Detection of High Molecular Weight Organic Tracers in Vegetation Smoke Samples by High-Temperature Gas Chromatography−Mass Spectrometry

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High-temperature high-resolution gas chromatography (HTGC) is an established technique for the separation of complex mixtures of high molecular weight (HMW) compounds which do not elute when analyzed on conventional GC columns. The combination of this technique with mass spectrometry (i.e., HTGC−MS) is not so common and application to aerosols is novel. The HTGC and HTGC−MS analyses of smoke samples taken by particle filtration from combustion of different species of plants provided the characterization of various classes of HMW compounds reported to occur for the first time in emissions from biomass burning. Among these components are a series of wax esters (long chain alcohols esterified with long chain fatty acids) with up to 58 carbon numbers, aliphatic hydrocarbons (C_{15}−C_{40}; C_{max} = C_{31}; odd predominance), triglycerides, long chain methyl ketones (up to 37 carbons; C_{max} = C_{33}; odd predominance), alkanols (up to 40 carbons; C_{max} = C_{32}; even predominance), and a series of triterpenyl fatty acid esters (e.g., α- and β-amyryl stearate) which have been characterized as novel natural products. Long chain fatty acids with more than 32 carbon numbers are not present in the smoke samples analyzed. The HMW compounds in smoke samples from the burning of plants from Amazonia indicate the input of directly volatilized natural products in the original plants during their combustion. However, the major organic compounds extracted from smoke consist of a series of lower molecular weight polar components, which are not natural products but the result of the thermal breakdown of cellulose and lignin. In contrast, the HMW natural products may be suitable tracers for specific sources of vegetation combustion because they are emitted as particles without thermal alteration in the smoke and can thus be related directly to the original plant material.

Introduction

Chemical fingerprints of emission sources have commonly been utilized to distinguish specific inputs from point sources. Regional vegetation cover has been shown to produce distinct compound signatures and molecular markers (*1*−*7*). It is therefore useful to apply these biogenic marker constituents, from both natural and combustion emissions, as tracers in tropospheric chemistry. In addition, the detailed knowledge of the major compounds of different vegetation mixes derived from both natural and combustion emission processes permits the choice of a few key compounds which are the characteristic tracers (e.g., refs *8*−*11*). For instance, levoglucosan (1,6-anhydro-β-D-glucose) can be used as a specific tracer of vegetation biomass burning in aerosols (*12*).

Aerosols are composed of chemical compounds from multiple sources. Advances have been made in atmospheric organic chemistry in terms of point source correlations and molecular marker analysis to distinguish between anthropogenic and biogenic organic matter (e.g., refs *4, 5, 7, 13*−*33*). Thermally altered (pyrolysis) and directly emitted molecular markers may be used for tracing biomass burning (*12, 34*). This concept has been applied preliminarily for smoke samples from Norway (*35*), Oregon (*4*), China (*36, 37*), and Amazonia, Brazil (*17*). For example, retene, a thermal alteration product from resin diterpenoids (e.g., abietic acid), has been found in aerosols in Elverum, Norway, and in Oregon, and at trace levels in Los Angeles, California (*4, 9, 10, 35, 38*), and China (*37*). Retene was not detectable in aerosols of the Harmattan or in urban samples of Nigeria, nor in rural aerosols of southeastern Australia or Amazonia, Brazil (*5, 17, 39*). The explanation for this is the absence of conifers in those regions. On the other hand, levoglucosan was the major component in smoke and aerosols from many different areas and climatic zones (*12*).

In general, biogenic and anthropogenic hydrocarbons are the most extensively studied organic compounds of the lipid fractions in aerosol particles (e.g., refs *2*−*5, 7, 13, 14, 20, 21, 25, 28,* and *29*). Only a few cases report the composition of polar compounds (e.g., refs *2*−*5, 10, 11, 13*−*15, 25, 28, 29*). Aside from the chemical composition, the conventional GC techniques are generally limited to the identification of compounds with up to 40 carbon numbers. The reason for this is the final temperature limit of GC analysis on the most popular columns. In this regard, the analysis of organic tracers by high-temperature gas chromatography (HTGC) and HTGC−mass spectrometry (MS) may enable the characterization of high molecular weight (HMW) organic compounds. These components have not been reported previously in aerosols due to their nonelution on conventional GC columns with lower temperature limits.

The aim of this work is to evaluate and indentify the occurrence of HMW tracers ($>C_{40}$) from smoke aerosols by HTGC and HTGC−MS. A series of burning experiments was conducted utilizing dominant plant species from the Amazon forest. Smoke samples were taken by particle filtration from combustion of different species of plants so that the particulate organic compounds could be used for source correlation to distinguish specific inputs of thermally altered

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and directly emitted natural products from biomass combustion. Various extract fractions of differing polarities have been analyzed, and many HMW compounds were characterized for the first time in smoke aerosols. The carbon number range of many homologous series (e.g., n-alkanes, alkanones, alkanols) was extended. Additionally, HTGC−MS analyses enabled the identification of known HMW compounds and a novel class of natural products, which have been characterized for the first time. Moreover, these compounds indicate direct volatilization of natural products from plants. In general, the HMW compounds identified in the smoke samples are natural or altered products from the original plants which are volatilized during biomass combustion. In other words, this work establishes that there are organic compounds in smoke aerosols, which are not detected by GC analysis on traditional columns.

