis, 1997), was fairly constant at around  $4 \mu\text{g m}^{-3}$  STP throughout the entire campaign. The data from the SFU samples indicated that most of the PM<sub>10</sub> aerosol mass and OC were contained in the coarse (2–10  $\mu\text{m}$  EAD) fraction, i.e., when averaged over all samples, 70% of the PM<sub>10</sub> aerosol mass and 60% of the OC were in the coarse fraction.

### 3.2. Results from the detailed organic analyses and comparison of the data from Balbina with those from the hot 1998 summer period in Gent

From the detailed analyses for organic compounds, the percentage contributions of different compound classes to the identified EEOC were calculated. Such calculations were carried out for the total filter samples and also for the separate fine and coarse filters of the Hi-Vol samples from Balbina, and the results were then averaged

Table 2

Summary of mass spectral data obtained for the unknown compounds U<sub>1</sub>, U<sub>2</sub>, U<sub>3</sub>, and U<sub>4</sub>

Label	Derivative	Formula	MW	t <sub>r</sub> (min)	Ions m/z	Rel.Ab.	Assignment ions					
U <sub>1</sub>	Methyl ester	C <sub>9</sub> H <sub>14</sub> O <sub>5</sub>	202	16.04	171	25	M <sup>++</sup> -CH <sub>3</sub> O <sup>•</sup>					
					160	49	M <sup>++</sup> -CH <sub>2</sub> CO					
					139	46	M <sup>++</sup> -(CH <sub>3</sub> O <sup>•</sup> + CH <sub>3</sub> OH)					
					128	40	M <sup>++</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + H <sup>•</sup> )					
					127	19	M <sup>++</sup> -(CH <sub>3</sub> CO + CH <sub>3</sub> OH)					
					111	20	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + CH <sub>3</sub> OH)					
					100	100	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + CH <sub>3</sub> CO <sup>•</sup> )					
					97	34	M <sup>++</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + CH <sub>3</sub> OH)					
					59	43	CH <sub>3</sub> OCO <sup>+</sup>					
					TMS ester	C <sub>13</sub> H <sub>26</sub> O <sub>5</sub> Si <sub>2</sub>	318	22.5	303	21	M <sup>++</sup> -CH <sub>3</sub> <sup>•</sup>	
									276	32	M <sup>++</sup> -CH <sub>2</sub> CO	
									275	20	M <sup>++</sup> -CH <sub>3</sub> CO <sup>•</sup>	
									185	50	M <sup>++</sup> -(CH <sub>3</sub> CO <sup>•</sup> + TMSOH)	
	158	49	M <sup>++</sup> -(TMSOCO <sup>•</sup> + CH <sub>3</sub> CO <sup>•</sup> )									
	147	26	TMSO <sup>+</sup> =Si(CH <sub>3</sub> ) <sub>2</sub>									
	117	17	TMSOCO <sup>+</sup>									
	111	33	M <sup>++</sup> -(TMSOCO <sup>•</sup> + TMSOH)									
	Methyl ester, methoxime <sup>a</sup>	C <sub>10</sub> H <sub>17</sub> O <sub>5</sub> N	231	18.17/18.35					231	3/6	M <sup>++</sup>	
									200	19/61	M <sup>++</sup> -CH <sub>3</sub> O <sup>•</sup>	
					199	21/33	M <sup>++</sup> -CH <sub>3</sub> OH					
					172	23/31	M <sup>++</sup> -CH <sub>3</sub> OCO <sup>•</sup>					
					168	13/18	M <sup>+</sup> -(CH <sub>3</sub> O <sup>•</sup> + CH <sub>3</sub> OH)					
					140	100/100	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + CH <sub>3</sub> OH)					
126					19/33	M <sup>+</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + CH <sub>3</sub> OH)						
U <sub>2</sub>					Methyl ester	C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>	202	18.18	187	8	M <sup>++</sup> -CH <sub>3</sub> <sup>•</sup>	
									171	100	M <sup>++</sup> -CH <sub>3</sub> O <sup>•</sup>	
	157	23	M <sup>++</sup> -(CH <sub>3</sub> + H <sub>2</sub> CO)									
	155	34	M <sup>++</sup> -(CH <sub>3</sub> + CH <sub>3</sub> OH)									
	139	63	M <sup>++</sup> -(CH <sub>3</sub> O <sup>•</sup> + CH <sub>3</sub> OH)									
	138	50	M <sup>+</sup> -2xCH <sub>3</sub> OH									
	129	49	M <sup>++</sup> -CH <sub>3</sub> OCOCH <sub>2</sub>									
	111	40	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + CH <sub>3</sub> OH)									
	100	73	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + C <sub>3</sub> H <sub>7</sub> <sup>•</sup> )									
	97	73	M <sup>++</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + CH <sub>3</sub> OH)									
	74	59	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> <sup>+</sup>									
	59	59	CH <sub>3</sub> OCO <sup>+</sup>									
	TMS ester	C <sub>14</sub> H <sub>30</sub> O <sub>4</sub> Si <sub>2</sub>	318	24.021					303	3	M <sup>++</sup> -CH <sub>3</sub> <sup>•</sup>	
					215	9	M <sup>++</sup> -[CH <sub>3</sub> + (CH <sub>3</sub> ) <sub>2</sub> SiOCH <sub>2</sub> ]					
					147	14	TMSO <sup>+</sup> =Si(CH <sub>3</sub> ) <sub>2</sub>					
					117	13	TMSOCO <sup>+</sup>					
					U <sub>3</sub>	Methyl ester	C <sub>11</sub> H <sub>18</sub> O <sub>6</sub>	246	19.21	215	21	M <sup>++</sup> -CH <sub>3</sub> O <sup>•</sup>
										187	5	M <sup>++</sup> -CH <sub>3</sub> OCO <sup>•</sup>
	155	100	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + CH <sub>3</sub> OH)									
	146	35	M <sup>++</sup> -CH <sub>3</sub> OCOC <sub>3</sub> H <sub>5</sub>									
	127	28	M <sup>++</sup> -(2CH <sub>3</sub> OCO <sup>•</sup> + H <sup>•</sup> )									
	113	21	M <sup>++</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + CH <sub>3</sub> OCOH)									
	TMS ester	C <sub>17</sub> H <sub>36</sub> O <sub>6</sub> Si <sub>3</sub>	420	25.75		405	5	M <sup>++</sup> -CH <sub>3</sub> <sup>•</sup>				
287						2	M <sup>++</sup> -(CH <sub>3</sub> + TMSOCO <sup>•</sup> + H <sup>•</sup> )					
261						1	M <sup>++</sup> -TMSOCOC <sub>3</sub> H <sub>6</sub>					
245	7	M <sup>++</sup> -(CH <sub>3</sub> + TMSOCOC <sub>3</sub> H <sub>7</sub> )										
213	4	287-(CH <sub>3</sub> ) <sub>3</sub> SiO										
171	5	264-TMSOH										
147	24	TMSO <sup>+</sup> =Si(CH <sub>3</sub> ) <sub>2</sub>										

