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ANALYTICAL ANALYSIS OF ROMAN AMPHORAE

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Abstract

The analysis of organic residues present in ancient pottery can give important information for archaeologists. Diets, habits, technologies and original use of the vessels can be identified through this studies.

Fourier transform infrared spectroscopy (FT–IR) and gas chromatography coupled with mass spectrometry (GC–MS) were used in order to analyse organic resinous materials from the interior surfaces of Roman amphorae belonging to the archaeological collection of DRASSM and Museum of Arles Antique. In addition, wine amphorae from Grand Congloué 2 shipwreck were analysed. The FTIR spectra obtained by the technique of KBr micropellets, prepared directly with the materials scraped from the amphora without any further sample preparation, provided enough information to establish their diterpenoic nature. GC–MS enabled to identify dehydroabietic acid, 7-oxodehydroabietic acid, 7-hydroxy-dehydroabietic acid, 15-hydroxy-7-oxodehydroabietic acid, methyl dehydroabietate, retene. The presence of diterpenoids and retene provided evidence that the amphorae examined were waterproofed with a pitch produced from resinous wood of plants from the *Pinaceae* family or mainly consist of *Coniferae* species. Moreover presence of retene in samples indicates that pitch was heated. Wine and fish amphorae were studied. Some fish amphorae samples did not show the presence of pitch in GC-MS analyses. This work studies for the first time pitch of an fish amphorae in the laboratory of IMBE.

KEYWORDS: ROMAN AMPHORAE, GC-MS, FT-IR, PITCH, DITERPENOIDS, WINE AMPHORAE, FISH AMPHORAE, GRAND CONGLOUÉ 2

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It has been a period of intense learning for me, not only in the educational arena, but also on a personal level. Writing this thesis has had a big impact on me. I would like to reflect on the people who have supported and helped me so much throughout this period.

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1. Introduction

Presentation of the laboratory

The laboratory work and the interpretation of the results has been done at IMBE[1] laboratory in IRPNC[2] team of University of Avignon (France). One of the main research axis of the team is the study of artistic and archaeological materials. Those studies have contributed over several years to the chemical and analytical knowledge of natural plant products by microchemical, chromatographic (HPLC with UV-vis/fluorimetry detector, GC-MS) and spectroscopic (FT-IR, fluorimetry, UV-vis spectrometry, colorimetry) techniques.

The laboratory develops analytical methods that enable the identification of chemical markers, characteristic of the natural materials used in cultural heritage (resins, dyes, pigments, binding media, etc.). This approach includes the comprehension of the mechanisms of thermal and photochemical degradation suffered by the identified markers.

In chemistry field, the team works on the analytics, identification and use of natural substances in fine arts and archaeology. The research addresses biomarkers and markers of natural or anthropogenic degradation of different materials (resins, colors). The studies concern the sectors of artwork restoration and cultural heritage conservation. The metabolomic approach of ancient and fresh plant compounds involves collaborations with botanists and specialists in natural substances. The cooperation with different national and international groups of scientists (European projects mostly) put the laboratory team in the center of the thematic and allows is to be aware of the new advances in this field of science.

Presentation of the subject and the aim of the research work

This study concerns DRASSM[3] collection of amphorae from Grand Congloué 2 shipwreck and Museum of Arles (both – France) collections. Roman amphorae were discovered in 1952 by Commander Cousteau in the bay of Marseille in France (wreck of Grand Congloué 2). He concluded that most of the ship's wine cargo had been stored in amphorae produced by the wealthy Sestius family from Cosa, a port of Rome. The wrecks of Grand

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[1] IMBE – l'Institut Mediterraneen de la Biodiversite et d'Ecologie marine et continentale

[2] IRPNC – (Ingéniérie de la Restauration des Patrimoines Naturel et Culturel) – Ecological Restoration of Ecosystems and Cultural Heritage.

[3] DRASSM – Le Departement des recherches archeologiques subaquatiques et sous-marines (The Department of Underwater Archaeological Research)

Congloué are about 40 m long, loaded with Greek, Greco-Italian and Roman amphorae. The finds were on a slope at 28 - 44 m depth. It is interesting that it took experts 25 years of study to determine that there are actually two superimposed ships, which sank close to a century apart.

The shipwreck Grand Congloué 1 dates to the second century BC. Its cargo consisted in essence of about 400 wine amphorae of Greco-Roman origin, and 7000 pieces of dishes from Campania. About 30 Greek amphorae completed the lot. The shipwreck Grand-Congloué 2, dating to the late second or very early first century BC, contained more than a thousand Roman wine amphorae of the type Dressel 1A. Recent studied have proven that they came from Cosa in Etruria, the present-day Tuscany (Olmer *et al*.).

The aim of this study is to determine the molecular composition of the organic substances used to proof the amphorae (pitch) and the content. The objective of this research work is to characterize the presence of this type of substances by using spectroscopic (FT-IR) and chromatographic (GC-MS) techniques.

The presented work is a part of a bigger project of Hitomi Fujii (Ph.D. student of the University of Avignon), who is working on Roman amphorae under the project "Chromatographic study of archaeological organic materials". The shipwreck of Grand Congloué 2 is also a subject of studies of Hitomi Fujii under the project "The characterization of resinous material inside Roman amphorae and the identification of content" (University of Avignon).

The work "Analytical analysis of Roman amphorae" has been done under guidance of Ph.D. student Hitomi Fujii and the supervisory guidance from Professors Catherine Vieillescazes and Carole Mathe de Souza (University of Avignon). Gabriele Favero was the supervisor from Consortium side (Sapienza University of Rome). The studies were performed under European programs, i.e. program Erasmus Mundus Master in ARCHaeological MATerials Science (ARCHMAT) (University of Avignon is an associate partner of ArchMAT program, 2013-2017).

2. Background information

Before the presentation of the work itself, the general and specific information about amphorae will be presented in this section. The background information of this paper consists of four parts. The commercial amphora and amphorae types will be discussed in the first section. Following by information about contents of the amphorae and pitch and their importance in amphora studies. Special focus will be done on previous studies and literature review to provide a link between historical importance of amphorae with the modern analytical studies of them. Finally, the analytical techniques used in this studies will be described.

2.1 Amphora

The word *amphora* comes from the Greek amphoreus (αμφορέας), meaning jar with two handles, which derives from "amphi" (on both sides) + "phoreus" (bearer) (Fig. 1). Eastern Mediterranean was the place of origin of the amphora. In the fifteenth century BCE on the Syrian-Lebanese coast Canaanites introduced the idea of pottery transport jars. Egyptians, Phoenicians, Greeks and Romans, all of them had some particular shapes and styles of amphora. Because of their slowness to degrade, they can be found throughout Mediterranean, dating from about 1500 B.C. to 500 A.D. (Twede, 2002).

Fig. 1. Amphora (Source: University of Avignon, 2015)

Amphorae in past performed the same functions that are expected from packages today. Our modern civilization has developed so many new things, that we sometimes see everything as something unique and we think that in the past there was nothing similar to our nowadays technologies. At the same time we should always bear in mind that modern technologies are based on cultural and practical needs that remain the same as in the past. In this particular case use and importance of the commercial amphorae will be discussed.

2.1.1 Commercial amphora

Amphorae is a good example of past packaging technologies. Although it could be possible that other types of packages were also used in the past, now we mostly can talk about amphora as an example. The modern terms, like "logistics", "packaging", "ergonomically efficient" are perfectly applied to such ancient objects as amphorae. Amphorae were ergonomically efficient, cause their size and shape were intended for handling by one person and they were easy to carry. Amphorae were the object of the first recorded logistical system for managing reusable shipping containers. And indeed they were one of the earliest consumer packages in human history. Our traditional view on packaging lays on modern conception of square shape. In the past, however, it was the amphorae shape that was successful for shipping and handling (Fig. 2).

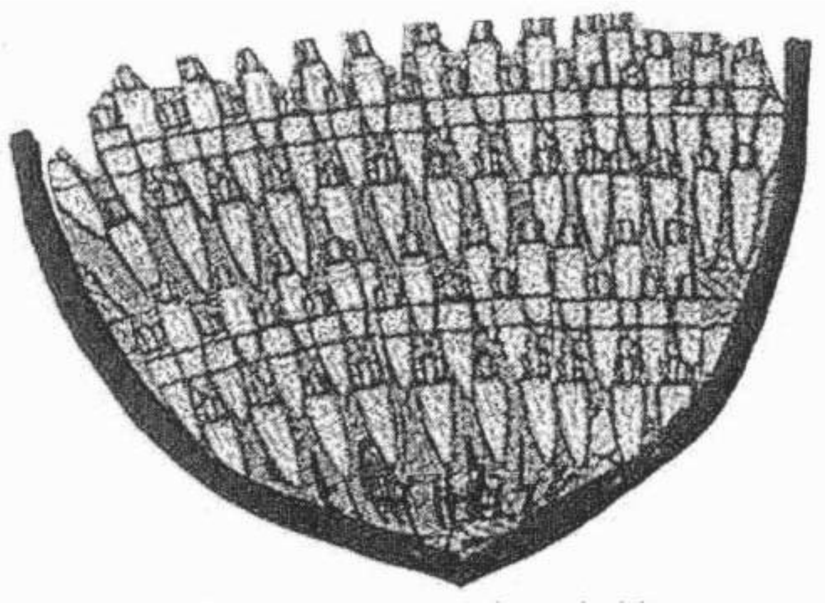

Fig. 2. Amphora stowage aboard ship (Source: Diana Twede, 2002)

The pointed base served as a third handle, below the weight, useful when one inverts a heavy vessel to pour from it (Grace, 1961). Moreover, there were advertising claims depicted on amphorae: Peacock and Williams translate the following tituli picti from a jar found in London: "Lucius Tettius Africanus finest fish sauce (liquam) from Antipolis, product of Africanus." (Twede, 2002).

As we can see, amphorae were truly one of the best examples of ancient economy packages. It is important to mention that amphorae were different from other types of ceramic jars. Mainly because they were not made for any domestic or day-to-day use but were designed specifically for shipping and storing. They were used for simple and strictly utilitarian purpose of either storing or transporting some commodity, like a large quantity of liquid (wine, olives, oils, and processed fish sauce) or dry products such as grain, nuts and salted fish.

Wine together with olive and grain formed so called "big three" of Roman cuisine. And number four, according to some studies, was taken by fish products (Ejstrud, 2005). While it is quite well known fact that wine was transported in amphorae, less known about fish transportation. In general, amphorae were not primarily intended as containers of fish or fish products, but occasionally they could be used for this purpose (Lund and Gabrielsen, 2005). Garum as well as the other types of fermented fish-sauce was a popular part of Roman cuisine and was transported all over the Roman Empire (Ejstrud, 2005). Not only Mediterranean countries were involved in fish trading. Gallant mentions that fish from the Black Sea "was a luxury item, aimed at a very restricted market" in Mediterranean area (Lund, Gabrielsen, 2005).

Particularly interesting information has Bo Ejstrud's article (Ejstrud, 2005). In there it is mentioned that the investigation on four West Europe archaeological sites had been done, they are: Nijmegen, Avenches, Saint-Romain-en-Gal and Rome (Fig. 3). In general very interesting picture of the average consumption of wine, olive and garum is given in this article. The results showed that average volumes of amphorae on these Mediterranean sites 62% was wine, 28% and 10% were oil and garum, respectively (Table 1).

Due to studies of Ejstrud, we know more about amphorae types containing certain types of food. For example, a typical Dressel 20 amphora had the capacity of 60-70 litres of olive oil, and the average Dressel 7 amphora contained about 14-18 litres of garum (Table 2).

Table1

The average volumes of wine, oil and fish (garum) amphorae on the Mediterranean sites.

	Relative volumes, %
Wine	62.25
Oil	27.92
Garum	9.83

In table 2, the general overview is done on some amphorae types capacity.

Table 2

The capacity and possible contents of some amphorae types.

Type	Content	m (litre)
Dressel 6A	Garum	26
Dressel 7	Garum	16
Dressel 8	Garum	21
Dressel 9	Garum	42
Dressel 10	Garum	16
Dressel 11	Garum	16
Dressel 12	Garum	20
Dressel 14	Garum	26
Dressel 16	Garum	10
Dressel 6B	Oil	20
Dressel 20	Oil	66
Dressel 1	Wine	26
Dressel 2-5	Wine	28
Dressel 43	Wine	17.5

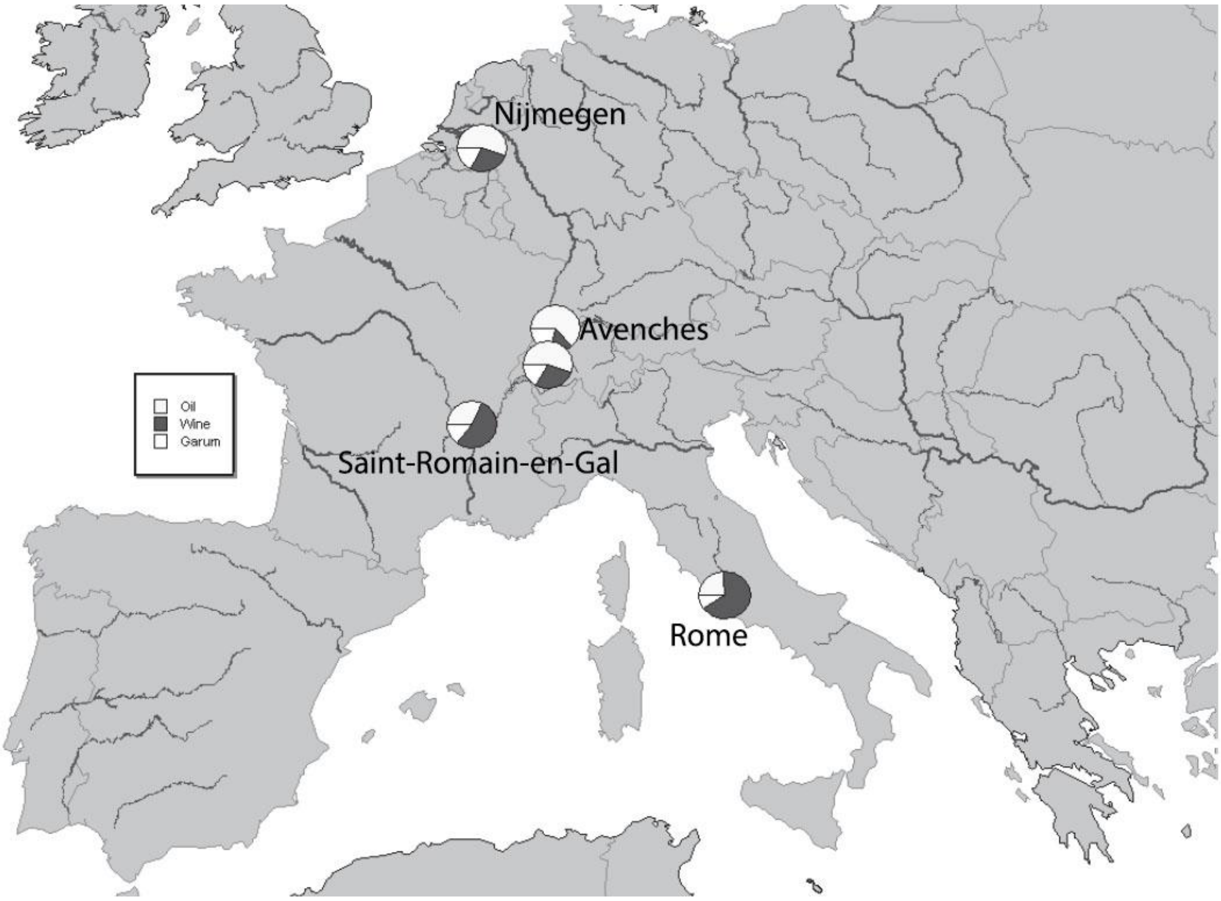

Fig. 3. Relative volumes of oil, wine and garum in Western Europe. (Source: Ejstrud, 2005)

2.1.2 Types of amphorae

It is known, there are many types of amphorae. Here only some of them will be discussed, Beltran and Dressel types. Heinrich Dressel grouped amphorae into types based on their form and place of manufacture. Thanks to the typology began by Dressel, amphorae now provide reliable spatial and temporal information about Roman trade throughout the Mediterranean zone.

Distribution maps of amphorae finds in Gaul (Fig.4) show distinct concentrations along coasts and rivers, the main trade routes for their transport in the South of France. Hereinafter the amphorae of different types and typologies will be briefly described.

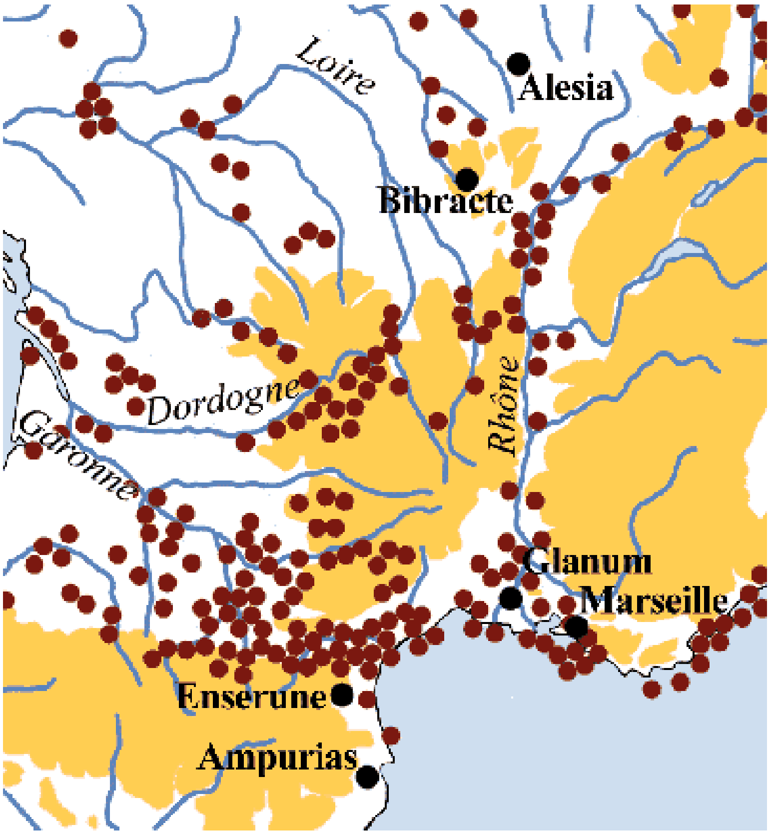

Fig. 4. Distribution of Dressel I amphorae of all types in Gaul. Yellow areas show elevations over 200 m (Source: http://steelerslounge.com/2016/01/latest-storage-reviews/248644/)

Beltrán 2A

This type of amphora (Fig. 5) has a broad, long and cylindrical or flared neck, with a wide and hooked rim, long flattened recurved handles and an ovoid body which widens towards the base and ends in a long, hollow, sharp spike. The form can be subdivided into other forms that are dependent upon the size of the vessel. The larger form is generally called Beltrán 2 A1 or Pelichet 46, while the smaller form is known as Beltrán 2-A2 or Augst 29. (Here and for other following amphorae the source was: http://archaeologydataservice.ac.uk/archives/view/amphora_ahrb_2005/cat_amph.cfm)

Origin: Beltrán 2A was manufactured at many workshops in the modern southern Spanish provinces of Huelva, Cádiz, Málaga and Granada.

Contents: This type carried a range of fish-based products including garum.

Fig. 5. Beltrán 2A type of amphora (Source: Museu Arqueològic de Barcelona David Peacock)

Beltrán 2B

This has a thick everted rim with a tapering lip and long handles sharply bent over directly below the rim (Fig. 6). There is a wide neck and a body which widens towards the base with a longish spike, either hollow or solid. In the latest stage of production, the handles are joined to the rim. There is also a smaller variant (parva) of this form.

Origin: Widely produced along the southern Spanish coast.

Contents: Fish-based products, although some inscriptions could refer to wine.

Fig. 6. Beltrán 2B (Source: Courtesy of Museo Arqueolõgico de Granada Simon Keay)

Dressel 1

The earliest Roman amphorae were Dressel type I, originating in Italy from the late 2nd century BCE to the early 1st century CE. Many came from Cosa on the Mediterranean coast. This was the most common type of late Republican Roman amphora (Fig. 7). Following an early classificatory scheme by Lamboglia (1955), the type is conventionally sub-divided into three sub-types, known as the Dressel 1A, 1B and 1C, which are still used today. These sub-types are distinguished largely on the basis of differences in the shape of the rim (discussed critically by Tchernia, 1986: 312-20). The Dressel 1A has a pronounced triangular rim, often quite difficult to distinguish from the rim of the Greco-Italic type; the rim of the Dressel 1B has a thick near vertical collar rim; the rim of the Dressel 1C takes the form of a narrow mouth and a high collar, which flares outwards in the earlier versions, and which Will (1982) suggests is directly derived from her Greco-Italic form Will 1E. There are few significant differences in the shape of the bodies of these three sub-types although those of the Dressel 1A and B tend to be heavier and more cylindrical while that of the Dressel 1C tends to be more spindle-like. Furthermore, the neck of the Dressel 1C tends to be wider at the bottom closer to its junction with the shoulder. A broad scheme to distinguish between the varieties of Dressel 1A and 1B handles and spikes has been suggested by Stockli (1979), based mainly on the size of these features, but its practical use is perhaps doubtful given the nuances of form which are sometimes apparent in the general class of Dressel 1 amphora. The Dressel 1 is sometimes stamped on the rim and very occasionally on the neck. Where present, the stamp normally consists of two or three letters, sometimes more, or a symbol (such as an anchor or trident) or both. Alphabetical symbols were used in the *ager cosanus*, particularly at the kiln at Albinia, while elsewhere the stamps are quite often in the form of names (e.g. *Sestius*).

Fig. 7. Dressel 1C. (Source: Courtesy of Prof. D.P.S. Peacock David Peacock)

Contents. *Tituli picti* (painted inscriptions) make it clear that the predominant content carried was wine (Tchernia, 1986). However, spondylus shells, resin and hazelnuts have been found in examples of the Dressel 1B, while *garum* has been suggested as a possible content for examples of the Dressel 1C at *Pompeii,* and olives were found in a Dressel 1C from the Cavalière wreck.

Dressel 7

This type has a straight mouth, with a thick external band, a heavy cylindrical neck (10-15 cms diameter) around 12-20 cm long, flattened handles which have a median furrow groove on the external face and an ovoid body. The spike is 15-20 cms long, hollow. It can be ascribed to the broader Dressel 7-11 and Beltrán 1 groupings (Fig.8).

Origin. This type was produced in a myriad of workshops such as Gallineras, El Rinconcillo and Cerro del Mar in the coastal areas of southern Spain (Cádiz and Málaga provinces). Production has also been attested along the west coast of Morocco at Khédis and Sala, as well as at Volubilis.

Contents. Tituli picti suggests several types of fish-sauce.

Fig. 8. Dressel 7 (Source: Courtesy of the Trustees of the British Museum David Williams)

Dressel 8

This form has a bell shaped mouth with a thickened short rim which has a concave outer face, a heavy cylindrical neck with long flattened handles sharply bent over below the rim and a 'radish-shaped' body which has a long hollow spike (Fig. 9).

Contents. *Tituli picti* suggests fish-sauce.

Fig. 9. Dressel 8.

Dressel 9

This type has a bell mouth with a rim which has a concave outer face, sometimes similar to Dressel 7 or Dressel 8 rims (Fig. 10); a cylindrical neck generally smaller than Dressel 7 or Dressel 8, flattened handles, sharply bent below the rim and straight to the body; and a piriform or ovoid body which has a long hollow spike ending in a flat bottom.

Contents. *Tituli picti* suggests fish sauce

Fig. 10. Dressel 9. (Source: Musée Archaéologique Intercommunal d'Istres David Williams)

Dressel 12

A short everted rim and long slim neck with ovoid handles (Fig.11). The body is cylindrical with a short solid spike. The rim becomes gently wider towards the top. The shoulder is noticeably present, usually supporting the handles, but there is no ridge. These handles generaly appear on long-necked amphorae, attaching near the top of the neck progressing vertically downwards to the shoulder. The handle appears to be ovoid or elliptical in section.

Contents. *Tituli picti* suggest fish-based products.

Distribution. Spain and Italy (Beltrán, 1970), but rare in the northern provinces.

Fig. 11. Dressel 12 type. (Source: City Hall of Puerto Real, Cádiz (Lazaro Lagóstena) Villanueva site)

Dressel 14

This has a thickish beaded rim and ovoid handles with a shallow groove down the centre (Fig. 12). The cylindrical body has a long hollow spike. In the southernmost part of Portugal, near Castro Marim, a production centre was identified in the late 19th century which produced amphorae similar to the Dressel 14 but with a short neck and an oval body.

Contents. *Tituli picti* suggest fish-based products. The discovery of kilns in Portugal confirm this suggestion.

Fig. 12. Dressel 14 type. (Source: Courtesy of Jewry Wall Museum, Leicester David Peacock)

2.2 The Chemistry of Resinous Substances

Amphorae were obtained by cooking clays at moderate temperatures. Due to high porosity of clay they were permeable and unsuitable for storing liquids. Thus, waterproofing was made necessary before amphorae could be used for transportation and storage purposes. From Plinii and Columella – the Roman authors of the first century B.C. – we know that a material called *pix* (pitch) was used for waterproofing. With this product, internal waterproofing was carried out on every type of ceramic recipient for wine and probably for any type of food container (Font *et al.*, 2007).

Pitch is the residue after the distillation of volatile resin components in an open vessel. It is an organic substance obtained by combustion of resin exudates or resinous wood, insoluble in water but soluble in organic solvents like acetone, methanol and dichloromethane. Usually pitch has a variable colour from light ochre to black. This substance was probably preferred to other organic compounds for its capacity to impart a particular aromatic strength to the wine, so called flavor enhancement (Izzo *et al.*, 2012). When obtained from pine resin, it may be called pine pitch; when obtained from other plant resins, it may be called more generally wood pitch. The resinous substances secreted by trees have been widely used either in their natural form or as tar and pitch to waterproof the planking of ships and vessels (Duce *et al.*, 2014).

A resin is one of a number of natural products defined as a plant exudate. Resins are non-cellular, water insoluble substances and serve to protect higher plants, if wounded, from excessive water loss and the invasion of microorganisms. Resins often comprise both volatile and non-volatile fractions. The derivatives produced by heating resin, as well as resinous wood, are collectively referred to as pyroligeneous substances. These include tar, the initial pyrolysate, and pitch (Gianno, 1990). Resin-producing trees are found over vast areas encompassing much of the torrid and temperate parts of the world. Resin preserves reasonably well and possesses a wide array of functional attributes. The properties of adhesiveness, insolubility in water, inflammability, healing and poisoning properties, fragrance, plasticity, vitreosity, colorability, pigment mediability, and resistance to spoilage are qualities that apply, to a greater or lesser degree, to all resins (Gianno, 1998). As such, these natural substances have played a role in most communities. The ancient Greeks, and probably not only them, noticed that the pine resin had not only helped to seal amphorae and isolate it from moisture, but also had played the role of a curing agent and helped to keep the wine during transporting it by sea (Zlateva *et al.* 2015). The pine resin was also used to suppress the smell of goat skin, which was used as vessel for a short distance transport of wine. Resin made from pine trees was most often used as the barrier lining for wine amphora. For this reason, Plutarch claimed that the pine tree is sacred to Dionysos (Twede, 2002).

The major components of resins are terpenoids. They have been found to survive in a large number of archaeological contexts from around the world and are distributed widely in plants from marine and terrestrial sources. Survivability and visibility of this compound class in a range of burial environments is quite high. Terpenoids occur widely in the sedimentary record, such as deep-sea sediments, fossil resin, petroleum, coal and so on (Simoneit et al, 1986). The term terpene derives from 'terpen' and is attributed to Kekule who used it to describe $C_{10}H_{16}$ hydrocarbons in turpentine oil.

Terpenoids are divided up into special classes of mono-, sesqui-, di-, and triterpenoids which have 10, 15, 20, and 30 carbon atoms per molecule respectively. At normal temperatures the first two of the classes are usually liquids, whereas di- and triterpenoids normally are solids. It should be also noted that di- and triterpenoids have never so far been found together in resins. On this basis, they can be divided in two main groups.

In this work focus will be on diterpenoids. The main group of diterpenoid (C_{20} compounds) resin producers are the Coniferae families (Pinaceae, Cupressaceae and Araucariaceae). The second main group comes from trees of the sub-family Caesalpinioideae of the enormous Leguminosae family. Diterpenoids serve as valuable marker compounds of terrigenous resinous plants. The most abundant sources of resin in temperate regions are trees of the genus *Pinus*. Diterpenoid compounds possess mainly abietane, pimarine and labdane skeletons. In 'soft' resins (i.e. those containing no polymerized structures), such as those derived from Pinaceae, abietane and pimarine compounds are predominant. The Pinaceae, and especially Pinus, generally have resins with a high content of abietic acid (AA) (Fig. 13), a tricyclic molecule, and a small number of abietane isomers (Mills and White, 1994).

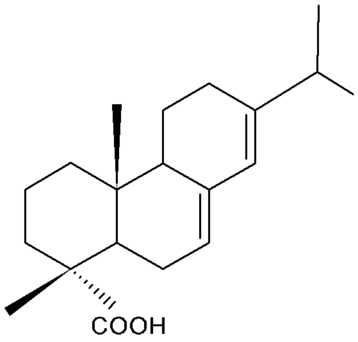

Fig. 13. Abietic acid

The double bonds in abietane acids are conjugated and in fresh Pinus resins will undergo significant modification during treatment. Warming of the resin (e.g. during distillation to remove oil of turpentine) induces isomerization reactions leading to a mixture enriched in abietic acid at the expense of other abietane molecules (Mills and White, 1977). The solid product remaining is referred to as rosin or colophony.

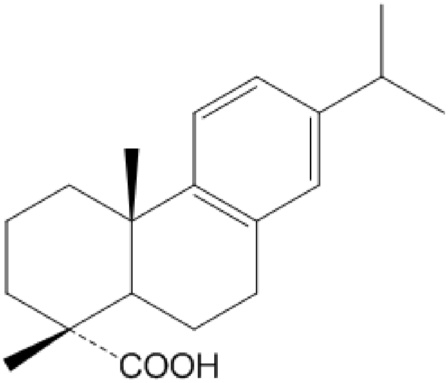

Fig. 14. Dehydroabietic acid

Terpenoids are susceptible to a number of alterations mediated by oxidation and reduction reactions. For example, the most abundant molecule in aged Pinus samples is dehydroabietic acid (DHA) (Fig. 14), a monoaromatic diterpenoid based on the abietane skeleton which occurs in fresh (bleed) resins only as a minor component. This molecule forms during the oxidative dehydrogenation of abietic acid, which predominates in rosins. Further atmospheric oxidation (autoxidation) leads to 7-oxodehydroabietic acid (Fig. 15) (Pollard, Heron, 2008). In general, oxygenated products (such as 7-oxo-DHA or 7-oxo-15-hydroxy-DHA) are the consequence of an aging process due to contact with the atmosphere.

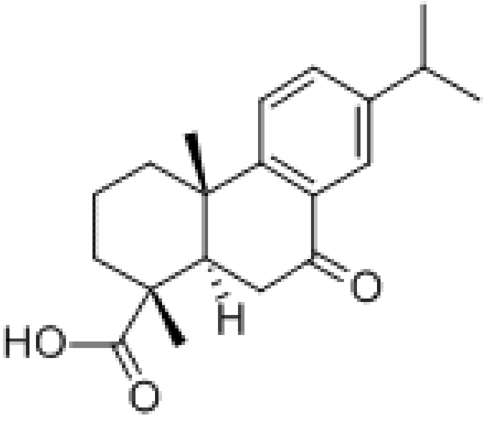

Fig. 15. 7-oxo-dehydroabietic acid

When resin or resinous wood is heated strongly, significant changes in resin composition occur, leading to the formation of tar and pitch. Chemical changes include thermal dehydrogenation, decarboxylation and demethylation which give rise to a large number of potential alteration products of varying aromaticity. Stable end products of these reaction pathways include retene (Fig. 16), a triaromatic defunctionalized diterpenoid with the formula $C_{18}H_{18}$. Retene is the product formed predominantely when the process is produced at high temperatures (Font *et al.*, 2007). Intermediates also include dehydroabietane, dehydroabietin, simonellite, the nor-abietatrienes and tetrahydroretene, although some of these molecules are resent in low abundance in relatively fresh bleed resins.

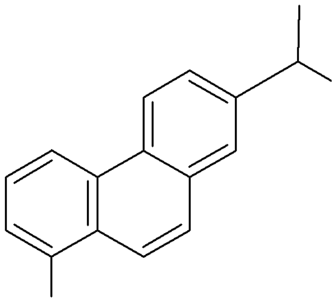

Fig. 16. Retene

Methyl dehydroabietic acid (DHAM) (Fig. 17) is formed when resin is heated in presence of wood because CH_3OH released when wood is heated to high temperatures reacts easily with dehydroabietic acid (DHA), which is absent when the sealing material is produced by pyrolysis of the resin alone. The simultaneous presence of retene and methyl dehydroabietate highlights that the resin was heated in the presence of wood obtained from plants of the Pinaceae family.

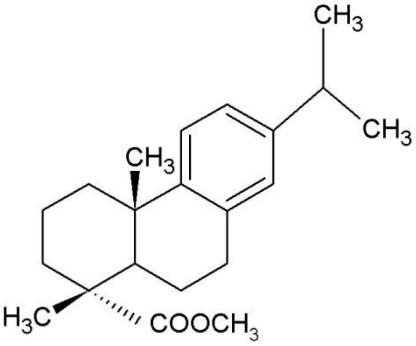

Fig. 17. Methyl ester of dehydroabietic acid

To sum up, abietic acid is the main component in resins of Pinaceae origin. During the heating process abietic acid (AA) can be converted into dehydroabietic acid through dehydrogenation. A series of other transformations can produce many other intermediate organic compounds when the thermal treatment is maintained and is more intense (Fig. 18). Although the main reaction is dehydrogenation of AA to DHA, decarboxylation of DHA produces dehydroabietin. Increasing aromatization of dehydroabietin as well as decarboxylation of DHA generates norabietamene. Norabietamene is further dehydrogenated to tetradydroretene and retene. Further retene dealkylation produces phenanthrene (Fig. 18).

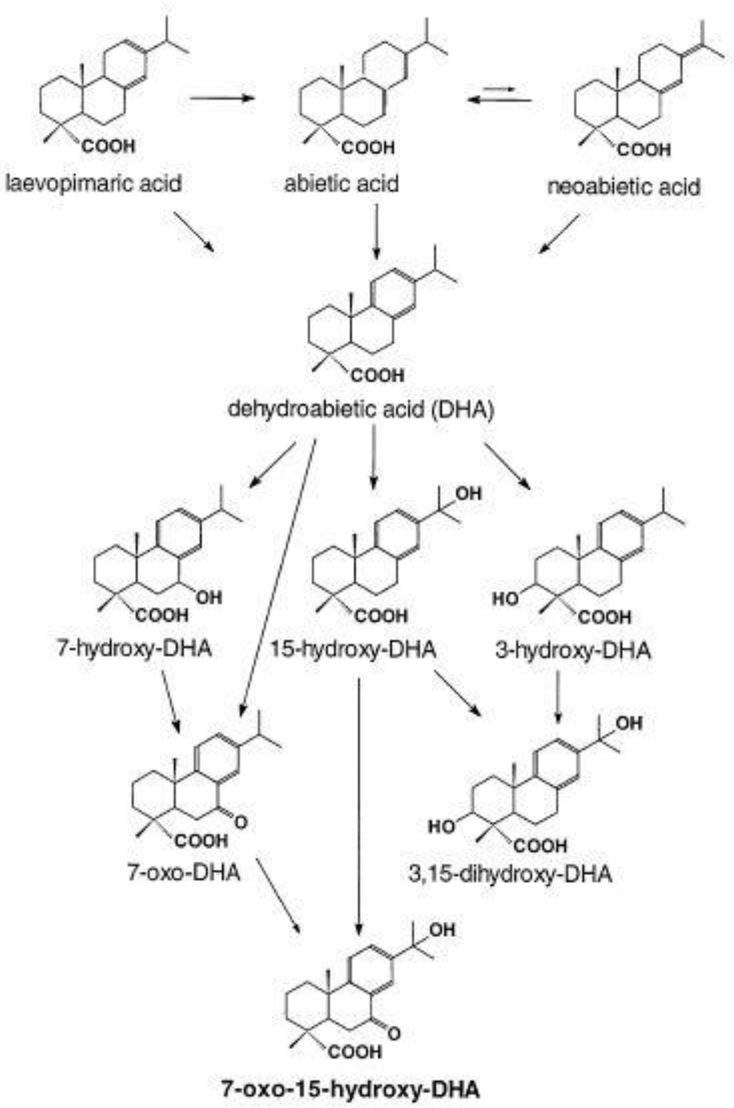

Fig. 18. Oxidation scheme of abietanes (Source: Pastorova *et al*, 1997)

Identification of ancient resin is not a straightforward task. Although ancient resins have been researched for a long time, their chemical complexity has hindered confident assignments. Visual characteristics and examination of simple chemical or physical properties may offer little or no clue as to the identity of resin samples, whether ancient or modern. Consequently, chemical analysis must be performed in order to characterize which molecular species are present.

2.3 Previous studies

The first important study of amphora was performed in 1899 by Heinrich Dressel who recorded examples of painted inscriptions and shapes. Another notable researcher was American archaeologist Virginia Grace (in 1940-1970s). Her work has been decisive in calling attention to the importance of amphora. As a result of her work, amphorae and their stamped handles are now useful as a tool for dating and serve as a primary indicator for tracing and understanding ancient trade in the Mediterranean. Callender was also one of the pioneers in studying amphorae. He described amphorae as simply a carriers of their contents and stresses the differences between amphorae and the other classes of pottery. Pottery, by his opinion, were manufactured and sold as objects to be used in their own right, while amphorae were simply carriers of their contents: "it was after all the latter (i.e. the particular commodity that they were destined to carry) which was being sold and not the amphora" (Callender, 1950).

The identification of a wide variety of resins in archaeological and art historical contexts were pioneered by Mills and his coworkers at the Research Laboratory of the National Gallery in London (Mills, 1977). Shackley (1982) used gas chromatography to examine resinous crusts, believed to represent the former vessel contents, from a sixth century storage jar from a site in Israel. GC analyses indicated the major constituents of the residue were dehydroabietic and 7-oxo-dehydroabietic acid. While the presence of Pinus-type resin was confirmed, firm conclusions about the nature of the deposit were not possible. Historically, similar resins were used (1) in the production of unguents, (2) for caulking and waterproofing, and (3) in resinated wine. Evershed *et al.* in 1985 performed studies on pitch from the Mary Rose ship. Through studies they have found out the evidence that pitches from Mary Rose were from pine wood.

One of the most recent studies were performed by J. Font *et al.* In this work, the resinous materials from the interior surfaces of two Roman and one Iberian amphora were studied with Fourier transform infrared (FT-IR) spectroscopy. Gas chromatography-mass spectrometry (GC-MS) was also used in order to compare the results with those of FTIR. The diterpenoic nature of samples from amphorae was established. Note that this work has repeated Font's procedures in GC-MS and FT-IR analyses.

In works of Izzo *et al.* the pitch of Roman amphorae from Monte Poro, Calabria (Italy) was studied by FT-IR and GC-MS. In the work it was discovered that the presence of monocarboxylic acids and terpenic species can prove that the organic residues were of vegetable origin and mainly consist of vegetable-based resins. The presence of methyl dehydroabietic acid shows the link to the use of wood tar and not only to the pine pitch. Izzo *et al.* also stated that absence of typical oxidation products of abietic acid might be due to the different conditions of conservation. In Colombini's studies on pottery vessels from Roman times (Colombini *et al.*, 2005) it was established that the presence of characteristic diterpenic biomarkers enables to assess the use of both pine resin and pine pitch. In the work of Regert the prehistoric glues were analysed. In this article, the triterpenoids and diterpenoids were connected with the historical periods. It was shown that during prehistoric times, people mostly used birch bark tars. During Bronze Age, pine resin began to be utilized in a big amounts. It was also shown that diterpenoids like dehydroabietic, abietic and 7-oxodehydroabietic acids are markers of pine resins (Regert, 2004).

In general in amphorae resin, waterproofing materials and pitch can be studied along with organic residues. Amphorae have been studied and classified by archaeologists, historians, economists and ceramic petrologists. Recently with the development of technologies and specific techniques the analytical, mainly chemical, research of amphora has been possible.

2.4 Analytical techniques

There has been conducted many works in the study of amphorae, mainly archaeological and historical. With the help of new analytical techniques, it is possible to dive into the past and to recheck and prove the information obtained from those studies or even to discover some new data. Artefacts such as amphorae were used frequently in the past to store and transport foodstuffs and other natural products. Consequently, traces of these substances may survive, preserved on the surface of the amphora. Similarly, organic molecules can occlude in the permeable ceramic matrix. These chemical remnants offer valuable clues to the use of pottery and other artefacts and may provide novel identifications of organic substances in the archaeological record (Pollard, Heron, 2008). In general, to make the connection between amphorae themselves and their contents it is important to study the organic residues of the amphora. And means of analytical chemistry are very helpful in this case.

Most modern techniques for determining molecular structures are based on spectroscopy, which involves interactions of electromagnetic radiation (light) with molecules. The spectral range which is used in the determination of molecular structure is broadly classified into X-ray, ultraviolet (UV), visible (vis), and infrared (IR) radiations, and microwaves and radiowaves, in order of decreasing frequency (i.e. energy) or increasing wavelength (Fig.19)

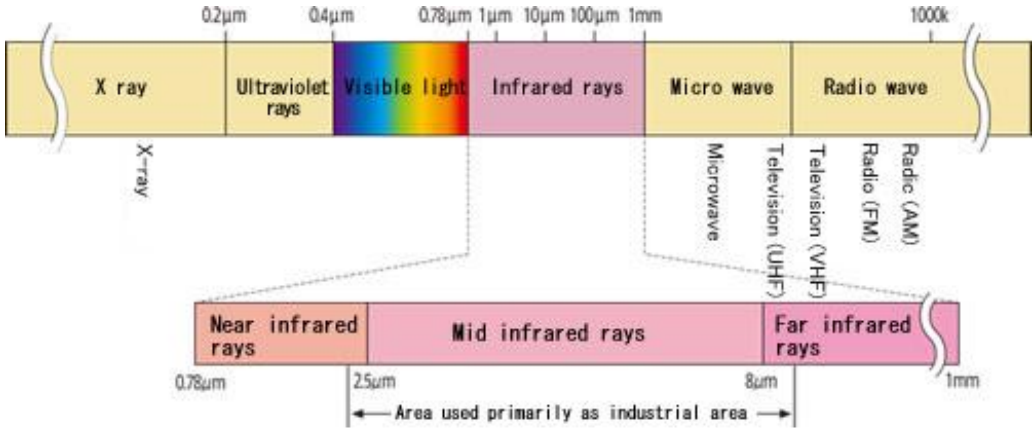

Fig.19 Electromagnetic spectra

(Source: http://www.apiste-global.com/fsv/technology_fsv/detail/id=1204)

Molecular spectroscopic techniques, i.e. infrared play an important role in classifying materials and assessing the state of oxidation. Fourier Transform Infrared Spectroscopy (FT-IR) gives information on the functional groups and on the degree of oxidation and/or aromatization correlated with the degradation of the organic material. The technique is suitable as an initial prospective screening technique. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Different materials consist of unique combination of atoms and therefore no two compounds produce the exact same infrared spectrum. Infrared spectroscopy can result in a positive identification (qualitative analysis) of different kind of material and in addition, the size of the peaks in the spectrum is a direct indication of the amount of material present.