Experimental Section

Samples. Controlled fires were set by burning dry leaf and stem litter of different representative plant species collected at various locations in the Amazonian forest (Brazil). The plants collected and burned were the following: *Avicennia sp.* (mangrove), *Bertholettia excelsa* (Brazil nut), *Carapa guineensis* (Andiroba), *Clusia sp.* (Clusia), *Dipterix odorata* (Cumaru), *Rizophora sp.* (Rizophora), *Simaruba amara* (Marupá), *Theobroma grandiflorum* (Cupuaçu), and *Vismia guineensis* (Vismia). Sampling was carried out at the site of collection by filtration of the smoke using a standard high-volume air sampler fitted with a quartz fiber filter (annealed prior to use for 3 h at 560 °C; Gelman Science Inc., Ann Arbor, MI). These filters are capable of retaining 0.3 μm diameter particles at a minimum efficiency of ~99% and those >0.3 μm with greater efficiency. Smoke was sampled for 6 min at a flow rate of 1.5 m^3/min, yielding a black filter. After sampling, each collection filter was placed into a precleaned 300 mL jar with a Teflon lined cap. After adding 5 mL of CH$_2$Cl$_2$ as preservative, the jar was stored under refrigeration whenever possible until laboratory workup was initiated.

Sample Extraction, Separation, and Derivatization. The filters were extracted three times using ultrasonic agitation for 15 min periods each with 200 mL of CH$_2$Cl$_2$. This solvent was used because it had been previously utilized to extract HMW compounds (e.g., wax esters) from plants (*4, 29, 31*). The extractions were carried out in the filter storage jars. The solvent extract was concentrated first on a rotary evaporator and then using a stream of filtered nitrogen gas to a volume of approximately 5 mL. The extracts were then filtered using a Gelman Swinney filtration unit (Gelman Science Inc., Ann Arbor, MI) fitted with an annealed glass fiber for the removal of insoluble particles. The resultant filtrates were then adjusted to 5.0 mL exactly by addition of CH$_2$Cl$_2$.

A 1.0 mL aliquot of the filtrate was transferred to a vial in order to methylate the carboxylic acids to methyl esters by addition of diazomethane (CH$_2$N$_2$) in diethyl ether. After concentration, the derivatized extract was subjected to thin-layer chromatography (TLC) using silica gel plates (0.25 mm thickness of silica, Alltech) and eluted with a mixture of hexane and diethyl ether (9:1). The TLC plates had been cleaned prior to use by repetitive elution with methanol and CH$_2$Cl$_2$. After each washing, the top centimeter of silica gel was scraped off in order to remove contaminants. Before sample application, the TLC plates were activated in an oven at 120 °C for 45 min. The TLC elution regions corresponding to hydrocarbons, esters, ketones (and aldehydes), alcohols, and origin were visualized by UV light and iodine vapor. The different regions were defined by elution of a standard compound mixture spotted on the same plate where each smoke sample was fractionated. After separation, the regions

containing the different polarity classes were scraped off, eluted with CH$_2$Cl$_2$, concentrated by rotary evaporation followed by nitrogen blowdown, and transferred to 2 mL vials. Carbon disulfide and cyclohexane (1:1) were used for dilution since they were shown to be the best solvent mixture for HTGC analyses of mixtures containing HMW compounds (*40*). The alcohol and the origin fractions were converted to the trimethylsilyl ethers prior to HTGC and HTGC−MS analyses by reaction with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) (Pierce).

Instrumental Analysis. Gas chromatography was performed on a 20 m × 0.3 mm i.d. custom-made glass capillary column coated with 0.1 μm of OV-1701-OH (88% methyl, 7% cyanopropyl, 5% phenylpolysiloxane; Ohio Valley Specialty Chemical, Co.). An on-column injector (Carlo Erba) was mounted on a Hewlett-Packard (HP) model 5890 gas chromatograph. The column temperature was maintained at 40 °C for 2 min then programmed to 390 °C at 10 °C/min and held isothermal for 20 min. The flame ionization detector and on-column injector were operated at 390 °C and 40 °C, respectively. Helium was used as carrier gas at a flow rate of 1.5 mL/min. GC data were acquired with a Hewlett-Packard ChemStation.

HTGC−MS analyses were carried out on a Hewlett-Packard model 5973 MSD coupled to a Hewlett-Packard 6890 gas chromatograph. The GC operating conditions were the same as described above. The on-column injector and the transfer line temperatures were set at 40 °C and 390 °C, respectively. The mass spectrometer was operated in the electron impact mode and 70 eV ion source energy. Molecular markers were identified by GC retention indices, mass spectra, and in some cases by comparison with authentic standards or characterized mixtures.