Table 2 (continued)

Label	Derivative	Formula	MW	$t_r$ (min)	Ions $m/z$	Rel.Ab.	Assignment ions			
U <sub>4</sub>	Methyl ester	C <sub>10</sub> H <sub>16</sub> O <sub>5</sub>	216	19.15	185	63	M <sup>++</sup> -CH <sub>3</sub> O <sup>•</sup>			
					184	72	M <sup>++</sup> -CH <sub>3</sub> OH			
					174	52	M <sup>++</sup> -CH <sub>2</sub> CO			
					153	98	M <sup>++</sup> -(CH <sub>3</sub> O <sup>•</sup> + CH <sub>3</sub> OH)			
					143	15	M <sup>++</sup> -CH <sub>3</sub> OCOCH <sub>2</sub>			
					142	37	M <sup>++</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + H <sup>•</sup> )			
					141	24	M <sup>++</sup> -(CH <sub>3</sub> CO <sup>•</sup> + CH <sub>3</sub> OH)			
					125	30	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + CH <sub>3</sub> OH)			
					124	10	M <sup>++</sup> -(2xCH <sub>3</sub> OH + CO)			
					114	50	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + CH <sub>3</sub> CO <sup>•</sup> )			
					111	49	M <sup>++</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + CH <sub>3</sub> OH)			
					101	100	M <sup>++</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + CH <sub>2</sub> CO)			
					TMS ester	C <sub>14</sub> H <sub>28</sub> O <sub>5</sub> Si <sub>2</sub>	332	25.09	317	6
	290	3	M <sup>++</sup> -CH <sub>2</sub> CO							
	289	3	M <sup>++</sup> -CH <sub>3</sub> CO <sup>•</sup>							
	243	3	M <sup>++</sup> -TMSO <sup>•</sup>							
	199	6	M <sup>++</sup> -(CH <sub>3</sub> CO <sup>•</sup> + TMSOH)							
	185	10	M <sup>++</sup> -(TMSO <sup>•</sup> + CH <sub>3</sub> CO <sup>•</sup> + CH <sub>3</sub> )							
	172	4	M <sup>++</sup> -(TMSOCO <sup>•</sup> + CH <sub>3</sub> CO <sup>•</sup> )							
	Methyl ester, methoxime <sup>a</sup>	C <sub>11</sub> H <sub>19</sub> O <sub>5</sub> N	245	21.08/21.32	245	31/12	M <sup>++</sup>			
214					81/79	M <sup>++</sup> -CH <sub>3</sub> O <sup>•</sup>				
213					68/19	M <sup>++</sup> -CH <sub>3</sub> OH				
186					58/23	M <sup>++</sup> -CH <sub>3</sub> OCO <sup>•</sup>				
172					63/65	M <sup>++</sup> -CH <sub>3</sub> OCOCH <sub>2</sub>				
154					100/67	M <sup>++</sup> -(CH <sub>3</sub> OCO <sup>•</sup> + CH <sub>3</sub> OH)				
140					21/100	M <sup>++</sup> -(CH <sub>3</sub> OCOCH <sub>2</sub> + CH <sub>3</sub> OH)				

<sup>a</sup>In the case of the methyl ester, methoxime derivatives, retention times ( $t_r$ ) and relative ion abundances are given for the two (*syn* and *anti*) isomers.

over the samples of the same type. The average percentage contributions, as obtained from the samples that were acidified prior to the dichloromethane extraction, are shown in Fig. 1, where they are compared with the average data from total filter samples from the 1998 hot summer period in Gent. Fatty acids were the major identified compounds in Balbina, and the unsaturated acids, oleic (FC<sub>18:1</sub>) and linoleic (FC<sub>18:2</sub>) acid, exhibited a very high relative abundance (Fig. 2). The high abundance of these unsaturated fatty acids and especially of linoleic acid, which is very sensitive to oxidation, is worth noting. The average concentrations of the fatty acids at Balbina and during the 1998 hot summer period in Gent were 149 and 121 ng m<sup>-3</sup>, respectively, and thus comparable. The fatty acids in Balbina undoubtedly result from biogenic emissions, but in Gent, anthropogenic sources may also be quite important. Meat cooking, tire wear, and road dust have all been indicated as sources of fatty acids in urban aerosols (Rogge et al., 1991, 1993b; Seinfeld and Pandis, 1997). Fig. 1 further shows that the tropical aerosols from Balbina contained only traces of