Different kinds of bonds vibrate with different frequencies and radiative excitation of a particular vibration corresponds to absorption of IR radiation of a particular frequency (energy). The absorption pattern plotted against the radiation frequency is the IR spectrum. Since functional groups have characteristic bonds and hence characteristic vibrational frequencies, IR spectroscopy may be used analytically to identify functional groups in a substance.

IR radiation is normally described by its wavenumber ($\bar{\nu}$ in cm^{-1} where $\bar{\nu} = 1/\lambda$) and the range is typically 4000-400 cm^{-1} (corresponding to λ of 2.5-25 μm). Another difference is that transmittance ($T = I / I_0$) is recorded in IR spectra rather than absorbance. Characteristic absorption bands (peaks) which are useful for identifying particular molecular structural features are summarized in Table 1.

Table 3 lists the characteristic IR absorption bands due mainly to bond stretching vibrations of the main functional groups of organic compounds. Most of the characteristic bands are above 1500 cm^{-1}; the region below 1500 cm^{-1} is called the fingerprint region where many peaks correspond to various C-O, C-C and C-N single bond stretching and bending vibrations.

Table 3

Characteristic IR absorptions of some functional groups[a]

alkane	C-H	2850-3960 (m-s)		
alkene (arene)	C(sp^2)-H	3020-3100 (m)	$C=C$	1620-1680 (m-w)[b]
alkyne	C(sp)-H	~3300 (s)	$C\equiv C$	2100-2260 (m-w)
alcohol (ether)	O-H[c] free O-H	3200-3600 (s, br) 3590-3650 (m)	$C-O$	1050-1250 (s)
aldehyde (ketone)	C(O)-H	~2720 and 2820 (w)	$C=O$	1630-1750 (s)[d]
carboxylic acid	O-H	2500-3300 (s, br)	$C=O$	1710-1780 (s)[d]
amine	N-H	3300-3500(m, br)	$C-N$	1020-1230 (m)

a. Absorption bands are given in cm^{-1} with indications of their intensities in parentheses: s, strong; m, medium; w, weak; br, broad;

b. The skeletal vibrations of the benzene ring are typically four bands of variable intensities in the region 1450-1600 cm^{-1}

c. H-bonded OH.

d. The wavenumber of the stretching band for carbonyl compounds RC(O)X is characteristically dependent on the nature of the X group.

The mass spectrometric method

The research of amphora's contents also strongly relies on structural information at a molecular level, and thus the application of mass spectrometry (MS) plays a prominent role. The coupling of mass spectrometry with gas chromatography (GC) make MS the most powerful tool for investigation of the complex and aged mixtures of organic molecules encountered as constituents of historic and archaeological objects.

Mass spectrometry (MS)[4] is a useful technique for determining the molecular formula of an organic compound as well as structures of parts of a molecule if not its whole structure. In this method, the masses of ionized molecules and their ionic fragments are measured, so the technique is fundamentally different from the spectroscopic methods (UV, IR).

Mass spectrometry (MS) can determine the molecular formula of a molecule ionized by loss of an electron following collision with a high-energy electron in an electron beam. In

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[4] The term *spectroscopy* is used for techniques involving interactions between molecules and electromagnetic radiation. In MS, a beam of electrons is normally used to energize and ionize molecules, and the term *spectrometry* is used.

addition, the ionic fragments formed by subsequent decomposition of the molecular ion provide important information about the molecular structure. Molecular formulas were once deduced from elemental analyses combined with molecular weights usually determined by the effect of the compound upon the boiling point (an elevation) or freezing point (a depression) of a solvent; these measurements were time- and labour-consuming tasks, and required appreciable amounts of pure compounds. Mass spectrometry now allows us to obtain the same information (and much more) in less time with only one minute amounts of material.

In a mass spectrometer, a sample of the compound under investigation is introduced as a molecular beam into a high vacuum chamber and ionized (usually) by bombardment with a beam of high-energy electrons (typically 70 eV), as illustrated in Figure 20.

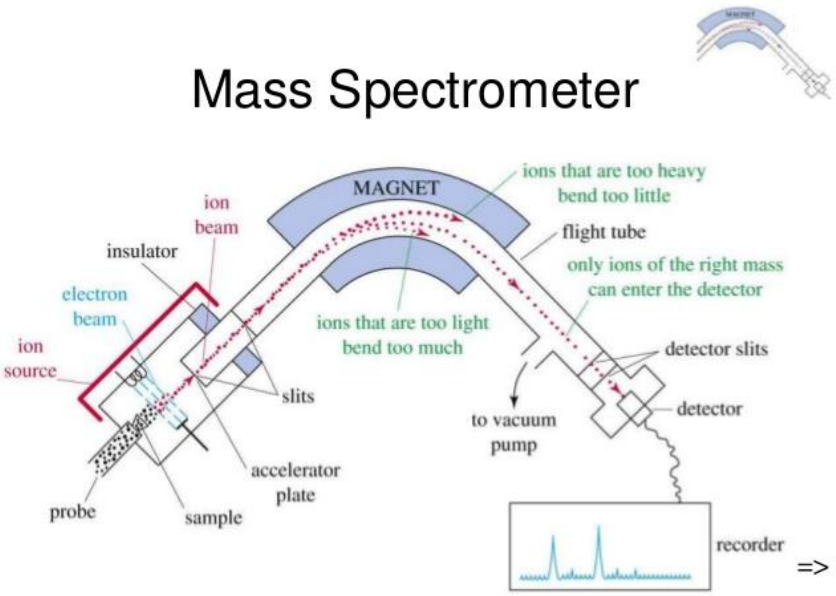

Fig.20 Schematic representation of mass spectrometer (Source: http://www.slideshare.net/banuman35/mass-spectrometrymassspec2013-pravisankar)

In this electron impact (EI) ionization mass spectrometric method, the molecular ion (a radical cation), formed by ejection of an electron following collision with one of the high-energy electrons, mainly decomposes into fragment radicals and cations (Fig. 21).

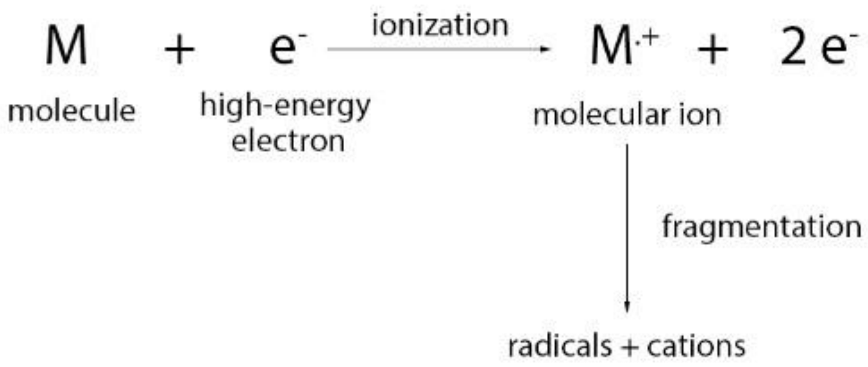

Fig. 21. Electron ionization

The cationic species (the molecular ion and its charged fragments) are separated by their mass (more exactly, their mass-to-charge ratio, m/z) to provide a mass spectrum by plotting the intensity of each ion against its mass (or m/z ratio). The separation is achieved by diverting the flow of gaseous ions with a magnetic field (the ions are deflected according to their m/z) or by their time of flight (the velocity of an ion depends on its m/z).

A conventional low resolution mass spectrometer records intensities of whole-number m/z ratios, and the highest (most intense) peak in the spectrum is called the base peak; intensities of all other peaks are given relative to this. The molecular ion (identified as $M^{\cdot+}$, M^+, or sometimes simply as M in spectra) generated in the ionization chamber by loss of an electron will appear at the highest m/z value in the mass spectrum if it is sufficiently stable to reach the detector before fragmenting.

Gas chromatography (GC) and mass spectrometry (MS) can be combined to analyse mixtures of compounds. In order to determine the structure of an organic compound, generally a pure sample and purification of compounds depends on intermolecular interactions. Chromatography is the most useful technique for separation and purification of organic compounds (Varella, 2013)

The gas chromatograph separates a mixture, and the individual components pass directly into the mass spectrometer so that individual mass spectra can be recorded. The quantitative analysis of the components of the mixture is carried out by the GC and, at the same time, identification of the components is achieved by MS. Gas chromatography combined with mass spectrometry (GC-MS) found wide application in the chemical characterisation of different organic compounds. High sensitivity is the main advantage of this analytical technique and thus very small amount of samples is required for the analysis. Gas chromatography is a separation technique that separates a mixture of volatile compounds for further individual analysis of each component by MS.

3. Materials and methods

3.1 Analysed samples

A set of samples was received from Museum of Arles collection and DRASSM collection of Grand Congloué 2 shipwreck near Marseille, France. The resinous materials were studied and are presented into three categories:

– 16 samples from Grand Congloué 2 shipwreck (Fig. 22). Dark resinous layers in large quantity with little impurity. Some grains of white sand and pieces of sea shell, and probably fish bones. Amphorae have been dated as of beginning of II-I century B.C. And provenance was defined as from Cosa in Italy. In Table 4 the list of Grand Congloué 2 samples are presented.

– 9 samples from other amphorae collection. Table 5 contains the list of samples. The amphorae are Dressel I and Dressel II types, Haltern 70 and Lamboglia 2 are presented as well. Amphorae' provenance is mostly Italian coast. The content presumably was wine.

– 21 samples of fish amphorae with presence of fish, brine or fish sauce (garum) were from collections of Museum of Arles Antique, France (Fig. 23). Preliminary studies shows that the reuse of amphorae was unlikely. Pitch keeps the original material. Presence of fish, brine or sauce. Samples of mud brown ochre and yellow colour, fine-grained. Translucent dark brown resinous layer. Dated as I B.C. - I A.D. In Table 6 the list of fish amphorae samples is indicated.

Since archaeological work is still in progress, the archaeologists have not definitively assessed the typology and provenance of all the amphorae that have been discovered.

Fig. 22. GC2.SN.11

The samples were carefully extracted mechanically with cutting tools from amphorae's inner surfaces by scratching the waterproofing coating – the pitch. In total, 46 samples were analysed. Among them 25 were wine amphorae samples and 21 were samples from amphorae containing fish. 24 samples were analysed by both FT-IR and GC-MS instruments, 6 only by FT-IR and 16 only by GC-MS instruments. Among the samples 41% of the amphorae were Dressel I type.

Fig. 23. ARL 9 amphorae

Table 4

Samples from Grand Congloué 2 shipwreck.

#	Sample	Amphora type
1	GC2.SN.2	Dressel I A
2	GC2.SN.3	Dressel I A
3	GC2.SN.4	Dressel I A
4	GC2.SN.5	Dressel I A
5	GC2.SN.6	Dressel I A
6	GC2.SN.8	Dressel I A
7	GC2.SN.9	Dressel I A
8	GC2.SN.10	Dressel I A
9	GC2.SN.11	Dressel I A
10	Li 2.83	Dressel I
11	24210	Dressel I
12	24255	Dressel I
13	24265	Dressel I
14	24268	Dressel I
15	24270	Dressel I
16	24281	Dressel I

Table 5

Wine amphorae samples (apart from Grand Congloué 2 samples)

#	Sample	Amphora type	Provenance
1	AV22	Dressel II/4	?
2	AV23	Dressel I	?
3	AV24	Dressel I	?
4	AV25	Dressel I	?
5	C98	Dressel II/4	Pompei
6	CB4155	Dressel II/4	Italy(?)
7	GE3932	Haltern 70	Baetica (Spain)
8	SL2878	Lamboglia 2	Adriatic
9	4928	?	Italy

Table 6

Samples from Museum of Arles. Fish amphorae.

#	Sample	Amphora type	Provenance
1	ARL3	Beltran II A	
2	ARL4	Dressel 9	
3	ARL5	Dressel 9	
4	ARL6	Dressel 8	
5	ARL7	Dressel 1C	
6	ARL8	Pompei 7(?)	
7	ARL9	Dressel 9	
8	ARL12	Beltran II B	
9	RL15	Dressel 8	
10	RL16	Beltran II A	
11	RL17	Dressel 8	
12	RL18	Beltran II A	
13	RL19	Beltran II A	
14	RL20	Beltran II A	
15	RL21	Dressel 8	
16	Amphora 1	?	
17	2928	Pompei 7	Baetica (Spain)
18	SL 2930	Pompei 7	Baetica (Spain)
19	2970	Dressel 9	Baetica (Spain)
20	6028	Dressel 12	Baetica (Spain)
21	Amphora a poix	?	

3.2 Analytical *methods*

The nature of organic residues and pitch were analyzed with Fourier-transformed infrared spectroscopy (FT-IR) and gas chromatography-mass spectrometry (GC-MS). FTIR allows the identification of the class of substance analysed based on the transitional vibrations of the functional groups. GC-MS permits a more specific identification of organic compounds present in the samples.

3.2.1 Reagents and standards

Potassium hydroxide (KOH), and N,O bis(trimethyl)silyltrifluoro acetamide (BSTFA) containing 1% trimethylchlorosilane were purchased from Thermo Scientific, Bellefonte, PA, U.S.A. The solvents acetone from Sigma-Aldrich Chromasolv, dichloromethane were from SupraSolv Merck KGaA Darmstadt Germany. KBr of infrared analysis was from Fisher Chemical, Loughborough, Leies, UK. Sodium carbonate (Soda ash) Na_2CO_3 was from Fluka, BioChemica, Switzerland. Methanol ultrapure 99.8+% from AlfaAesar, Thermofisher, Karlsruhe, Germany.

3.2.2 FT-IR analysis

Samples were analyzed in FT-IR KBr pellets. All samples of fish amphora were ground, homogenized and prepared for analysis by FT-IR and GC-MS. Samples (1 mg) were extracted using 5 mL of acetone. After drying, the extracts were mixed with KBr, compressed as micropellets (10 Tons pressure) and then analyzed in Thermo Scientific™ Nicolet™ iS™10 FTIR Spectrometer (Fig. 24). Thermo Scientific™ OMNIC™ Specta Software program was used for instrumental control and spectra acquisition. All the spectra were collected in the range of 400 to 4000 cm^{-1} with 4 cm^{-1} resolution. The raw data from the FTIR analysis was collected in 32 scans.

Fig. 24. Thermo Scientific™ Nicolet™ iS™10 FTIR Spectrometer (Source: Dauren Adilbekov, 2016)

3.2.3 GC-MS analysis

GC-MS analysis, which permits the separation and identification of single molecular species in complex mixtures, has been successfully used to characterize waterproofing materials (Colombini *et al.*). In the analysis of organic materials in ancient objects, it should be taken into consideration that their chemical composition may have been profoundly changed by treatment before use, such as heating or distillation, and by ageing.

Samples of 8 mg each were taken for the GC-MS analysis. 1.5 mL of acetone and dichloromethane (1:2, v/v) mixture was added and the mixture was sonicated for 5 minutes. After filtration with PTFE (polythetrafluoroethylene) filters, 1.0 mL and 1.0 mL of dichloromethane and potassium hydroxide (KOH) of 0.5M were added. Centrifugation (4000 rpm for 15 min) was performed for the separation of organic phase. Again 1.0 mL of KOH 0.5M was added, again, followed by centrifugation (4000 rpm for 15 min) was done again. After separation of the organic phase, sodium carbonate (Na_2CO_3) was added to avoid water. Samples were filtered with PTFE and dried in a sample concentrator. The reaction of derivatisation was done with BSTFA (N,O-bis (trimethylsilyl)trifluoroacetamide) with 1% TMCS (trimethylchlorosilane). (Pierce).

GC/MS analyses were carried out with a Thermo Scientific™ Focus gas chromatographic system mounted with a Thermo Scientific Al 3000 auto-injector (Fig. 25), coupled with a ITQ™ 700 Series GC-Ion Trap Mass Spectrometer (Thermo Fisher Scientific, Austin, TX

USA). GC separation was performed on a fused silica capillary column TG-5MS (Thermo Fisher Scientific, Austin, TX USA) stationary phase 5% diphenyl-95% dimethyl-polysiloxane.

Fig. 25. GC-MS Thermo Scientific™ ITQ700 Focus (Source: Dauren Adilbekov, 2016)

A volume of 1 μL for each sample was injected into the injector chamber in splitless mode at a ratio of 1:20. And injector temperature was set at 250°C. Molecular components were eluted using helium at a constant flow of 1.2 mL/min. The following temperature program was used: initial temperature 50 °C for 2 min, 50-220°C at 8 °C/min, 220-260°C at 2 °C/min, 260-330°C at 10 °C/min.

Mass spectra was recorded in Electron Impact (EI) mode with an electron ionization voltage of 70 eV and a mass range of 50-650 m/z. Ion trap and interface transfer line were respectively at 250 °C and 300 °C. Thermo Xcalibur™ 2.2 software (Thermo Fisher Scientific Inc.) was used for instrumental control and data acquisition. Mass spectra peak assignment were based on a comparison with internal mass spectrum databank (from commercial standards and from fresh and artificially aged resins and oils) and NIST databank (NIST MS Search 2.0).

4. Results and discussion

4.1 FT-IR

In this section the FT-IR results of Grand-Congloué 2, other wine amphorae and fish amphorae samples will be discussed.

4.1.1 Grand Congloué 2 samples

The FT-IR spectrum of the GC2.SN.5 sample of wine amphora is shown on Fig. 26. The FT-IR spectrum shows the typical transmittance profile of a diterpenoid resin such as that of the Pinus species (Izzo *et al.*, 2013). It is possible to observe the stretching bands of O-H from alcohol groups at 3428-3429 cm^{-1}. It is also possible to observe the stretching vibrations due to $–CH_2$ and $–CH_3$ groups at 2955, 2929 and 2868 cm^{-1} awardable to hydrocarbon skeleton of the resin. Also it is possible to see the shoulder band at about 1720 cm^{-1}. The stretching vibrations due to aromatic ring at 1605, 1496 cm^{-1}, 886 and 821 cm^{-1} are present. Other bands are those at 1459 and 1384 cm^{-1} due to the $–CH_2$, $–CH_3$ bending and at 1235 cm^{-1} due to the OH bending.

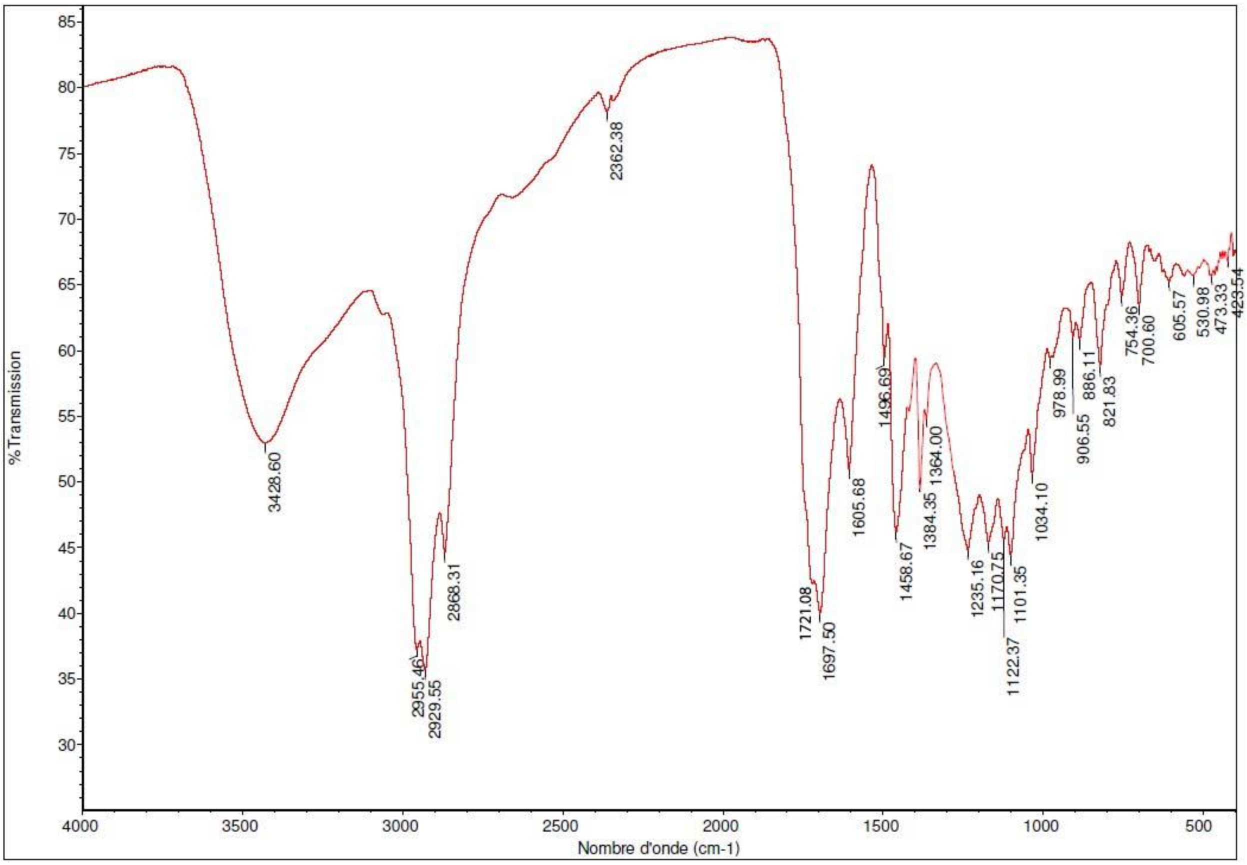

Fig. 26. FT-IR spectrum of GC2.SN.5 sample

4.1.2 Wine amphorae samples

Fig. 27 shows the FT-IR spectrum of the pitch of SL2878 sample. It is possible to observe the stretching bands of O-H from alcohol groups at 3428 cm^{-1}. It is also possible to observe the stretching vibrations due to -CH$_2$ and –CH$_3$ groups at 2955, 2930 and 2868 cm^{-1} awardable to hydrocarbon skeleton of the resin. Carbonilic group is at 1724 and 1697 cm^{-1}. The stretching vibrations due to aromatic groups at 1605 and 1497 cm^{-1}, 885 and 821 cm^{-1} are also present. The 1458 and 1384 cm^{-1} bands are due to methyl bending bands at 1242 and 1173 cm^{-1} are different bending signals from COOH.

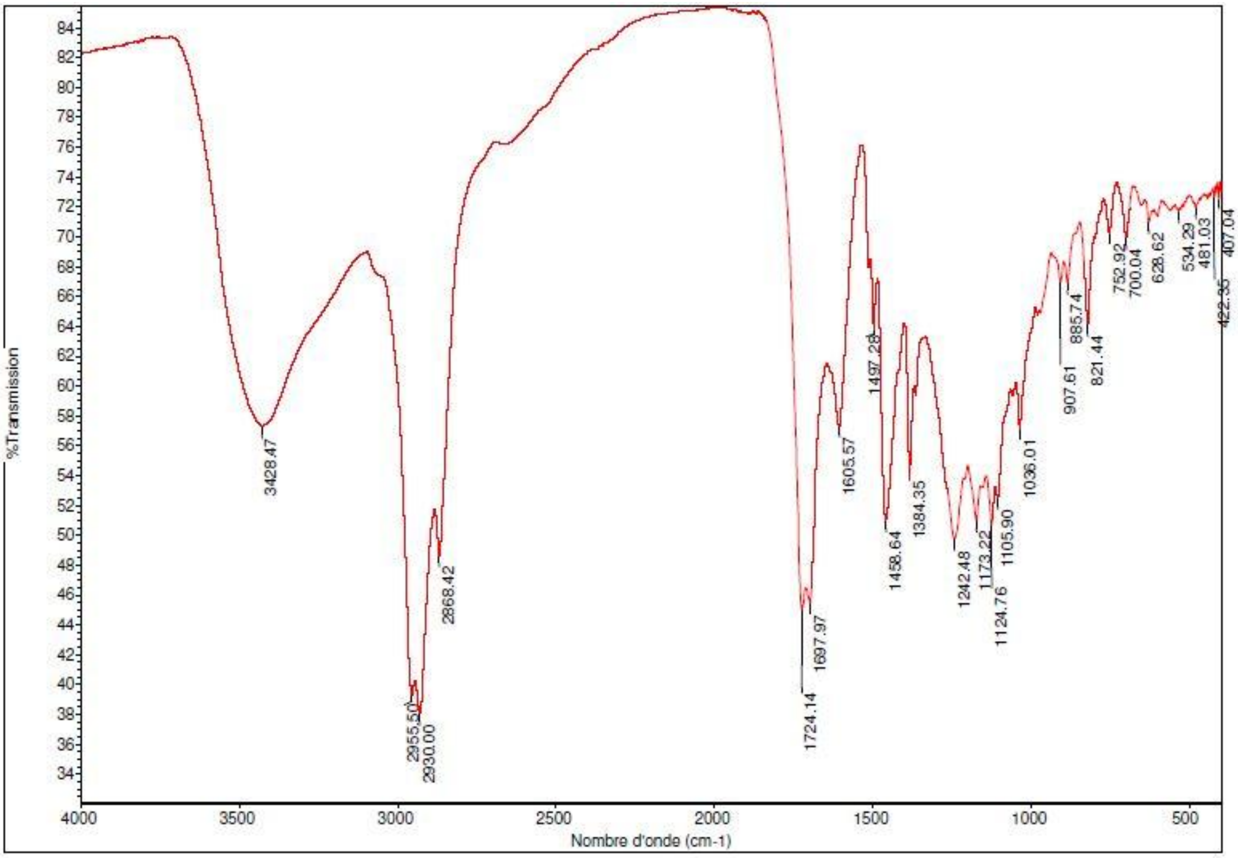

Fig. 27. FT-IR spectrum of the sample SL2878

4.1.3 Fish amphorae samples

The FT-IR spectrum of the ARL 9 sample of amphora that probably contained fish is shown on Fig. 28. It is possible to observe the stretching bands of O-H from alcohol groups at 3420 cm^{-1}. It is also possible to observe the stretching vibrations due to $–CH_2$ and $–CH_3$ groups at 2955, 2929 and 2868 cm^{-1} awardable to hydrocarbon skeleton of the resin. Ketones are observed at 1724 cm^{-1}. The stretching vibrations due to aromatic ring at 1606 and 1497 cm^{-1}, 886 and 821 cm^{-1} are also present. Other bands are those at 1457 and 1383 cm^{-1} due to the $–CH_2$, $–CH_3$ bending and at 1238 and 1172 cm^{-1} due to the OH bending.

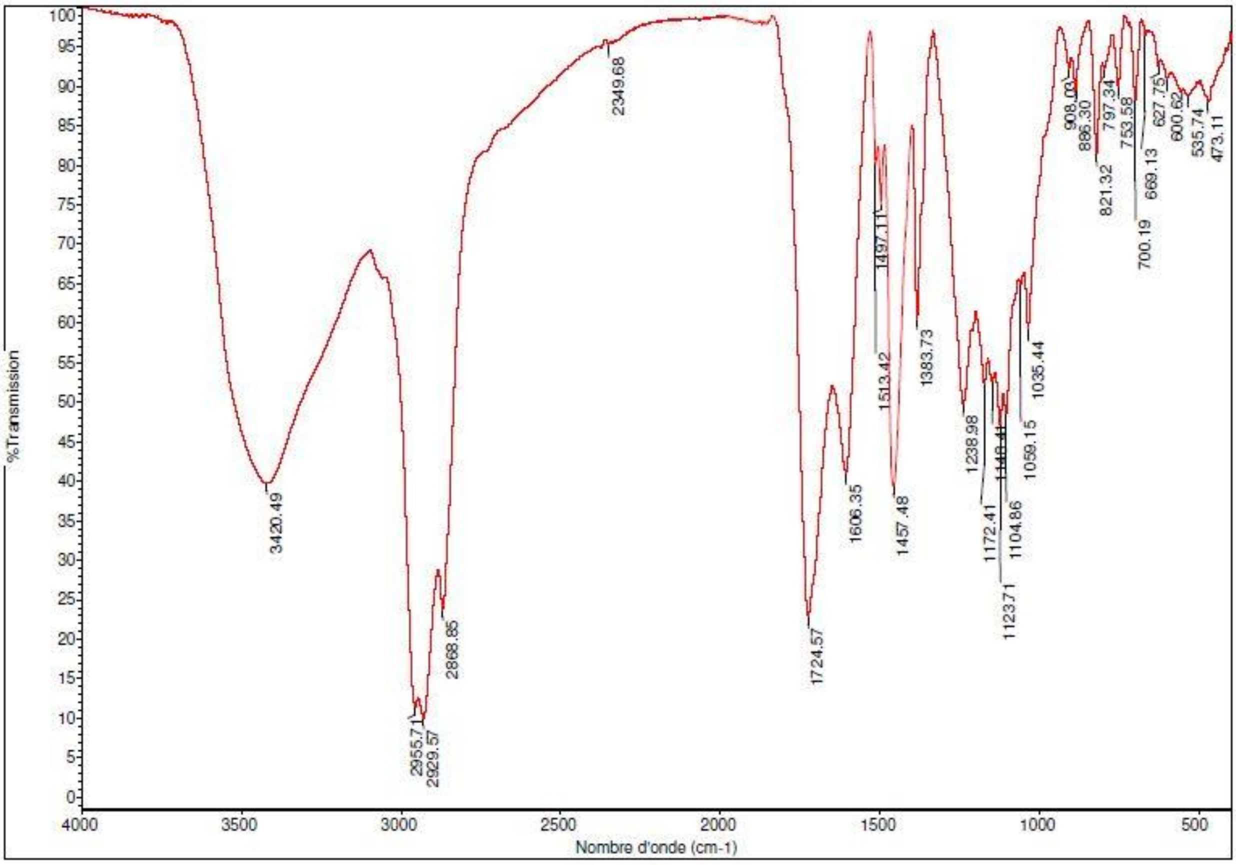

Fig. 28. FT-IR spectrum of ARL9 fish amphorae sample

Complete list of FT-IR results of all other samples could be found in Appendix 6 section.

4.2 GC-MS

In this section the results of GC-MS analysis are presented. GC-MS was applied to wine and fish amphorae samples. GC-MS technique was used in order to corroborate the results obtained with FT-IR spectroscopy. Pitch marker, degradation products and methyl esters are discussed in this part. 9 wine and 21 fish amphorae samples were analysed by GC-MS.

4.2.1 Wine amphorae samples

Different chemical markers of natural resin were found (Fig. 29 and Fig. 30). Wine amphorae samples contain diterpenic compounds, specific of resins exuded from conifer trees. In fact, all identified compounds came from abietic acid, a molecule present in fresh confer resins (Ménager *et al*., 2014).

GE3932 sample (Fig. 29): the presence of monocarboxylic acids (in this case palmitic acid) and terpenic species shows that the organic residues were of vegetable origin or mainly consist of vegetable-based resins. Moreover, the presence of characteristic diterpenic biomarkers permits to recognize the use of pine resin and pine pitch, while the presence of dehydroabietic acid methyl ester is likely linked to the use of wood tar and not only the pine pitch (Izzo *et al.*, 2013). Retene was found as well. And these two compounds (retene and methyl dehydroabietic acid) are the indicators of the presence of a Pinacea pitch. In particular, the occurrence of methyl dehydroabietate indicates that this substance was produced by destructive distillation of the softwood, rather than by processing of the isolated resin (Mills and White, 1994). During pyrolysis of wood methanol is formed, which converts diterpenoid acids to their corresponding methyl esters (Colombini *et al.*, 2005).

A molecule of abietic acid undergoes degradation reactions through time leading to dehydroabietic acid. Dehydroabietic acid also undergo different reactions of oxidation leading to 7-oxodehydroabietic acid and 7-hydroxy-dehydroabietic acid. Such compounds are widely cited in the literature (Berg *et al*., 2000). All above mentioned compounds were detected in the GC-MS analysis of the sample. Table 7 shows the important compounds that were found in wine amphorae samples.

Table 7

Summary of results obtained by GC-MS of wine amphorae samples.

Compounds	AV22	AV23	AV24	AV25	C98	CB4155	GE3932	SL2878	4928
Norabietanes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
Retene	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
DHAM	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
7-oxo-DHAM	Yes	Yes	No	Yes	Yes	No	Yes	Yes	Yes

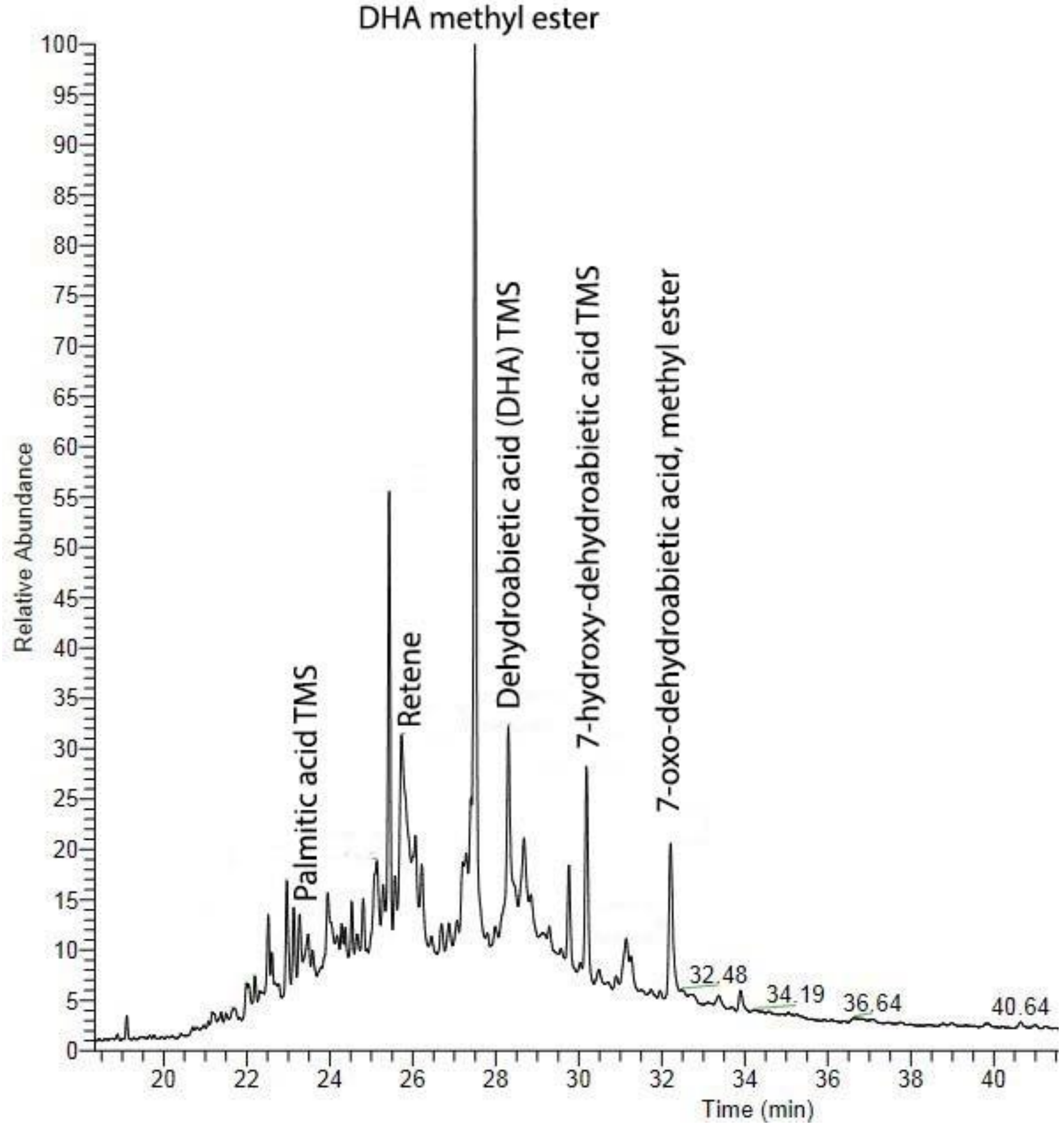

Fig. 29. Total ion chromatogram of GE3932 wine amphorae sample

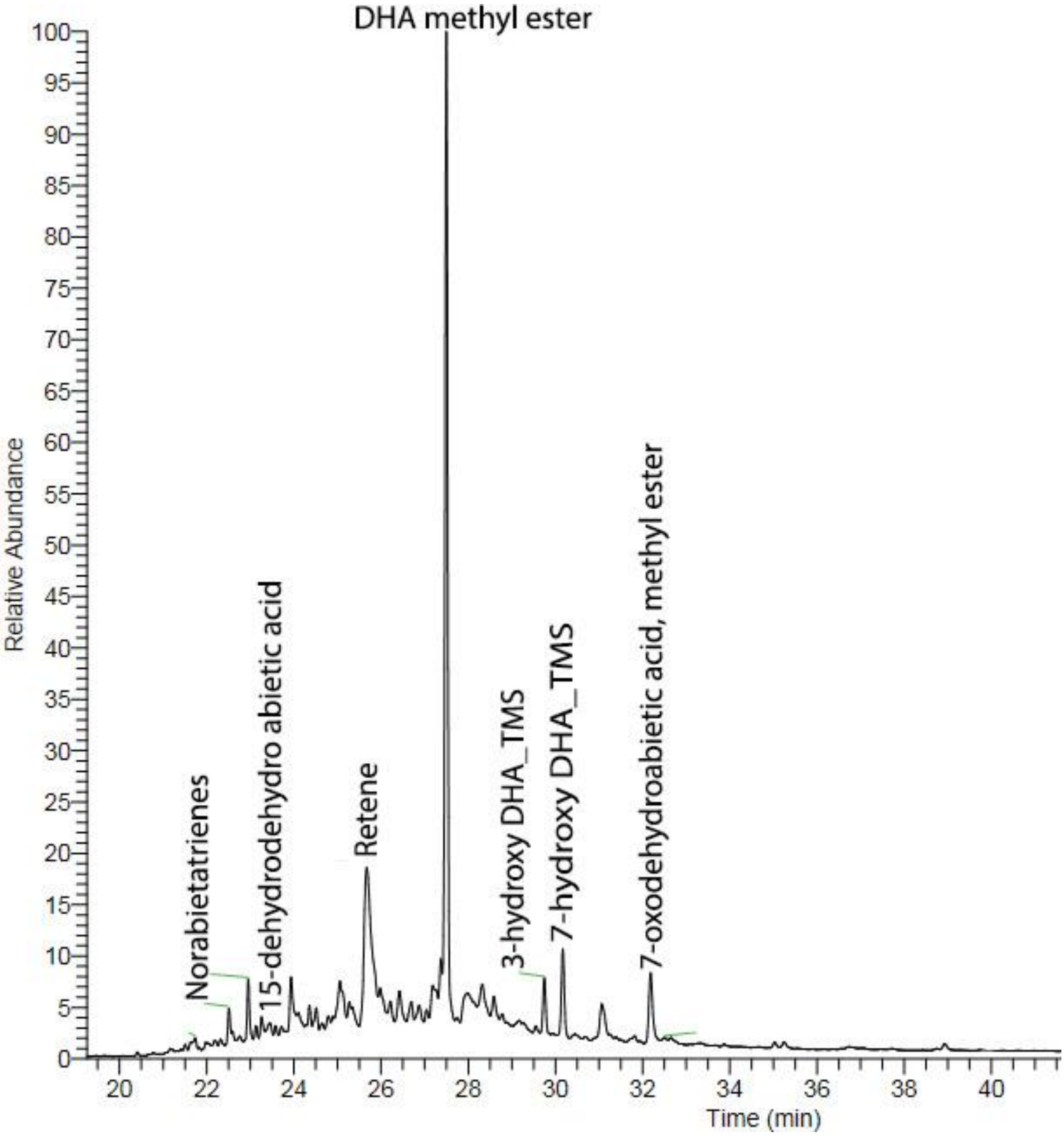

Fig. 30. Total ion chromatogram of SL2878 wine amphorae sample

SL2878 sample (Fig. 30): several tricyclic diterpenoid acids with abietane skeleton are encountered in the range 20-40 min. It was possible to detect the presence of the methyl esters of tricyclic diterpenoids, such as 7-oxodehydroabietic acid (7-oxoDHA). Dehydroabietic and 3-hydroxy-dehydroabietic acids are present as well. These two compounds are indicators that the used pitch was obtained from a destructive distillation of resinous wood. During wood distillation, in fact, gaseous methanol is produced and reacts easily with diterpenic acids to produce methyl-dehydroabietate. This compound is usually absent when pitch is produced by pyrolysis of the resin alone; this conclusion agrees also with the presence of band at 1724 cm^{-1} in the FT-IR spectrum of Fig.27.

In addition, 15-didehydroabietic acid, 7-hydroxy-dehydroabietic acid, and norabietanes were found. The GC-MS chromatogram shows also the presence of retene which is considered a marker for pine pitch since it appears when the resin is heated to high temperatures. (Font *et al.*, 2007).

Fig. 31 shows the oxidation undergone by some diterpenoid compounds of pine pitch due to the incorporation of one or more oxygen atoms. The relative degree of oxidation is indicated by the position of the various compounds.