Results and Discussion

Previous reports (*40−42*) on the application of HTGC in the analysis of HMW compounds showed that the general analytical procedure used in environmental molecular organic studies needs to be changed slightly in order to identify the HMW compounds present in the samples. Basically the main changes are the technique of injection and the solvent used to dilute the sample prior to its injection. The cold on-column technique proved appropriate for identification of the HMW compounds (>C$_{70}$) (*40*). With regard to the solvent, cyclohexane and CS$_2$ are found to be best after testing the different common solvents (*40*). Both were effective in dissolving the HMW waxes to above C$_{70}$. However, dissolution of the compounds is not the only point to be considered. The appropriate solvent must also promote a good partition phenomenon during the chromatographic process. For instance, toluene, which is a good solvent for polycyclic aromatic hydrocarbons, could not be utilized to analyze these compounds in the present experiment because it hindered the partition phenomenon on the column phase (*43*). The same problem was observed when different smoke fractions were analyzed using CH$_2$Cl$_2$ as solvent.

Nine plant smoke extracts and 81 fractions of differing polarities have been analyzed. However, only representative examples containing HMW compounds are described in this report. HMW components are present in smoke from all the plants analyzed but differ in abundance, chemical functionality, and structure. Technically, HMW compounds are defined and characterized as those components eluting above 300 °C in the GC analyses. These components are determined by HTGC analysis of the derivatized total extracts of the smoke samples, which denote their importance in the lipid fraction.

The total extract of smoke from burning of the Vismia plant, for example, presented a series of compounds eluting above 350 °C as shown in the GC trace (Figure 1). The major
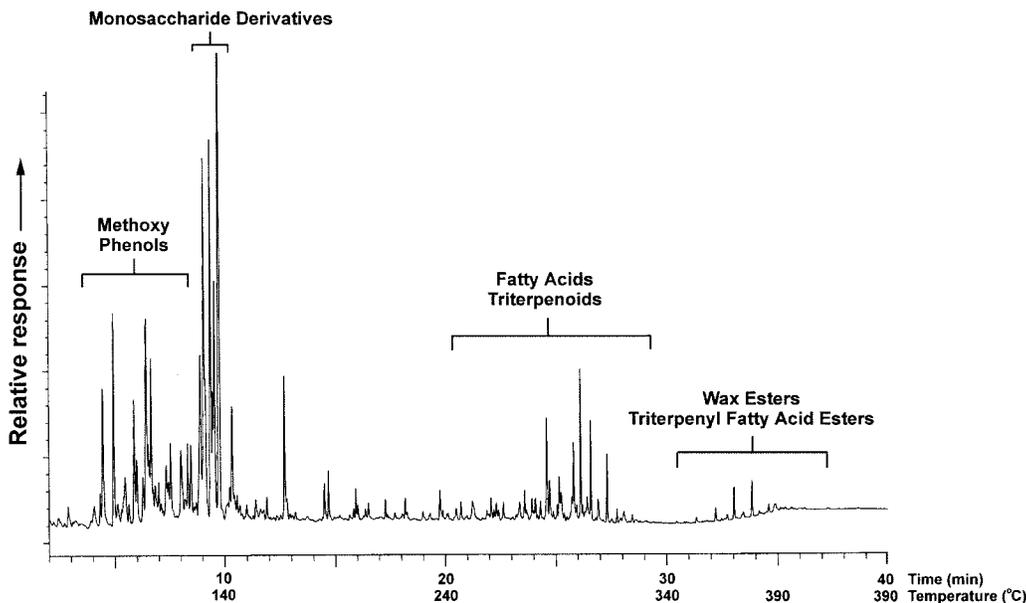
FIGURE 1. Typical gas chromatogram (HTGC) of the total extract (methylated and silylated) from fine particles of smoke from burning of Vismia.

compounds consist of levoglucosan (1,6-anhydro-β-D-glucose) and other monosaccharide derivatives from the thermal breakdown of cellulose (*12*). Among these monosaccharide derivatives, levoglucosan, mannosan, and galactosan could be positively elucidated by co-injection with the authentic standards. The second most abundant class of compounds comprises various methoxyphenols which were produced by thermal degradation of lignin (*34*). Typically, these two classes of components encompass approximately 85% of the total extractable organic compounds from the smoke samples analyzed. Compounds of relatively HMW (e.g., triperpenoids and fatty acids) and eluting earlier than 310 °C (temperature limit of conventional GC columns) are also present in the total extracts but at lower abundances than the lower molecular weight compounds discussed above. Considering the scope of this report, compounds eluting earlier than 300 °C are not discussed in further detail and will be considered in a separate report.

Various compounds elute late in the GC traces (>350 °C) of the total extracts. The detection of HMW compounds in some samples (with no prior fractionation) demonstrates their magnitude in smoke from biomass burning. Because many of these compounds have not been reported previously, it was necessary to separate the total extracts into different polarity classes in order to increase the confidence in the results as well as to minimize background in the mass spectra. Analyzing isolated fractions enabled the determination of compounds at higher concentration levels and consequently the acquisition of better mass spectra. Furthermore, some compounds were detectable only after fractionation of the total extracts, demonstrating the importance of this procedure. Although separation of smoke extract samples into different fractions may be considered cumbersome and time-consuming, this is a necessary step to properly characterize the chemical structures of the HMW compounds present. Nevertheless, once an organic tracer is identified, it can be easily and specifically detected by HTGC−MS in total extracts using the single-ion monitoring technique.