alkanes, whereas these compounds were abundant in the urban aerosols from Gent. In contrast, for the class of oxidative degradation products, the percentage contributions were similar for the total filter samples from both sites. As explained in more detail below, included in this compound class were the known dicarboxylic acids and related compounds (Table 1), the unknowns which were characterized in the current study (Table 2), and some other unknown related compounds. The average concentrations of the oxidative degradation products in the total filter samples from Balbina and the 1998 hot summer period in Gent were 14 and 28 ng m<sup>-3</sup>, respectively. As seen in Fig. 1, the oxidative degradation products were clearly much more important in the fine size fraction than in the coarse aerosol at Balbina. This suggests that they were mainly formed by gas-to-particle conversion processes and thus correspond to secondary organic aerosol.

Figs. 3a and b show partial total ion current GC/MS chromatograms for the methylated fraction of total filter samples from Balbina and the 1998 hot summer period in Gent. The region displayed is from 4 to 24 min, where the

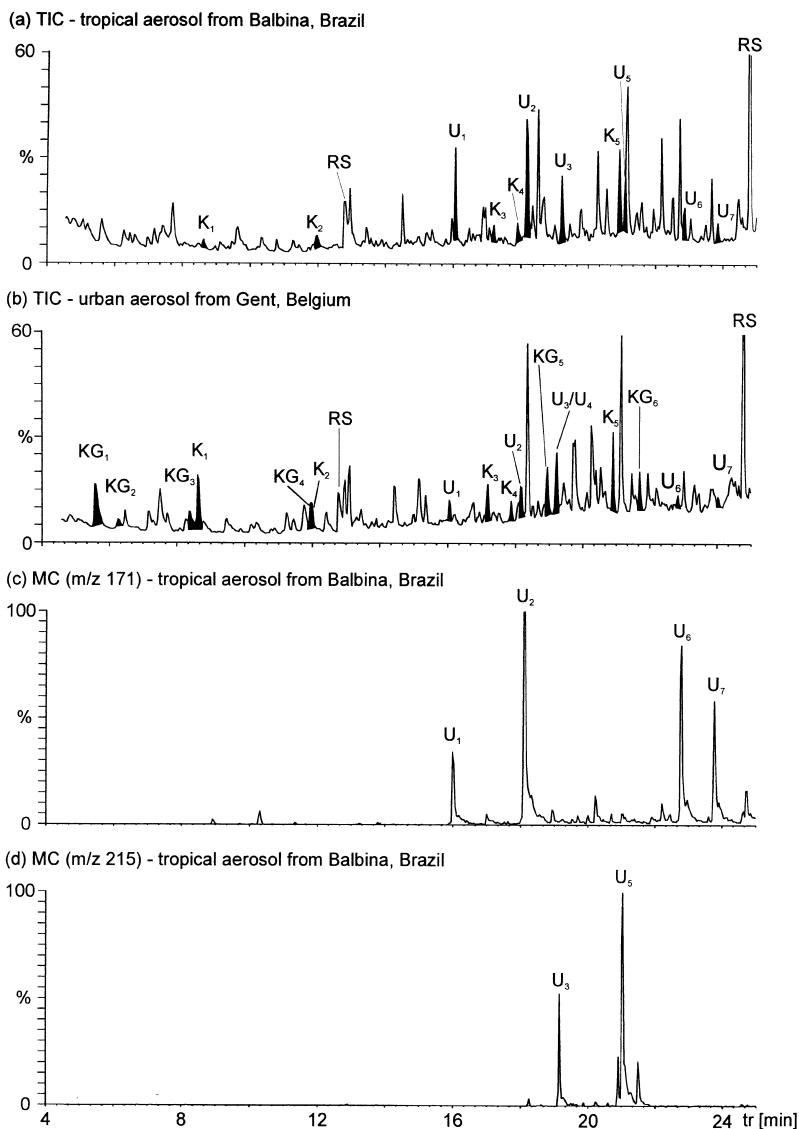


Fig. 3. Partial GC/MS total ion chromatogram obtained for the methylated extract of total filter samples collected in (a) Balbina, Brazil, and (b) Gent, Belgium. For abbreviations  $K_x$  and  $KG_x$ , see Table 1;  $U_x$  refers to unknown compounds which were characterized in the present work; RS: recovery standards. The two bottom panels show the corresponding mass chromatograms (MC) obtained for the methylated extract of a total filter sample collected in Balbina, Brazil, by using (c)  $m/z$  171 and (d)  $m/z$  215.

oxidative degradation products elute from the capillary column. A number of peaks labeled K or KG could be identified, with those labeled KG only observed in the Gent samples and those labeled K observed in the samples from both sites. A summary of relevant GC/MS data obtained for these known compounds is given in Table 1. Peaks labeled U in Figs. 3a and b refer to unknown compounds which contained fragment ions typical of methylated dicarboxylic acids, and, therefore, are also likely to be atmospheric oxidation products. These unknown compounds were present in the samples from

both Balbina and Gent. Figs. 3c and d show mass chromatograms for a methylated extract from Balbina, obtained by using ions at  $m/z$  171 and 215 which correspond to the  $[M-CH_3O]^+$  fragment ions of methylated  $C_7$  and  $C_9$  dicarboxylic acids, respectively.