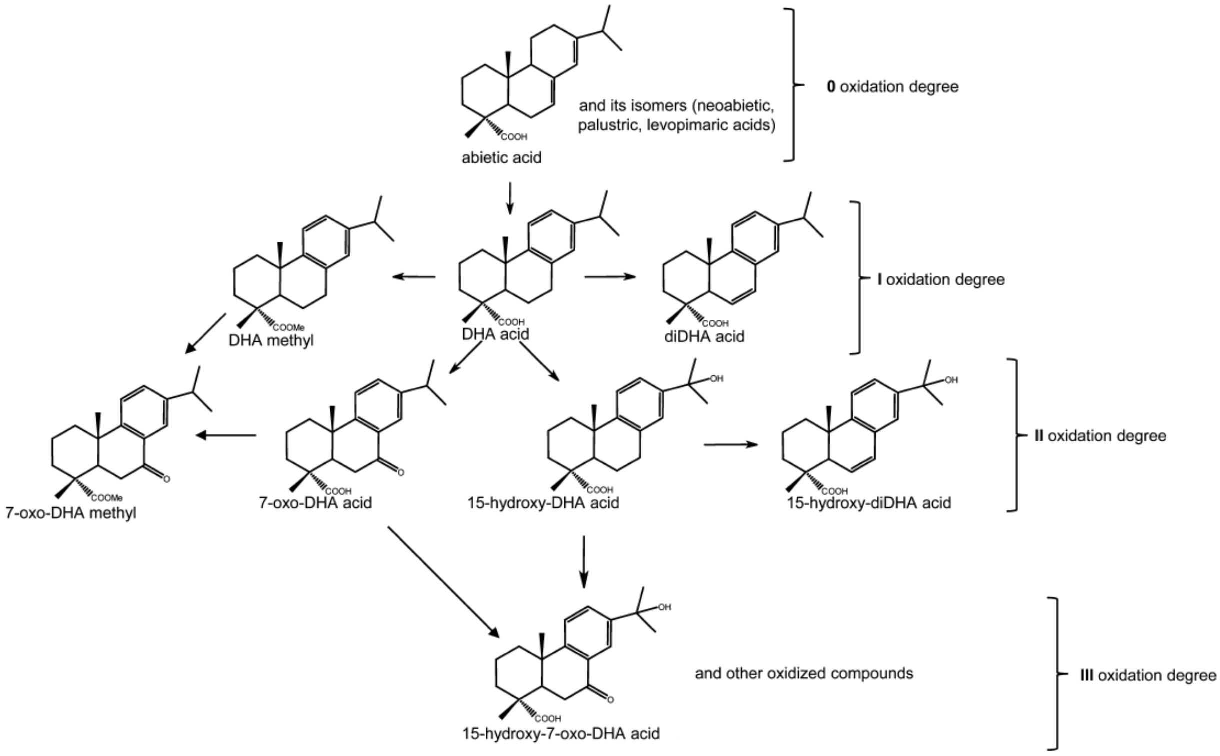

Fig. 31. Oxidation reaction paths of diterpenoid compounds of pine pitch with the relative state of aromatization and oxidation (0,I,II,III) linkable to the numbers of oxygen atoms incorporated.

4.2.2 Fish amphorae samples

The pitch markers such as retene and methyldehydroabietic acid were not detected in fish samples (except for ARL7 sample) from Museum of Arles. However, pitch can be found in four another samples that are from Baetica in Spain and in sample "amphore a poix (pitch)". This question needs further investigation.

The correspondent chromatogram in Fig. 32 shows the presence of methyl esters of saturated fatty acids such as palmitic acid. The presence of the methyl esters of tricyclic diterpenoids, such as 7-oxo-dehydroabietic acid (7-oxoDHA), 15-hydroxy-dehydroabietic acid (15HyDA) were not detected. These compounds are some of the typical oxidation products of a resin from the *Pinaceae* family (Colombini and Modugno, 2009). The reason is unknown. Only in four fish amphorae samples 15-hydroxy-7-oxo-dehydroabietic acid have been found. From the above mentioned data the following assumptions can be made: (i) either some of the fish amphorae did not contain pitch or (ii) during the sampling the pitch was not taken in enough quantities or (iii) during the sample preparation the pitch component was not taken in enough quantity. Further studies need to be applied in order to be able to answer this question. However, FT-IR analyses showed the presence of pitch ()

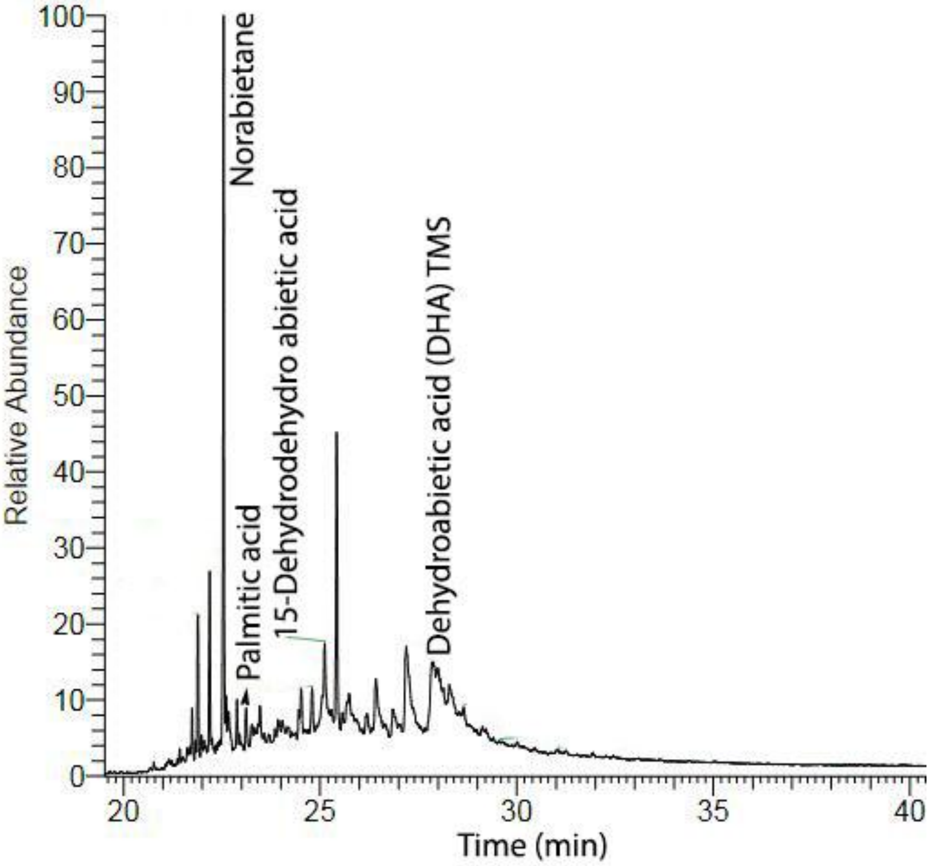

Fig. 32. Total ion chromatogram of ARL 9 obtained by GC-MS.

In most fish amphorae and some wine amphorae new compounds that have not been described in literature (at least in that the student had access) were found, they are androst 2-en-17-amine, 4,4-dimethyl-N-(2-phenylethyl)-,(5alpha)- and oleamide, N-trimethylsilyl. Further studies should be applied. Complete list of GC-MS analyses results of all other samples could be found in Appendix 7 section.

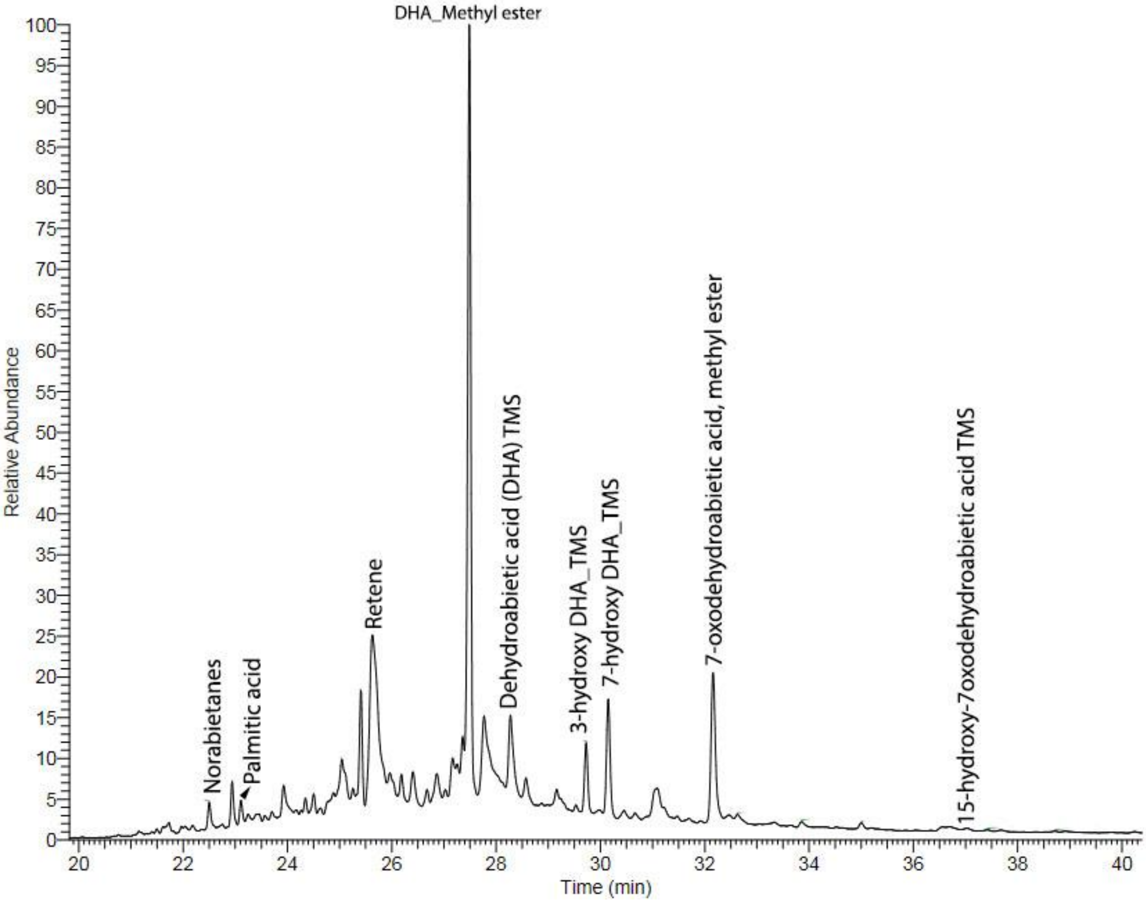

Fig. 33. Total ion chromatogram of 2970 fish amphorae sample.

Fig. 33 shows the chromatogram from another fish sample (2970). Here the pitch markers, i.e. retene, DHA methyl ester, 3-hydroxyDHA, 7-oxodehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid are detected. Results of the GC-MS analyses reveals the presence of two diagnostic peaks relative to retene and to the methyl ester of dehydroabietic acid. Retene is considered as a marker for pine pitch because when the resin is heated to high temperatures or distilled in a low oxygen environment to obtain a pitch, aromatisation, demethylation, and defunctionalisation reaction occur in the abietadiene and pimaradiene acids. This leads to the formation of a series of products as norabietatrienes and tetrahydroretene, and the final stable product of all these transformations is retene

(Colombini, 2005). The methyl dehydroabietate is formed when the resin is heated in the presence of wood because the methanol released when wood is heated to high temperatures reacts easily with diterpenic acids to produce above all methyl-dehydroabietate, which is absent when the pitch is produced by pyrolysis of the resin alone.

The simultaneous presence of abietanic acids, retene and methyl dehydroabietate highlights that the material contains a pitch obtained from a destructive of wood of plants of the *Pinaceae* family.

For all the organic samples considered in this study, it was not possible to identify with accuracy the species of Pine used to prepare the pitch since the profile of diterpenoid acids of an aged and thermal treated resin is very different from the one of fresh resin. Triterpenoids or labdane compounds were not found, indicating that the material does not originate from angiosperms or from conifers other than *Pinaceae* (Romanus *et al*., 2009).

5. Conclusion

Chemical analysis was performed in order to characterise the organic components of the pitch of Roman amphorae from DRASSM and Museum of Arles Antique collections. Samples were analysed by gas chromatography/mass spectrometry (GC-MS) and Fourier Transform Infrared spectroscopy (FT-IR) techniques. In brief, the combine use of both of these techniques showed great complementarity. FT-IR spectroscopy is a simple technique that in many cases can give fast and economical information about the nature of the coatings of amphorae. FT-IR spectroscopy reduces the number of steps necessary in the preparation of the sample since the micropellets of KBr are prepared directly from one single milligram of waterproofing pitch obtained from the amphorae under study.

Although GC-MS technique is destructive, it can give more precise information on the chemical composition of the samples. Conifer resins were discovered in GC-MS analyses of the pitch. Many identified byproducts indicated degradation reactions taking place in such archaeological material. For instance, the degradation products of abietane (dehydroabietic acid, 15-didehydroabietic acid, 15-hydroxy-7-oxodehydroabietic acid, 7-oxodehydroabietic acid) were found in the samples.

The use of pine resin, tar and pitch derived from plant resins is documented in antiquity not only as sealant or caulking materials but also as a medicine, antiseptic, or ritual balms. Scientific publications on wine amphorae are well presented in the literature. But it is still difficult to find the bibliography on ancient materials containing fish due to the fact that fatty acids (which fish comprise of) are very susceptible to deterioration. This work is adding a new information on amphorae from Grand Congloué 2 shipwreck, Museum of Arles and DRASSM amphorae collection. This work studies for the first time the pitch of fish amphorae in the IMBE laboratory at Avignon University.

Most of the studied wine samples and samples from Grand Congloué 2 showed the presence of pine resin and pine pitch. For wine samples this information is moreover confirmed by the presence of retene and of methyl esther of dehydroabietic acid (DHAM), which are products of the chemical reaction between gaseous methanol and diterpenic acids formed during the distillation of wood. The high degree of oxidation of diterpenoids, present in the organic residue collected from waterproofing treatment, suggests that resin was cooked in an oxidant atmosphere and/or was subjected to ageing processes by oxidation.

After completing the work, the student is able to distinguish pitch markers, degradation products of abietic acid and methyl esters. It was also possible to distinguish different organic families and to define exactly the botanical family of the material of which pitch was made of. We can have information on degradation and alteration of the pitch in archaeological artefacts as amphorae.

Clearly there is considerable further potential for using archaeological chemistry to identify a wide range of naturally occurring organic molecules used in the past. This will undoubtedly contribute substantially to our understanding of the relationship between human populations and their use of plant and animal resources, as well as in the determination of the myriad ways in which artefacts were used.

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Appendix 1. Identified compounds – FT-IR spectroscopy (Grand Congloué 2 amphorae samples)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
WINE	**GC2SN2**	**GC2SN3**	**GC2SN4**	**GC2SN5**	**GC2SN6**	**GC2SN8**	**GC2SN9**	**GC2SN10**
	cm^{-1}							
Stretching bands of O-H from alcohol groups	3435.47	3429.08	3428.47	3428.60	3428.86	3428.87	3428.74	3428.29
CH_2, $-CH_3$ groups (hydrocarbon skeleton of the resin)	2955.09	2955.44	2955.49	2955.46	2955.95	2954.98	2955.35	2955.21
	2928.37	2929.46	2929.31	2929.55	2930.68	2930.08	2929.98	2930.07
	2867.52	2868.04	2868.07	2868.31	2868.94	2868.62	2868.52	2868.57
Carbonilic group	1724.33	1723.42	1723.58	1721.08	1721.24	1721.00	1720.92	1721.26
	1694.08	1697.63	1697.57	1697.50	1697.70	1698.06	1697.88	1698.00
Aromatic ring	1605.05	1605.61	1605.49	1605.68	1607.07	1605.36	1605.70	1605.80
	1496.56	1496.88	1496.80	1496.69	1496.76	1495.88	1496.16	1496.48
	885.79	886.03	885.39	886.11	886.92	887.20	887.36	886.44
	821.46	821.76	821.79	821.83	822.73	822.26	822.47	822.06
CH_2, $-CH_3$ bending	1460.52	1458.65	1458.73	1458.67	1459.14	1458.92	1458.29	1459.08
	1384.00	1384.04	1384.09	1384.35	1384.25	1384.30	1384.27	1384.18
COOH	1233.05	1235.43	1235.58	1235.16	1235.53	1235.52	1235.79	1235.71
	1166.58	1171.40	1171.38	1170.75	1172.64	1171.20	1170.59	1171.38

Appendix 1. Identified compounds – FT-IR spectroscopy (Grand Congloué 2 amphorae samples) (cont.)

	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**
WINE	**GC2SN11**	**Li 2.83**	**24281**	**24270**	**24268**	**24265**	**24255**	**24210**
	cm^{-1}							
Stretching bands of O-H from alcohol groups	3428.57	3429.27	3435.22	3431.40	3431.25	3428.67	3429.07	3431.86
CH_2, $-CH_3$ groups (hydrocarbon skeleton of the resin)	2955.22	2955.46	2955.19	2954.74	2955.36	2954.96	2955.15	2955.47
	2930.08	2929.55	2930.07	2929.31	2929.11	2930.22	2930.07	2930.16
	2868.49	2868.19	2868.72	2868.38	2868.02	2868.62	2868.53	2868.69
Carbonilic group	1721.72	1723.48	1717.49	1721.10	1721.94	1721.02	1720.91	1721.35
	1698.04	1697.63	1698.19	1698.15	1697.39	1698.12	1697.94	1698.15
Aromatic ring	1606.09	1605.37	1606.29	1605.44	1605.70	1605.61	1605.47	1606.90
	1496.49	1496.88	1496.39	1495.31	1496.84	1496.27	1495.91	1496.68
	886.94	886.03	886.05	873.68	885.82	888.19	887.02	888.17
	821.85	821.81	822.55	822.93	821.58	822.72	822.95	822.30
CH_2, $-CH_3$ bending	1459.02	1458.55	1458.16	1456.32	1459.07	1458.96	1459.09	1458.01
	1384.29	1384.10	1384.38	1384.49	1384.19	1384.25	1384.18	1384.32
COOH	1235.52	1235.82	1235.74	1235.76	1235.70	1235.49	1235.89	1235.44
	1170.27	1171.61	1171.71	1171.63	1171.37	1170.80	1171.14	1172.45

Appendix 2. Identified compounds – FT-IR spectroscopy (wine amphorae samples) (cont.)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
WINE	**AV22**	**AV23**	**AV24**	**AV25**	**4928**	**SL 2878**	**GE 3932**	**C98**	**CB4155**
	cm^{-1}								
Stretching bands of O-H from alcohol groups	3428.60	3424.13	3428.85	3416.20	3412.79	3428.47	3420.26	3420.40	3439.73
CH_2, -CH_3 groups (hydrocarbon skeleton of the resin)	2956.27	2956.98	2955.31	2956.05	2955.71	2955.50	2955.11	2954.74	x
	2930.16	2929.46	2930.54	2929.19	2929.75	2930.00	2930.08	2929.12	x
	2868.76	2868.56	2869.12	2868.46	2868.17	2868.42	2868.60	2867.85	x
Carbonilic group	1721.54	1724.48	1721.31	1724.57	1721.10	1724.14	1716.84	1721.61	1798.38
	x	x	x	x	1697.96	1697.97	1697.40	1701.61	x
Aromatic ring	1605.97	1605.13	1607.18	1606.12	1606.13	1605.57	1607.78	1605.45	1632.78
	1497.24	1497.33	1496.42	1497.20	1497.28	1497.28	1496.97	1497.07	x
	886.69	887.29	x	885.10	885.22	885.74	886.09	885.94	874.54
	821.83	821.14	821.26	821.21	821.99	821.44	821.99	821.44	x
CH_2, -CH_3 bending	1459.34	1458.74	1458.65	1457.74	1458.42	1458.64	1458.38	1458.03	1425.41
	1384.45	1384.11	1384.35	1384.19	1384.34	1384.35	1384.43	1384.22	1385.05
COOH	1242.46	1239.00	1232.83	1238.98	1246.40	1242.48	1242.82	1241.66	x
	1174.26	1172.67	x	1171.45	1174.09	1173.22	1174.33	1173.00	x

Appendix 3. Identified compounds – FT-IR spectroscopy (fish amphorae samples)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
FISH	**ARL3**	**ARL4**	**ARL5**	**ARL6**	**ARL7**	**ARL8**	**ARL9**	**ARL12**
	cm^{-1}							
Stretching bands of O-H from alcohol groups	3411.47	3412.58	3420.88	3429.3	3408.55	3412.99	3420.49	3413.48
CH_2, $-CH_3$ groups (hydrocarbon skeleton of the resin)	2955.14	2955.51	2955.79	2955.07	2955.78	2955.59	2955.71	2955.46
	2929.15	2929.94	2929.45	2929.94	2929.17	2929.22	2929.57	2929.06
	2868.64	2869.14	2868.74	2869.26	2868.56	2868.47	2868.85	2868.8
Ketones	1726.01	1716	1724.46	1724.39	1725.38	1725.95	1724.57	1724.63
Aromatic ring	1614.45	1605.73	1604.57	1608.16	1607.13	1605.02	1606.35	1606.91
	1496.88	1497.03	1497.39	1449.08	1457.28	1497.12	1497.11	1496.61
	874	886.6	886.31	874.69	884.85	885.52	886.3	874.59
	821.11	821.32	821.14	821.03	821.14	820.82	821.32	821.61
CH_2, $-CH_3$ bending	1456.9	1456.28	1457.72	1449.08	1457.28	1457.76	1457.48	1456.68
	1384.66	1383.7	1383.77	1386.26	1383.66	1384.01	1383.73	1385.07
COOH	1237.16	1239.06	1239.28	1234.72	1238.77	1238.13	1238.98	1239.36
	1169.99	1172	1172.71	x	1171.28	1171.55	1172.41	1171.4

Appendix 3. Identified compounds – FT-IR spectroscopy (fish amphorae samples) (cont.)

	9	**10**	**11**	**12**	**13**	**14**	**15**
FISH	**RL15**	**RL16**	**RL17**	**RL18**	**RL19**	**RL20**	**RL21**
	cm^{-1}						
Stretching bands of O-H from alcohol groups	3430.39	3420.96	3409.72	3421.79	3428.04	3428.31	3412.94
CH_2, $-CH_3$ groups (hydrocarbon skeleton of the resin)	2955.27	2955.35	2955.11	2955.07	2956.56	2955.67	2955.37
	2929.04	2930.22	2929.75	2929.45	2929.35	2928.42	2929.27
	2868.51	2869.36	2868.87	2868.87	2868.58	2868.05	2868.8
Carbonilic group	1725.77	1723.75	1724.35	1724.36	1724.37	1724.3	1724.51
	x	x	x	x	x	x	x
Aromatic ring	1604.88	1616.14	1610.05	1609.56	1605.1	1605.32	1608.63
	1497.15	1496.94	1496.68	1497.07	1497.31	1496.7	1496.98
	885.96	874.01	874.78	874.77	886.56	871.72	874.51
	821.04	821.56	821.31	821.55	821.35	821.07	821
CH_2, $-CH_3$ bending	1456.54	1456.61	1456.88	1455.73	1458.92	1455.8	1455.22
	1383.67	1384.82	1384.47	1384.68	1384	1383.93	1384.15
COOH	1239.22	1239.06	1237.2	1238.27	1240.12	1239.97	1238.7
	1172.11	1171.57	x	1171.29	1173.4	1173	1171.7

Appendix 4. Identified compounds – GC-MS analysis (wine amphorae samples)

		1	2	3	4	5	6	7	8	9
#	**Compound**	**AV22**	**AV23**	**AV24**	**AV25**	**CB4155**	**GE3932**	**SL2878**	**C98**	**4928**
1	Pentane	7.95*	7.96	7.95	7.95	x	x	7.94	7.95	7.96
2	Benzene propanoic acid TMS	x	8.43	x	x	x	x	x	x	x
3	Nonanoic acid TMS	13.72	13.72	13.74	x	x	x	x	x	x
5	18_Norabieta_diene_TMS	22.53	22.96	22.53	22.51	x	22.51	22.51	22.52	22.5
4	18_Norabieta_diene_TMS	x	x	x	22.95	x	22.96	x	x	x
6	18-Norabieta 811013, TMS	x	x	x	x	x	x	22.95	22.96	22.95
7	palmitic acid TMS	23.12	23.13	23.13	x	23.13	23.13	x	x	x
8	10,18 - Bisnorabieta -5,7,9,11,13-pentaene	23.93	23.93	x	23.93	x	23.95	23.93	23.94	23.93
9	15-Dehydrodehydro abietic acid (Piti_TMS…)	24.37	24.37	24.37	24.35	x	24.37	24.36	24.36	28.6
10	Androst 2-en-17-amine, 4,4-dimethyl-N-(2-phenylethyl)-,(5alpha)-	25.43	25.42	25.44	x	25.43	25.43	x	x	x
11	Retene	x	25.62	25.74	25.73	x	25.72	25.67	25.7	25.63
12	7-isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a	26.21	26.21	26.23	26.2	x	26.21	x	26.21	26.21
13	DHA_Methyl ester	27.49	27.49	27.5	27.47	x	27.5	27.5	27.48	27.49
14	Dehydroabietic acid (DHA) TMS	x	x	28.3	x	x	28.3	x	28.3	28.3
15	Acetic acid	x	28.34	x	28.33	x	x	x	x	x
16	Oleamide, N-trimethylsilyl	x	x	28.68	x	28.68	28.67	x	x	x
17	3-hydroxy DHA_TMS	29.75	x	29.76	29.74	x	29.76	29.74	29.74	29.75
18	7-hydroxy DHA_TMS	30.18	x	30.19	30.16	x	30.18	30.16	30.16	30.16
19	7-oxodehydroabietic acid, methyl ester	32.2	32.2	x	32.19	x	32.2	32.18	32.18	32.18
20	7-oxodehydroabietic acid TMS	33.89	x	x	x	x	33.89	x	x	x
21	15-hydroxy-7oxodehydroabietic acid TMS	x	x	x	x	x	x	x	x	x

*** – retention time (min)**

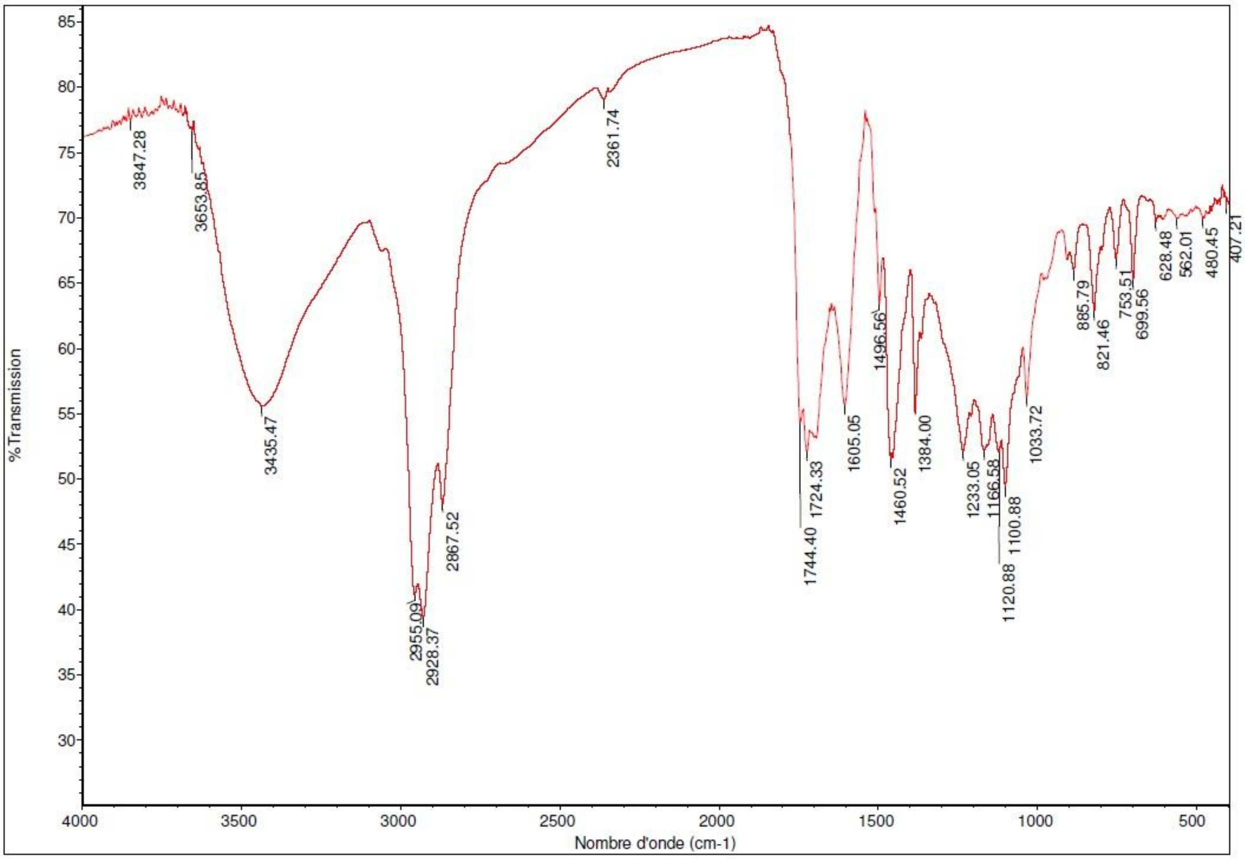
Appendix 5. **Identified compounds - GC-MS analysis (fish amphorae samples)**

		1	2	3	4	5	6	7	8	9	10	11
#	**#compound**	ARL3	ARL4	ARL5	ARL6	ARL7	ARL8	ARL9	ARL12	RL15	RL16	RL17
1	Pentane	7.95	7.95	7.95	x	7.95	7.95	7.95	7.95	7.95	7.95	7.95
2	Nonanoic acid TMS	13.65	x	13.73	13.73	13.73	13.74	13.74	13.74	x	x	x
3	18-Norabieta 811013, TMS	21.35/22.69	x	x	x	21.36	x	x	x	x	x	x
4	18-Norabietane	22.54	22.53	22.53	x	22.54	22.54	22.54	22.53	x	x	22.54
5	Palmitic acid	23.09	x	23.11	23.11	23.12	23.12	23.11	x	x	x	x
6	10,18 - Bisnorabieta -5,7,9(10),11,13 - pentaene	x	23.93	23.94	x	23.93	23.92	23.94	23.93	x	x	x
7	15-Dehydrodehydro abietic acid (Piti_TMS…237.95.355.73)	x	25.52	25.12	xx	25.12	25.12	25.11	25.75	25.12	x	x
8	Androst 2-en-17-amine, 4,4-dimethyl-N-(2-phenylethyl)-,(5alpha)-	25.42	25.42	25.42	25.42	25.42	25.42	25.42	x	25.42	25.42	25.41
9	Stearic acid	x	x	x	25.74	x	x	x	x	x	x	25.7
10	Retene	x	x	x	x	25.74	x	x	x	x	x	x
11	8-isopropyl-1,3-dimethylphenanthrene	27.25	27.22	27.21	27.27	27.25	27.25	27.19	27.22	x	27.22	x
12	DHA_Methyl ester	x	x	x	x	x	x	x	x	x	x	x
13	1,4-Naphthoquinone, 2-acetyl-5,8 …	x	x	28.03	x	x	x	x	x	x	x	x
14	Dehydroabietic acid (DHA) TMS	x	28.29	x	x	28.29	x	28.3	28.29	x	x	x
15	Acetic acid	x	x	28.34	x	x	x	x	x	x	x	x
16	Oleamide, N-trimethylsilyl	28.66	28.66	x	28.67	28.66	28.66	x	x	28.66	28.66	28.66
17	3-hydroxy DHA_TMS	x	x	x	x	x	x	x	x	x	x	x
18	7-hydroxy DHA_TMS	x	x	x	x	x	x	x	31.25	x	x	x
19	7-oxodehydroabietic acid, methyl ester	x	x	x	x	x	x	x	x	x	x	x
20	7-oxodehydroabietic acid TMS	x	x	x	x	x	x	x	x	x	x	x
21	15-hydroxy-7oxodehydroabietic acid TMS	x	x	x	x	x	x	x	x	x	x	x

Appendix 5. Identified compounds - GC-MS analysis (fish amphorae samples) (cont.)

#	#compound	12	13	14	15	16	17	18	19	20	21
		RL 18	RL19	RL20	RL21	amph1	2928	SL 2930	2970	6028	Amph a poix
1	Pentane	7.95	7.95	7.95	7.96	7.96	7.95	7.95	7.95	7.95	7.95
2	Nonanoic acid TMS	x	x	x	x	x	x	x	x	x	x
3	18-Norabieta 811013, TMS	x	x	x	x	x	x	x	22.94	22.5	22.94
4	18-Norabietane	22.54	22.53	22.54	22.53	x	x	22.5	22.5	x	22.5
5	Palmitic acid	x	x	x	x	x	x	x	23.11	x	x
6	10,18 - Bisnorabieta -5,7,9(10),11,13 - pentaene	x	23.92	x	x	23.94	x	23.92	23.93	23.94	23.94
7	15-Dehydrodehydro abietic acid (Piti_TMS…237.95.355.73)	25.12	x	25.11	x	x	x	24.34	24.34	24.35	24.35
8	Androst 2-en-17-amine, 4,4-dimethyl-N-(2-phenylethyl)-,(5alpha)-	25.41	25.41	25.41	25.41	25.41	25.4	25.41	25.4	25.4	25.41
9	Stearic acid	25.71	x	x	x	x	x	x	x	x	x
10	Retene	x	x	x	x	x	25.62	25.63	25.63	25.68	25.61
11	8-isopropyl-1,3-dimethylphenanthrene	x	x	27.21	27.23	x	x	x	x	x	x
12	DHA_Methyl ester	x	x	x	x	x	27.48	x	27.49	27.47	22.59
13	1,4-Naphthoquinone, 2-acetyl-5,8 …	x	x	x	x	x	x	x	x	x	x
14	Dehydroabietic acid (DHA) TMS	x	x	28.26	28.26	x	28.26	28.28	28.27	28.27	28.3
15	Acetic acid	x	x	x	x	28.32	x	x	x	x	x
16	Oleamide, N-trimethylsilyl	28.66	x	x	x	28.64	x	28.65	x	28.64	x
17	3-hydroxy DHA_TMS	x	x	x	x	x	x	29.72	29.73	29.72	x
18	7-hydroxy DHA_TMS	x	x	x	x	x	x	30.15	30.15	30.15	31.22
19	7-oxodehydroabietic acid, methyl ester	x	32.17	x	x	x	32.15	32.16	32.16	32.16	32.18
20	7-oxodehydroabietic acid TMS	x	30.15	x	x	x	x	x	x	x	x
21	15-hydroxy-7oxodehydroabietic acid TMS	x	x	x	x	x	37.03	37.03	37.03	37.04	x

Appendix 6. FT-IR spectra of the samples



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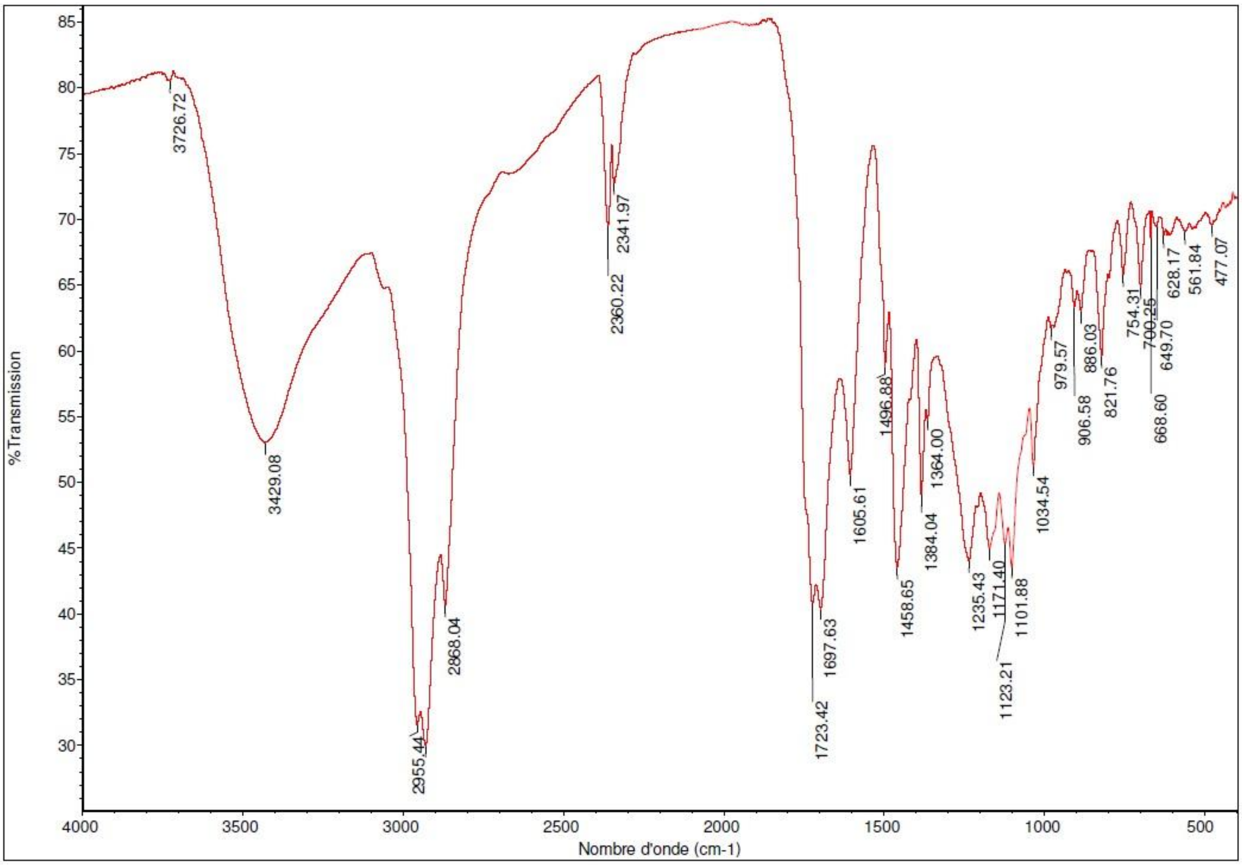

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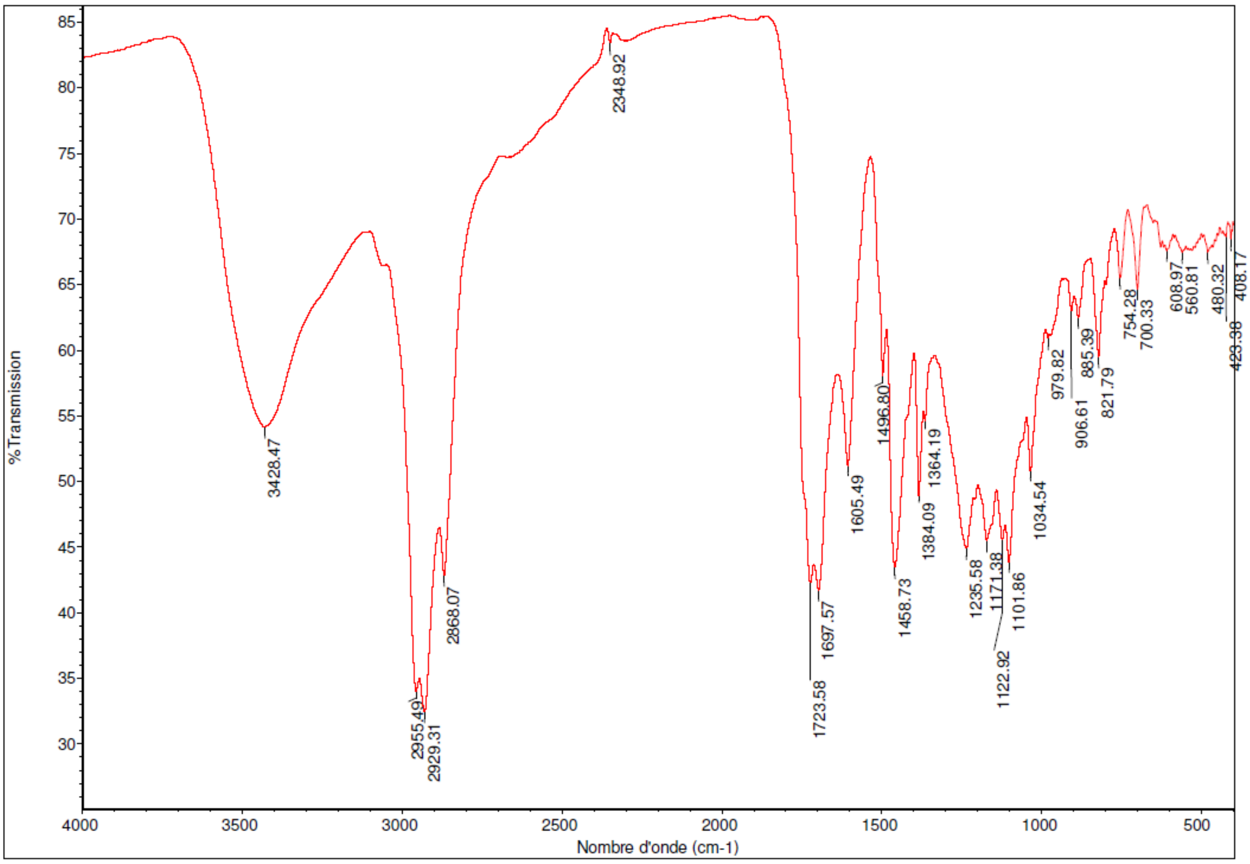