Hydrocarbons. Alkanes with more than 35 carbon numbers are present in some smoke extract samples. For instance, the sample obtained by burning the Castanha-do-Pará plant contains alkanes with more than 40 carbons (Figure 2). HMW alkanes have been characterized in geological samples (*40, 42*) and may also occur in waxes of tropical plants. Thus, the

HMW alkanes found in the smoke samples appear to be introduced directly from the vegetation being burned. Because hydrocarbons have not been detected in the blank experiments, the introduction of HMW alkanes by contamination can be eliminated. The major peak in the mass fragmentogram (Figure 2) is a C_n isoprenoid hydrocarbon of an unknown origin at this point.

Fatty Acids. Fatty acids can be readily detected in the methylated and silylated (BSTFA) total extract fractions of smoke from many plants analyzed (e.g., Figure 1), showing the high abundances of these compounds produced by plant burning. This is not unusual because fatty acids have been reported to occur as major compounds in many plant extracts (e.g., refs *4, 44, 45*) as well aerosol samples (e.g., refs *1, 2, 5, 13, 19, 29*). The free fatty acids in the smoke samples from plants of Amazonia generally range from C_{12} to C_{30} with a carbon number maximum (C_{max}) at 16. However, no fatty acids with chain lengths greater than C_{34} have been detected.

Wax Esters. Long chain wax esters (LCWE) are present in smoke from the burning of some plant species. For example, smoke aerosol from the burning of Cupuaçú presented LCWE from 38 up to 58 total carbon numbers with a strong even carbon number predominance, typical of that reported for plant wax (Figure 3). The LCWE series is comprised of mainly palmitic acid esterified with the fatty alcohols ranging from C_{22} to C_{34} and minor amounts of stearic and eicosanoic acids esterified with the C_{32} and C_{34} alcohols (Figure 3). Although wax esters have been described extensively in the literature, LCWE are reported as such only for a few cases of higher plant waxes (e.g., refs *46, 47*) despite their likely widespread occurrence (*42*). The reason for this may be that they were simply not detected when analyzed on conventional GC columns used to analyze lipid mixtures. LCWE are described here, for the first time, to occur in smoke aerosols. These natural products are found in abundances comparable to those of the *n*-alkanes (e.g., Figure 3) in some smoke samples, indicating their magnitude in biomass burning emissions. This compound signature is further evidence for direct volatilization of HMW compounds into smoke. In this regard, other classes of compounds may follow the same mechanism of introduction into smoke aerosols (*48*). Volatilization of natural product compounds has been proposed as a mechanism for the introduction of oxygenated organic compounds into smoke and ultimately into the atmosphere (e.g., refs *17,*
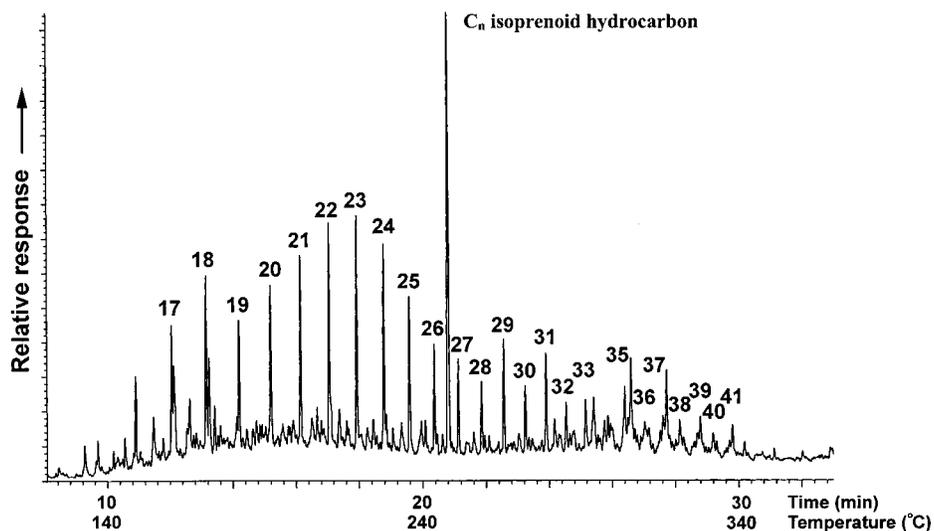
FIGURE 2. Mass fragmentogram (m/z 85) trace (HTGC−MS) of the fraction containing hydrocarbons from the smoke extract from burning of Castanha-do-Pará. Numbers refer to the carbon chain length of the n-alkanes.
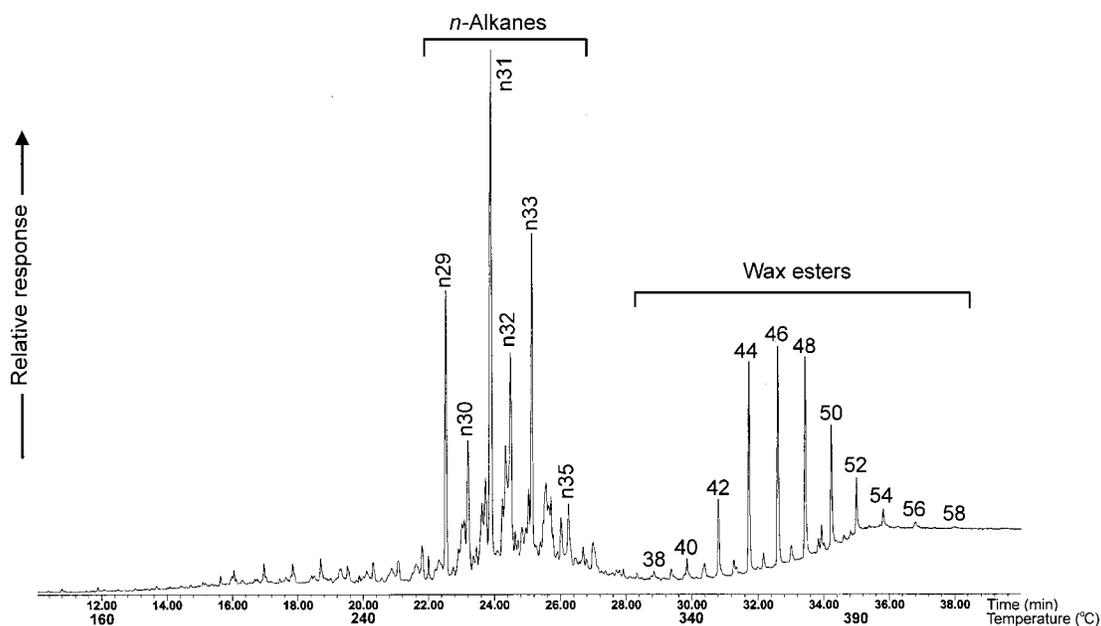