### 3.3. Results from derivatizations and analyses for characterizing unknown compounds

As indicated in Section 2.3, more samples were available for Gent than for Balbina. The derivatizations and

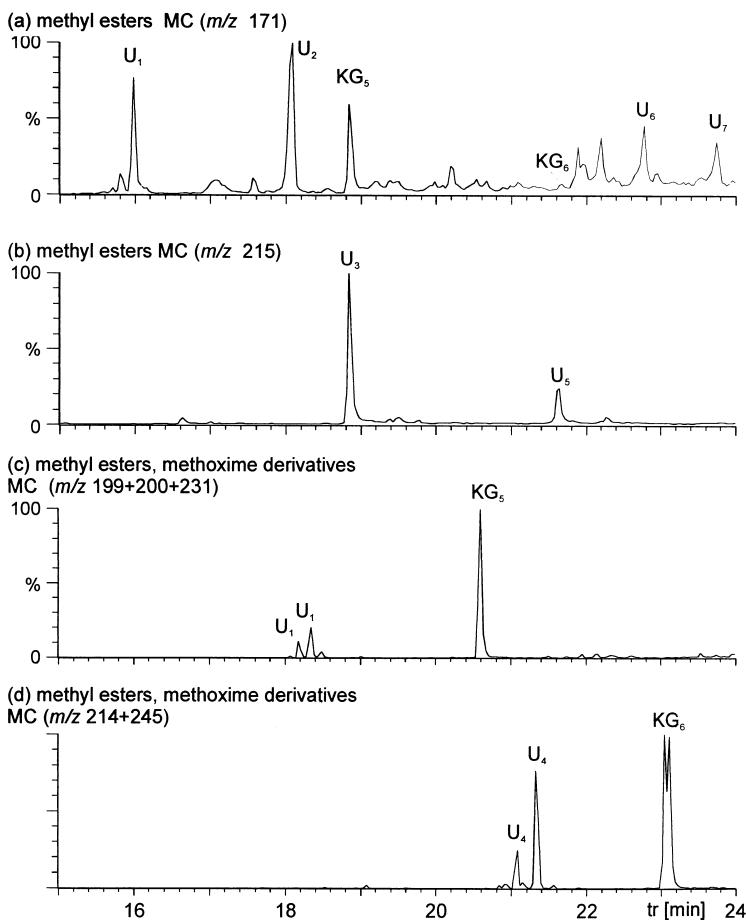


Fig. 4. Mass chromatograms obtained for the fraction containing the oxidative degradation products from pooled methylated extracts of Gent total filter samples (see text for details). The two top panels were obtained for the original methyl ester derivatives by using (a)  $m/z$  171 and (b)  $m/z$  215, whereas the two bottom panels were obtained after additional methoxime derivatization and were constructed by using (c)  $m/z$  199, 200, and 231, and (d)  $m/z$  214 and 245.

all further structural characterizations for the unknown compounds were therefore performed with total filter samples from the 1998 hot summer period in Gent. Of the five fractions obtained by silica gel solid-phase extraction of the pooled methylated extracts, fraction 4 was found to contain the unknown oxidative degradation products. This methylated fraction, the methoxime derivatives prepared from it, and the TMS esters prepared from the original non-methylated extract were analyzed by GC/MS. Table 2 summarizes the relevant mass spectral data for the various derivatives of the unknown compounds  $U_1$ ,  $U_2$ ,  $U_3$ , and  $U_4$ . It should be noted here that methoxime derivatization of the keto groups of the methyl esters resulted in two different isomers (*syn* and *anti*) with slightly different retention times ( $t_r$ ), which are both given in Table 2. Figs. 4a–d show mass chromatograms obtained on fraction 4 without (a, b) and with (c, d) subsequent methoxime derivatization. The mass spectra

of the different derivatives of unknown  $U_1$  are given in Fig. 5. For the other unknowns  $U_2$ ,  $U_3$ , and  $U_4$ , the spectra of the methyl ester derivatives are presented in Fig. 6.

The EI spectrum of the methyl ester of  $U_1$  (Fig. 5a) shows an intense peak at  $m/z$  171 which was interpreted as the  $[M-CH_3O]^+$  ion and indicates a molecular weight of 202. The spectrum of the corresponding TMS-derivative (Fig. 5b) shows a fragment ion at  $m/z$  303 which is due to the  $[M-CH_3]^+$  ion and indicates a molecular weight of 318 for the TMS-derivative and of 174 for the underivatized compound, and confirms the presence of two carboxylic functions. The presence of a keto group was revealed by methoximation of the methyl ester, which yielded two isomeric (*syn* and *anti*) derivatives (Fig. 4) showing an  $M^{++}$  ion at  $m/z$  231 (Figs. 5c and d). The formation of two isomeric (*syn* and *anti*) derivatives upon methoxime derivatization points to an