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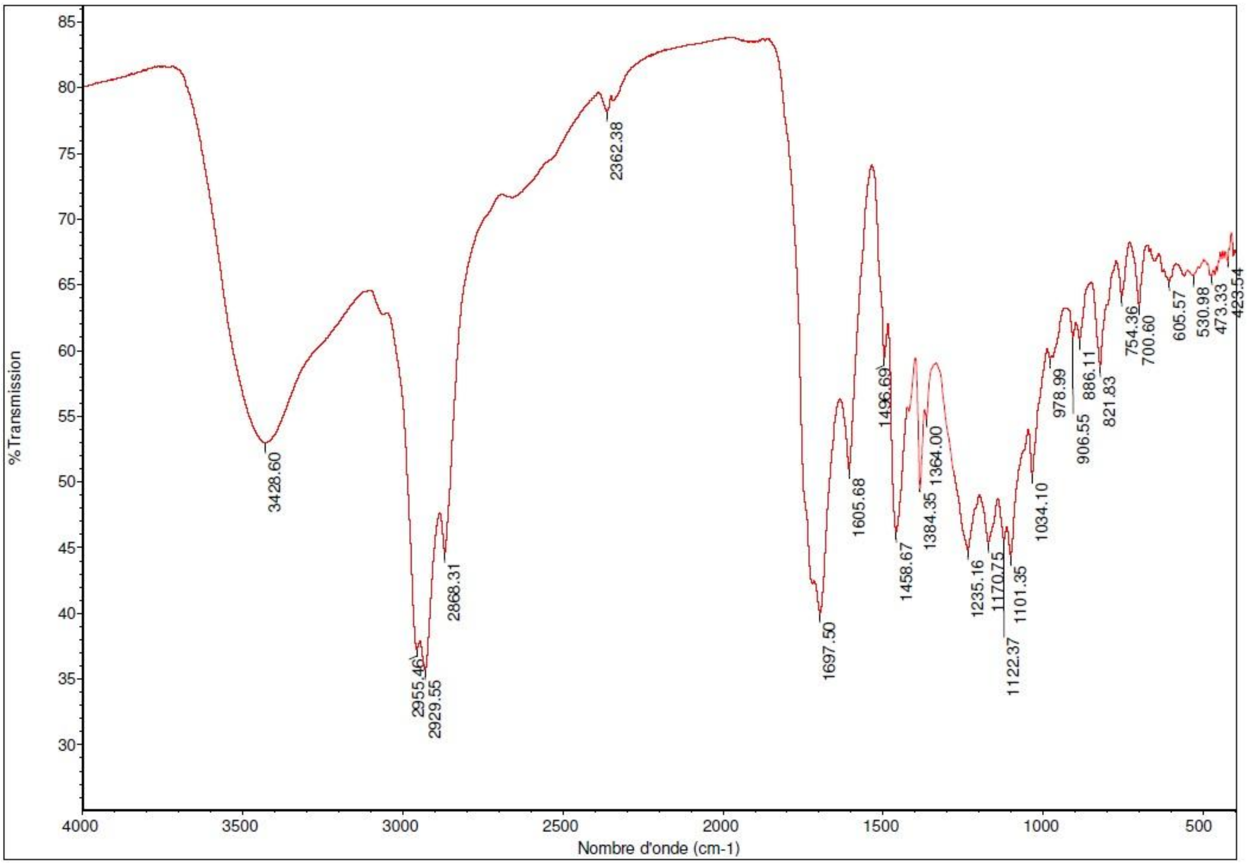

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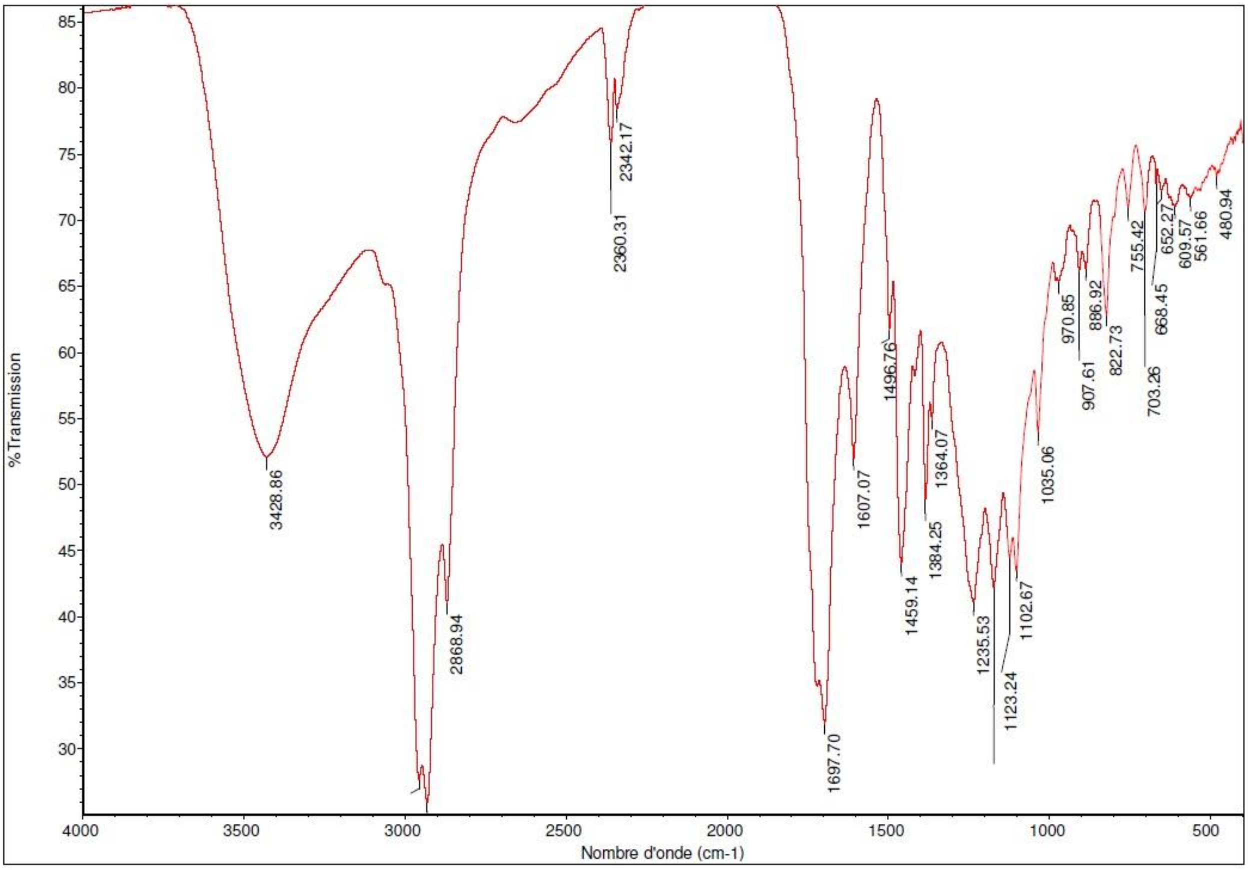

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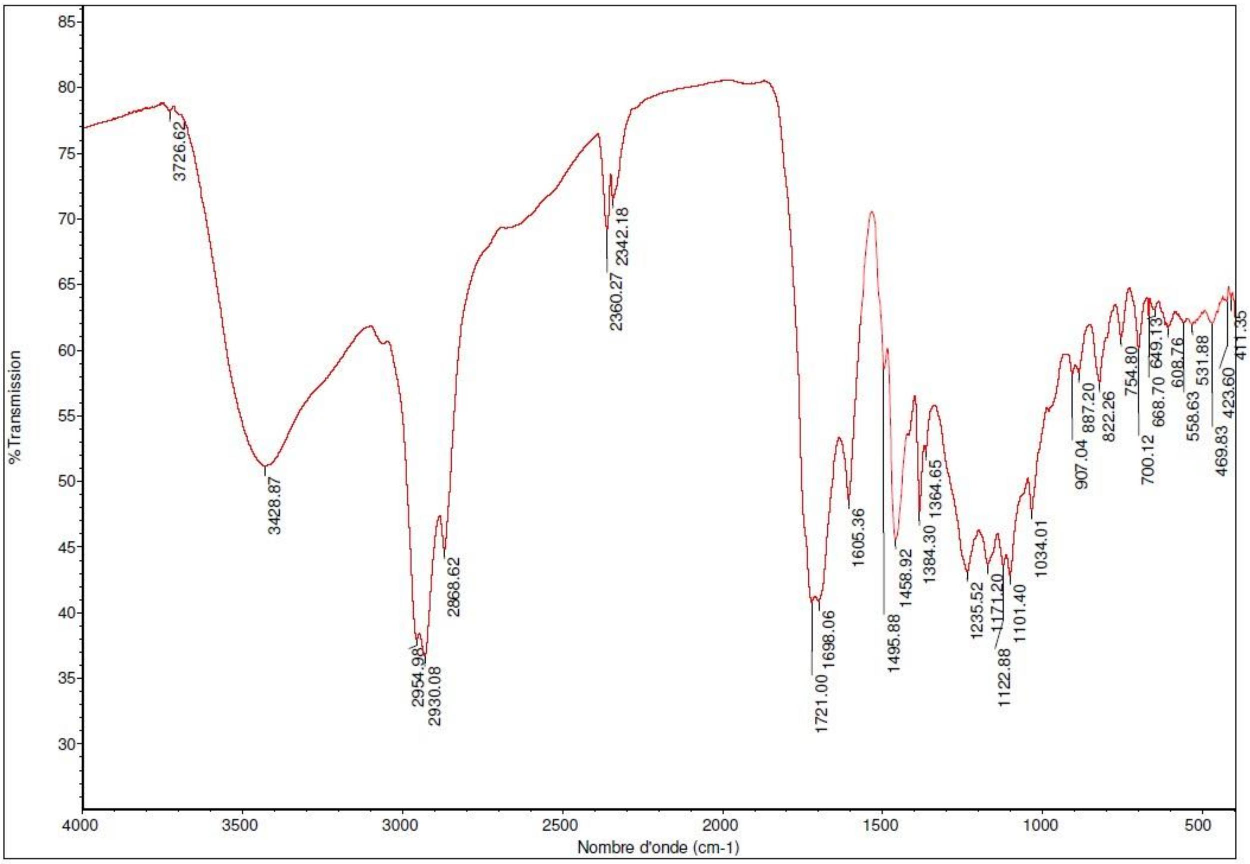

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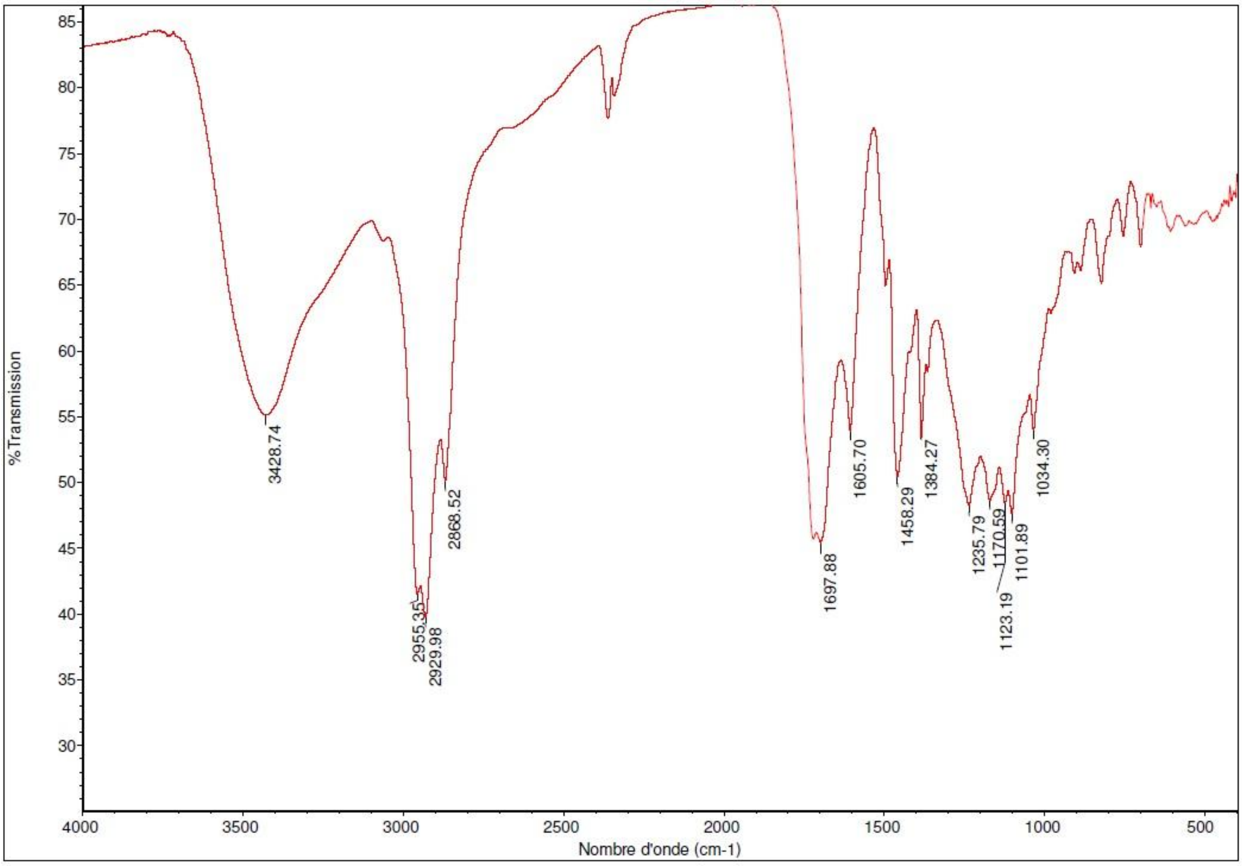

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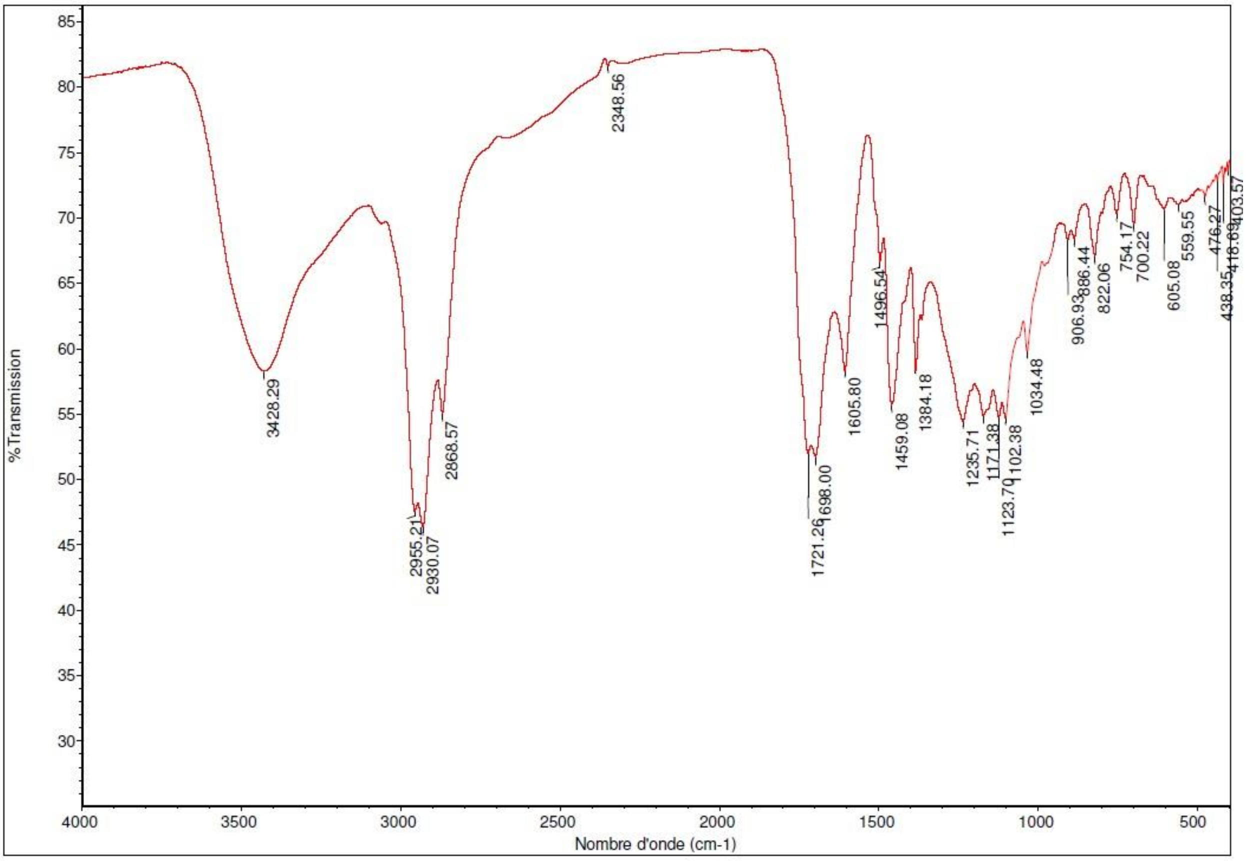

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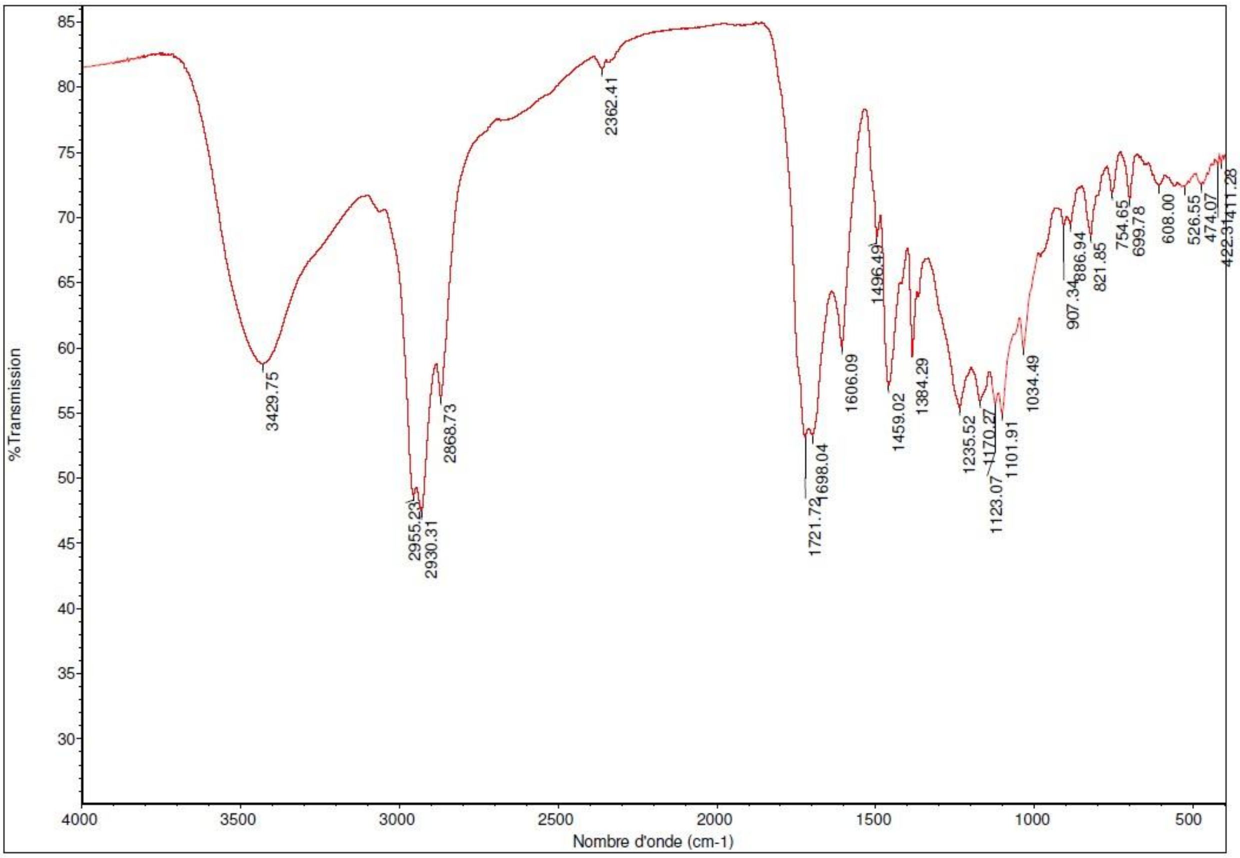

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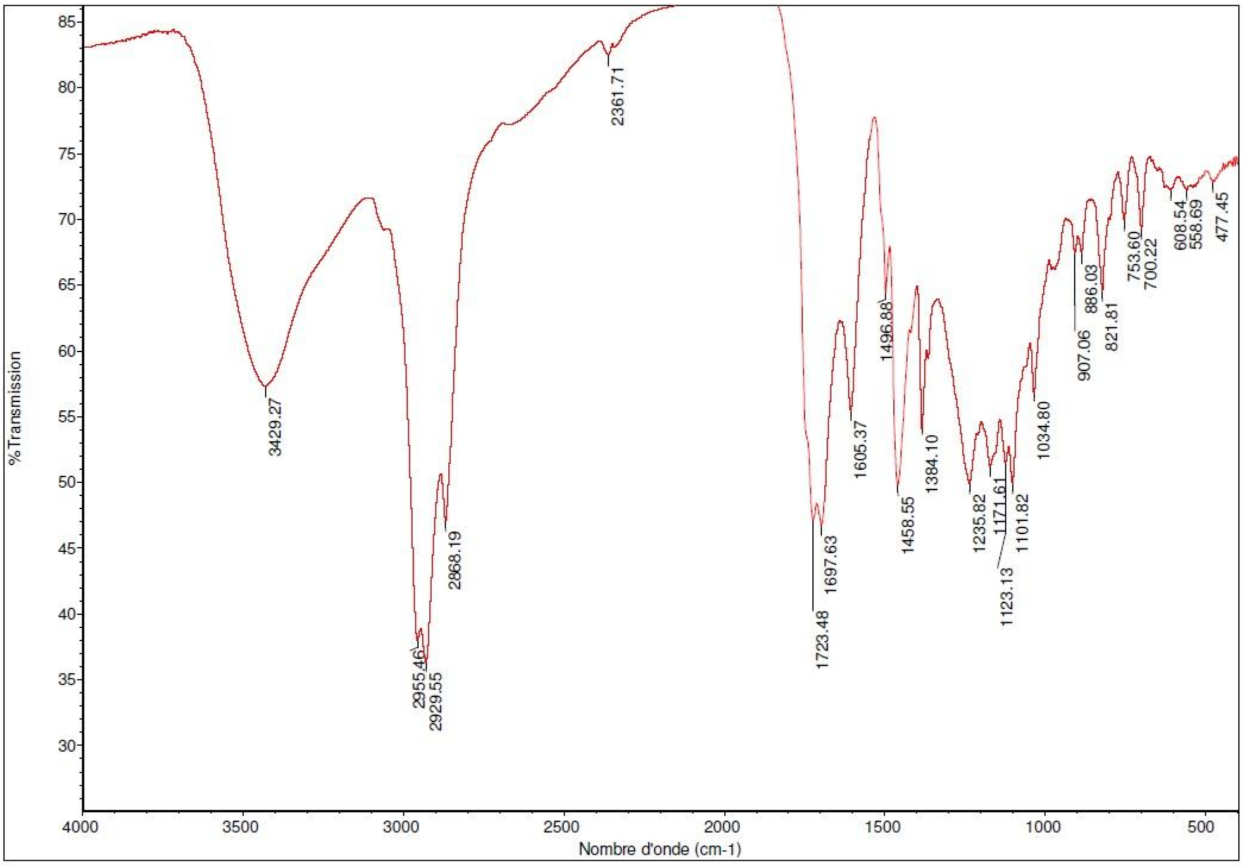