FIGURE 3. Representative total ion current trace (HTGC−MS) of the fraction containing wax esters from the smoke extract from burning of Cupuaçu. Numbers refer to the total carbon chain length of the wax esters; ni indicates the normal alkane carbon chain length.

34). However, only limited evidence of this mechanism has been documented. Therefore, the occurrence of LCWE in smoke may be considered as indicative of this process. This statement is reinforced by other organic markers characterized in this report. However, this comparison requires the extraction and characterization by HTGC−MS of the natural products of the original plant material.

Triglycerides. Intact triglycerides elute late (>350 °C) in the HTGC analyses of the polar fractions of some smoke samples (e.g., Figure 4). The major compounds are dipalmitoylolein ($C_{53}H_{100}O_6$, MW = 832), 1-palmitoyl-2-oleoyl-3-stearin ($C_{55}H_{104}O_6$, MW = 860), and triolein ($C_{57}H_{104}O_6$, MW = 884). The mass spectra of these compounds match with data for authentic standards. No fragments above 800 Da (e.g., the $M^{•+}$ ion) could be obtained due to the technical constraint of the HP 5973 MSD instrument which limits the MS data acquisition to a maximum of 800 Da. However, fragments below m/z 800 match with those of the authentic standards. Furthermore, the GC retention indices of the triglycerides found in the smoke samples are the same as

those obtained for triglyceride standards which enabled the structure confirmation of some compounds.

Many plants have triglycerides in their lipids, which are important energy storage molecules. It should be noted that these common energy storage lipids are rarely present in epicuticular waxes (46). They are commonly found in seeds, but no seeds were burned in these experiments, indicating that these compounds are internal constituents of the plants that were burned. Triglycerides have a very low vapor pressure and their presence in smoke is further evidence of their direct volatilization as HMW natural products during burning of plants. As in the case of the LCWE, this is the first report on the presence of these compounds in smoke aerosols.