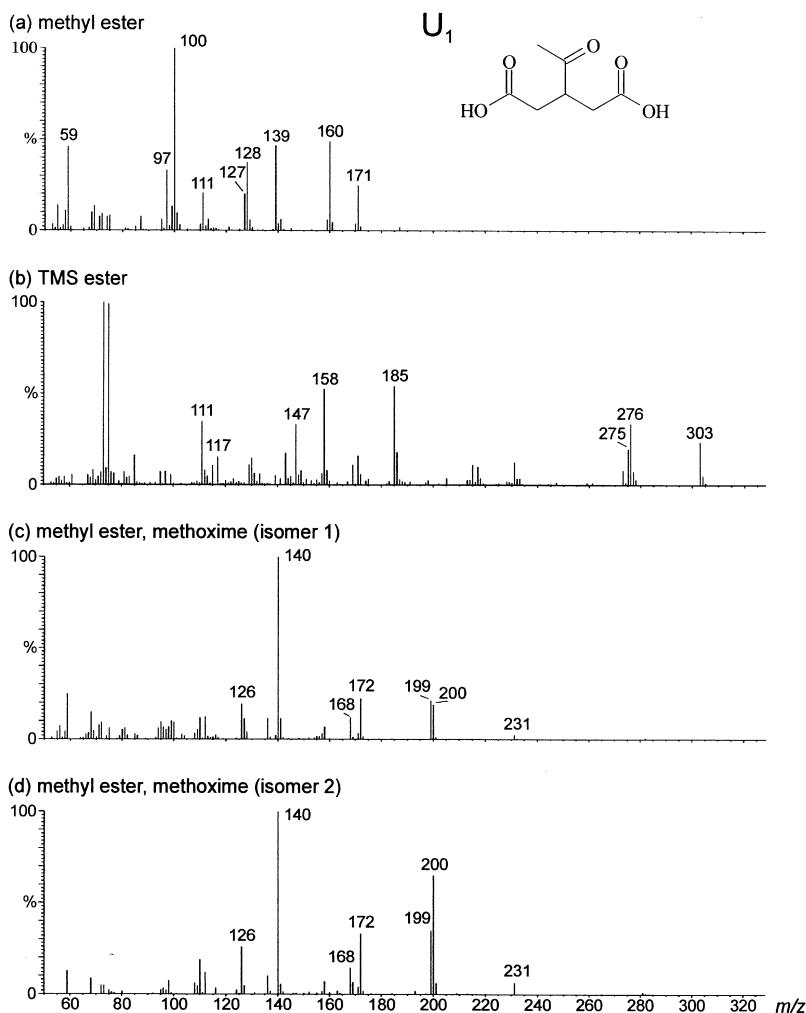


Fig. 5. Mass spectra obtained for the unknown  $U_1$  characterized as 3-acetyl pentanedioic acid: (a) methyl ester, (b) TMS ester, (c) and (d) methyl ester, methoxime derivatives.

asymmetric nature of the keto derivative. The ion at  $m/z$  160 in the spectrum of the methyl ester (Fig. 5a) corresponds to the loss of 42 units and is in agreement with the loss of ketene ( $\text{CH}_2\text{CO}$ ) from an acetyl derivative (Scheme 1a). Other features in the mass spectra of the methyl ester (weak  $[\text{M}-\text{CH}_3]^+$  ion at  $m/z$  187) and of the TMS-derivative ( $[\text{M}-\text{CH}_2\text{CO}]^+$  ion at  $m/z$  276 and  $[\text{M}-\text{CH}_3\text{CO}]^+$  ion at  $m/z$  275) support the presence of an acetyl group; this group must be located at the 3-position of pentanedioic acid, because in the case of 2-substitution we would expect keto-enol tautomerism and the formation of trimethyl derivatives upon reaction with diazomethane. Based on the combined mass spectral data, unknown  $U_1$  was tentatively identified as 3-acetyl pentanedioic acid.

The EI spectrum of the methyl ester of  $U_2$  (Fig. 6a) is similar to that of  $U_1$ ; it shows an intense peak at  $m/z$  171

which is due to the  $[\text{M}-\text{CH}_3\text{O}]^+$  ion and indicates an MW of 202. The spectrum of the corresponding TMS-derivative revealed a fragment ion at  $m/z$  303 which was interpreted as the  $[\text{M}-\text{CH}_3]^+$  ion and indicates an MW of 318 for the TMS-derivative and of 174 for the un-derivatized compound, and is consistent with the presence of two carboxylic functions. In contrast to  $U_1$ ,  $U_2$  was not found to contain a keto group since no reaction of the methyl ester occurred with methoxyamine. Based on the interpretation of the mass spectral data of both the methyl ester and TMS-ester derivatives,  $U_2$  was tentatively identified as 3-isopropyl pentanedioic acid. The ion at  $m/z$  187 in the spectrum of the methyl ester can be explained by the loss of a methyl substituent which is in close proximity to the carboxylic acid function (Scheme 1b) and supports the presence of a 3-isopropyl rather than a 3-*n*-propyl substituent. The