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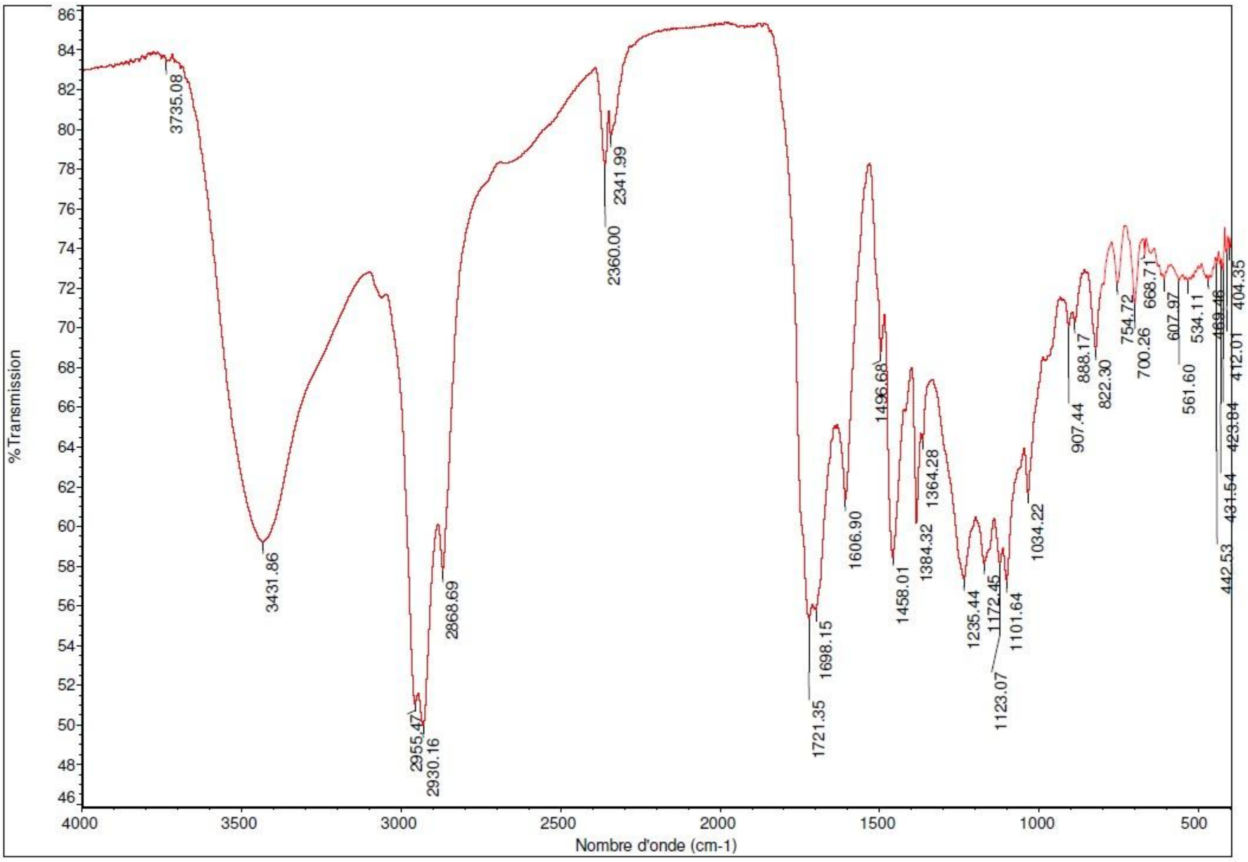
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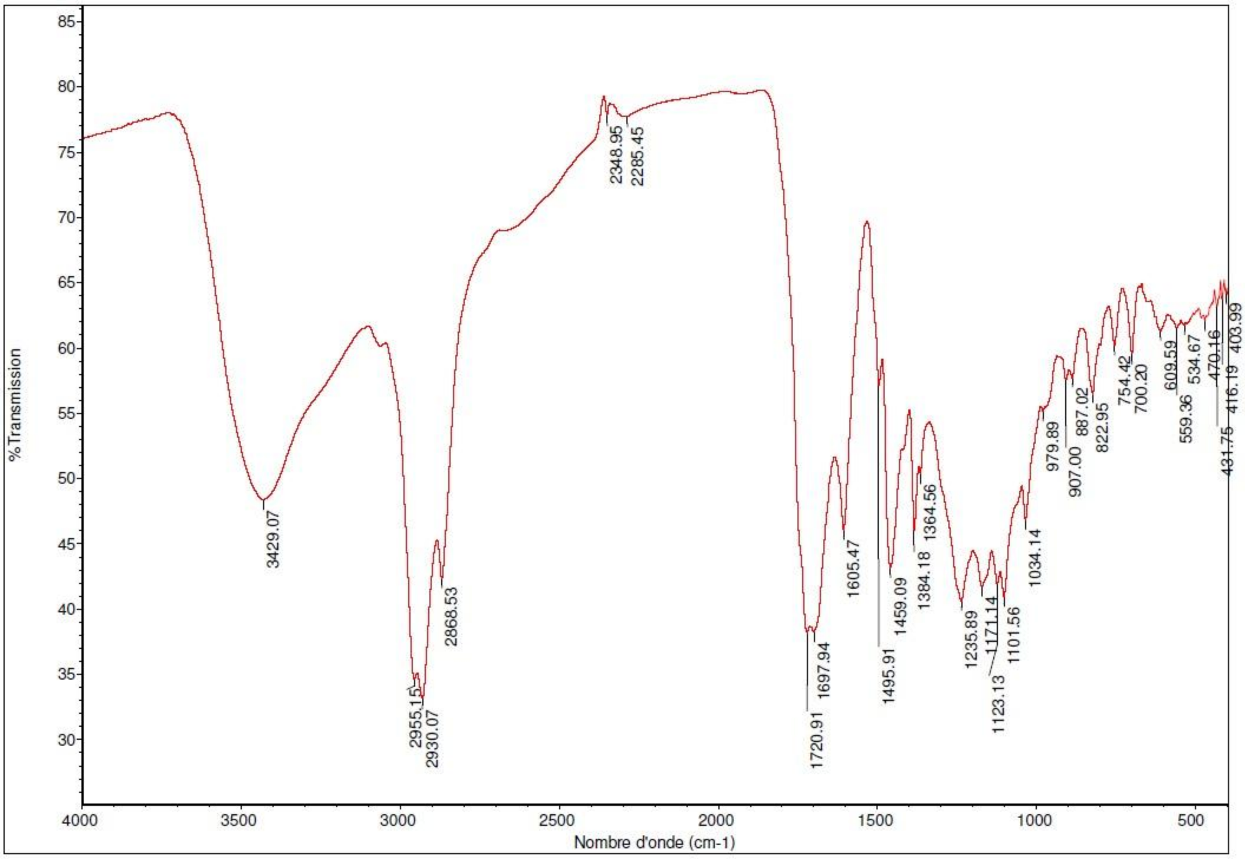
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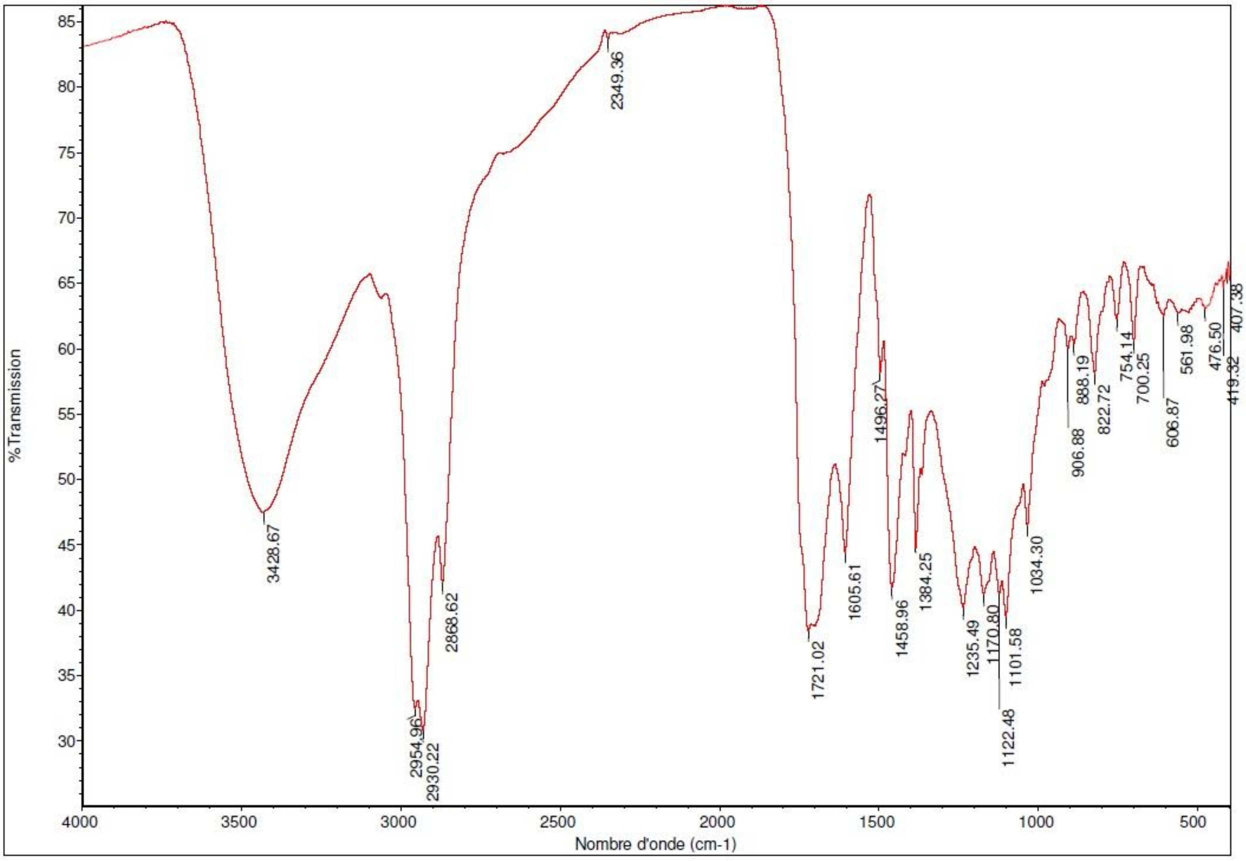
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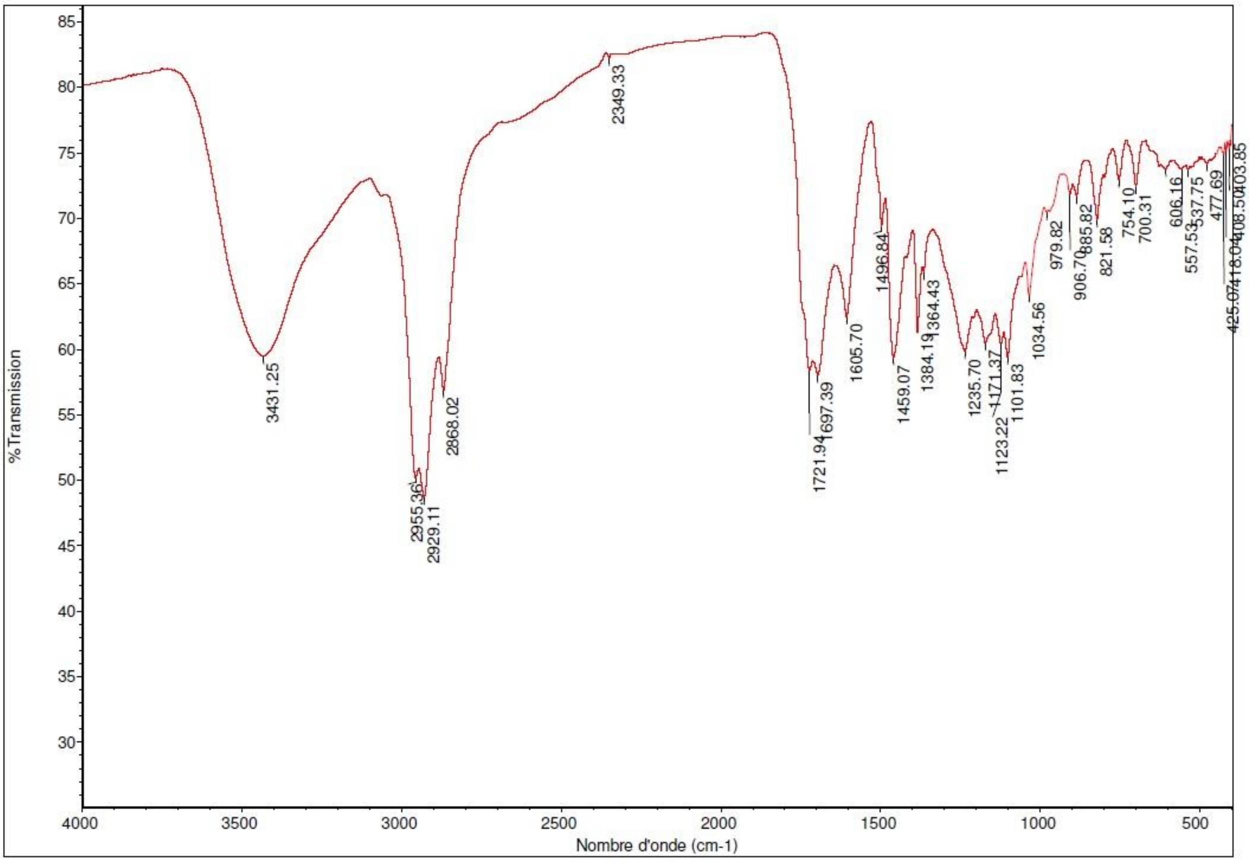
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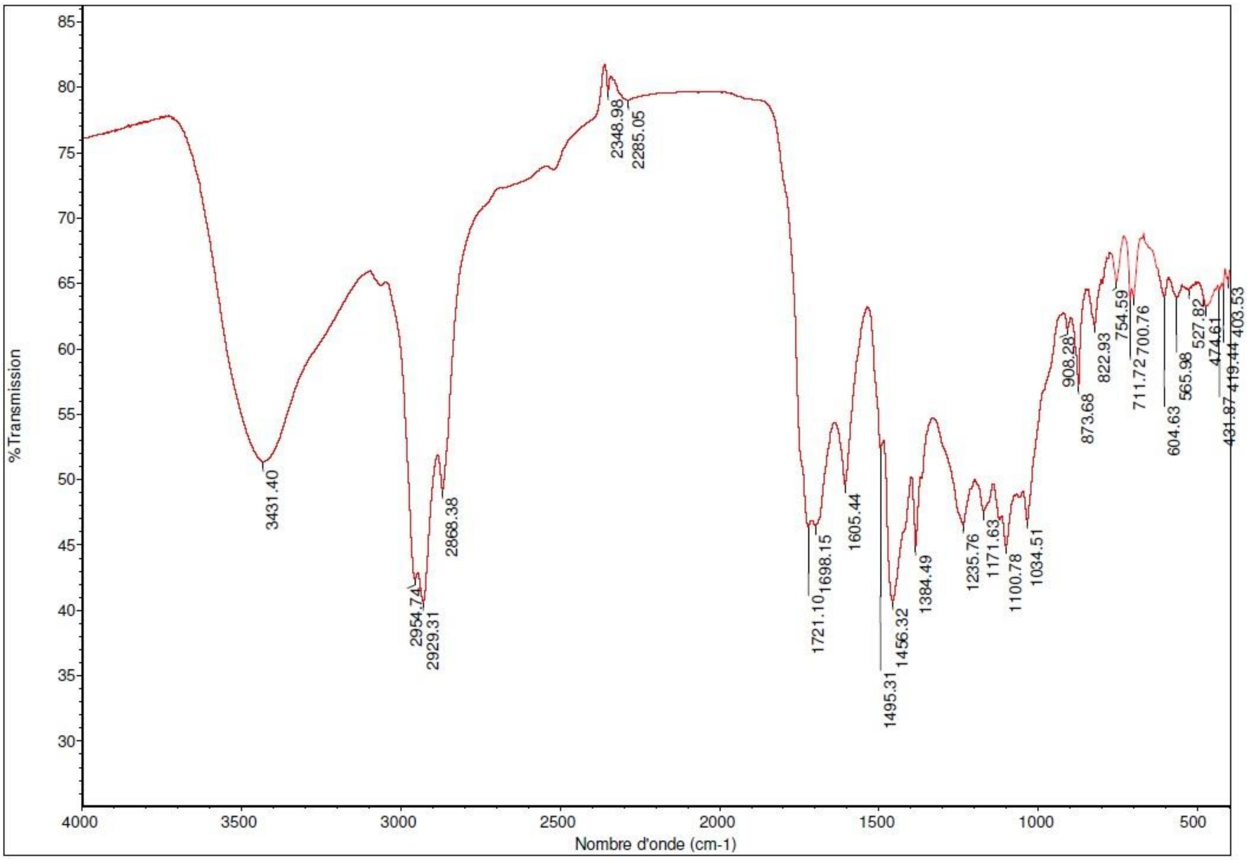
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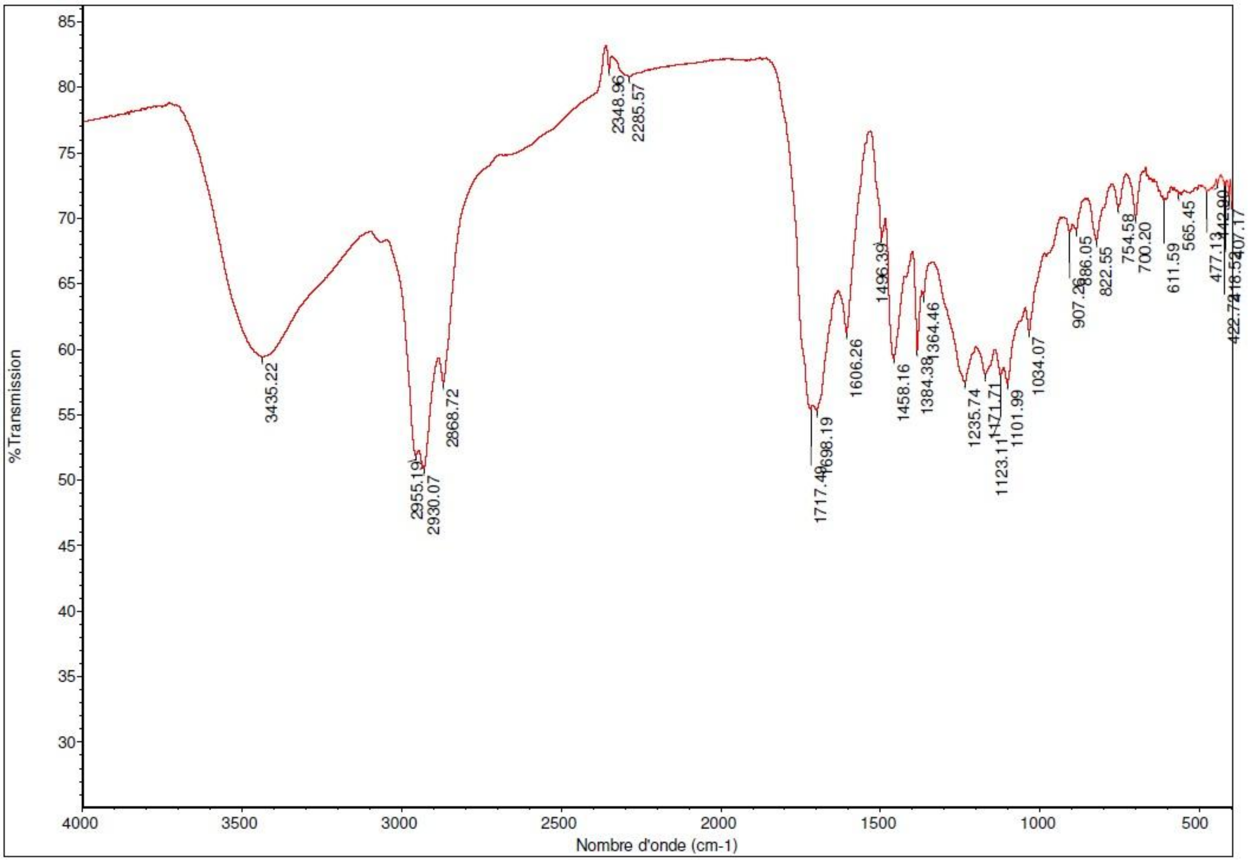
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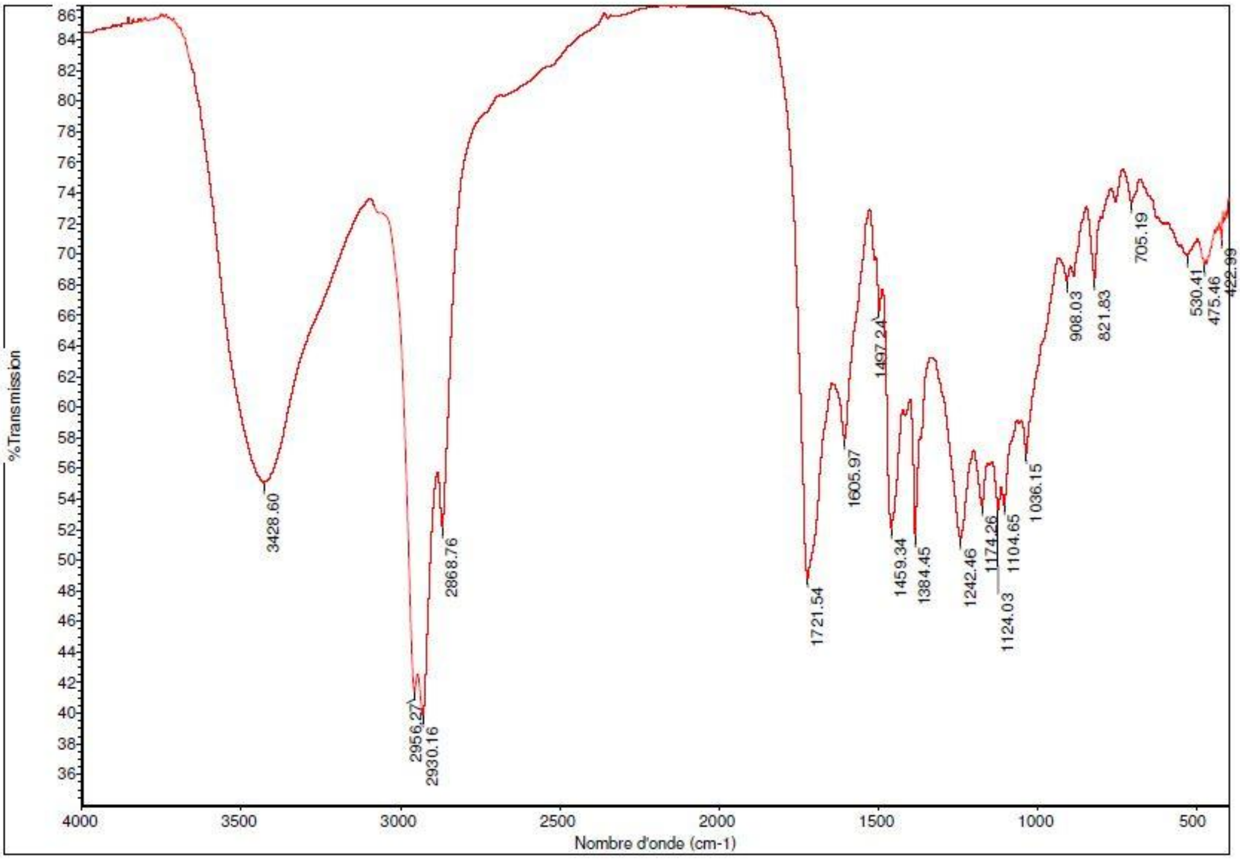
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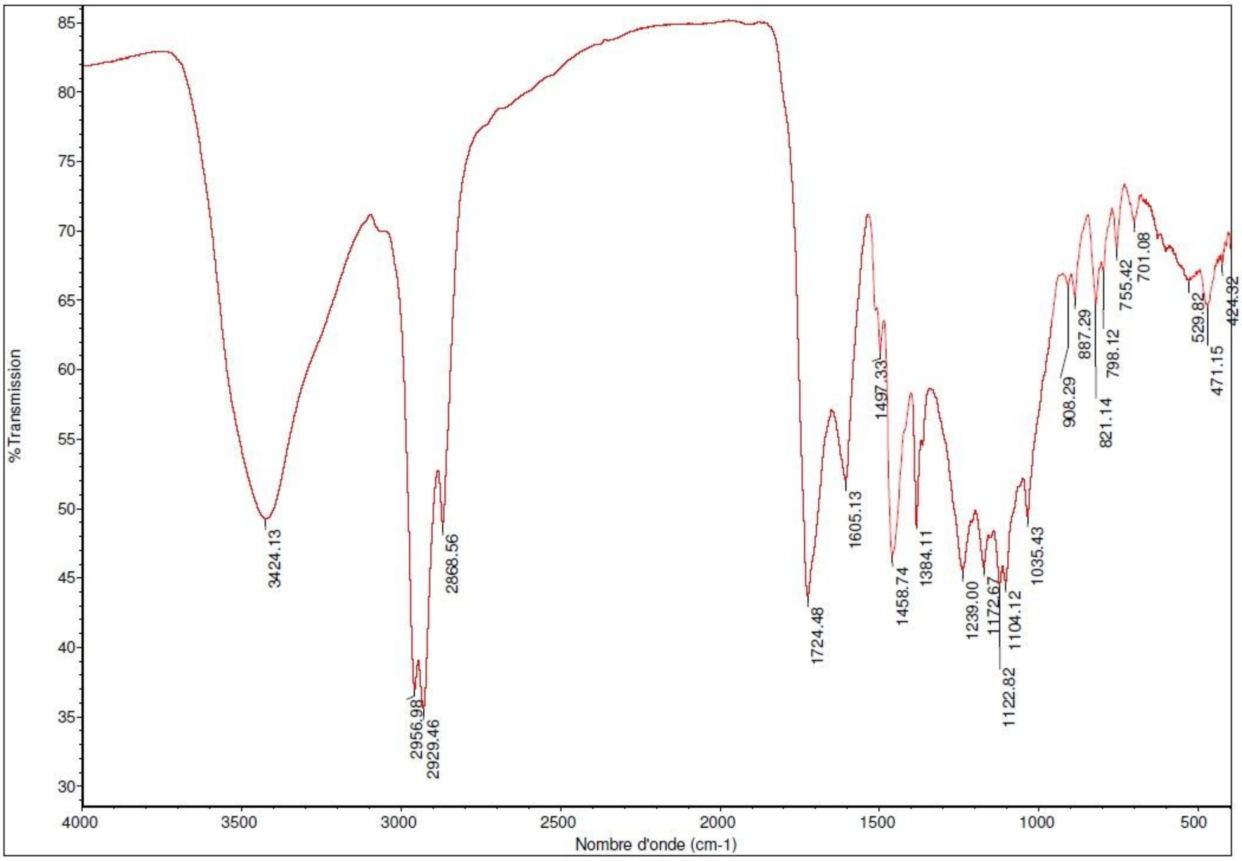
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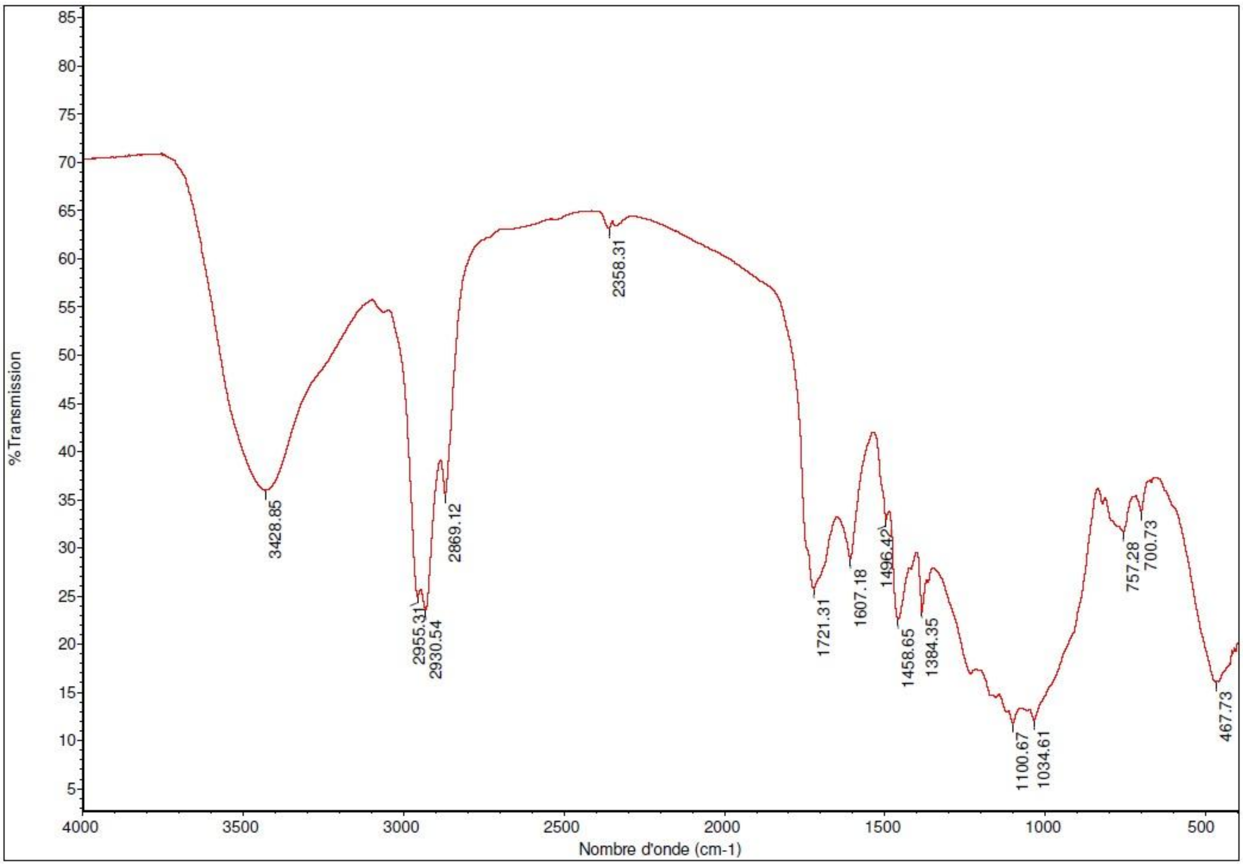
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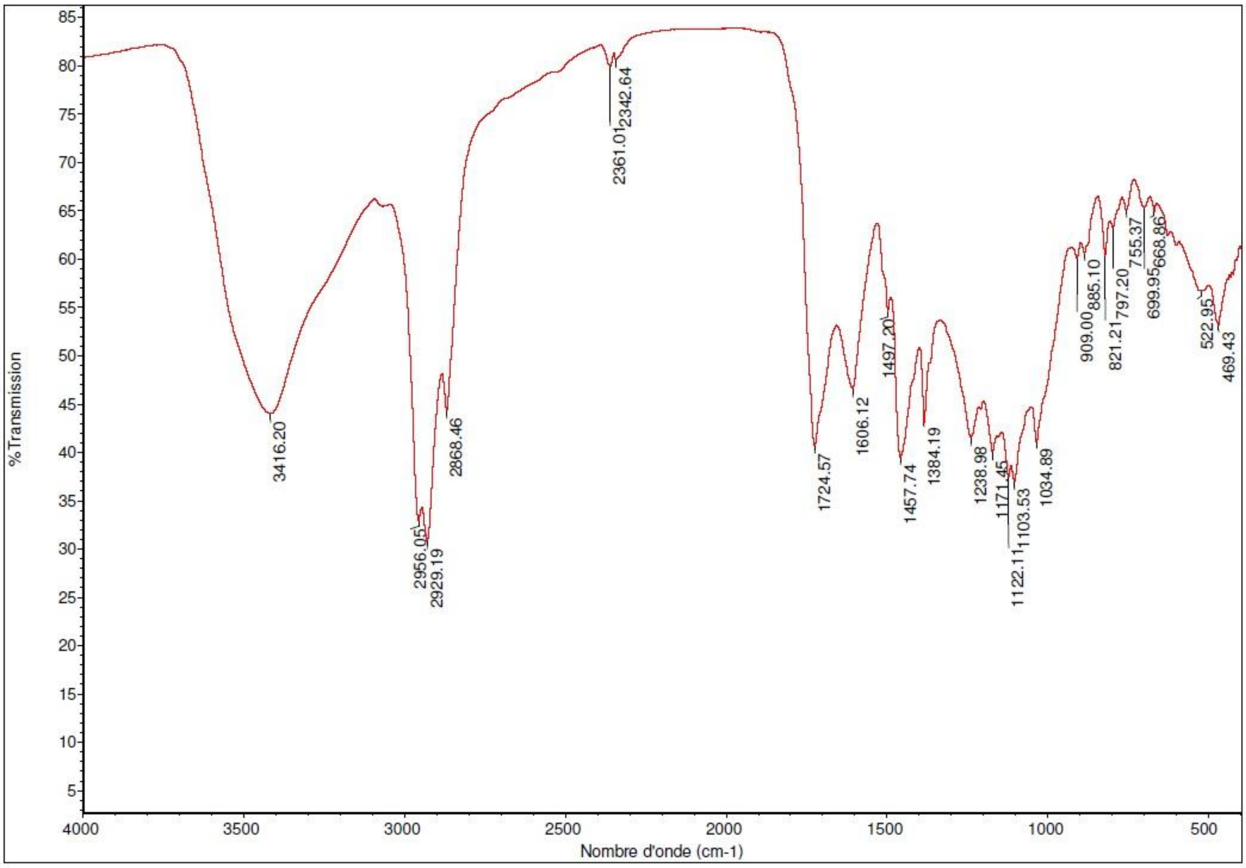
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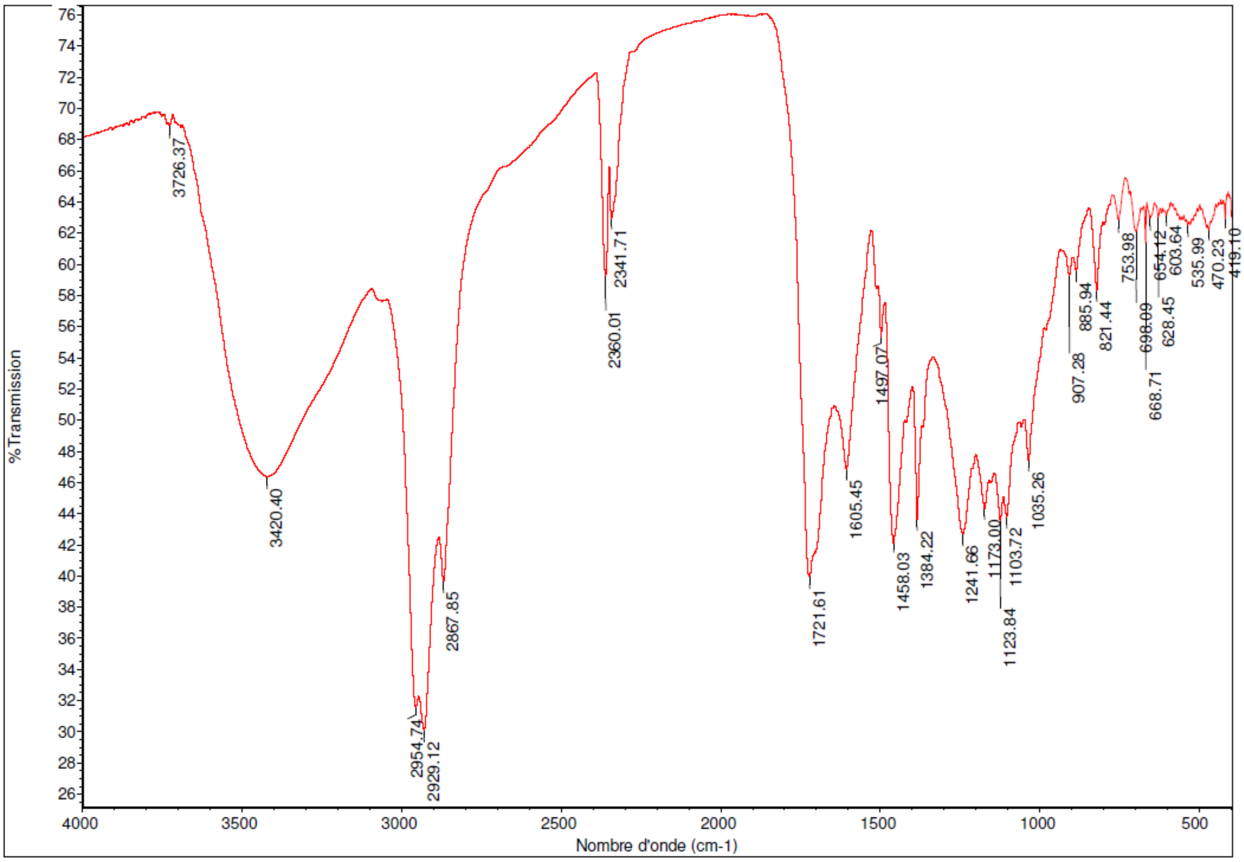
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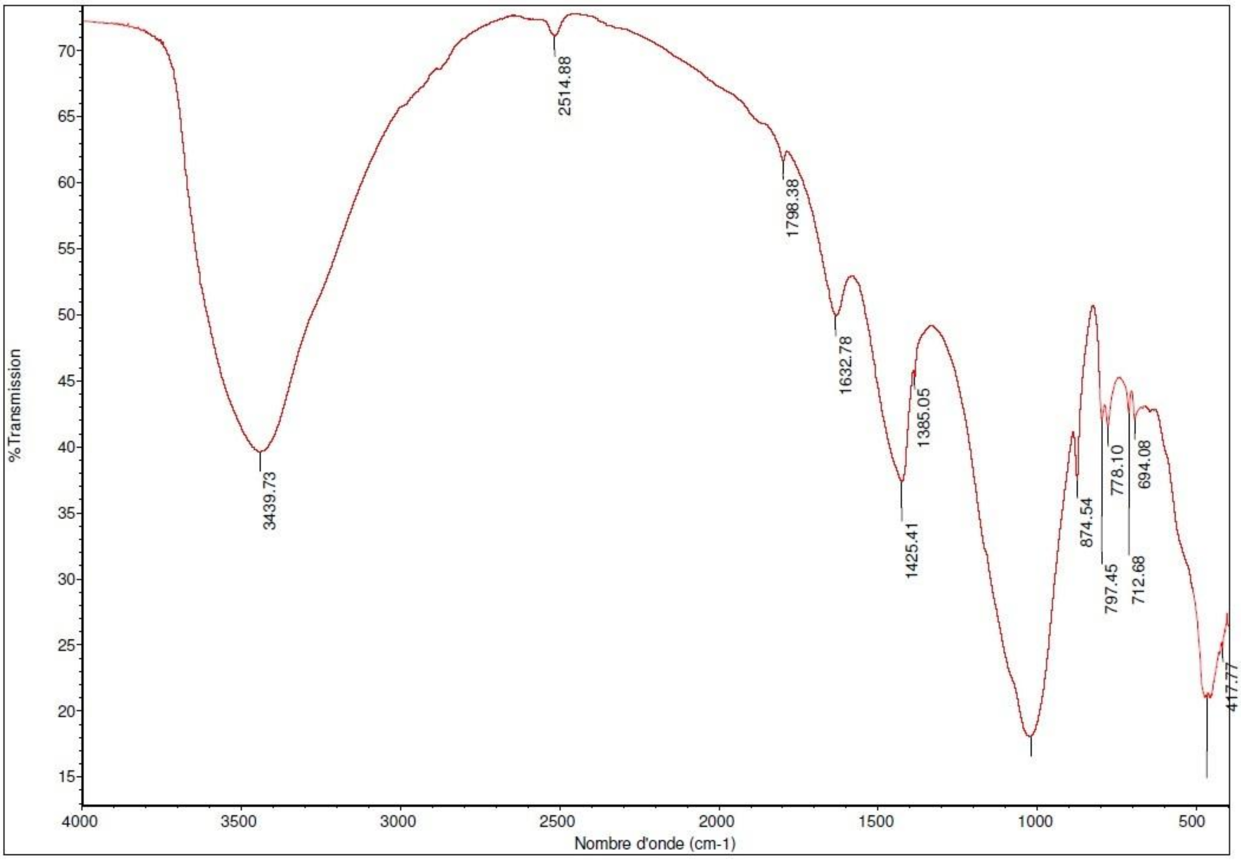
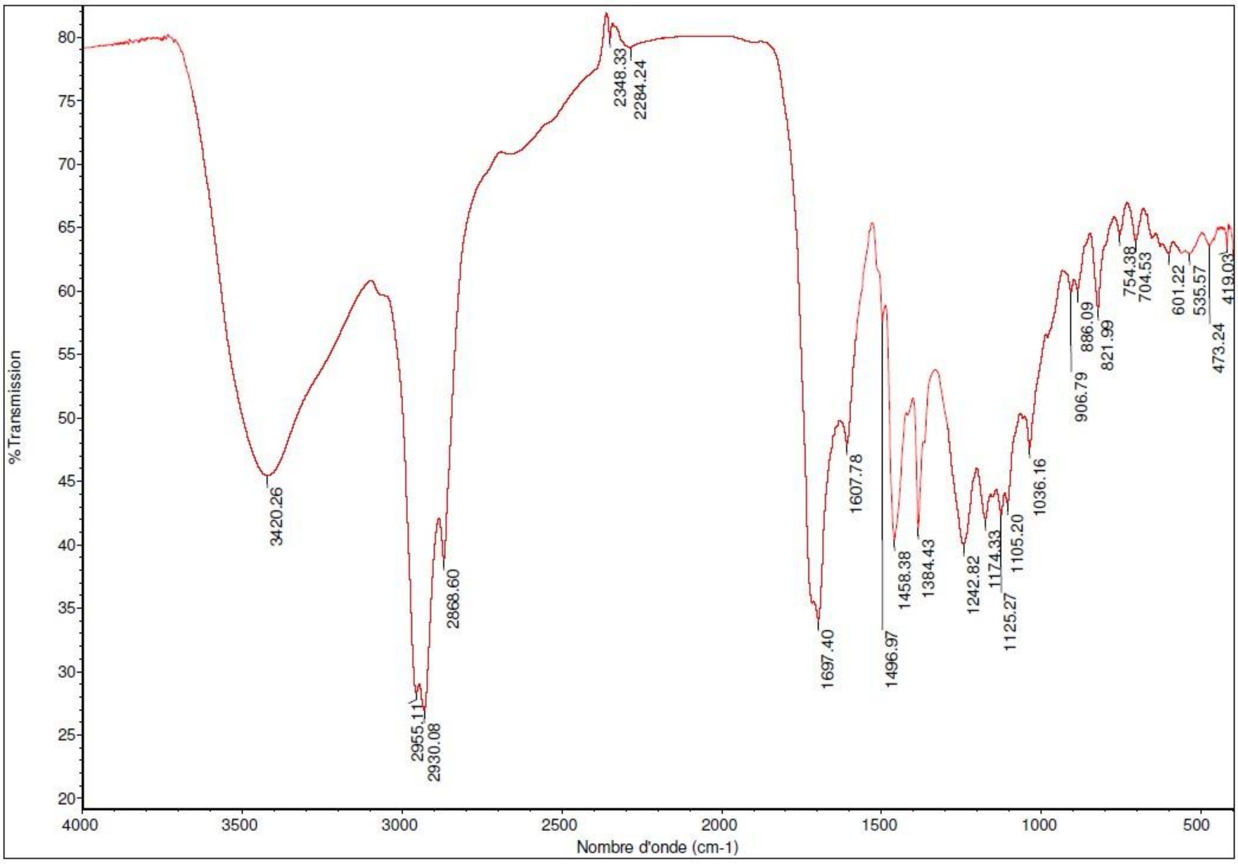
419.10

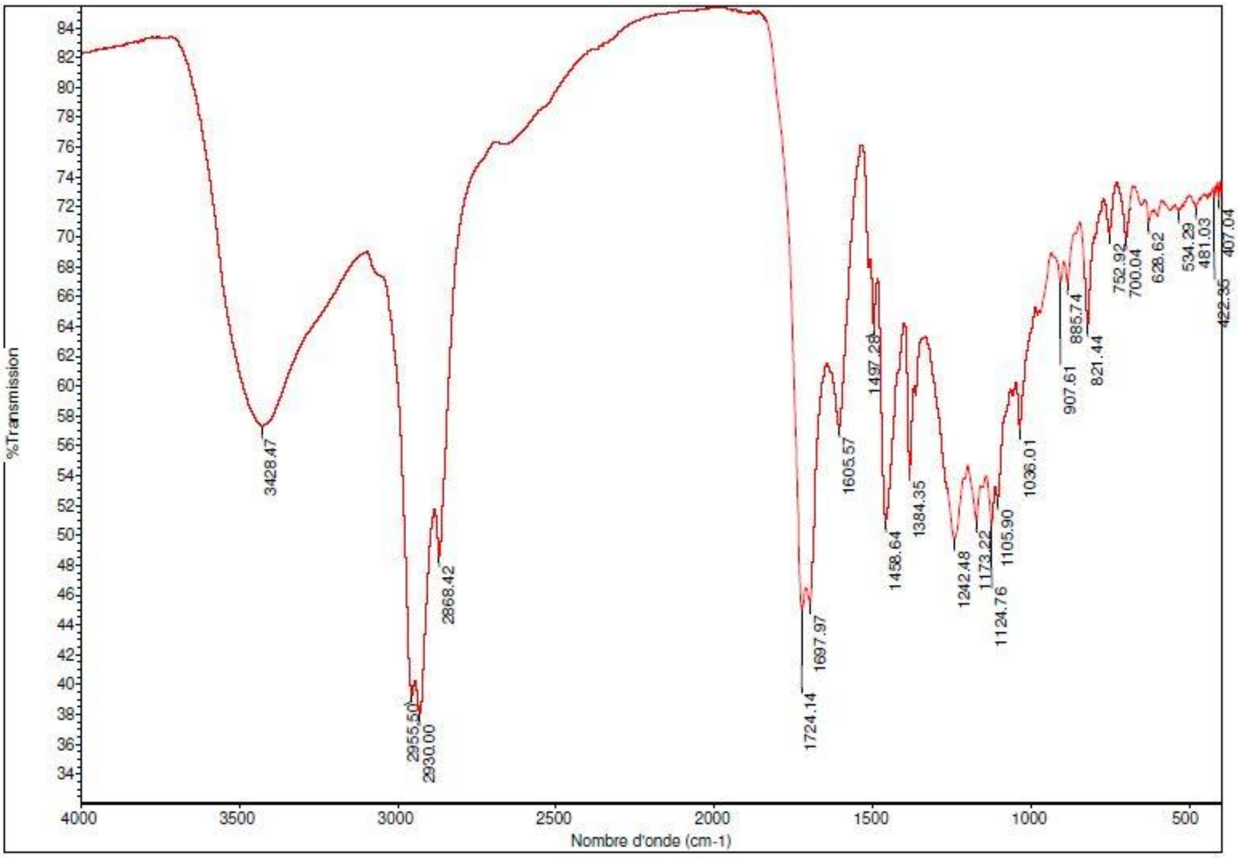
C98


%Transmission
70
65
60
55
50
45
40
35
30
25
20
15
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3439.73
2514.88
1798.38
1632.78
1425.41
1385.05
874.54
797.45
778.10
712.68
694.08
417.77

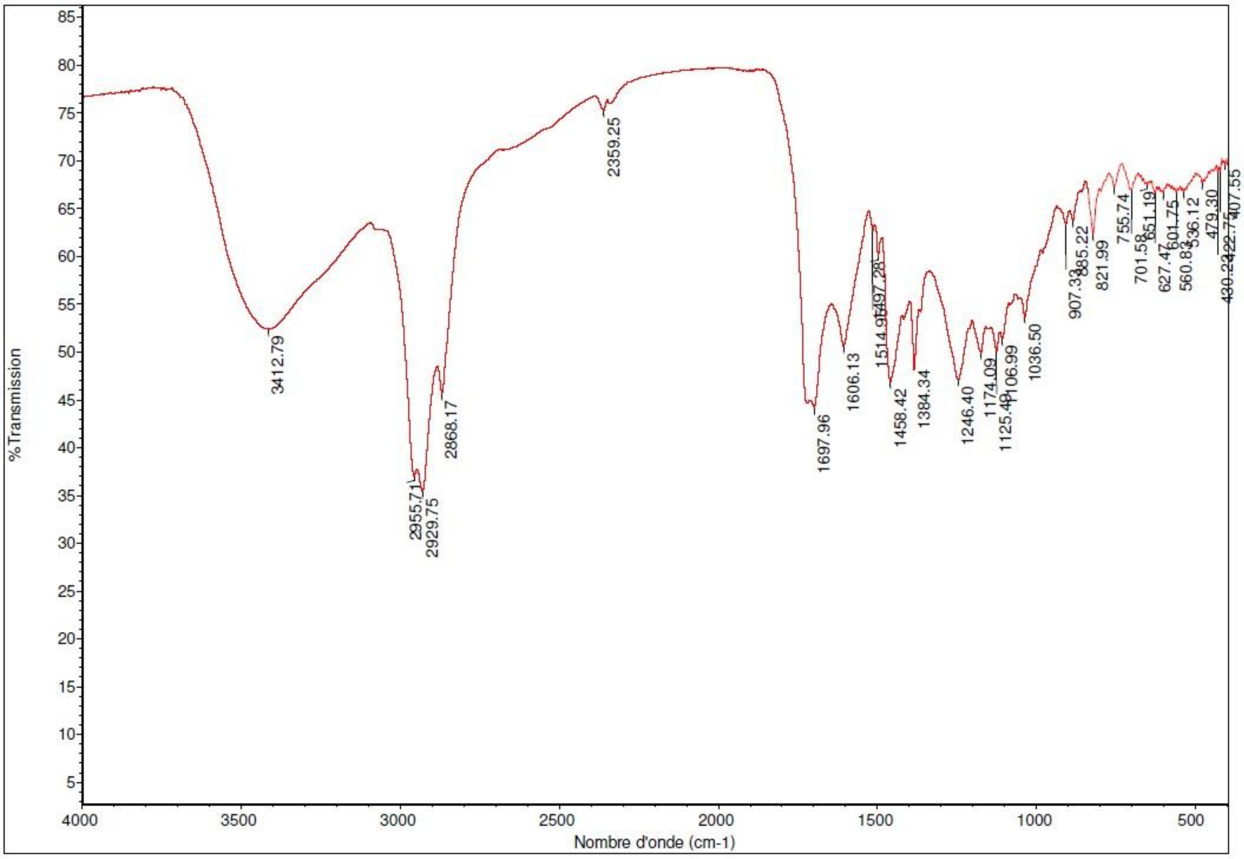
CB4155



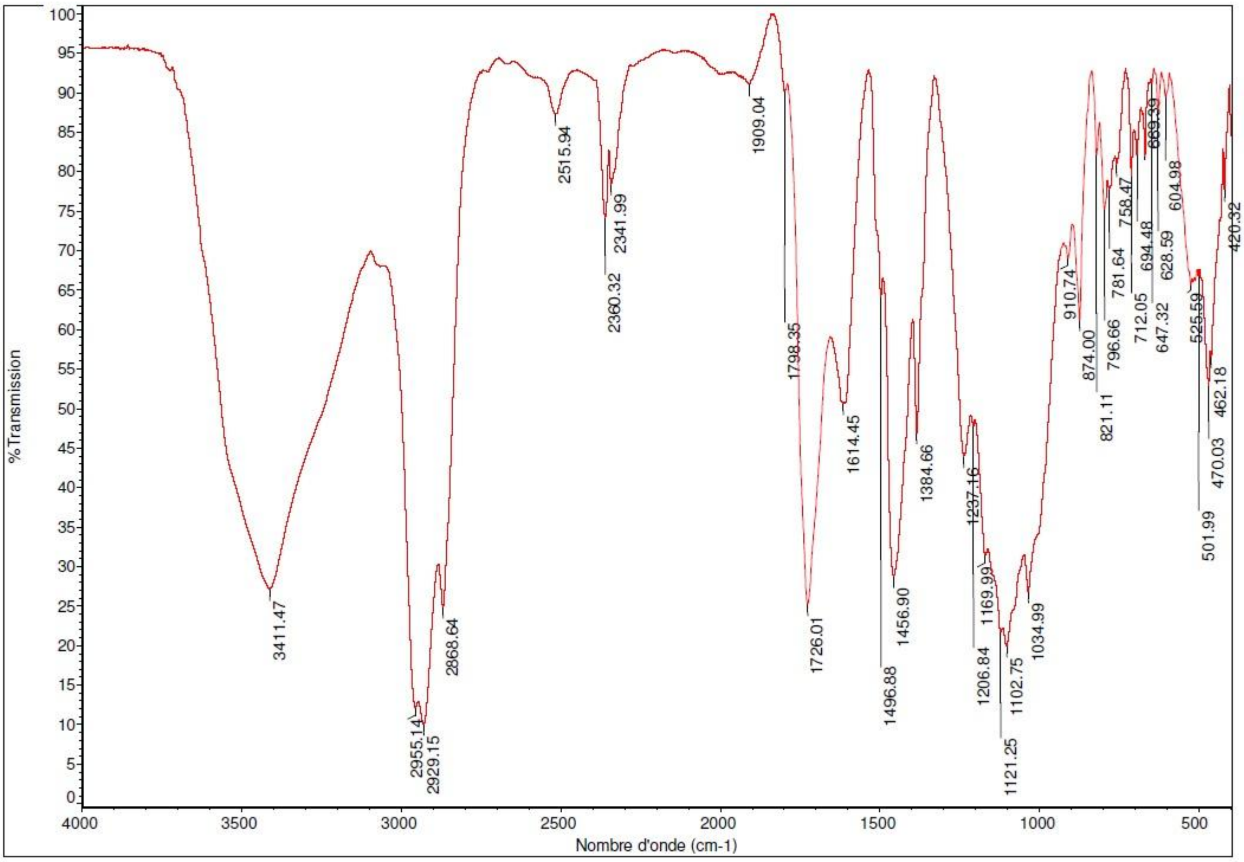
GE3932



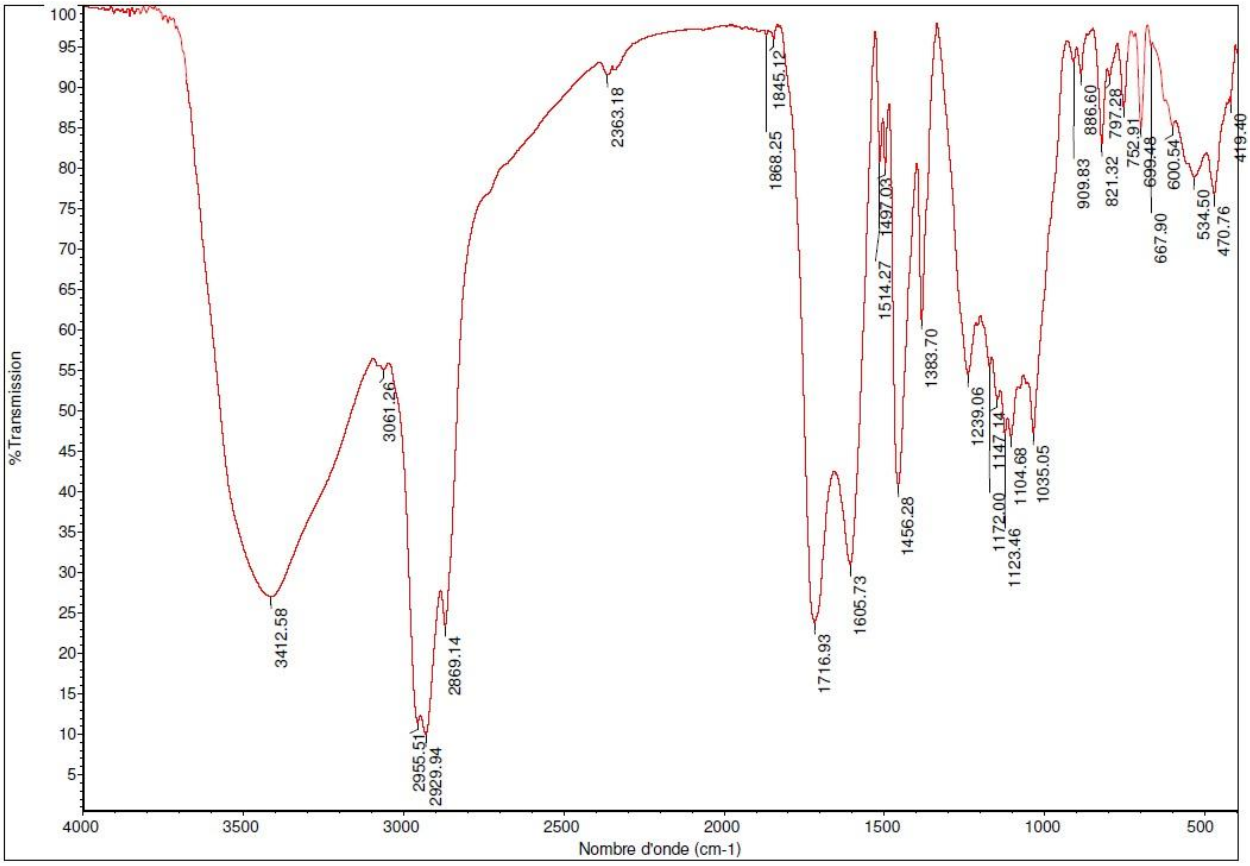
SL2878


%Transmission
Nombre d'onde (cm-1)
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500
3412.79
2955.71
2929.75
2868.17
2359.25
1697.96
1606.13
1514.96
1497.28
1458.42
1384.34
1246.40
1174.09
1125.49
1106.99
1036.50
907.33
885.22
821.99
755.74
701.58
651.19
627.47
601.75
560.83
536.12
479.30
430.22
422.75
407.55

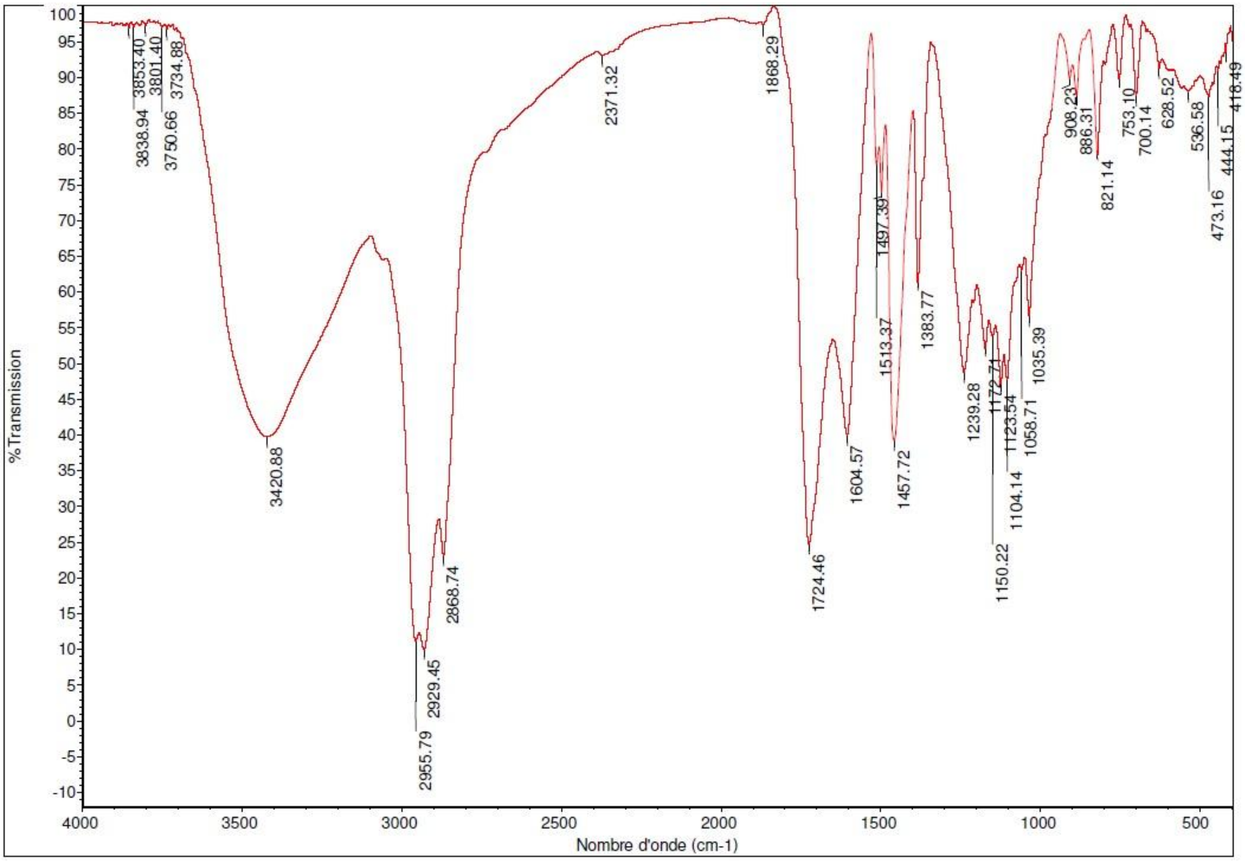
4928


% Transmission
Nombre d'onde (cm-1)
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
4000
3500
3000
2500
2000
1500
1000
500
3411.47
2955.14
2929.15
2868.64
2515.94
2360.32
2341.99
1909.04
1798.35
1726.01
1614.45
1496.88
1456.90
1384.66
1237.16
1206.84
1169.99
1121.25
1102.75
1034.99
910.74
874.00
821.11
796.66
781.64
758.47
712.05
694.48
647.32
628.59
609.39
604.98
525.59
501.99
470.03
462.18
420.32