Triterpenyl Fatty Acid Esters. Ester fractions separated from extracts of smoke particulate matter from the burning of different species of plants contained compounds, in relatively high abundance, eluting late in the total ion current traces of HTGC−MS analyses (Figure 5). The most intense peaks of these HMW components have mass spectra resembling the characteristic fragmentation pattern of pen-
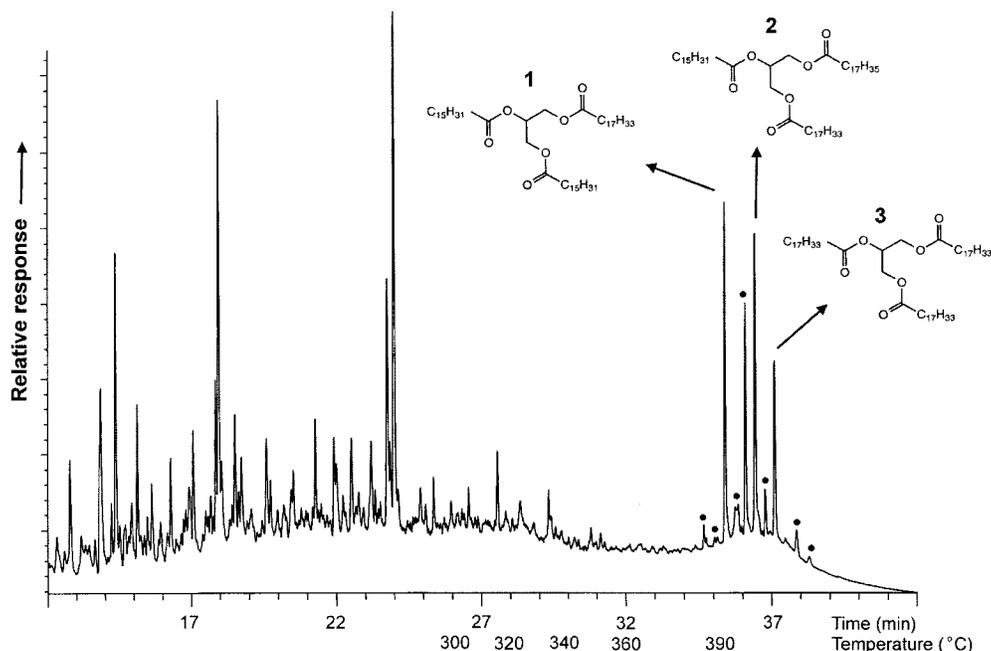
FIGURE 4. Representative gas chromatogram (GC–MS) of the fraction containing triglycerides in the smoke extract from burning of Andiroba: 1 = dipalmitoylolein, 2 = 1-palmitoyl-2-oleoyl-3-stearin, 3 = triolein, ● = unknown triglycerides.
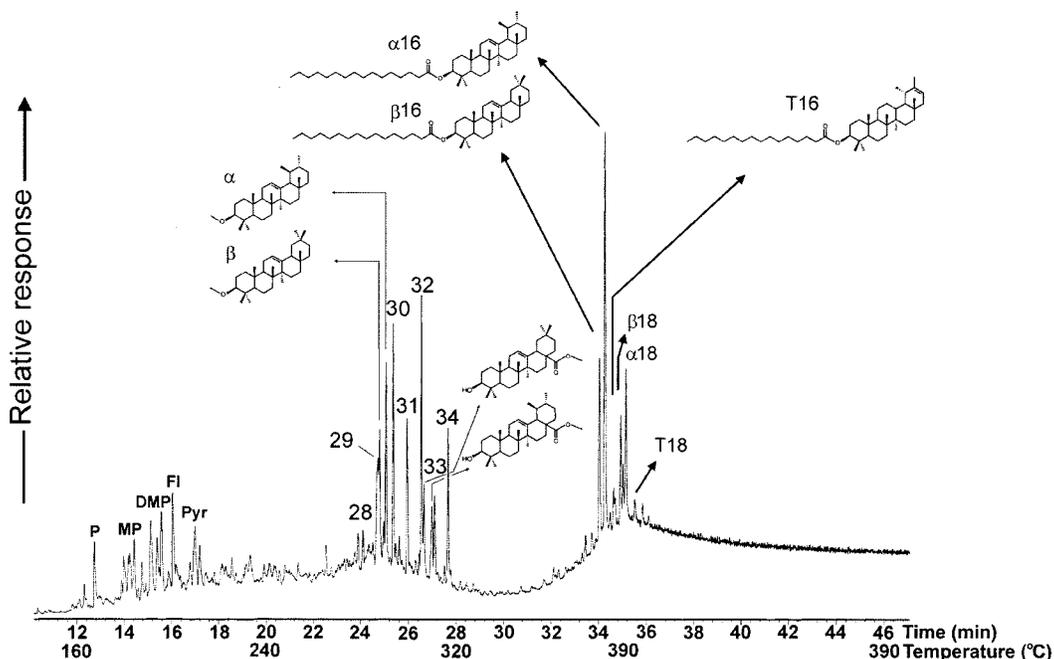

FIGURE 5. Representative total ion current trace (HTGC–MS) of the ester fraction from the smoke extract from burning of Castanha-do-Pará. Numbers refer to the carbon chain length of free fatty acids (analyzed as the methyl esters): P = phenanthrene; MP = methylphenanthrenes; DMP = dimethylphenanthrenes; Fl = fluoranthene, and Pyr = pyrene. α, β, and T are the esterified triterpenols α-amyrin, β-amyrin, and taraxasterol, respectively.

tacyclic triterpenoids with a double bond in their structure. For instance, the most intense peaks at long times are a homologous series with fragment ions at m/z 218 (base peak), 189, 203, and 409, typical of pentacyclic triterpenoids with the Δ^{12}-ursene and Δ^{12}-oleanene structures (Figure 6b). However, the retention indices (up to ~5700) and molecular ions (up to 720 Da) indicate the structures to be triterpenyl fatty acid esters (TFAE). Essentially, the fragmentation pattern of the TFAE consists of molecular ion (M·⁺), M–CH₃, M–fatty acid, and then fragments characteristic of the esterified triterpenol. The TFAE have acyl carbon chain lengths extending from 5 up to 20 carbon numbers (Figure 6a) (*49*). The relative intensities of the characteristic fragments in the

mass spectra of the HMW triterpenyl esters are given in Table 1. The dominant esters are with α- and β-amyrin and a minor amount with taraxasterol. The complete characterization as well as interpretation of the mass spectra is given elsewhere (*49*). These compounds are reported for the first time in smoke aerosol and are novel natural products believed to be constituents of the plants, analogous to the well-known steroid fatty acid esters.