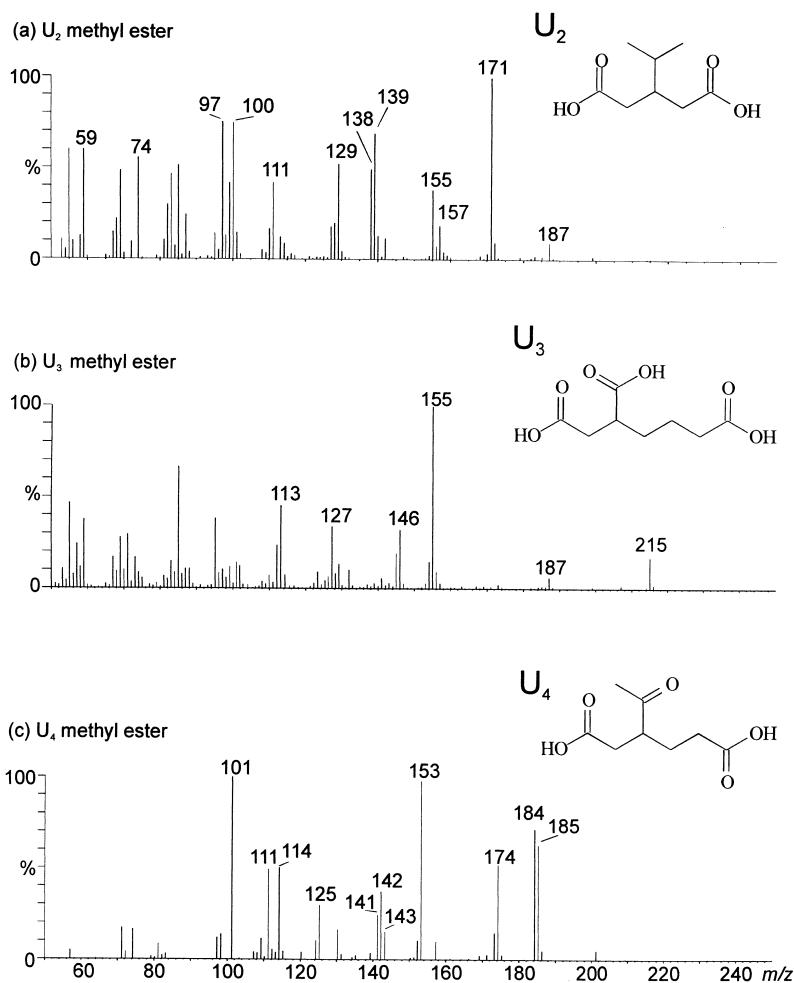
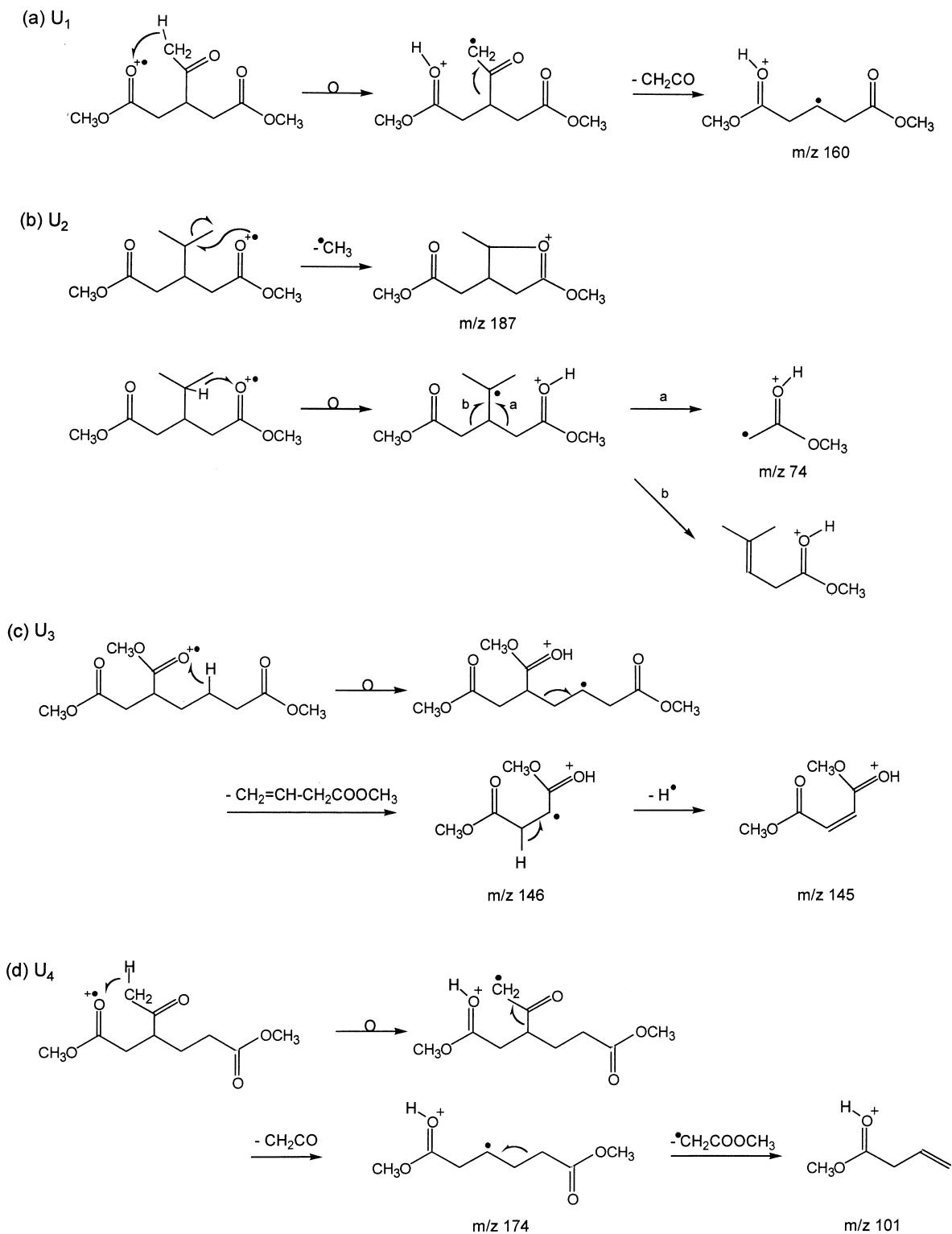


Fig. 6. Mass spectra obtained for the methyl esters of unknowns  $U_2$ ,  $U_3$ , and  $U_4$ .

ion at  $m/z$  74 can be explained by a McLafferty rearrangement; the presence of this ion and the formation of an ion at  $m/z$  129 are in agreement with 3-substitution (Scheme 1b).

The EI spectrum of the methyl ester of  $U_3$  (Fig. 6b) shows a peak at  $m/z$  215 which is due to the  $[M-CH_3O]^+$  ion and indicates an MW of 246. The spectrum of the corresponding TMS-derivative revealed a fragment ion at  $m/z$  405 which was interpreted as the  $[M-CH_3]^+$  ion and indicates an MW of 420 for the TMS-derivative and of 204 for the underivatized compound, and is thus consistent with the tricarboxylic nature of the compound. Based on the interpretation of the mass spectral data of both the methyl ester and TMS-ester derivatives, unknown  $U_3$  was tentatively identified as 3-carboxy heptanedioic acid. The formation of the ions at  $m/z$  145 and 146 can be explained by a McLafferty rearrangement (Scheme 1c) and supports the proposed structure.