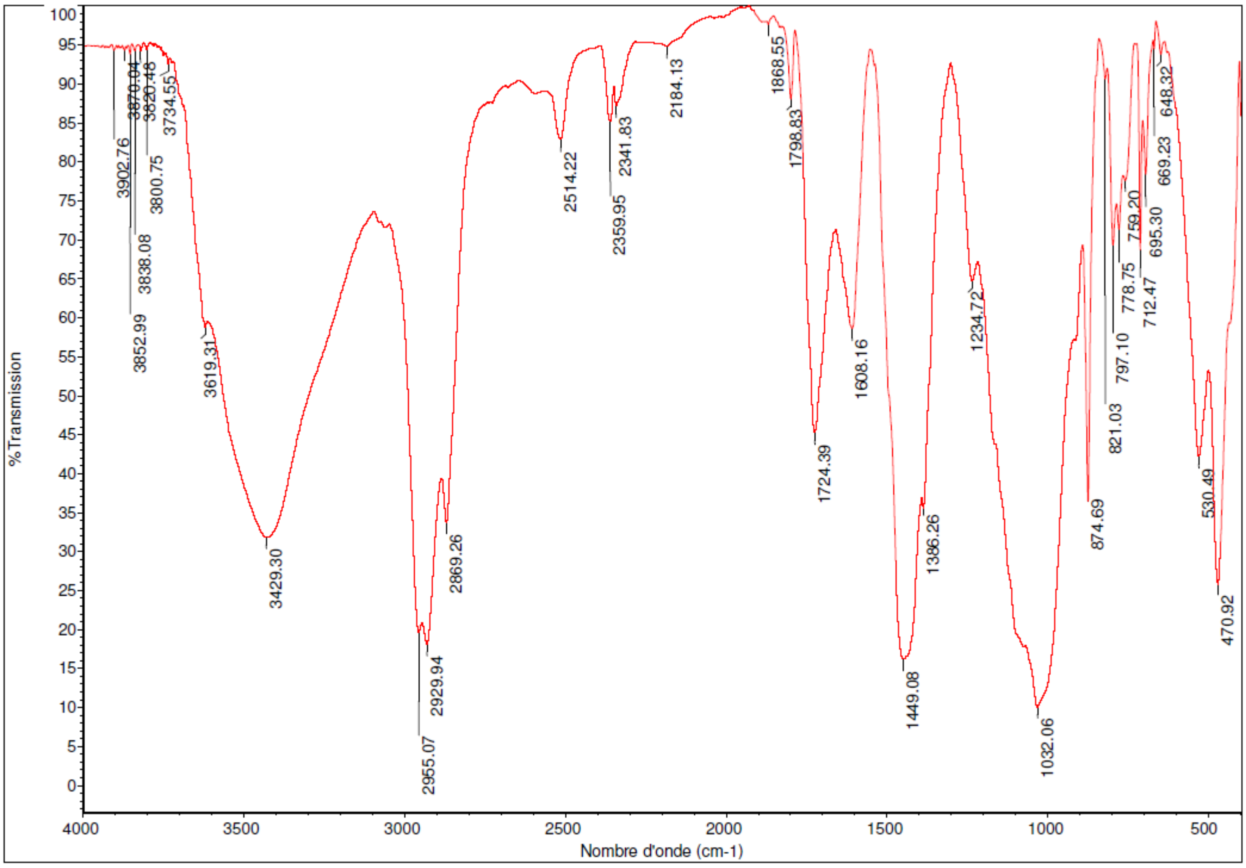
ARL 3


% Transmission
Nombre d'onde (cm-1)
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500
3412.58
3061.26
2955.51
2929.94
2869.14
2363.18
1868.25
1845.12
1716.93
1605.73
1514.27
1497.03
1456.28
1383.70
1239.06
1172.00
1147.14
1123.46
1104.68
1035.05
909.83
886.60
821.32
797.28
752.91
699.48
667.90
600.54
534.50
470.76
419.40

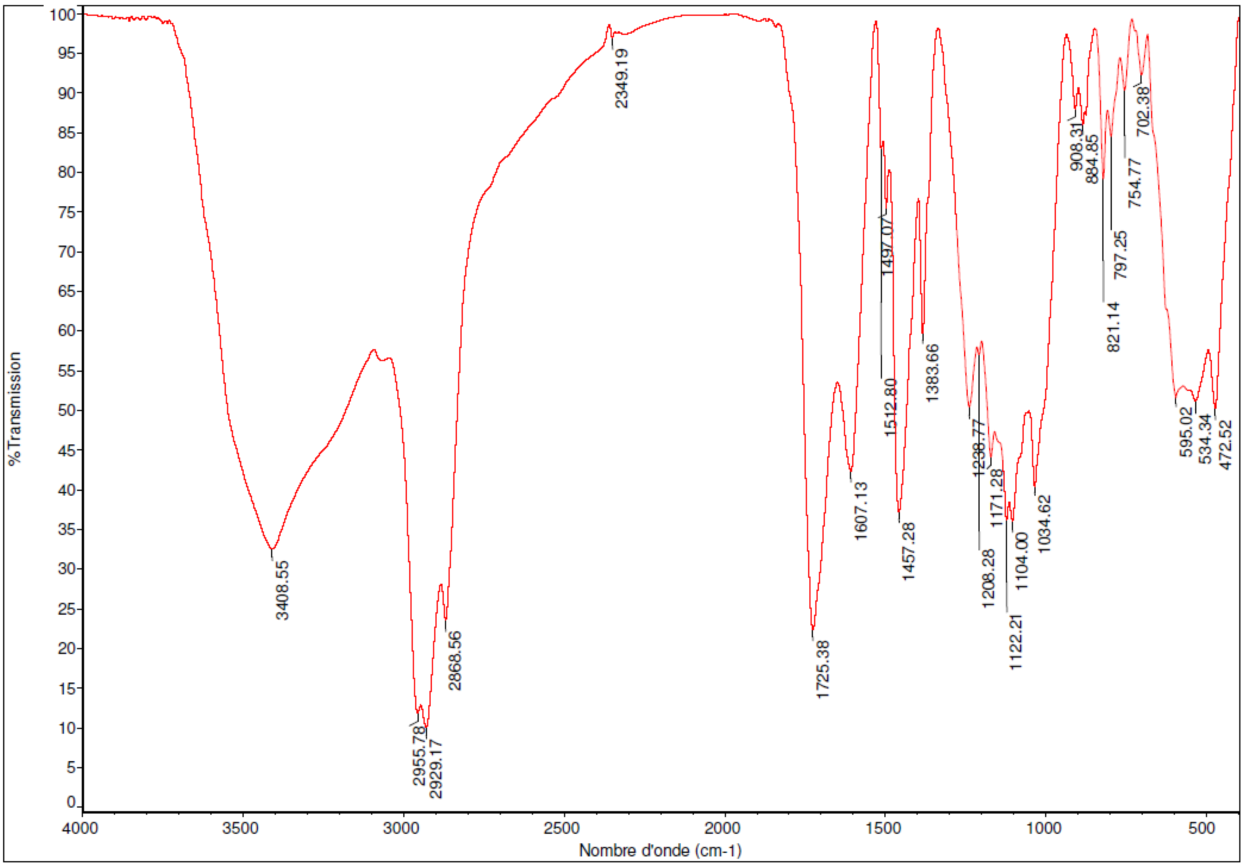
ARL 4


%Transmission
Nombre d'onde (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
3853.40
3838.94
3801.40
3750.66
3734.88
3420.88
2955.79
2929.45
2868.74
2371.32
1868.29
1724.46
1604.57
1513.37
1497.39
1457.72
1383.77
1239.28
1172.71
1150.22
1123.54
1104.14
1058.71
1035.39
908.23
886.31
821.14
753.10
700.14
628.52
536.58
473.16
444.15
418.49

ARL 5


%Transmission
Nombre d'onde (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
3902.76
3870.04
3852.99
3838.08
3820.48
3800.75
3734.55
3619.31
3429.30
2955.07
2929.94
2869.26
2514.22
2359.95
2341.83
2184.13
1868.55
1798.83
1724.39
1608.16
1449.08
1386.26
1234.72
1032.06
874.69
821.03
797.10
778.75
759.20
712.47
695.30
669.23
648.32
530.49
470.92

ARL 6


%Transmission
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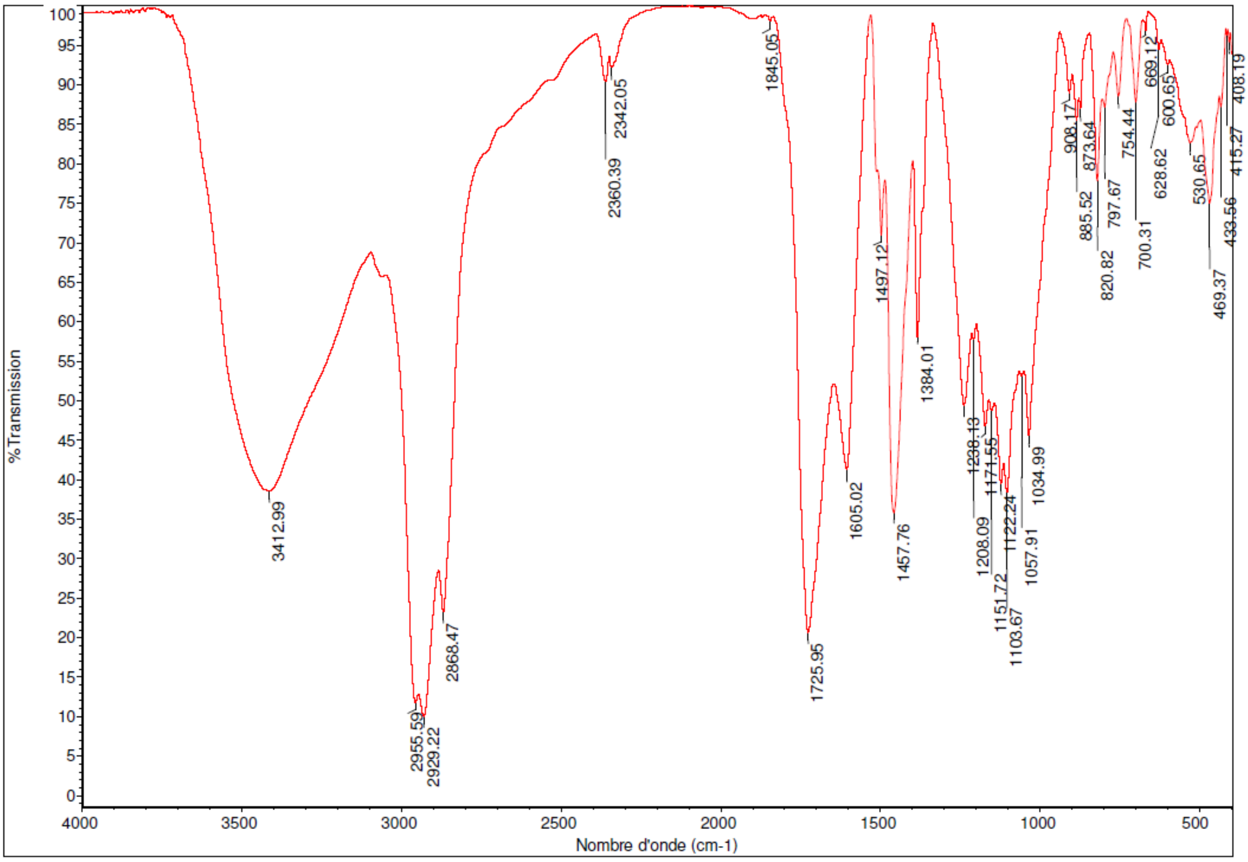
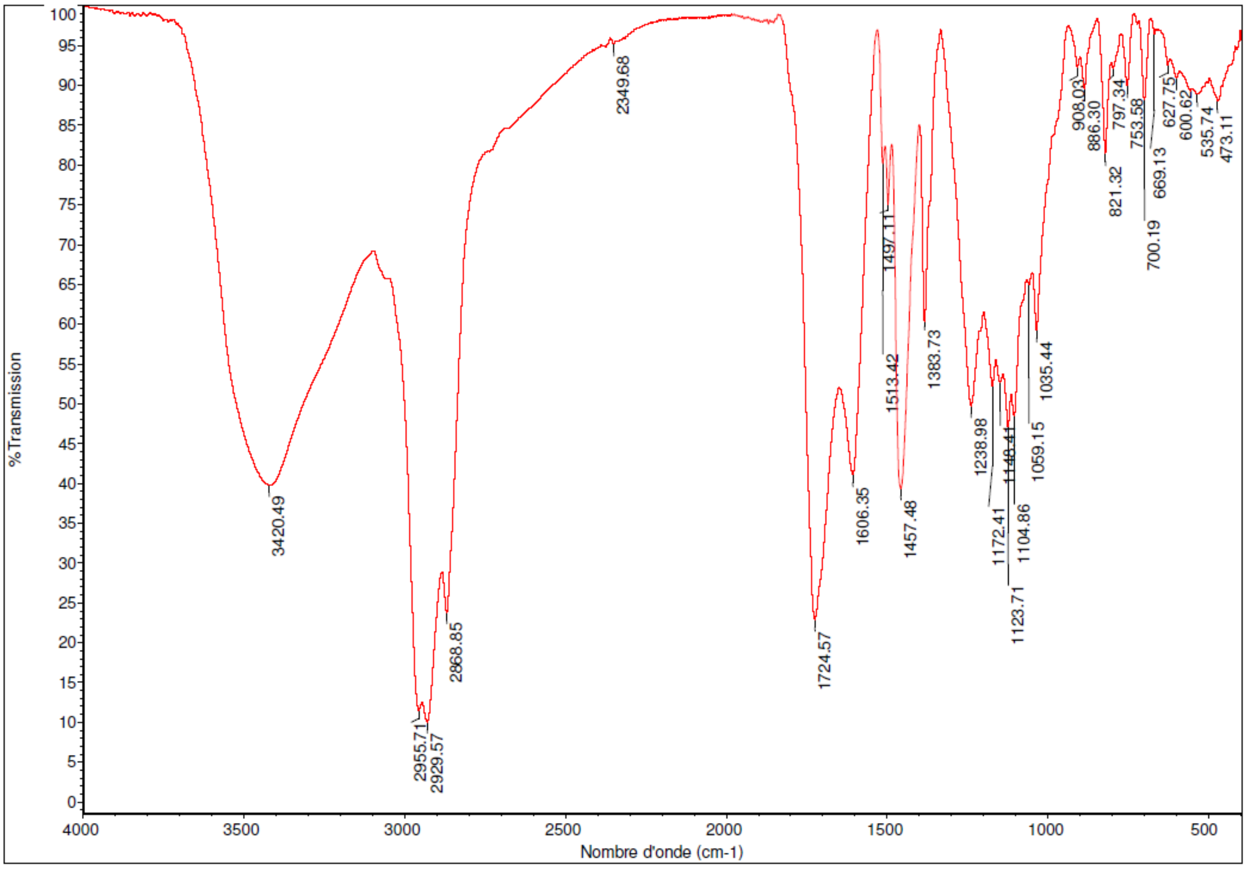
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3408.55
2955.78
2929.17
2868.56
2349.19
1725.38
1607.13
1512.80
1497.07
1457.28
1383.66
1238.77
1208.28
1171.28
1122.21
1104.00
1034.62
908.31
884.85
821.14
797.25
754.77
702.38
595.02
534.34
472.52

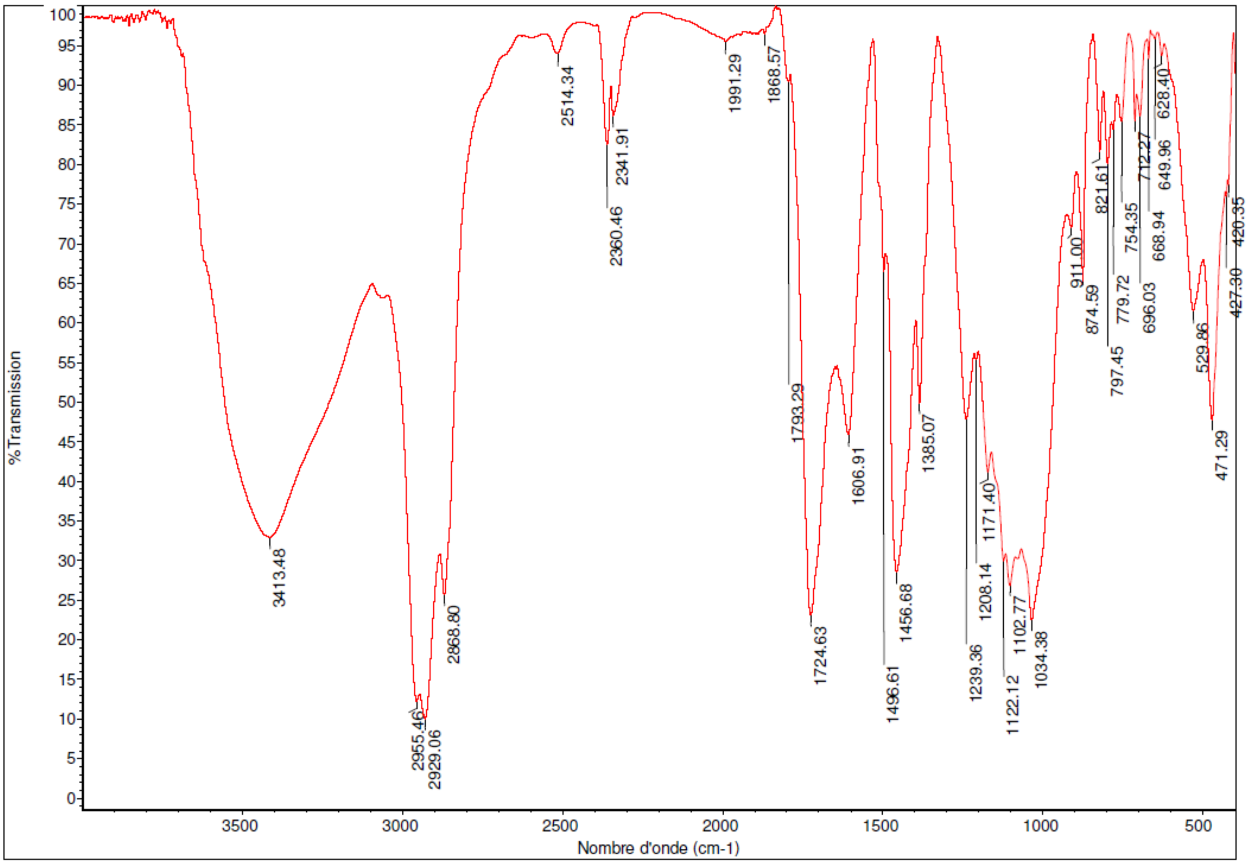
ARL 7


%Transmission
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3412.99
2955.59
2929.22
2868.47
2360.39
2342.05
1845.05
1725.95
1605.02
1497.12
1457.76
1384.01
1238.13
1208.09
1171.55
1151.72
1122.24
1103.67
1057.91
1034.99
908.17
885.52
873.64
820.82
797.67
754.44
700.31
669.12
628.62
600.65
530.65
469.37
433.56
415.27
408.19

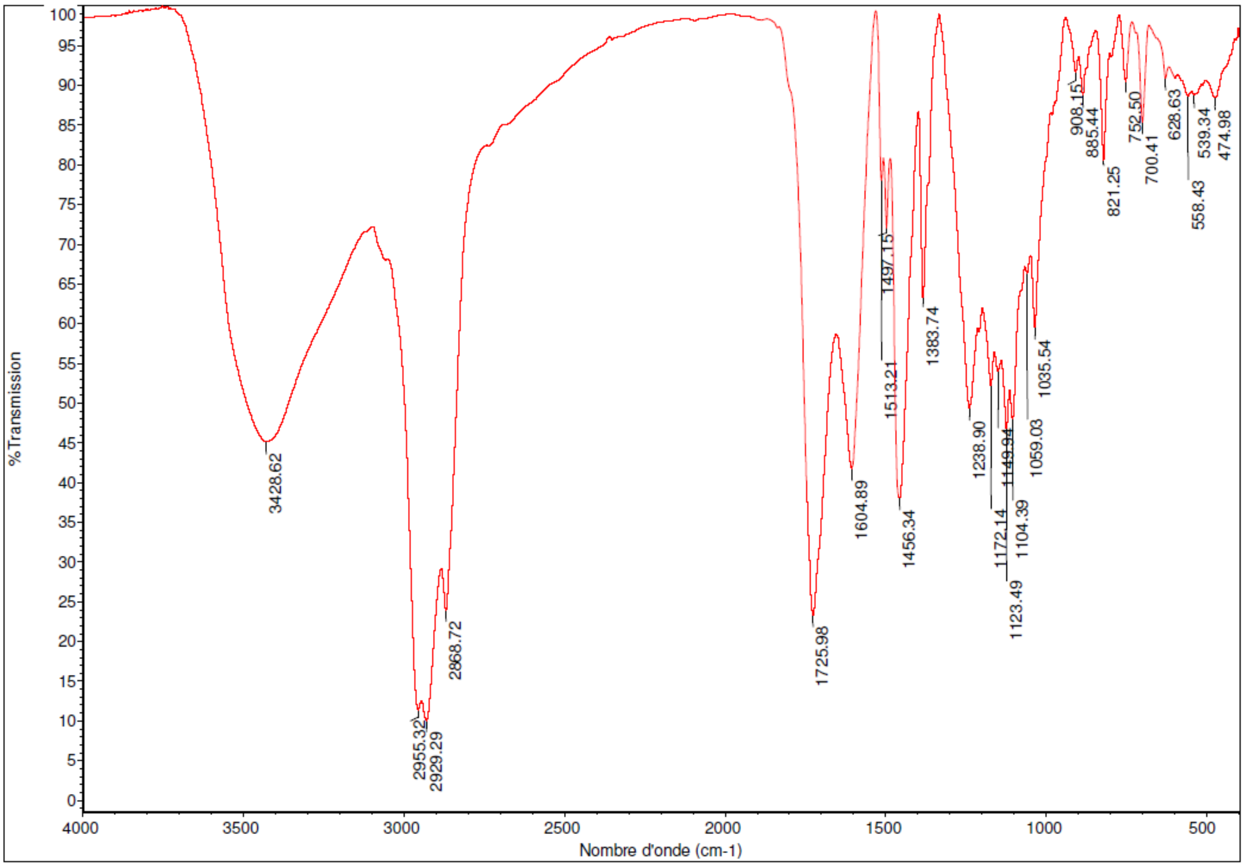
ARL 8


%Transmission
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3420.49
2955.71
2929.57
2868.85
2349.68
1724.57
1606.35
1513.42
1497.11
1457.48
1383.73
1238.98
1172.41
1148.41
1123.71
1104.86
1059.15
1035.44
908.03
886.30
821.32
797.34
753.58
700.19
669.13
627.75
600.62
535.74
473.11

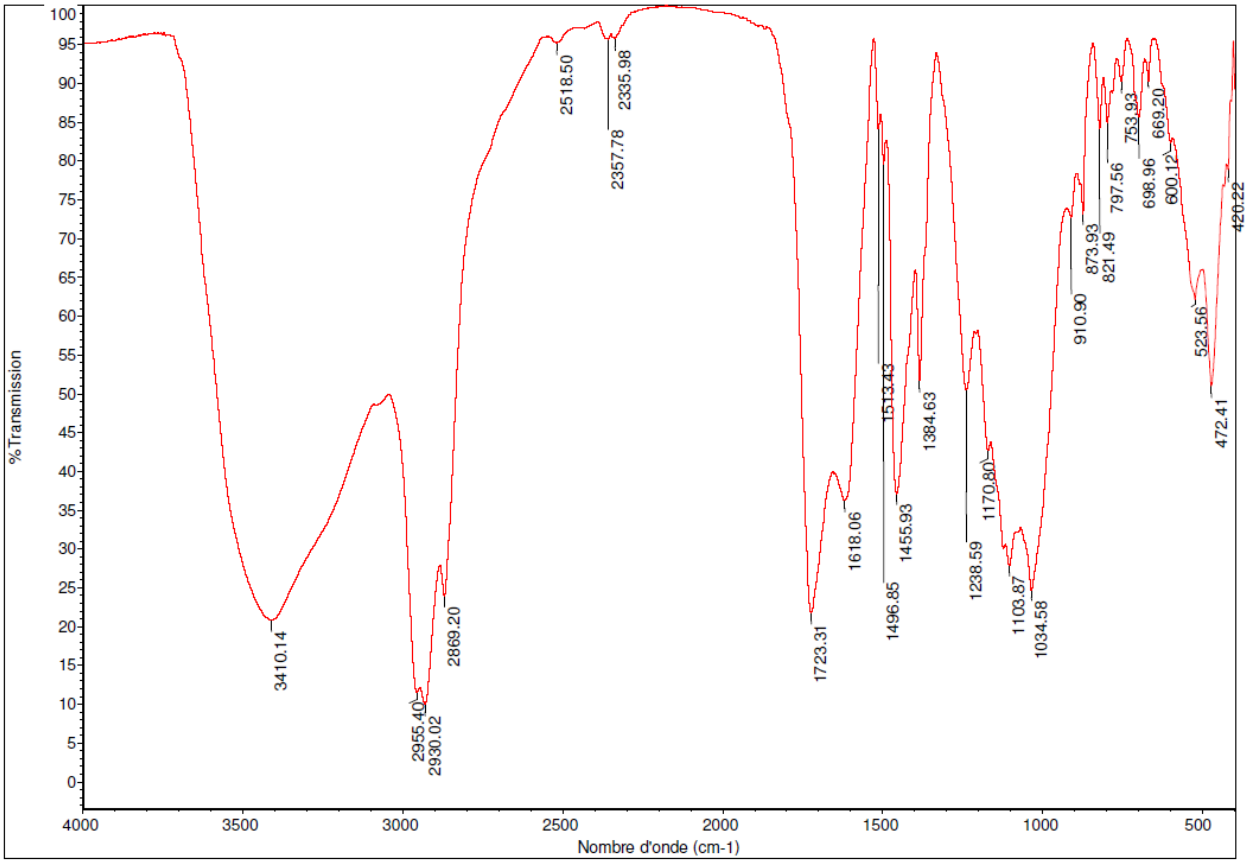
ARL 9


%Transmission
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3413.48
2955.46
2929.06
2868.80
2514.34
2360.46
2341.91
1991.29
1868.57
1793.29
1724.63
1606.91
1496.61
1456.68
1385.07
1239.36
1208.14
1171.40
1122.12
1102.77
1034.38
911.00
874.59
821.61
797.45
779.72
754.35
712.27
696.03
668.94
649.96
628.40
529.86
471.29
427.30
420.35

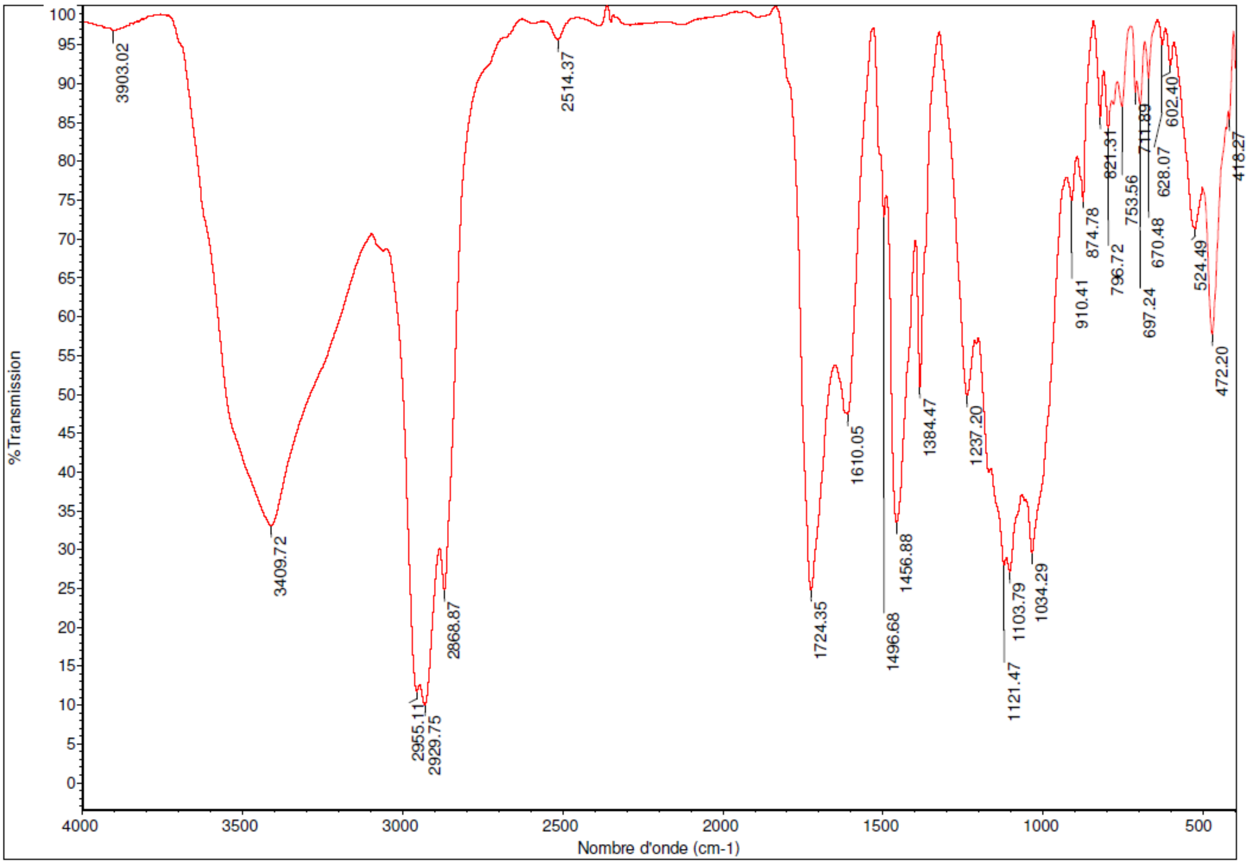
ARL 12


%Transmission
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3428.62
2955.32
2929.29
2868.72
1725.98
1604.89
1513.21
1497.15
1456.34
1383.74
1238.90
1172.14
1149.94
1123.49
1104.39
1059.03
1035.54
908.15
885.44
821.25
752.50
700.41
628.63
558.43
539.34
474.98

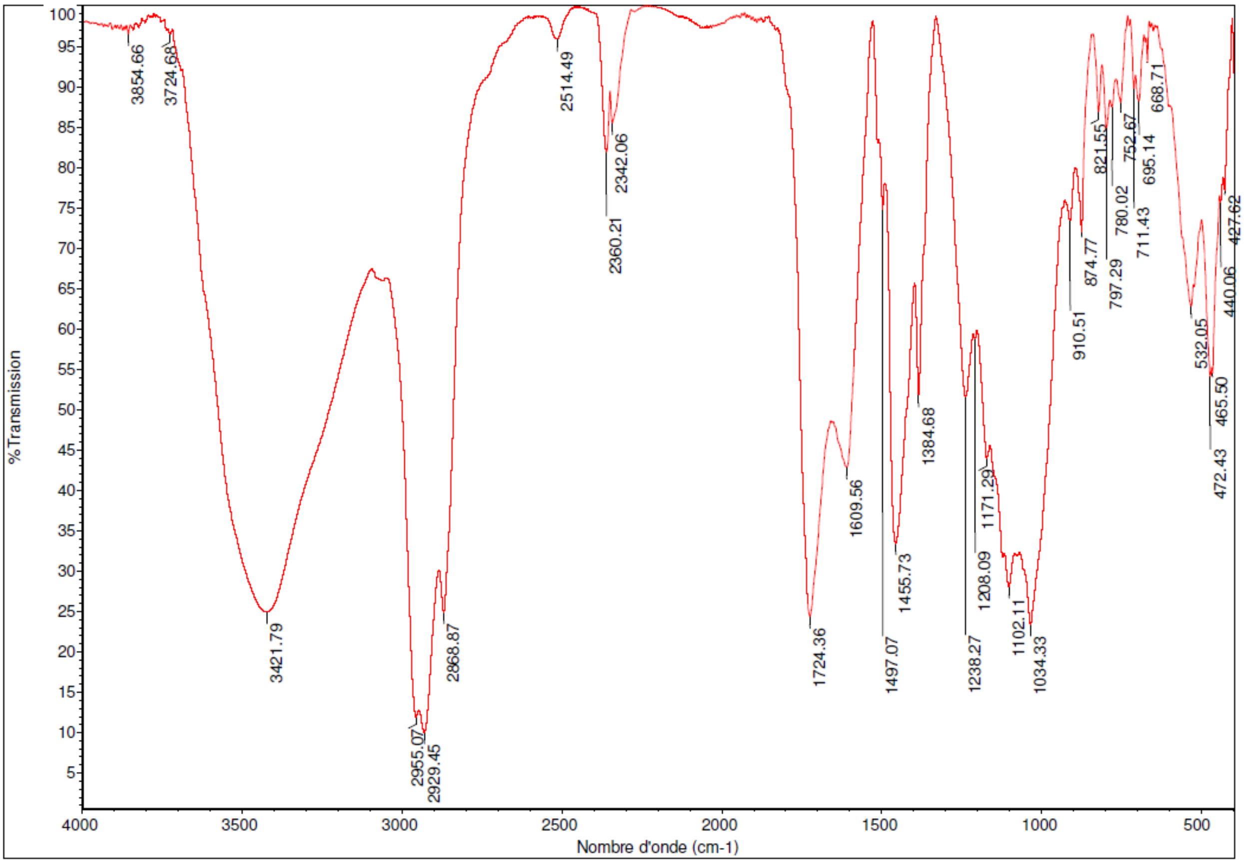
RL15


%Transmission
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3410.14
2955.40
2930.02
2869.20
2518.50
2357.78
2335.98
1723.31
1618.06
1513.43
1496.85
1455.93
1384.63
1238.59
1170.80
1103.87
1034.58
910.90
873.93
821.49
797.56
753.93
698.96
669.20
600.12
523.56
472.41
420.22

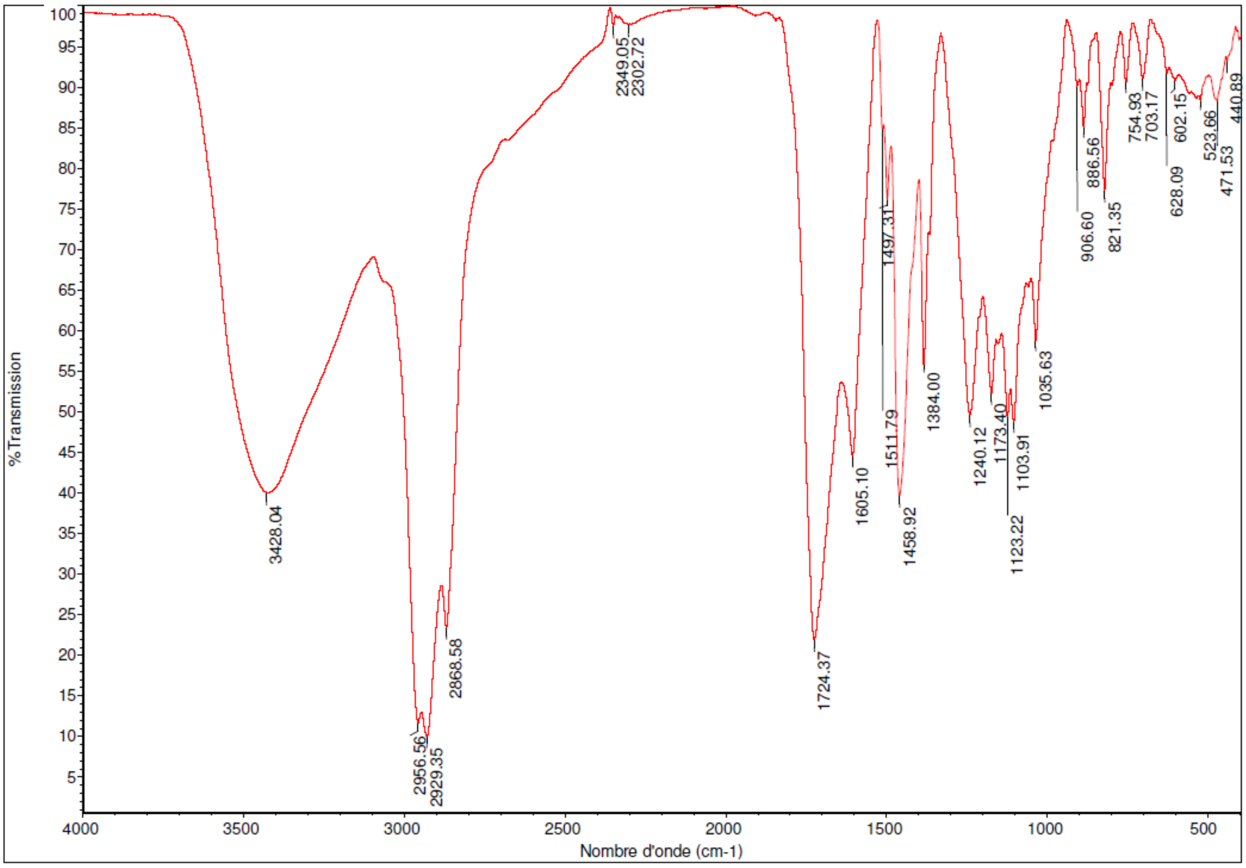
RL 16


100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
%Transmission
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3903.02
3409.72
2955.11
2929.75
2868.87
2514.37
1724.35
1610.05
1496.68
1456.88
1384.47
1237.20
1121.47
1103.79
1034.29
910.41
874.78
821.31
796.72
753.56
711.89
697.24
670.48
628.07
602.40
524.49
472.20
418.27

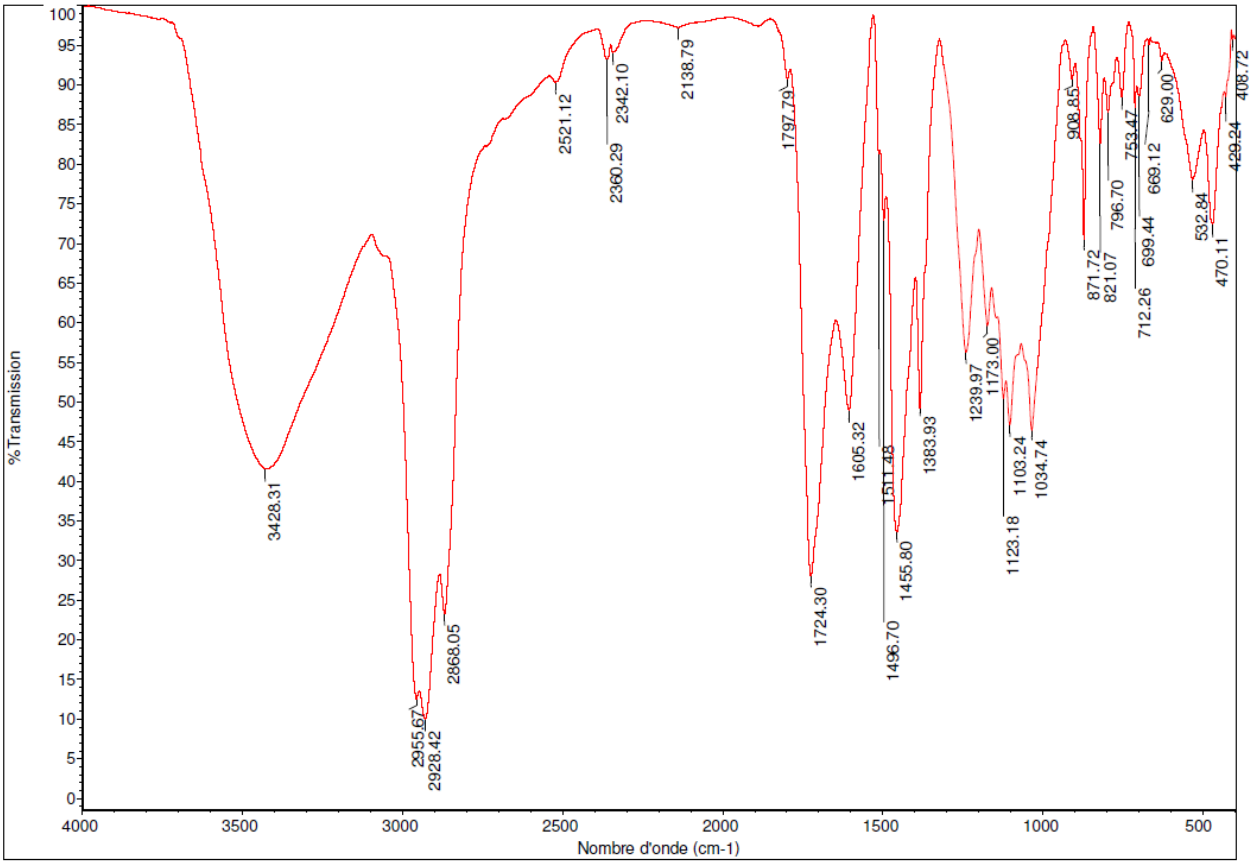
RL 17


100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
%Transmission
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3854.66
3724.68
3421.79
2955.07
2929.45
2868.87
2514.49
2360.21
2342.06
1724.36
1609.56
1497.07
1455.73
1384.68
1238.27
1208.09
1171.29
1102.11
1034.33
910.51
874.77
821.55
797.29
780.02
752.67
711.43
695.14
668.71
532.05
472.43
465.50
440.06
427.62

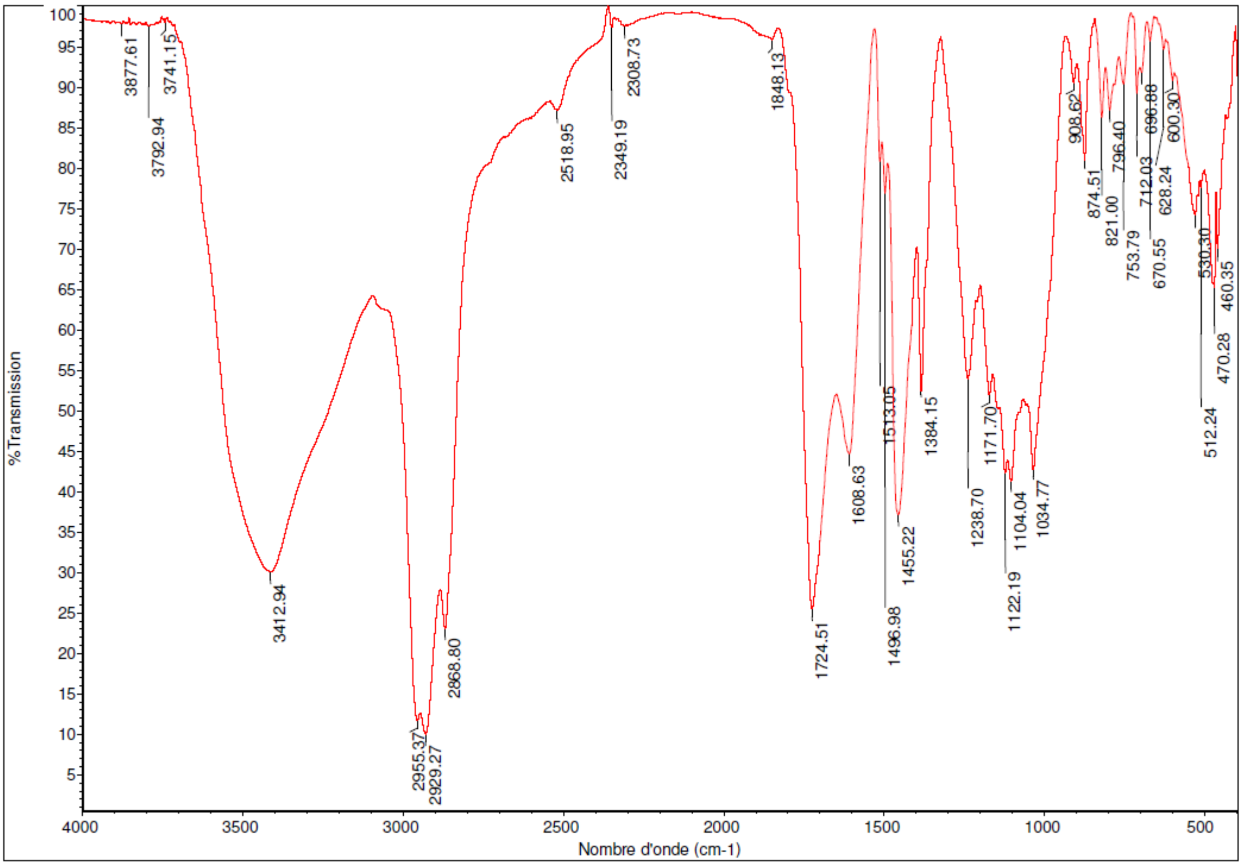
RL 18


%Transmission
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3428.04
2956.56
2929.35
2868.58
2349.05
2302.72
1724.37
1605.10
1511.79
1497.31
1458.92
1384.00
1240.12
1173.40
1123.22
1103.91
1035.63
906.60
886.56
821.35
754.93
703.17
628.09
602.15
523.66
471.53
440.89