Ketones. Many higher plants with alkanes as major constituents in their epicuticular lipids also contain appreciable amounts of ketones with the same carbon numbers (C_{29} and C_{31}) and odd predominance as the alkanes (*46*). The carbonyl group is either in the center of the chain, at C-15
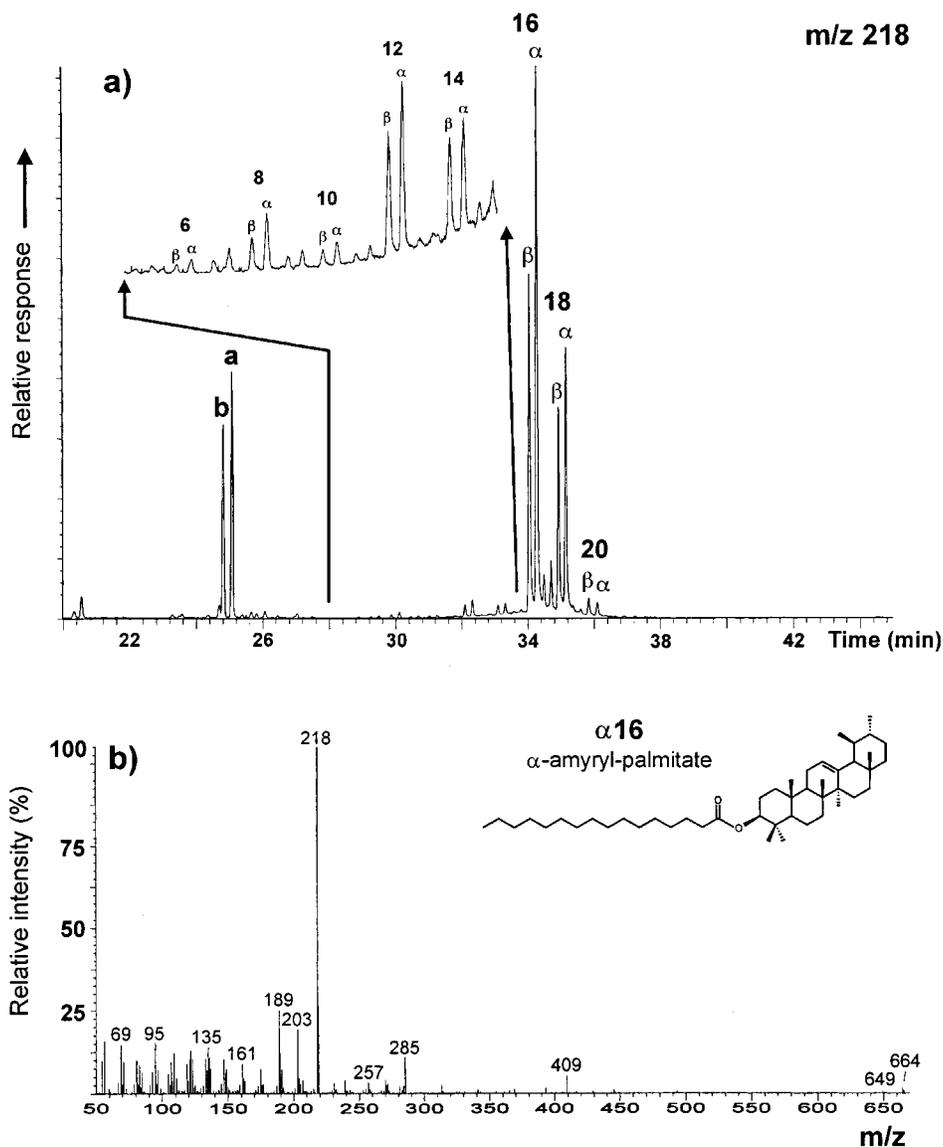
FIGURE 6. (a) HTGC—MS mass fragmentogram (*m/z* 218) showing the homologous series of amyryl alkanoates. Numbers refer to carbon chain length of the esterified fatty acids; α and β are the esterified triterpenols α-amyrin and β-amyrin, respectively; a and b are α-amyrin and β-amyrin methyl ether, respectively. (b) Mass spectrum of α-amyryl-palmitate, representative of the homologous series of triterpenols esterified to long chain fatty acids.

TABLE 1. Main Fragments and Their Relative Intensity (%) in the Mass Spectra of Triterpenyl Fatty Acid Esters