The EI spectrum of the methyl ester of  $U_4$  (Fig. 6c) shows a peak at  $m/z$  185 corresponding to the  $[M-CH_3O]^+$  ion and indicates an MW of 216. The spectrum of the TMS-derivative revealed a fragment ion at  $m/z$  317 which was interpreted as the  $[M-CH_3]^+$  ion and indicates an MW of 332 for the TMS-derivative and of 188 for the underivatized compound, and is thus in agreement with a dicarboxylic nature of the compound. The presence of a keto group was indicated by methoxime derivatization of the methyl ester which resulted in two isomeric (*syn* and *anti*) methoxime derivatives (Fig. 4) yielding an  $M^{+}$  ion at  $m/z$  245. Based on the interpretation of the mass spectral data of the methyl ester, TMS-ester, and methyl ester, methoxime derivatives (Table 2), unknown  $U_4$  was tentatively identified as 3-acetyl hexanedioic acid. The ion at  $m/z$  174 in the spectrum of the methyl ester is due to the loss of ketene ( $CH_2CO$ ) and supports the presence of an acetyl group (Scheme 1d). As already discussed for  $U_1$ , this acetyl

Scheme 1. Diagnostic electron impact fragmentations for methyl esters of unknowns  $U_1$ ,  $U_2$ ,  $U_3$ , and  $U_4$ .

group cannot be located at the 2-position because in this case we would expect keto–enol tautomerism and formation of a trimethyl derivative upon derivatization with diazomethane. The base peak at  $m/z$  101 can readily be explained by the combined loss of ketene and of a  $\text{CH}_3\text{COOCH}_2$  radical (Scheme 1d) and supports the proposed structure.

In addition to unknowns  $\text{U}_1$ ,  $\text{U}_2$ ,  $\text{U}_3$ , and  $\text{U}_4$ , other unknowns labeled  $\text{U}_5$ ,  $\text{U}_6$ , and  $\text{U}_7$  were found in both the tropical aerosol from Balbina and the urban aerosol from Gent (Fig. 3). For these unknowns, which were present in low concentrations at Gent, only a partial characterization could be achieved. Unknown  $\text{U}_5$  was isobaric to  $\text{U}_3$  and, therefore, is likely to correspond to an isomer of 3-carboxy heptanedioic acid. The mass chromatogram obtained by using  $m/z$  215  $[\text{M}-\text{CH}_3\text{O}]^+$  on the methylated extract shows that  $\text{U}_5$  can readily be detected in tropical aerosols (Fig. 3d). Unknowns  $\text{U}_6$  and  $\text{U}_7$  were isobaric to  $\text{U}_1$  and  $\text{U}_2$ , did not contain a keto group as no methoxime derivatization of the methyl esters took place, and, therefore, are likely to correspond to branched octanedioic acids. The mass chromatogram obtained by using  $m/z$  171  $[\text{M}-\text{CH}_3\text{O}]^+$  on the methylated extract (Fig. 3c) suggests that  $\text{U}_1$ ,  $\text{U}_2$ ,  $\text{U}_6$ , and  $\text{U}_7$  are present in comparable concentrations in tropical aerosols.

### 3.4. Atmospheric particulate concentrations of known and novel (unknown) oxidative degradation products at Balbina

Table 3 presents the atmospheric concentrations of various oxidative degradation products, as derived from the two total filter samples from Balbina, which were subjected to acidification prior to extraction with dichloromethane. Also included in Table 3 are other relevant aerosol parameters obtained for these samples, such as the PM, OC, and EC concentration data. The first sample (BWW03) was taken when the impact of mineral dust was maximum at the site, the other sample (BWW14A) is from the second (low dust) period of the campaign. Whereas the PM concentrations of the two samples differ by a factor of 4, the levels of OC and the sums of the oxidative degradation products (ODP) are nearly the same. The unknowns  $\text{U}_1$  and  $\text{U}_2$ , which were characterized in this work, are together responsible for almost half of the ODP concentration. The class of ODP corresponds to approximately 0.5% of the organic carbon of the total filter samples (Table 3). Consequently, compounds belonging to this class are only minor constituents of the organic aerosol; however, they are useful as indicators of atmospheric processes.

### 3.5. Discussion

With regard to the presence of known and unknown dicarboxylic acids and related compounds, it can be seen

Table 3

Atmospheric concentrations of oxidative degradation products and selected other aerosol parameters in two total filter samples from Balbina, Brazil

		BWW03 (25–26 March 1998)	BWW14A (5–6 April 1998)
PM	( $\mu\text{g m}^{-3}$ STP)	33.3	7.3
OC	( $\mu\text{g m}^{-3}$ STP)	3.4	3.0
EC	( $\mu\text{g m}^{-3}$ STP)	0.11	0.00
EEOC	( $\mu\text{g m}^{-3}$ STP)	0.52	0.51
ODP <sup>a</sup>	( $\text{ng m}^{-3}$ STP)	15.4	17.0
$\text{K}_1$	( $\text{ng m}^{-3}$ STP)	0.00	0.47
$\text{K}_2$	( $\text{ng m}^{-3}$ STP)	0.59	0.86
$\text{K}_3$	( $\text{ng m}^{-3}$ STP)	0.47	0.43
$\text{K}_4$	( $\text{ng m}^{-3}$ STP)	0.00	0.18
$\text{K}_5$	( $\text{ng m}^{-3}$ STP)	2.3	1.8
$\text{U}_1$	( $\text{ng m}^{-3}$ STP)	4.7	3.9
$\text{U}_2$	( $\text{ng m}^{-3}$ STP)	2.5	2.7
$\text{U}_3 + \text{U}_4$	( $\text{ng m}^{-3}$ STP)	0.8	1.6
$\text{U}_5$	( $\text{ng m}^{-3}$ STP)	0.3	1.7
Other	( $\text{ng m}^{-3}$ STP)	3.6	3.3