RL 19

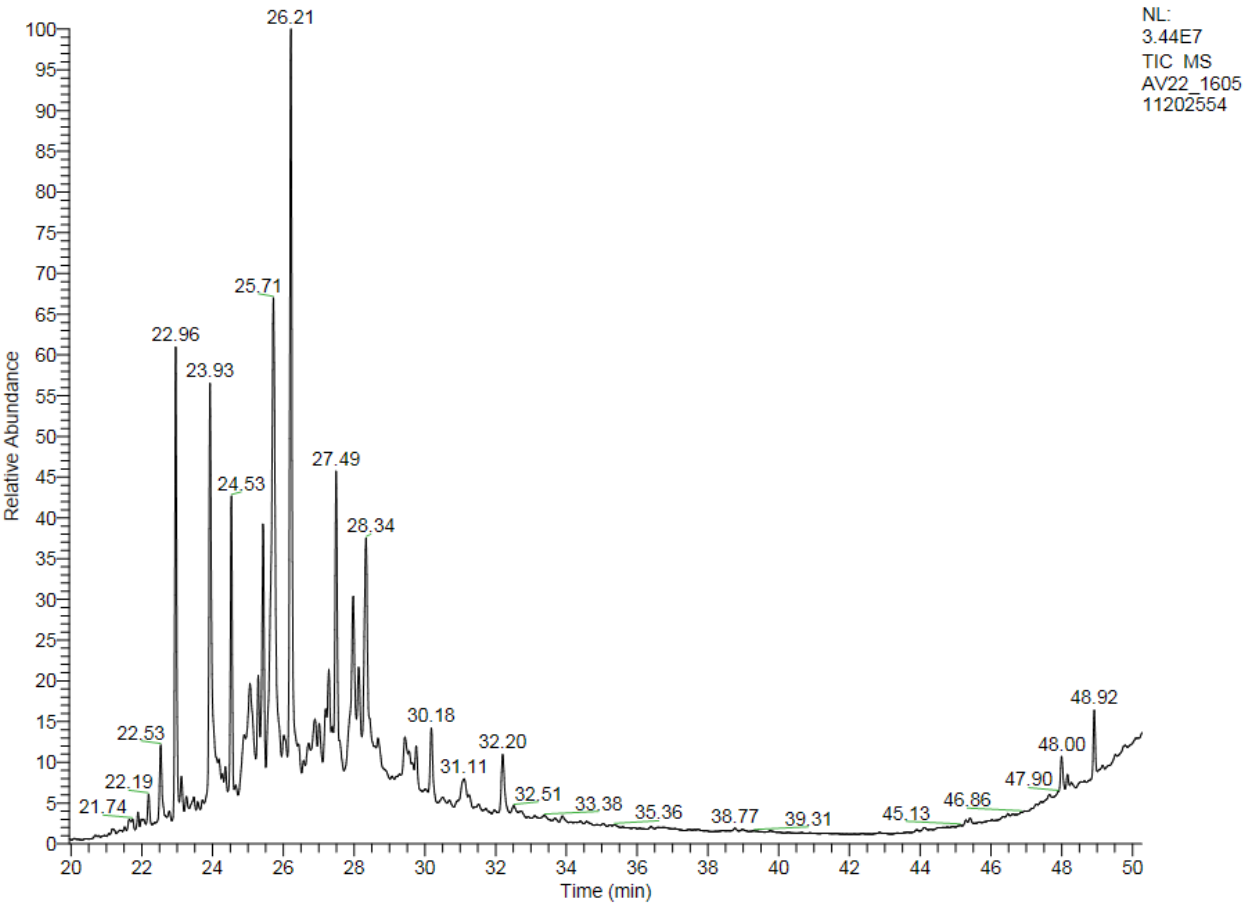

%Transmission
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3428.31
2955.67
2928.42
2868.05
2521.12
2360.29
2342.10
2138.79
1797.79
1724.30
1605.32
1511.48
1496.70
1455.80
1383.93
1239.97
1173.00
1123.18
1103.24
1034.74
908.85
871.72
821.07
796.70
753.47
712.26
699.44
669.12
629.00
532.84
470.11
429.24
408.72

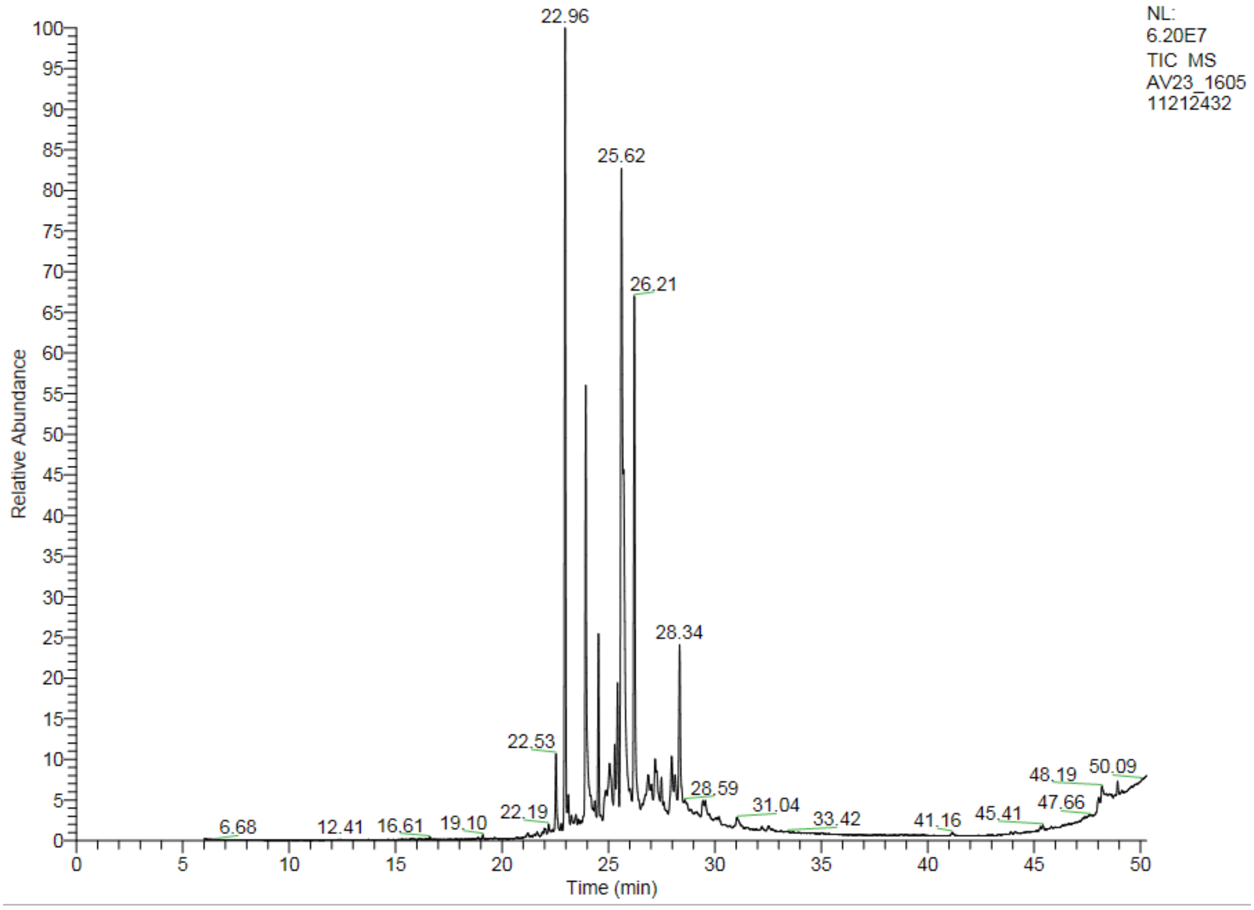
RL 20

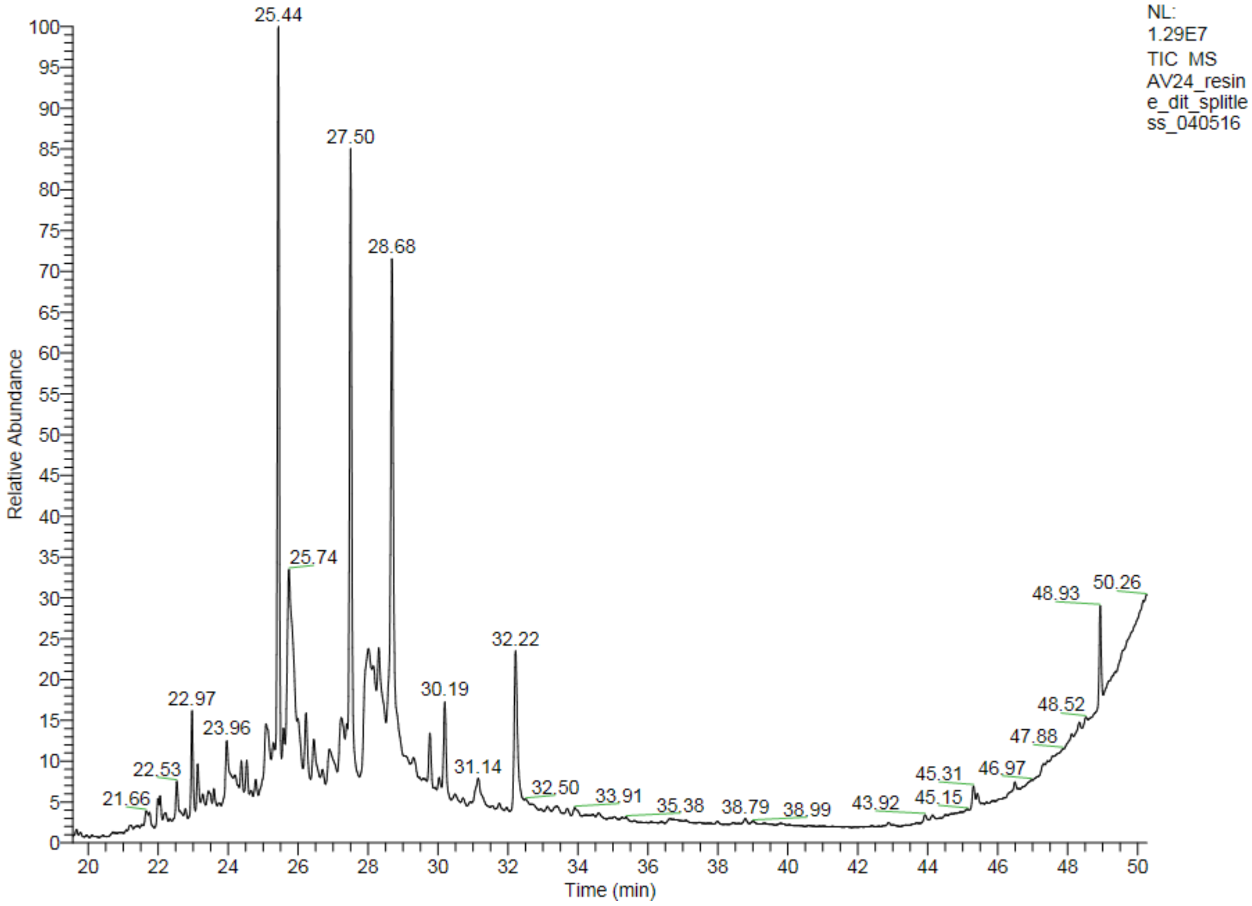

%Transmission
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500
Nombre d'onde (cm-1)
3877.61
3792.94
3741.15
3412.94
2955.37
2929.27
2868.80
2518.95
2349.19
2308.73
1848.13
1724.51
1608.63
1513.05
1496.98
1455.22
1384.15
1238.70
1171.70
1122.19
1104.04
1034.77
908.62
874.51
821.00
796.40
753.79
712.03
696.88
670.55
628.24
600.30
530.30
512.24
470.28
460.35

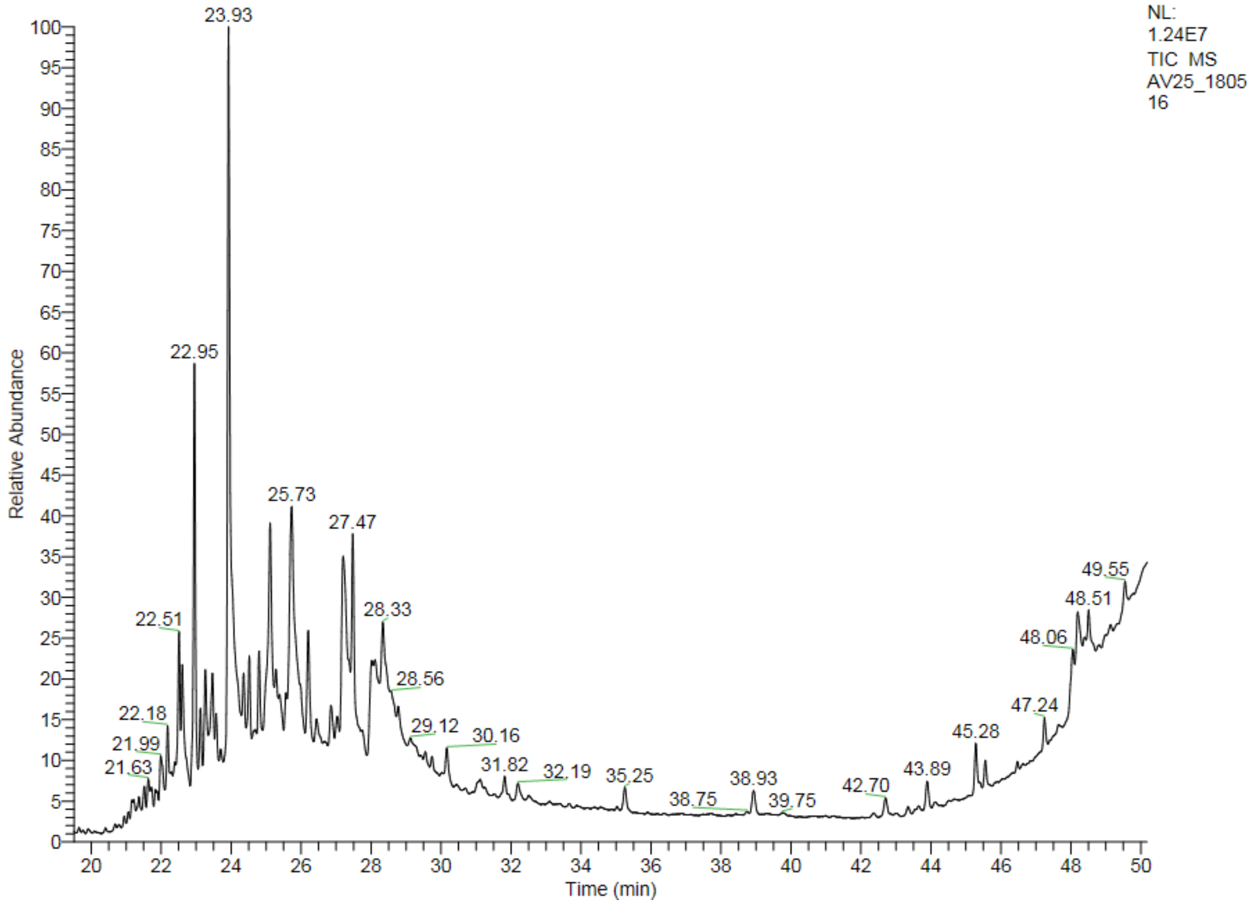
RL 21

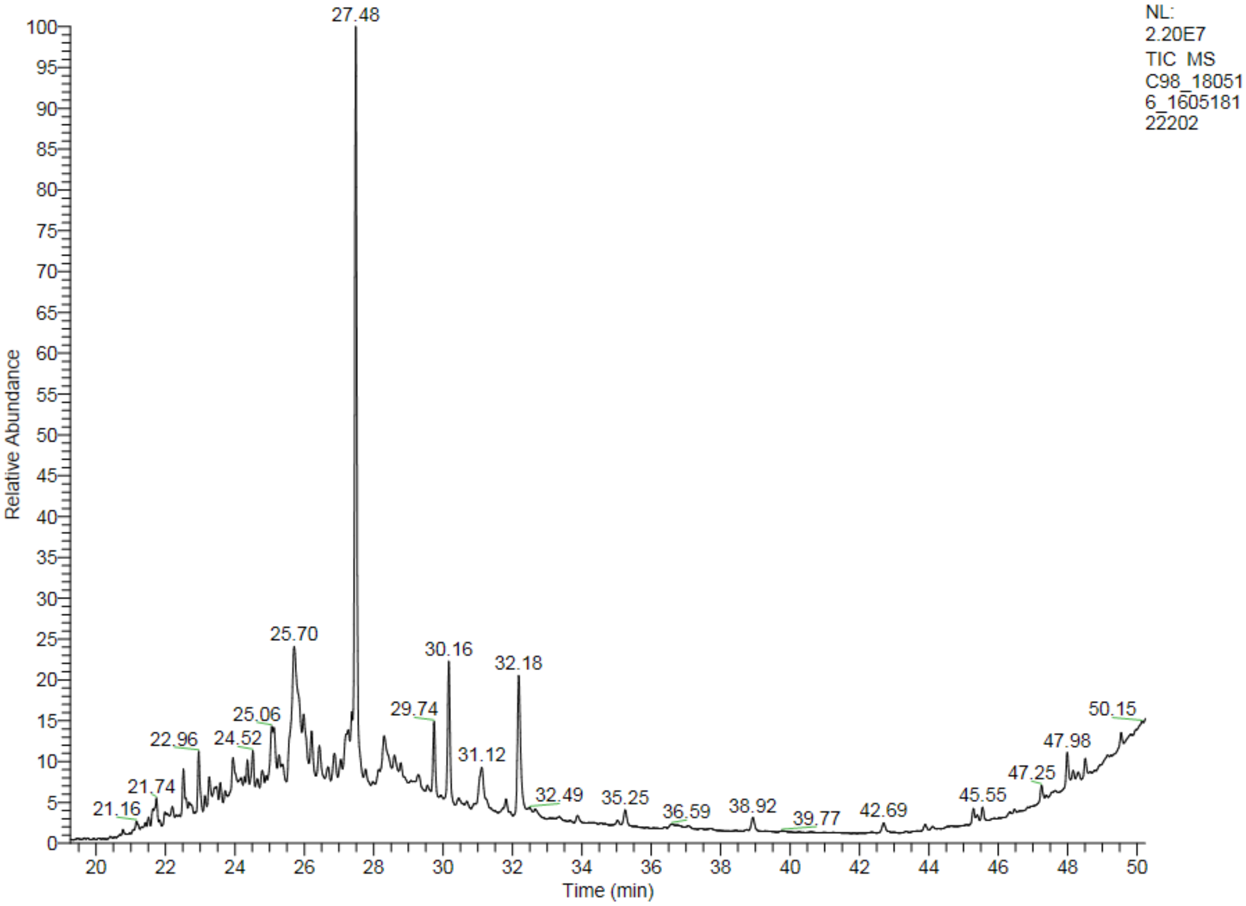
Appendix 7. **GC-MS results. Total ion chromatograms of the samples.**

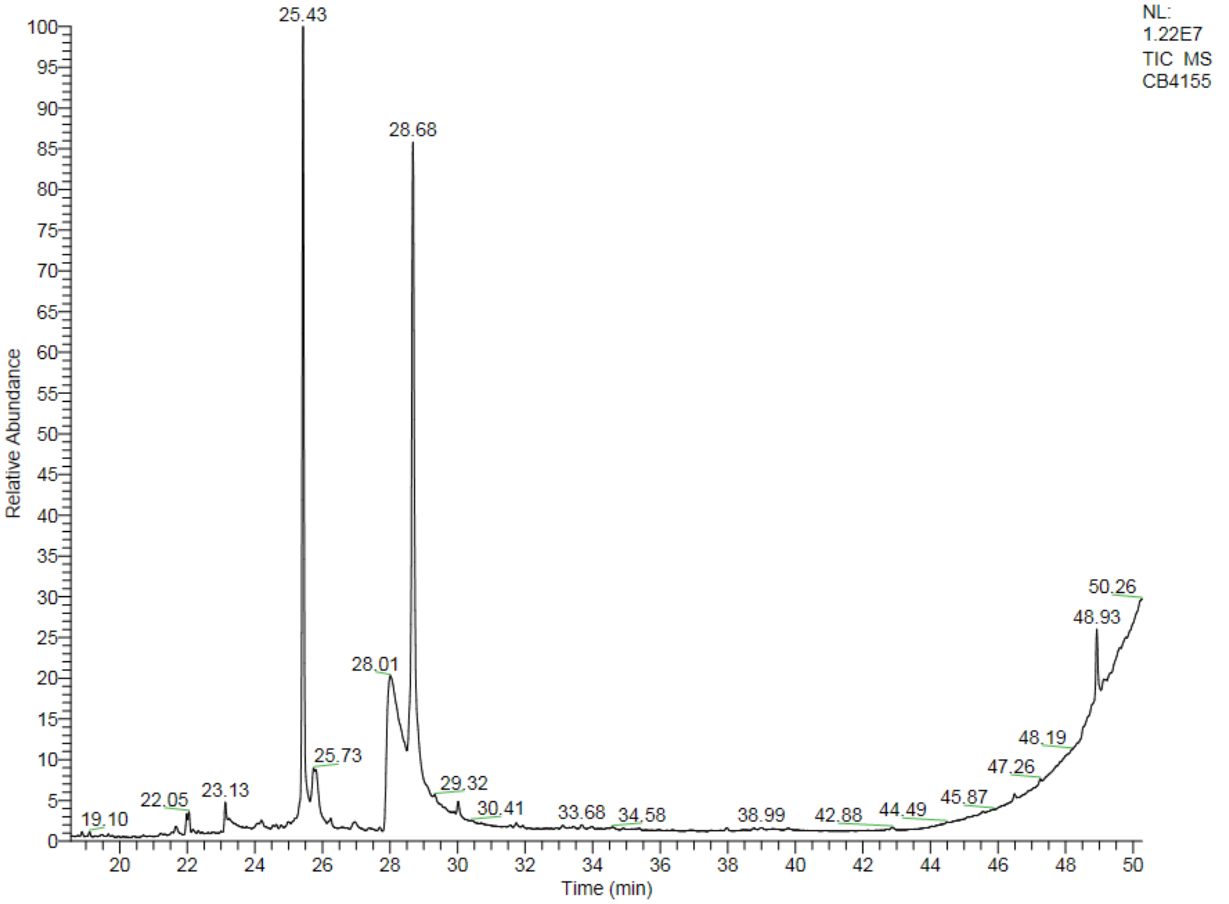





NL:
1.29E7
TIC MS
AV24_resine_dit_splitless_040516
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
Time (min)
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
25.44
27.50
28.68
25.74
32.22
30.19
22.97
23.96
22.53
21.66
31.14
32.50
33.91
35.38
38.79
38.99
43.92
45.31
45.15
46.97
47.88
48.52
48.93
50.26


NL:
1.24E7
TIC MS
AV25_180516
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
Time (min)
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
23.93
22.95
25.73
27.47
28.33
22.51
28.56
22.18
21.99
21.63
29.12
30.16
31.82
32.19
35.25
38.75
38.93
39.75
42.70
43.89
45.28
47.24
48.06
48.51
49.55


NL:
2.20E7
TIC MS
C98_18051
6_1605181
22202
Relative Abundance
Time (min)
27.48
25.70
30.16
32.18
29.74
50.15
25.06
22.96
24.52
47.98
31.12
21.74
47.25
32.49
35.25
45.55
21.16
36.59
38.92
39.77
42.69
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50