compound	M·+	base peak (100)	M—CH₃	M—fatty acid	other significant fragments
		Taraxasterol Esters			
taraxasteryl hexadecanoate	664 (1.7)	189	649 (0.4)	408 (13)	393 (7), 175 (17)
taraxasteryl octadecanoate	692 (1.2)	189	649 (0.2)	408 (14)	393 (11), 175 (15)
		Amyrin Esters			
β-amyryl dodecanoate	608 (0.5)	218	593 (0.7)	409 (4)	203 (37), 189 (17)
α-amyryl dodecanoate	608 (1.0)	218	593 (0.4)	409 (2)	203 (18), 189 (22)
β-amyryl tetradecanoate	636 (0.8)	218	621 (0.1)	409 (2)	203 (36), 189 (17)
α-amyryl tetradecanoate	636 (0.7)	218	621 (0.6)	409 (7)	203 (17), 189 (21)
β-amyryl hexadecanoate	664 (0.7)	218	649 (0.3)	409 (3)	203 (34), 189 (16)
α-amyryl hexadecanoate	664 (1.3)	218	649 (0.5)	409 (5)	203 (18), 189 (23)
α-amyryl heptadecanoate	678 (1.1)	218	663 (0.3)	409 (4)	203 (15), 189 (22)
β-amyryl octadecanoate	692 (0.6)	218	677 (0.3)	409 (3)	203 (32), 189 (17)
α-amyryl octadecanoate	692 (0.7)	218	677 (0.3)	409 (4)	203 (14), 189 (17)
α-amyryl nonadecanoate	706 (0.8)	218	691 (0.8)	409 (9)	203 (20), 189 (43)
β-amyryl eicosanoate	720 (0.7)	218	705 (0.3)	409 (6)	203 (32), 189 (16)
α-amyryl eicosanoate	720 (0.9)	218	705 (0.4)	409 (3)	203 (12), 189 (17)

for C_{29} and at C-16 for C_{31}, or toward one end, at C-9 for C_{29} and C-10 for C_{31}. These compounds are not found in these samples. However, a series of methyl ketones (alkan-2-ones) ranging from C_{25} to C_{37} are present in some samples (e.g.,
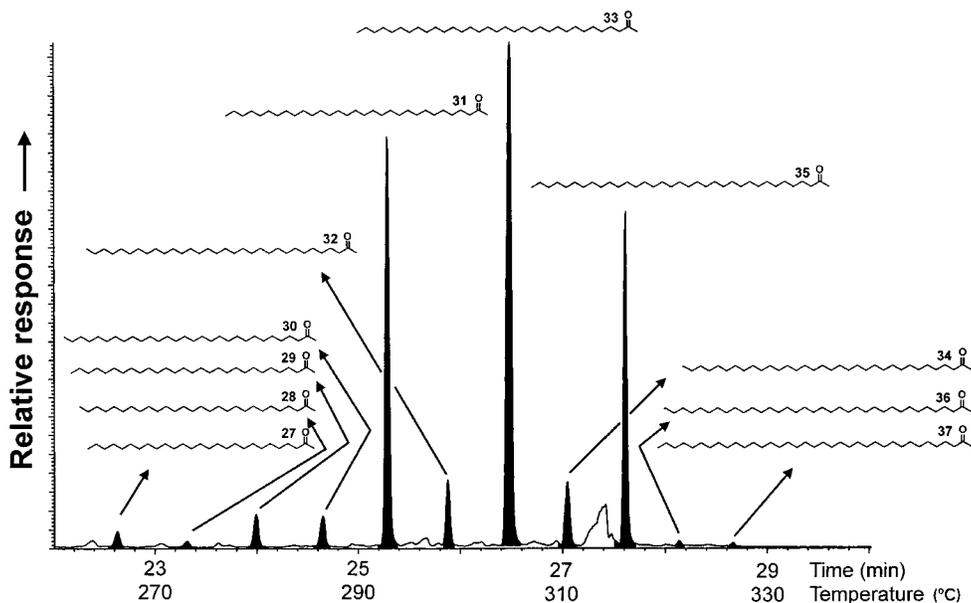
FIGURE 7. Mass fragmentogram (*m/z* 59) from HTGC−MS analysis of long chain methyl ketones found in the smoke extract from burning of Cumarú. Numbers refer to the carbon chain length of the structure of *n*-alkan-2-ones (above each structure).

Figure 7). The series has an odd carbon number predominance with C_{max} at C_{33}, but it does not have the same distribution as the wax alkanes from the same plant. Thus, oxidative formation from alkanes or alkanols does not explain their presence. These alkan-2-ones are therefore derived from unknown precursors or may be natural products.

Alcohols. Alkanols are present in smoke samples at highly variable concentrations which is due to their facile thermal dehydration to olefins and various precursor sources in the vegetation (e.g., free fatty alcohols, wax esters, etc.) (*17, 50*). The *n*-alkanol distributions in these smoke samples range from C_{24} to C_{40}, with a strong even carbon number predominance and C_{max} at C_{32}. The homologues $>C_{30}$ are found at trace levels in these samples. The homologues $<C_{30}$ are detected easily with conventional GC and GC−MS as the trimethylsilyl ethers, and therefore this compound group is not discussed in further detail.

In general, there are considerable amounts of high molecular weight organic tracers in smoke aerosols which cannot be detected by gas chromatography using conventional columns. Because the HMW compounds characterized here are, in general, natural products volatilized during biomass burning, their detection is important for quantitative analysis in comparative studies which evaluate biogenic versus anthropogenic components in aerosols.

Moreover, HTGC and especially HTGC−MS analysis enabled the identification of various HMW compounds reported for the first time in smoke aerosols. Additionally, novel natural products have been identified. These considerations alone demonstrate the potential of this technique, and as such there is no doubt that use of HTGC will increase. The HMW compounds identified from burning of Amazonian plants are, in general, natural products in contrast to the lower molecular weight components which are typically degradation products from thermal alteration of cellulose and lignin, comprising the major organic components of the smoke extracts.

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