<sup>a</sup>ODP represents the sum of all oxidative degradation products;  $\text{K}_1$ – $\text{K}_5$  are known products (see Table 1);  $\text{U}_1$ – $\text{U}_4$  are unknowns which were characterized in this work (see text);  $\text{U}_5$  was partially characterized, and Other represents the sum of other unknowns.

that the profiles observed for tropical and urban aerosols are different (Figs. 3c, d and 4a, b). Azelaic acid ( $\text{K}_5$ ), which originates from the oxidation of unsaturated fatty acids ( $\text{C}_{18:1}$  and  $\text{C}_{18:2}$ ) (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993), is the major known dicarboxylic acid in our tropical aerosol samples. The dicarboxylic acids  $\text{U}_1$  and  $\text{U}_2$ , identified in the present study as 3-acetyl pentanedioic acid and 3-isopropyl pentanedioic acid, respectively, gives rise to a higher total ion current GC/MS response than the known dicarboxylic acids  $\text{K}_{1-5}$  (Fig. 3a) and are present in higher concentrations (Table 3). Hence, their relevance as possible markers for atmospheric oxidation processes should be considered. Other known dicarboxylic acids could be identified in the urban aerosol (Table 1). Among these, 4-oxooctanedioic acid ( $\text{KG}_5$ ) has been reported to originate from the further oxidation of semivolatile fatty acids formed during oxidation of unsaturated acids (Kawamura and Gagosian, 1990), whereas 4-oxoheptanedioic acid ( $\text{KG}_6$ ) is believed to be an oxidation product of heptanedioic acid (Sakaguchi and Kawamura, 1994).

Possible biogenic precursors for the newly identified oxidative degradation products could not be pinpointed, but are likely to include monoterpenes and fatty acids. Recent investigations have dealt with the

characterization of ozone oxidation products of common monoterpenes, including  $\alpha$ -pinene, sabinene,  $\beta$ -pinene,  $\Delta^3$ -carene, and limonene (Yu et al., 1999; Koch et al., 2000). The identified oxidation products in these studies were different, however, from the oxidative degradation products characterized in the present study (more specifically, 3-isopropyl pentanedioic acid and the branched octanedioic acids) which may be due to more extensive oxidation of monoterpenes. The acetyl derivatives, 3-acetyl pentanedioic acid and 3-acetyl hexanedioic acid, are likely to originate from the further photochemical reaction of the dicarboxylic acids, pentane- and hexanedioic acid, with acetyl radicals, which may also be generated during photochemical oxidation processes.

It is worth noting that two tricarboxylic acids, namely, propane-1,2,3-tricarboxylic acid (labeled  $K_3$ ) and a newly characterized tricarboxylic acid, tentatively identified as 3-carboxy heptanedioic acid (labeled  $U_3$ ), were detected in both tropical and urban aerosols. These tricarboxylic acids are more polar and water soluble than the corresponding dicarboxylic acids of similar MW: for this reason they could enhance the capability of aerosols to act as cloud condensation nuclei and also influence the cloud formation processes by lowering the surface tension of droplets (Facchini et al., 1999).

#### 4. Conclusions

Using mass spectral approaches we have structurally characterized dicarboxylic acids and related compounds of similar polarity which are present in both tropical and urban aerosols. These compounds, denoted in the present study as “oxidative degradation products”, were enriched in the fine size fraction of the tropical aerosol and thus contributed to the secondary aerosol. They were also found to be important in urban aerosols collected during a period of increased ozone concentrations. Hence, these compounds may have significance as markers for atmospheric oxidation processes. In addition to known dicarboxylic acids and oxidative degradation products of fatty acids, a number of unknown novel compounds were tentatively identified or partially characterized. The latter compounds included tricarboxylic acids, acetyl dicarboxylic acids, and branched dicarboxylic acids. Among these compounds, the glutaric acid derivatives, 3-acetyl pentanedioic acid and 3-isopropyl pentanedioic acid, were found to be relatively important in tropical aerosols and equally abundant as azelaic acid, an oxidation product of the unsaturated fatty acids, oleic and linoleic acid. 3-Acetyl pentanedioic acid can possibly be formed by further photochemical reaction of glutaric acid with acetyl radicals which may also be generated during photochemical oxidation processes. 3-Isopropyl pentanedioic acid is likely to originate from the extensive photochemical oxidation of monoterpenes. Two tricar-

boxylic acids, propane-1,2,3-tricarboxylic acid and 3-carboxy heptanedioic acid, could be characterized. To our knowledge, they have not been reported previously in atmospheric aerosols.

#### Acknowledgements

The authors are indebted to the Belgian Federal Office of Scientific, Technical and Cultural Affairs, the Special Research Fund of the University of Antwerp (UIA), and the “Fonds voor Wetenschappelijk Onderzoek – Vlaanderen” for research support. G.R. was supported by the Max Planck Gesellschaft, Germany, and Environment – now at the California Institute of Technology. P.A. acknowledges FAPESP for financial support. The authors thank the Electronorte in Balbina, Brazil, for logistical support, and the University of Sao Paulo and the Max Planck Institute for Chemistry, Mainz, for assistance in the field work. This work is a contribution to the Large-scale Biosphere Atmosphere Experiment in Amazonia (LBA).

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