NL:
1.22E7
TIC MS
CB4155
Relative Abundance
Time (min)
25.43
28.68
50.26
48.93
28.01
48.19
25.73
47.26
29.32
23.13
45.87
22.05
30.41
33.68
34.58
38.99
42.88
44.49
19.10
0
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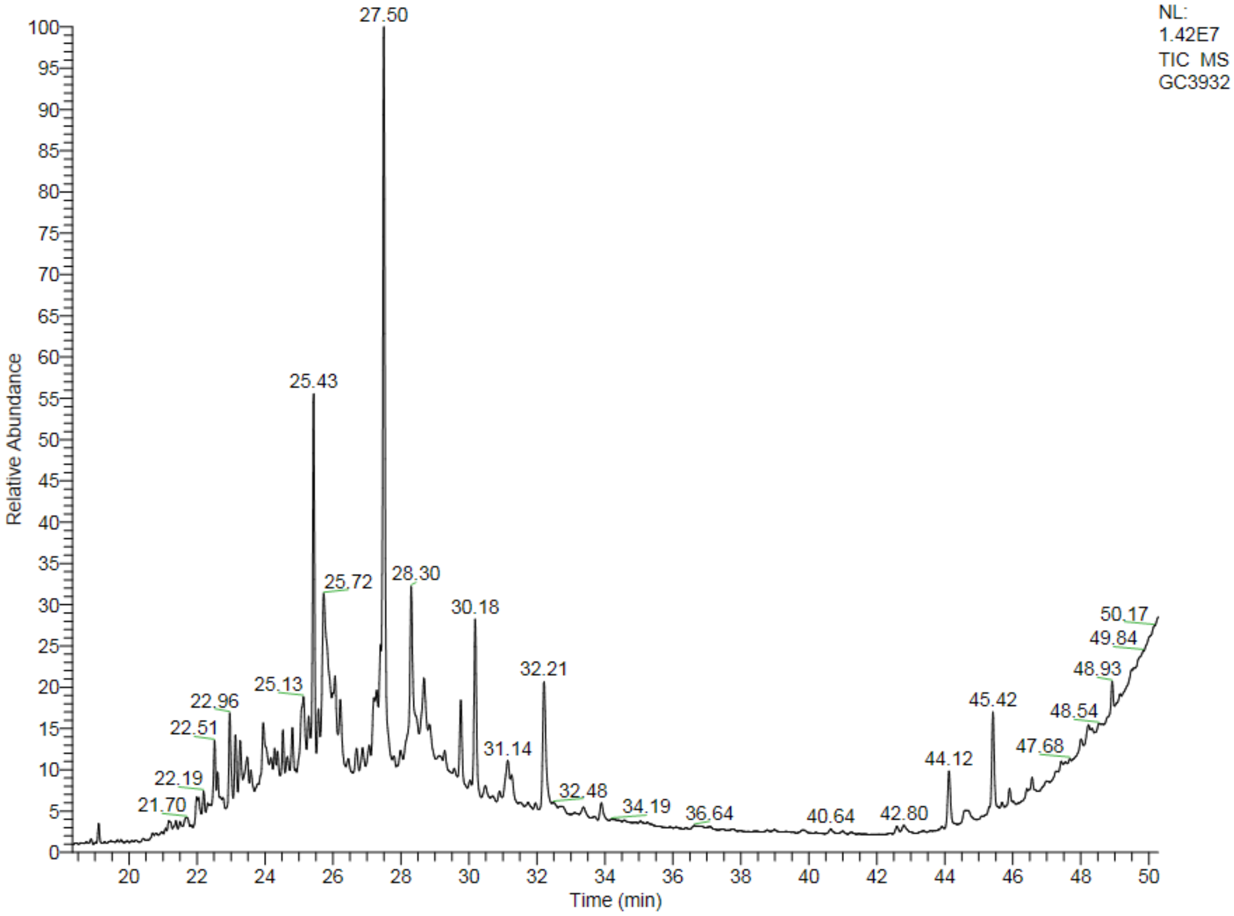
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21.70
32.48
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48.54
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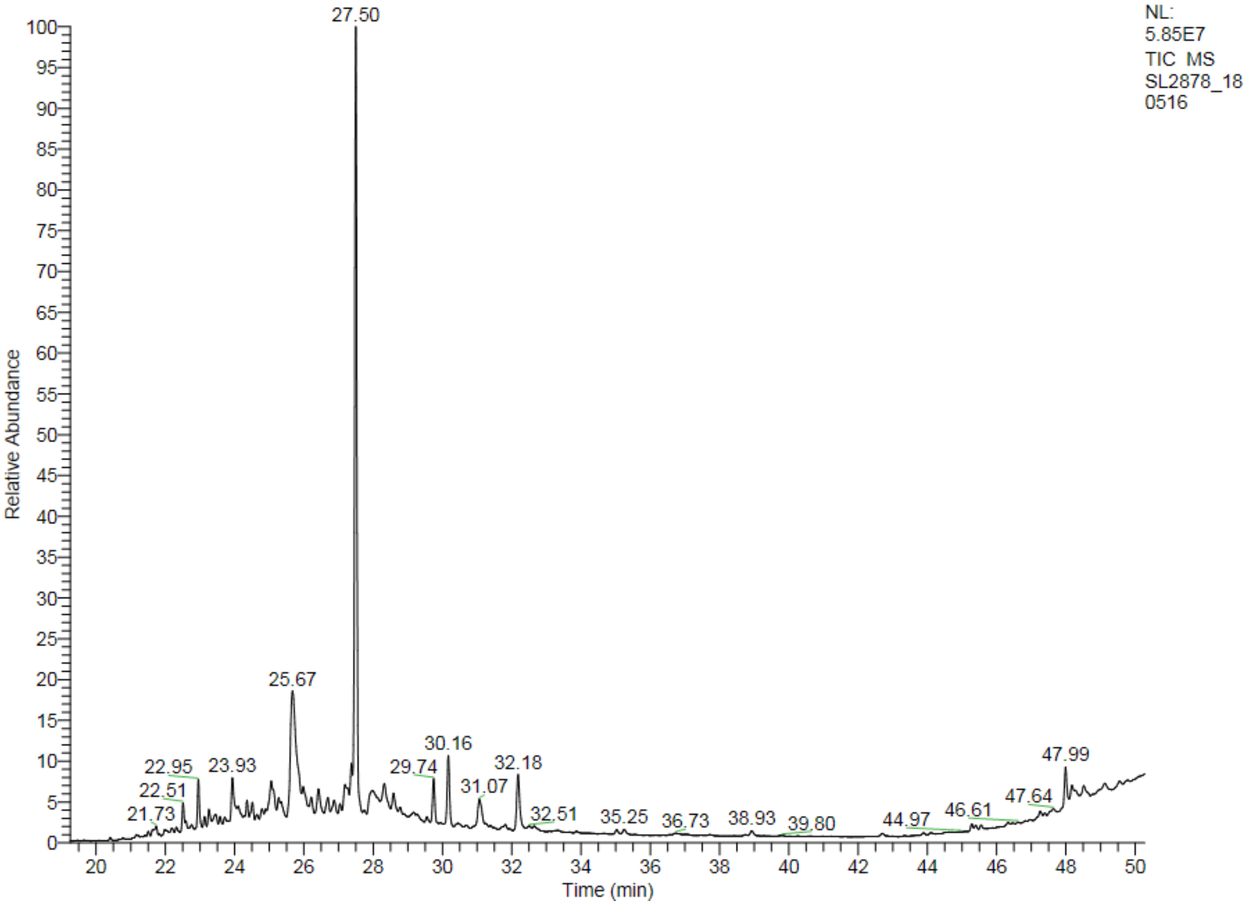
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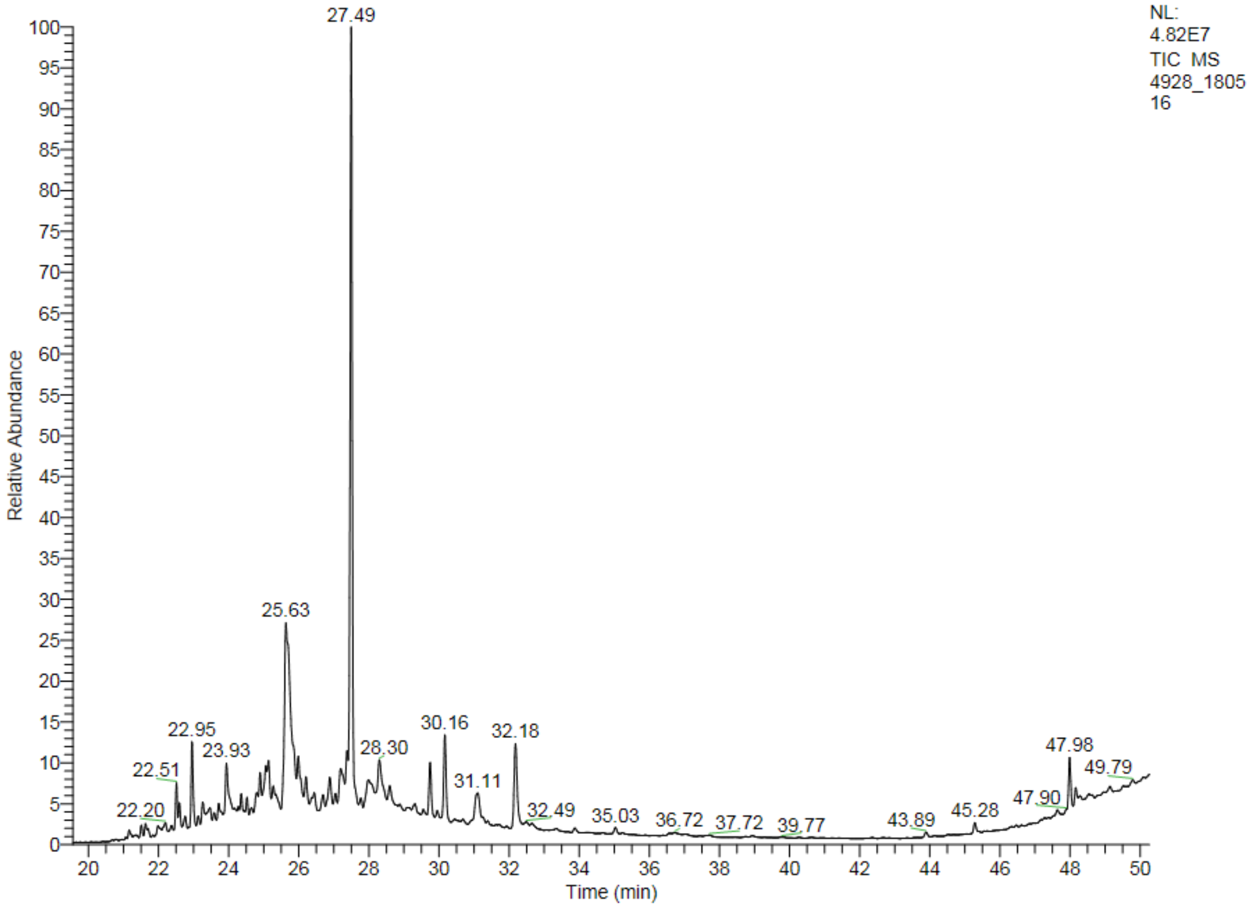
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32.18
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39.77
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47.90
47.98
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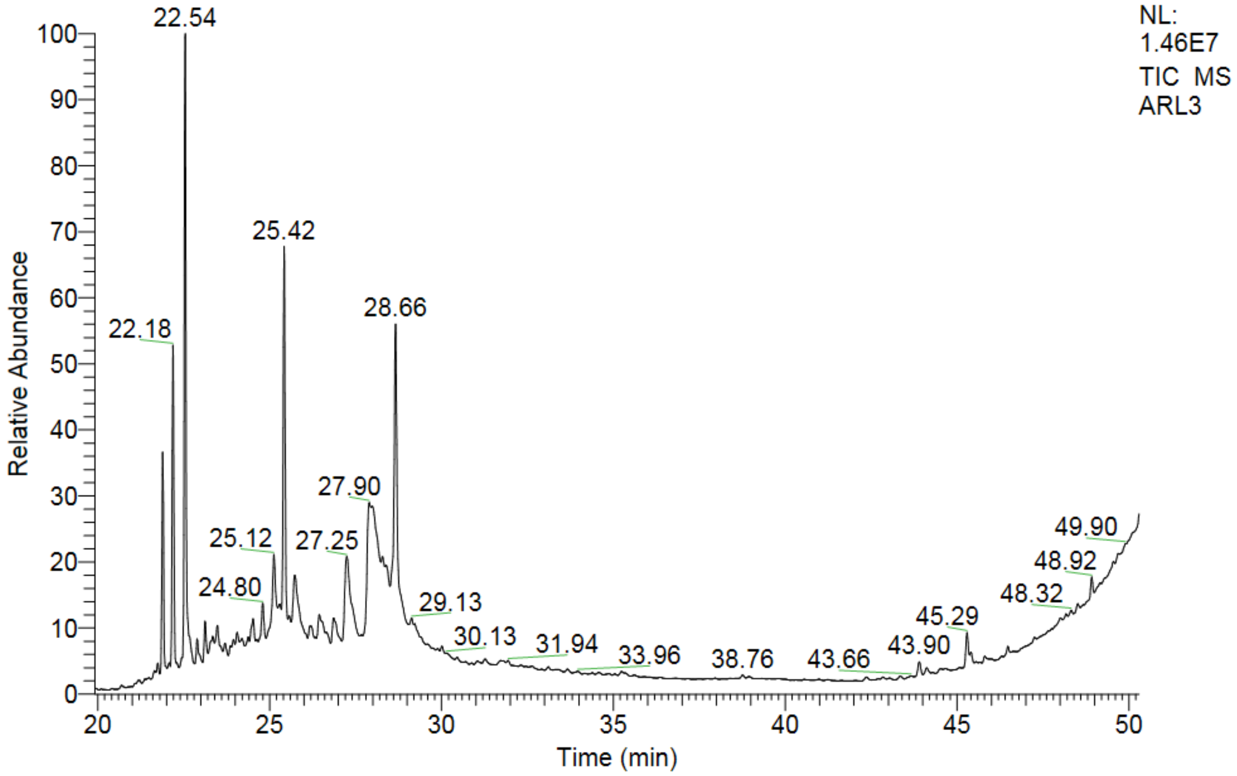
Time (min)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30.13
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33.96
38.76
43.66
43.90
45.29
48.32
48.92
49.90
Relative Abundance
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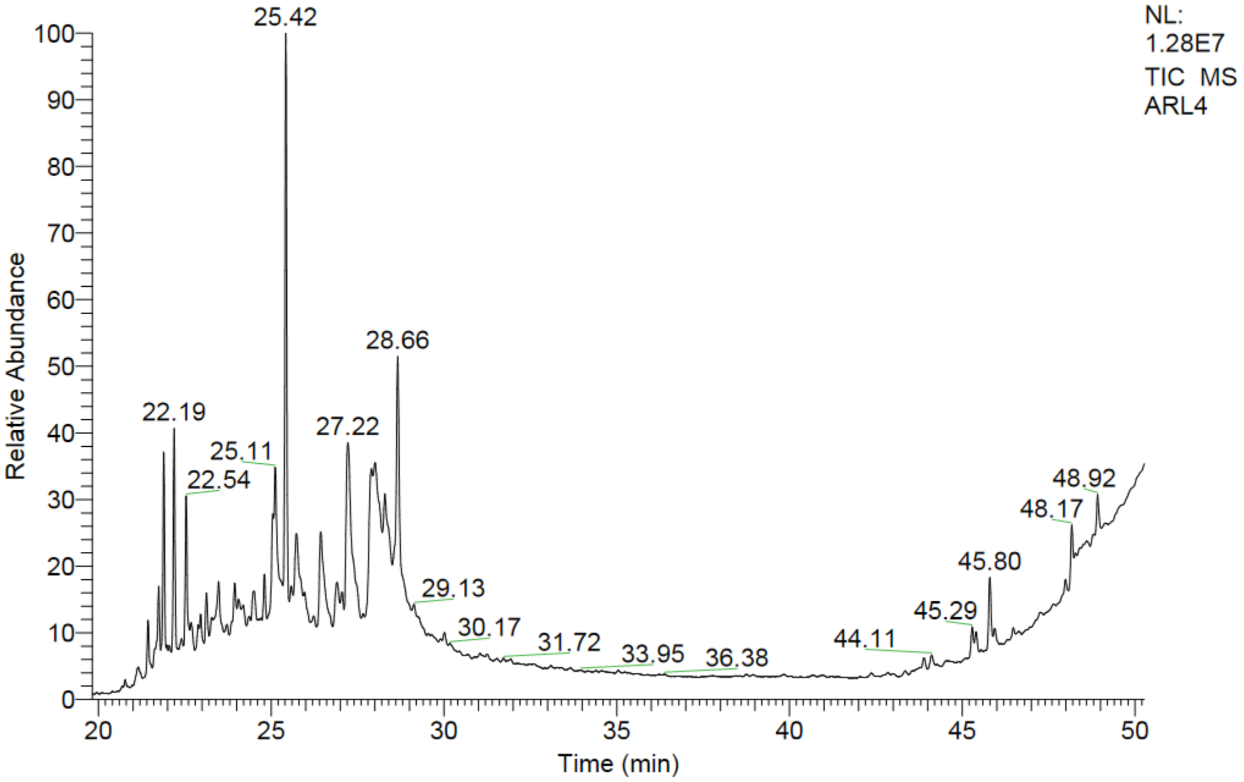
Time (min)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36.38
44.11
45.29
45.80
48.17
48.92
Relative Abundance
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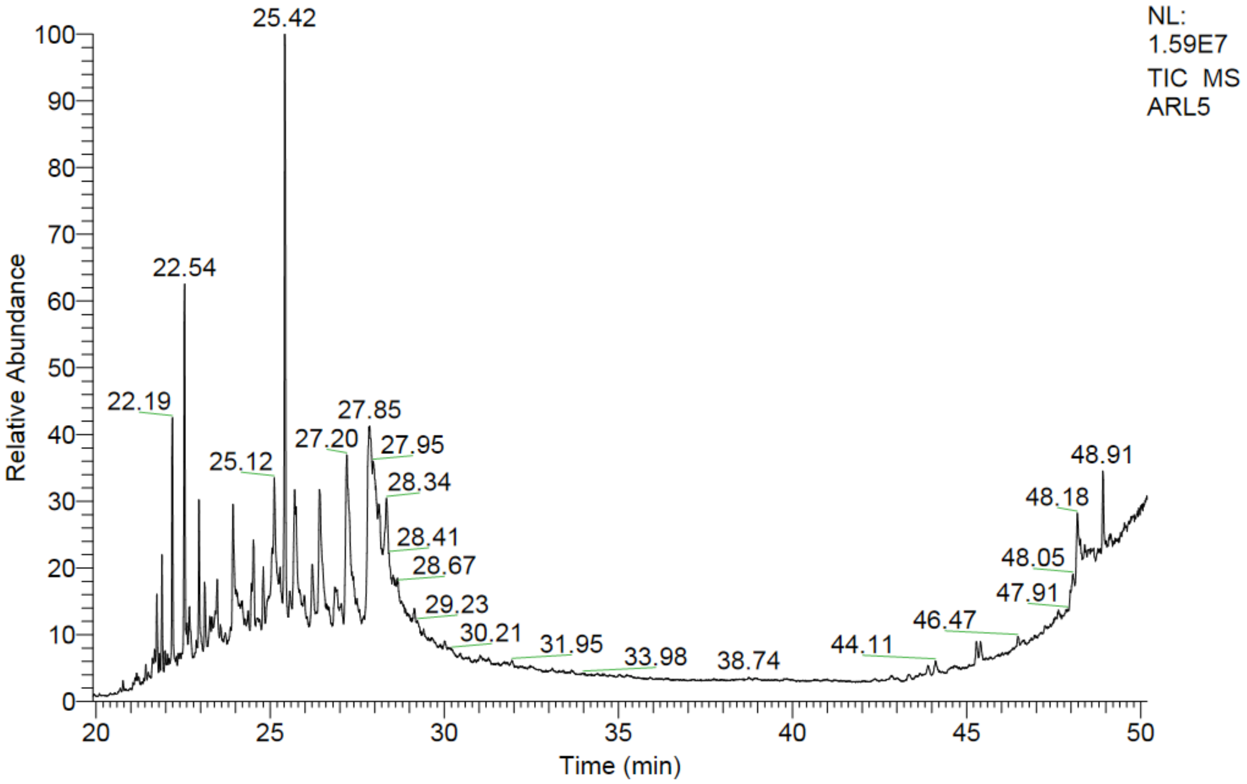
Time (min)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25.12
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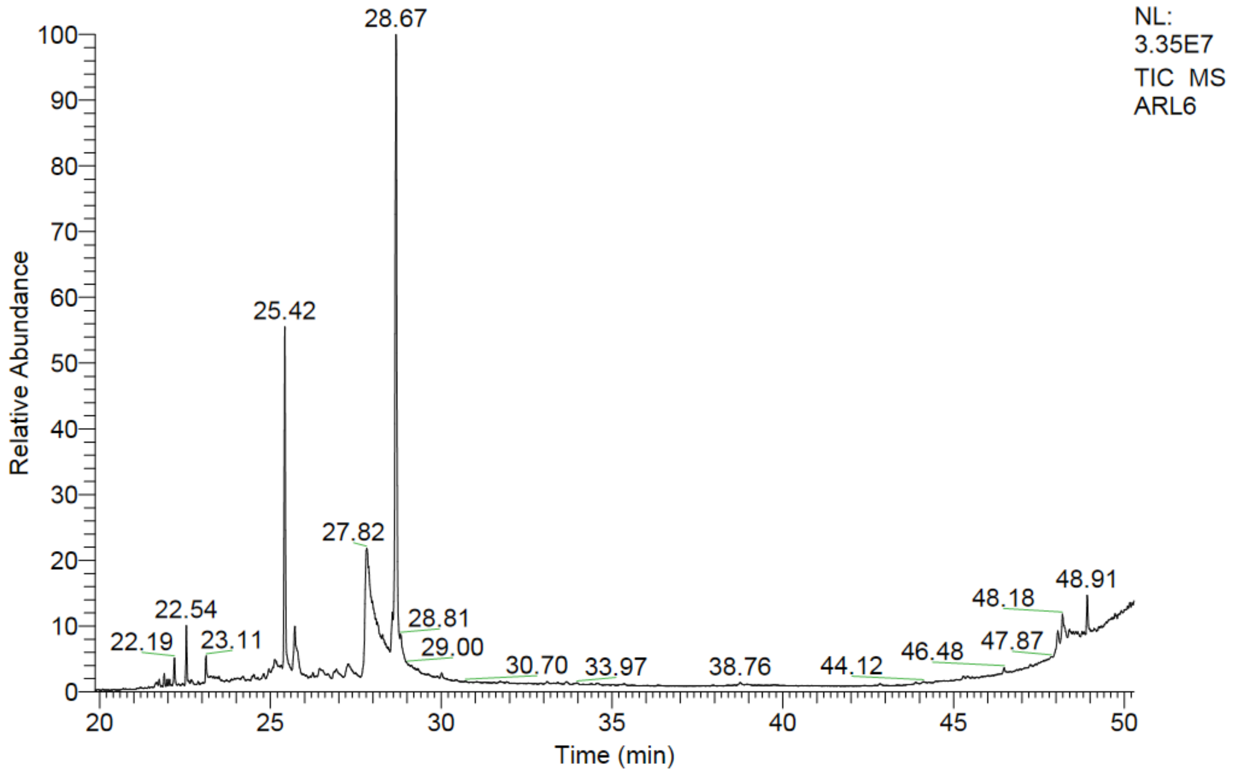
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Time (min)
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30
35
40
45
50
28.67
25.42
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22.54
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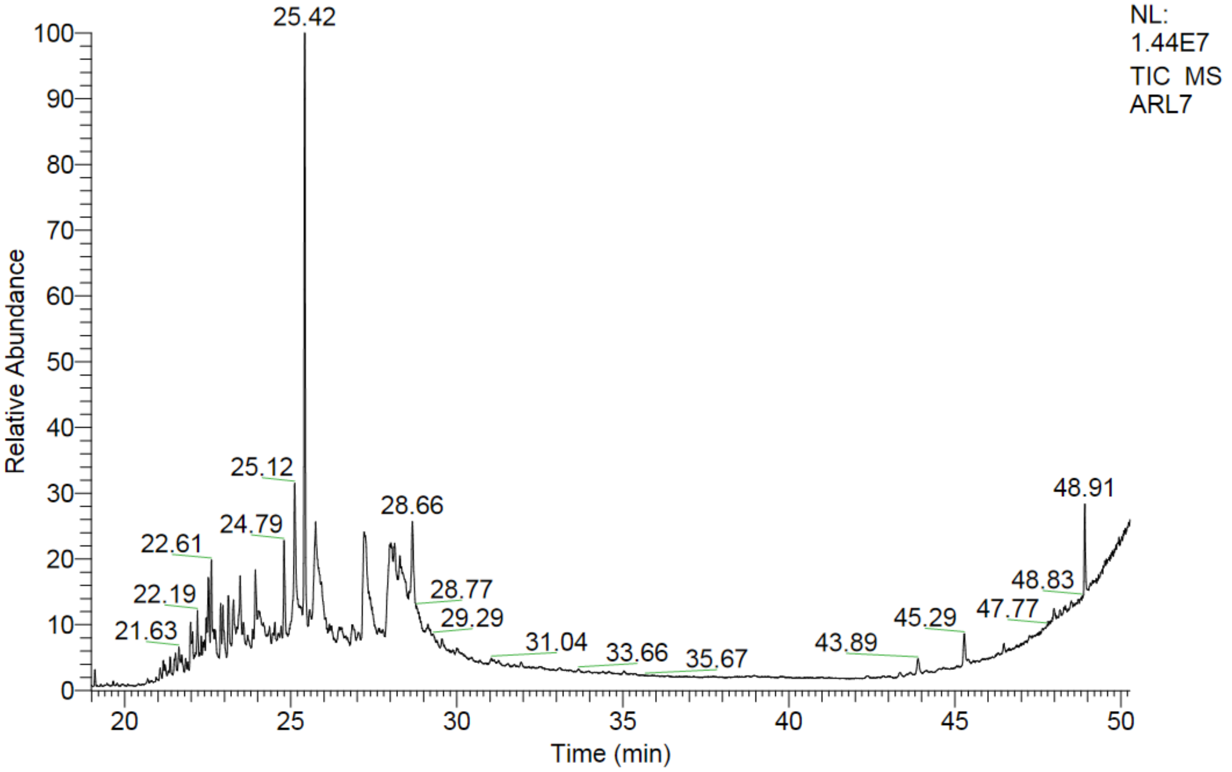
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28.66
28.77
29.29
31.04
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47.77
48.83
48.91
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35
40
45
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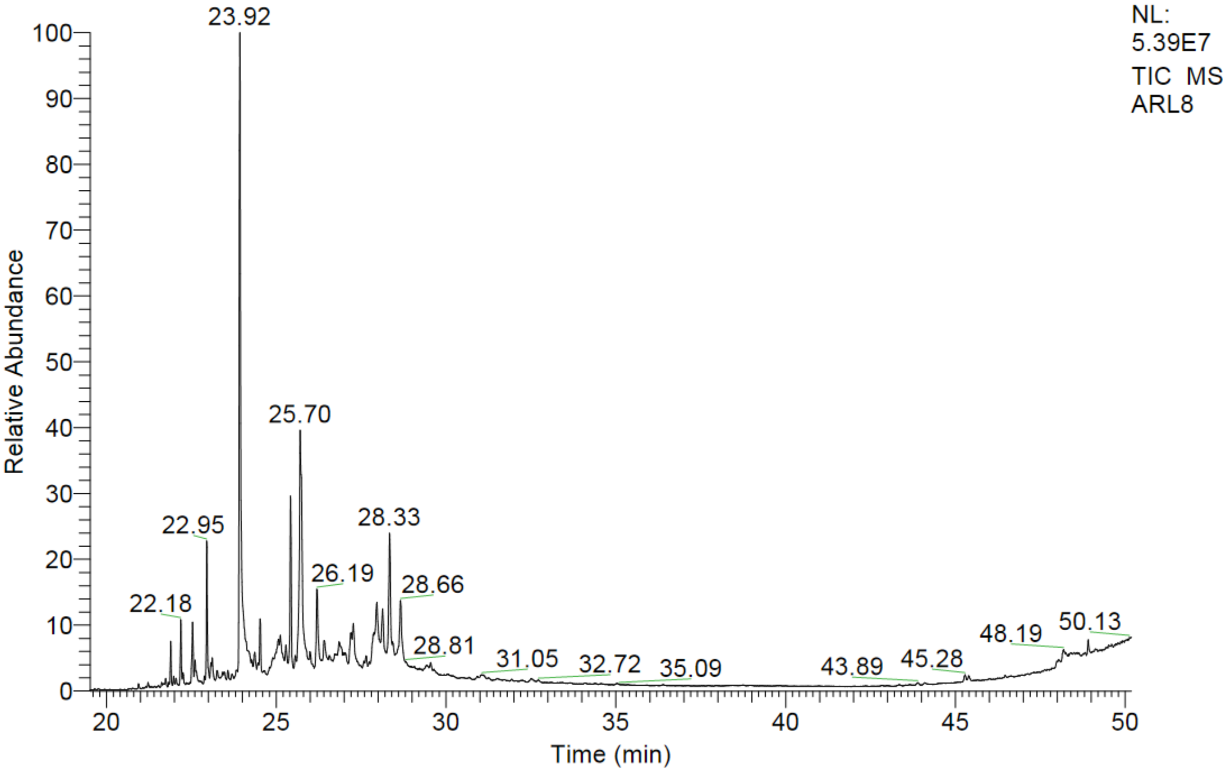
Time (min)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28.33
28.66
28.81
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43.89
45.28
48.19
50.13
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35
40
45
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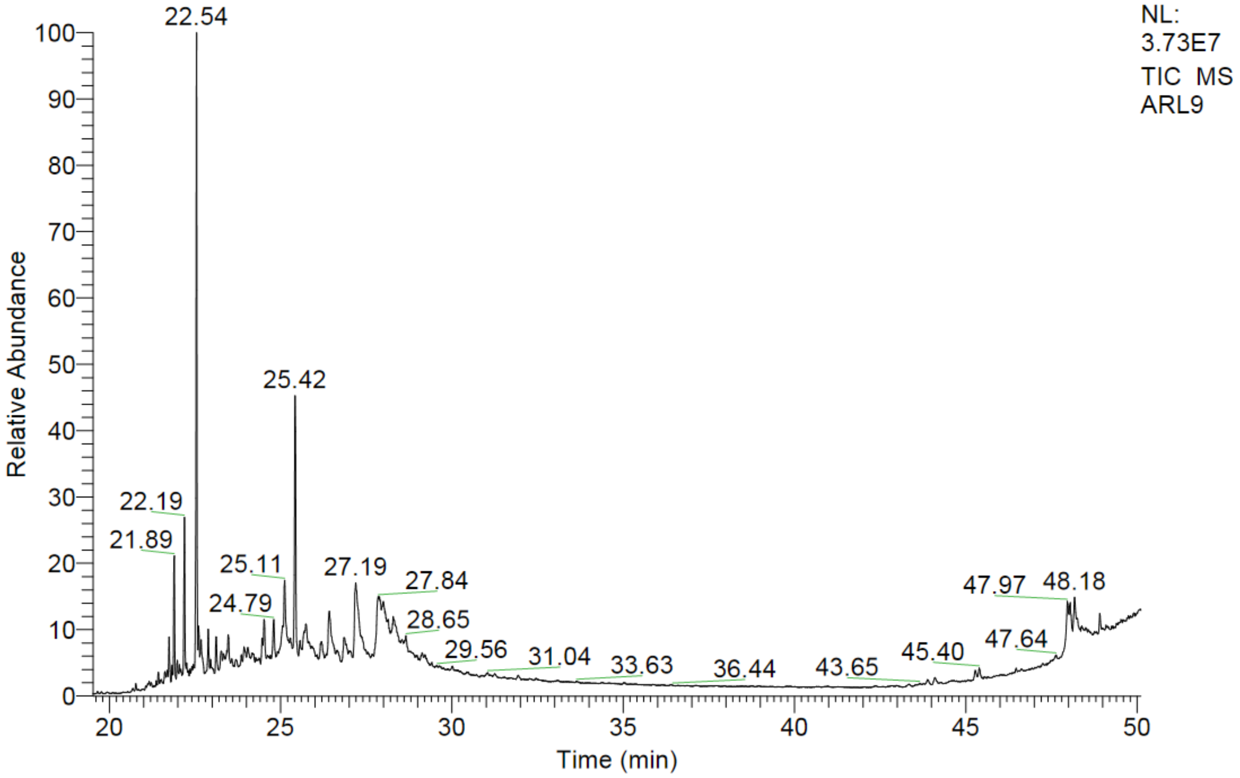
Time (min)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Time (min)
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21.89
25.11
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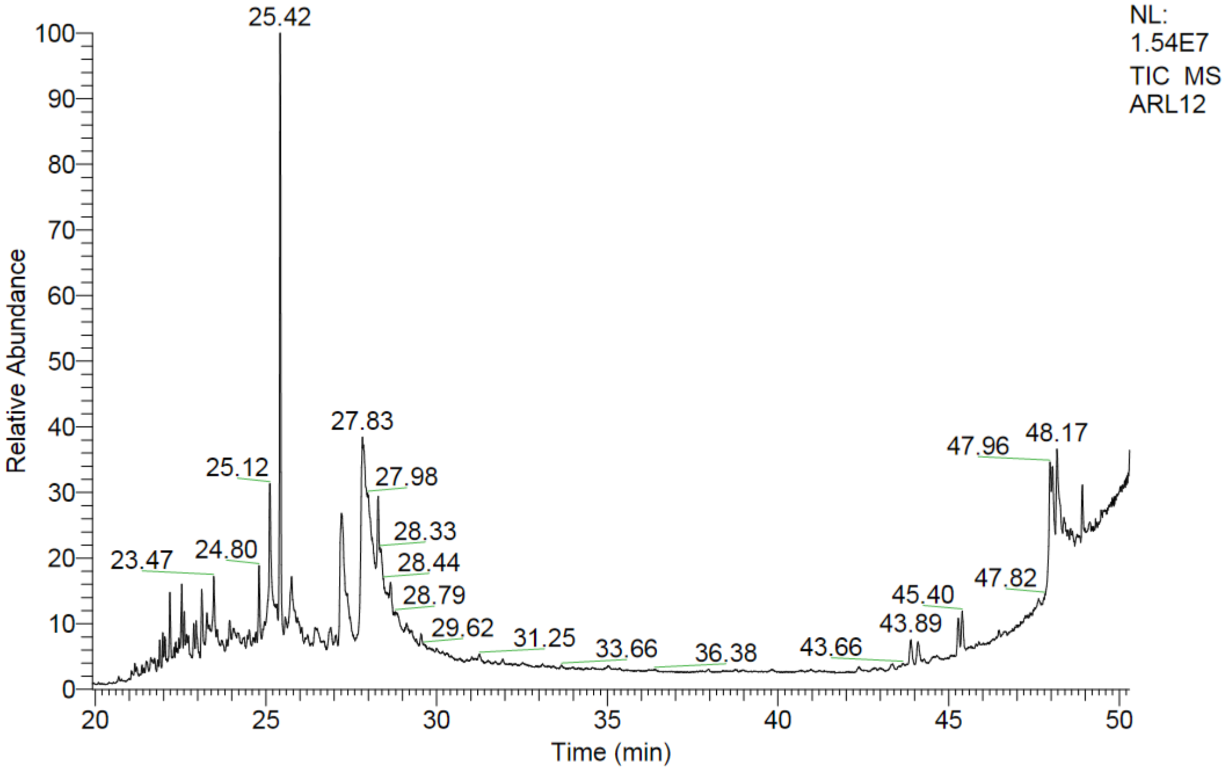
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Time (min)
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25.42
27.83
25.12
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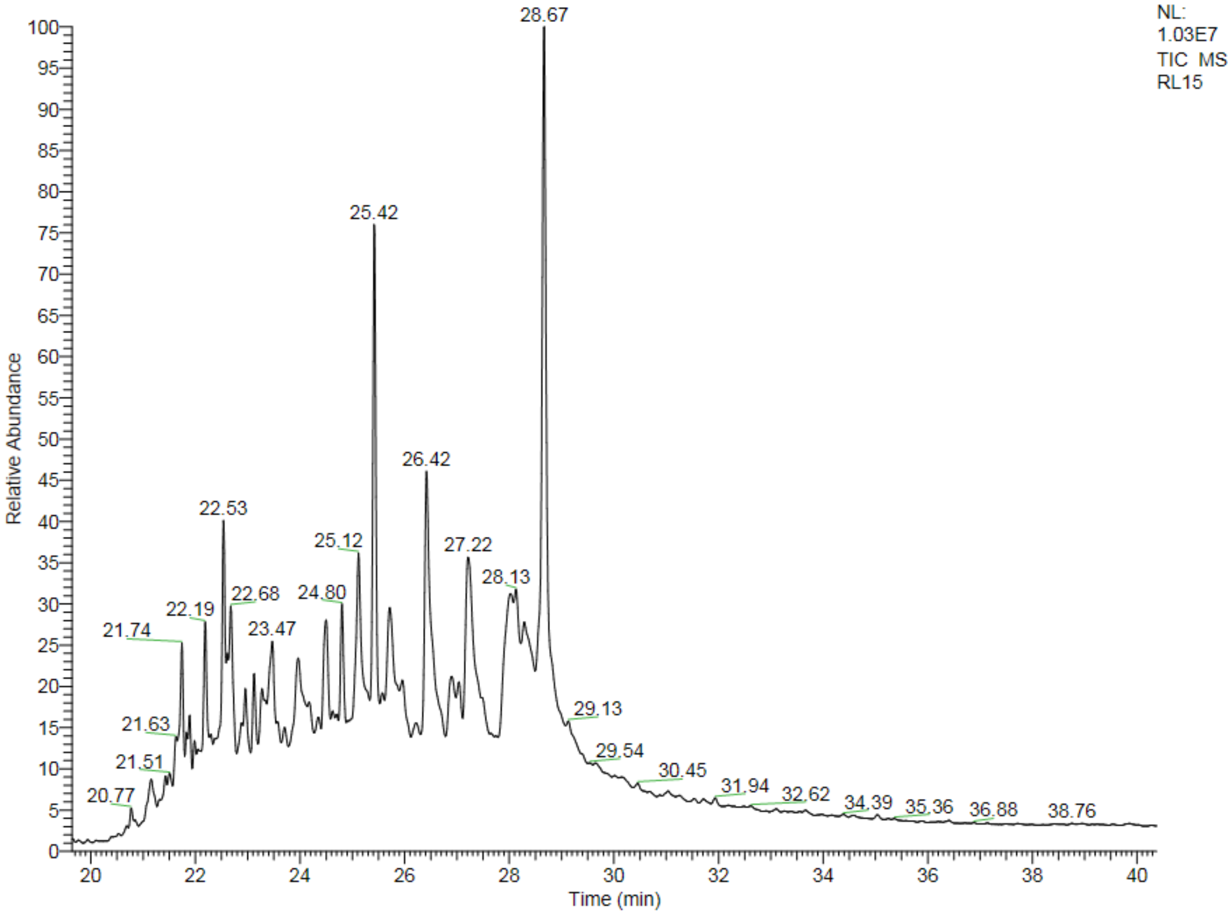
48.17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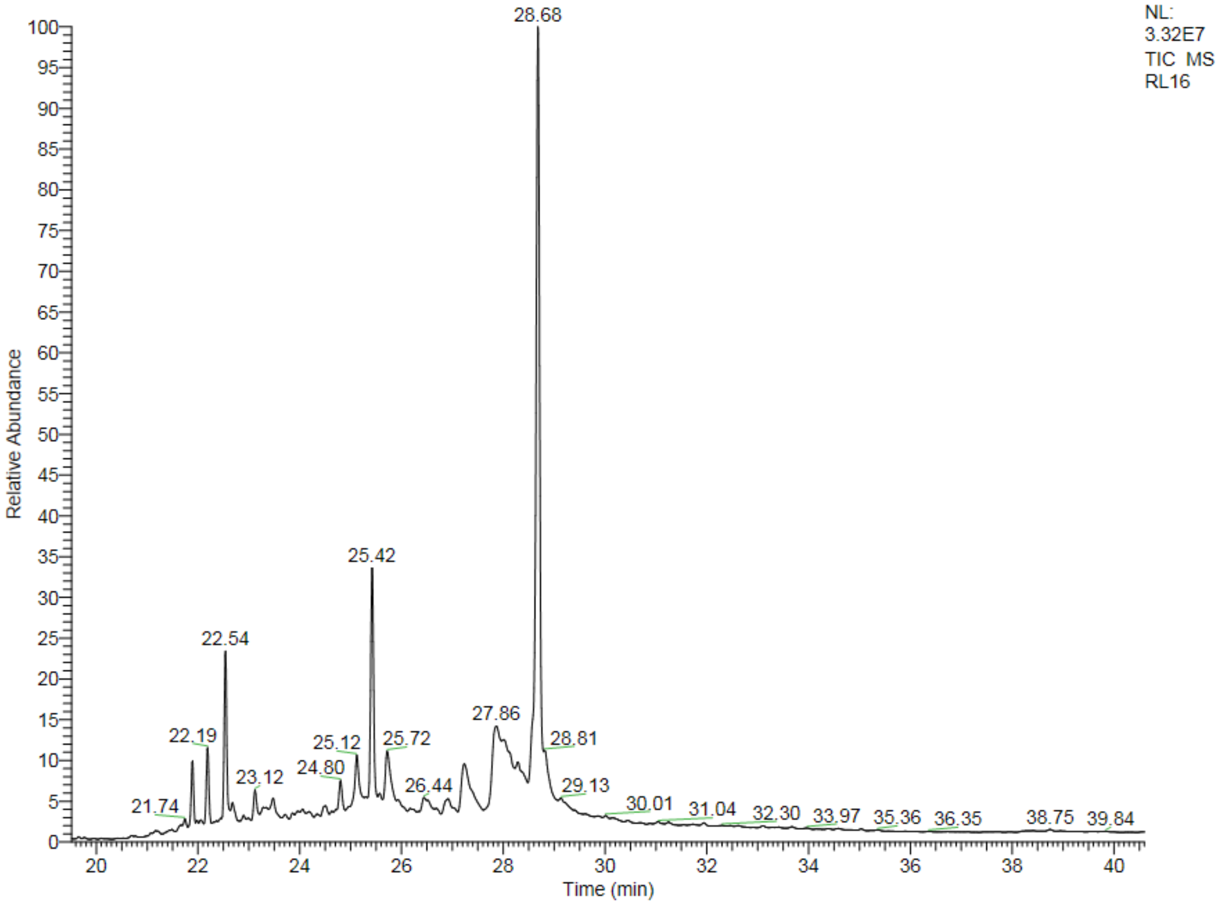
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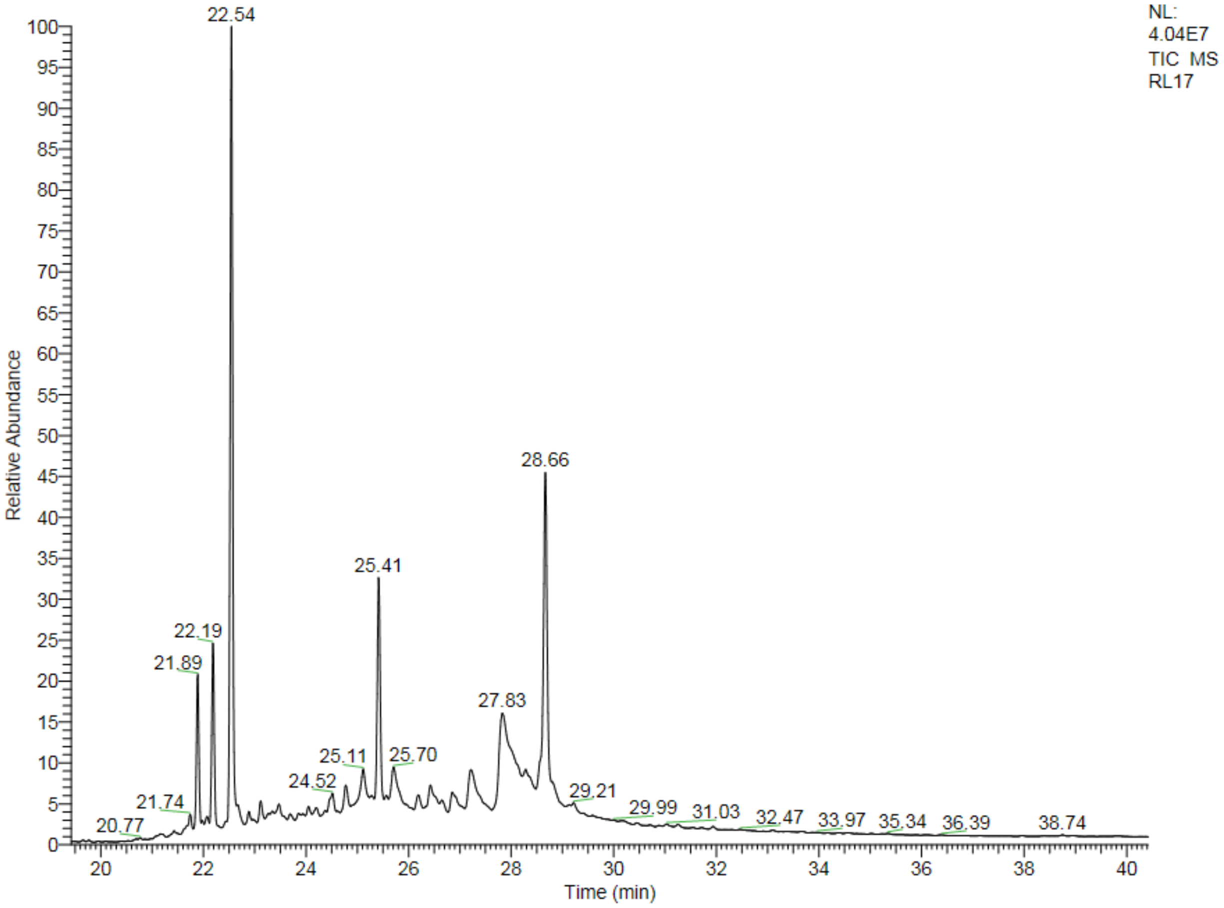
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33.97
35.34
36.39
38.74
20.77
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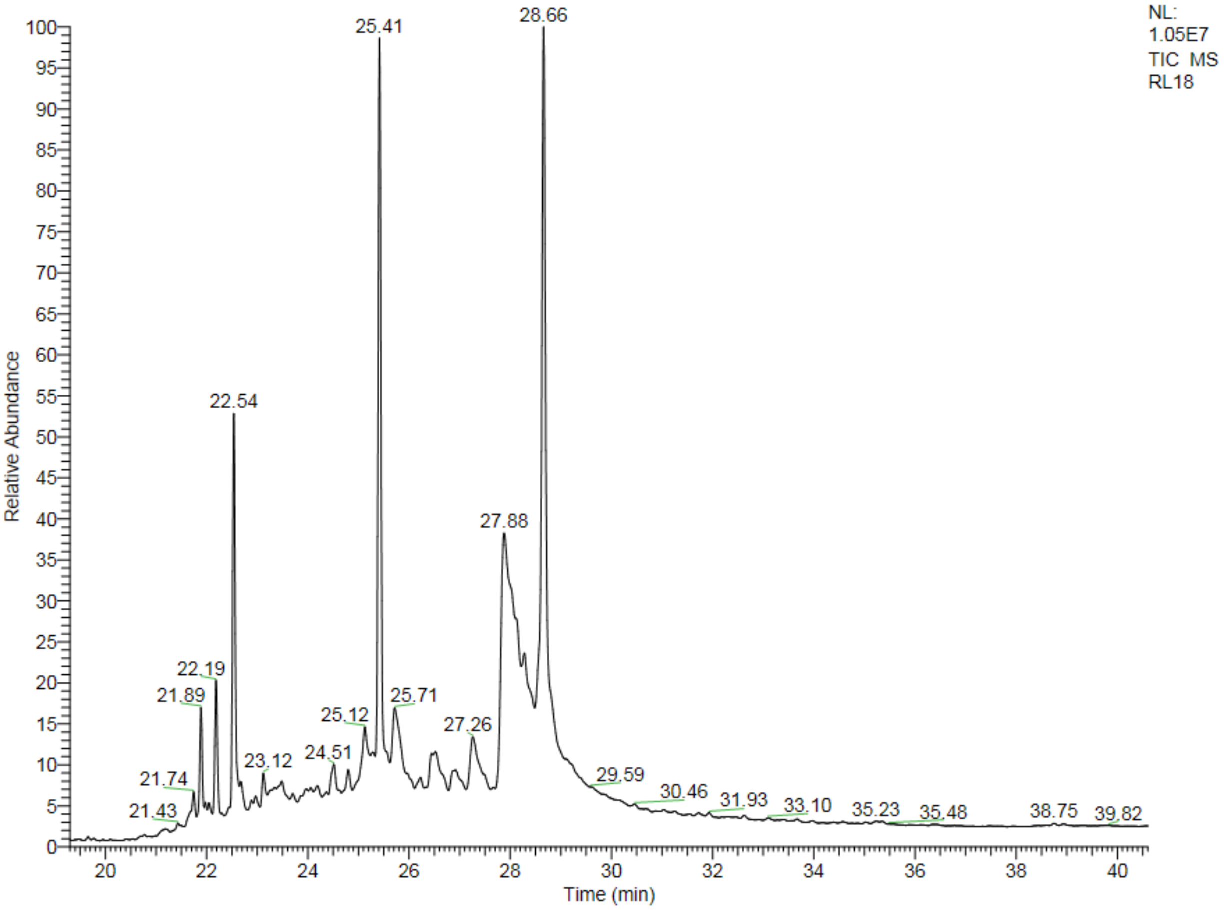
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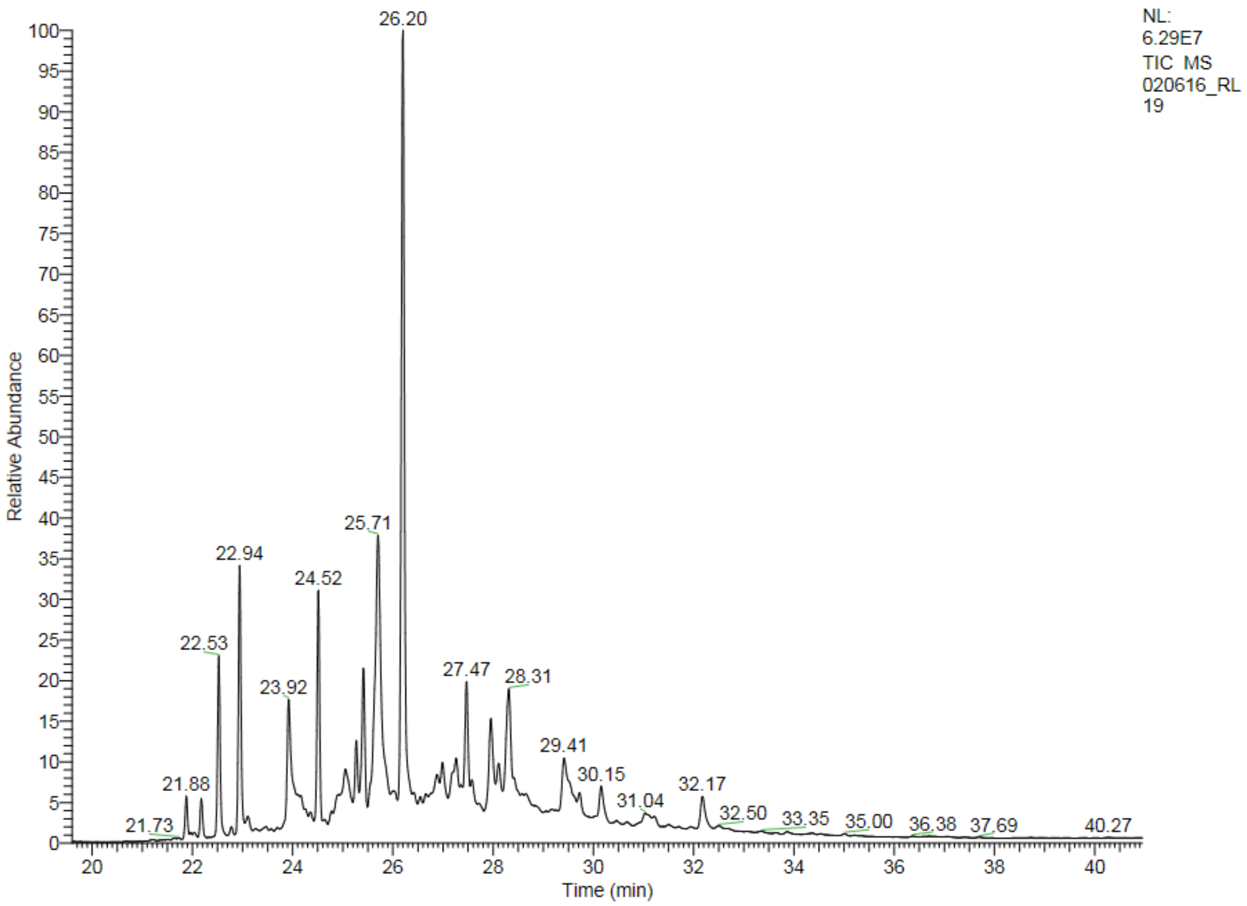
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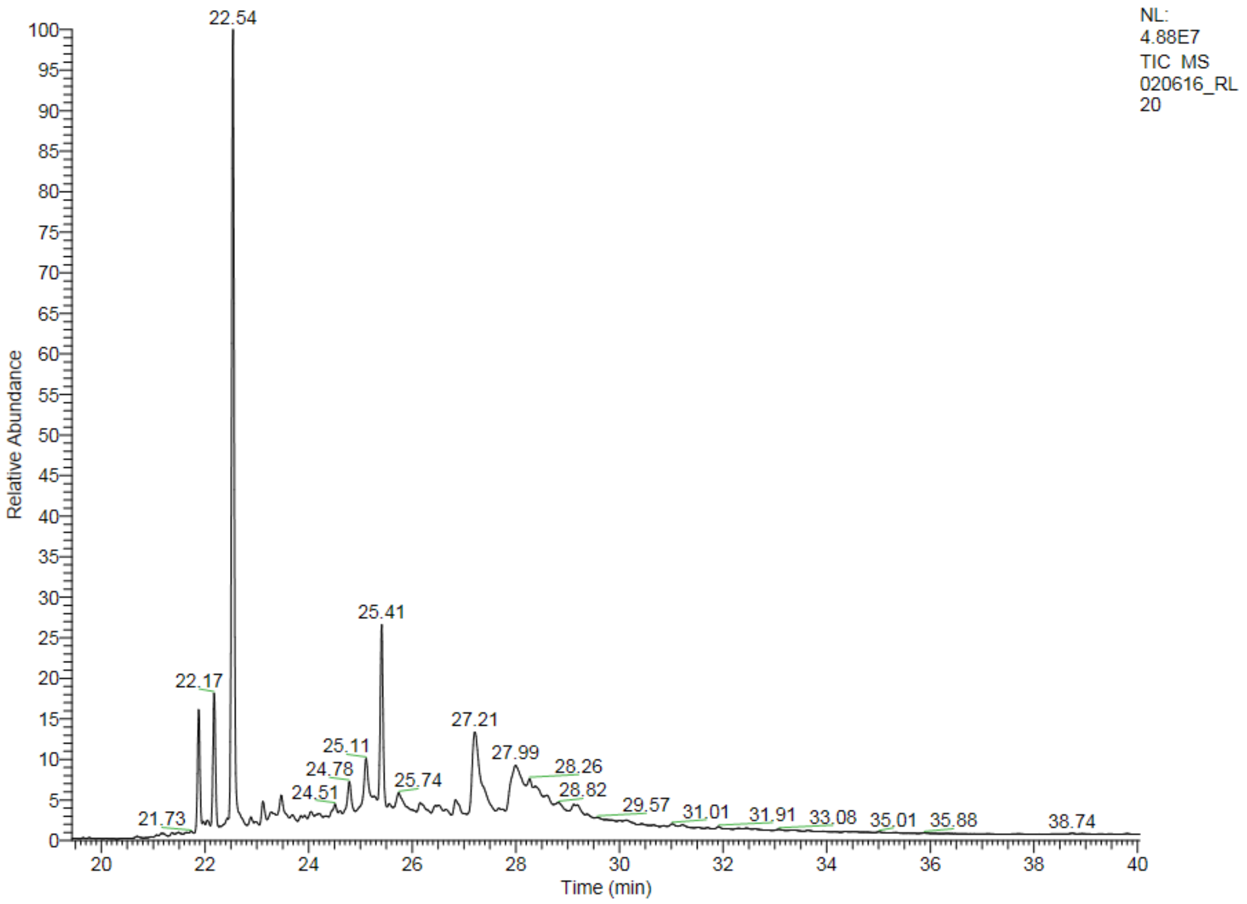
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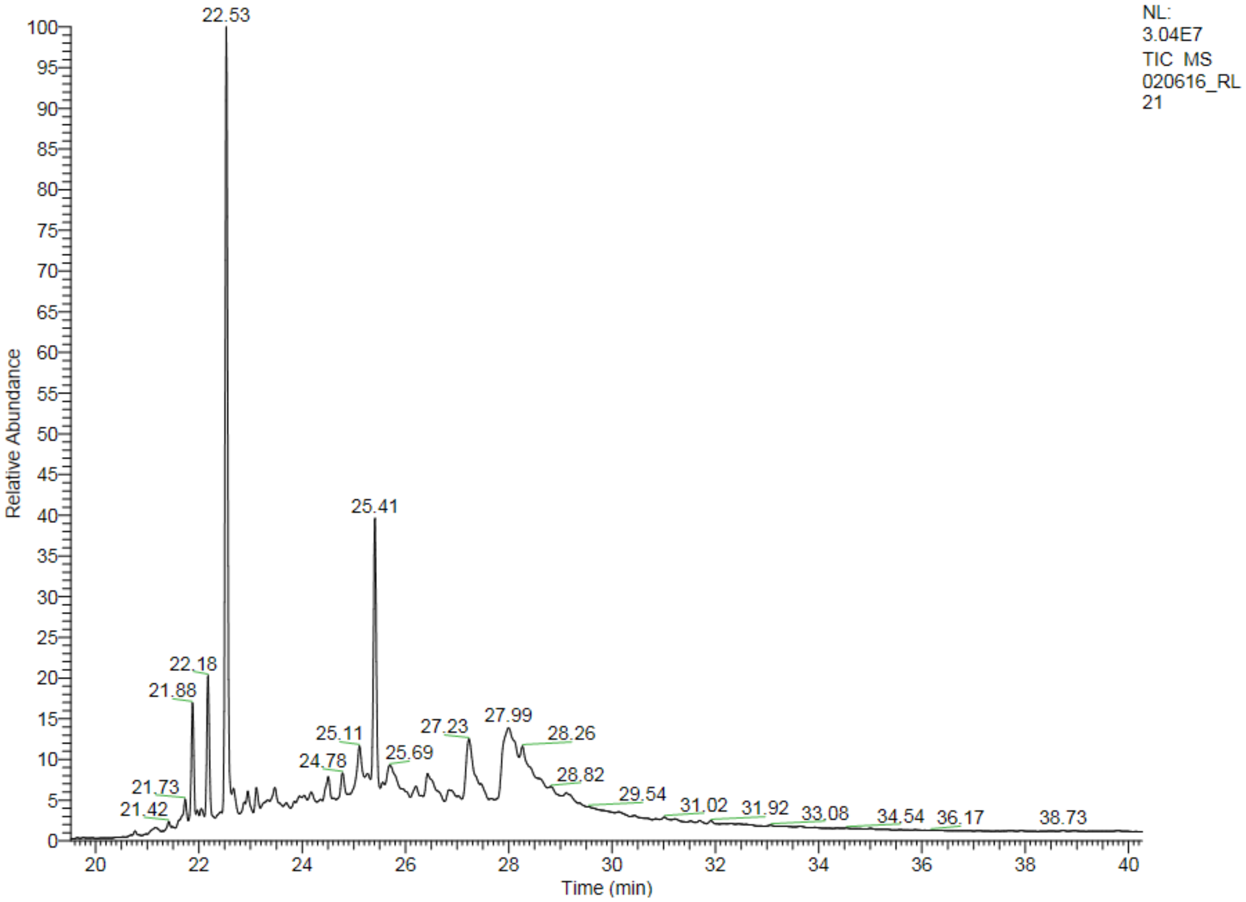
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33.08
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Relative Abundance
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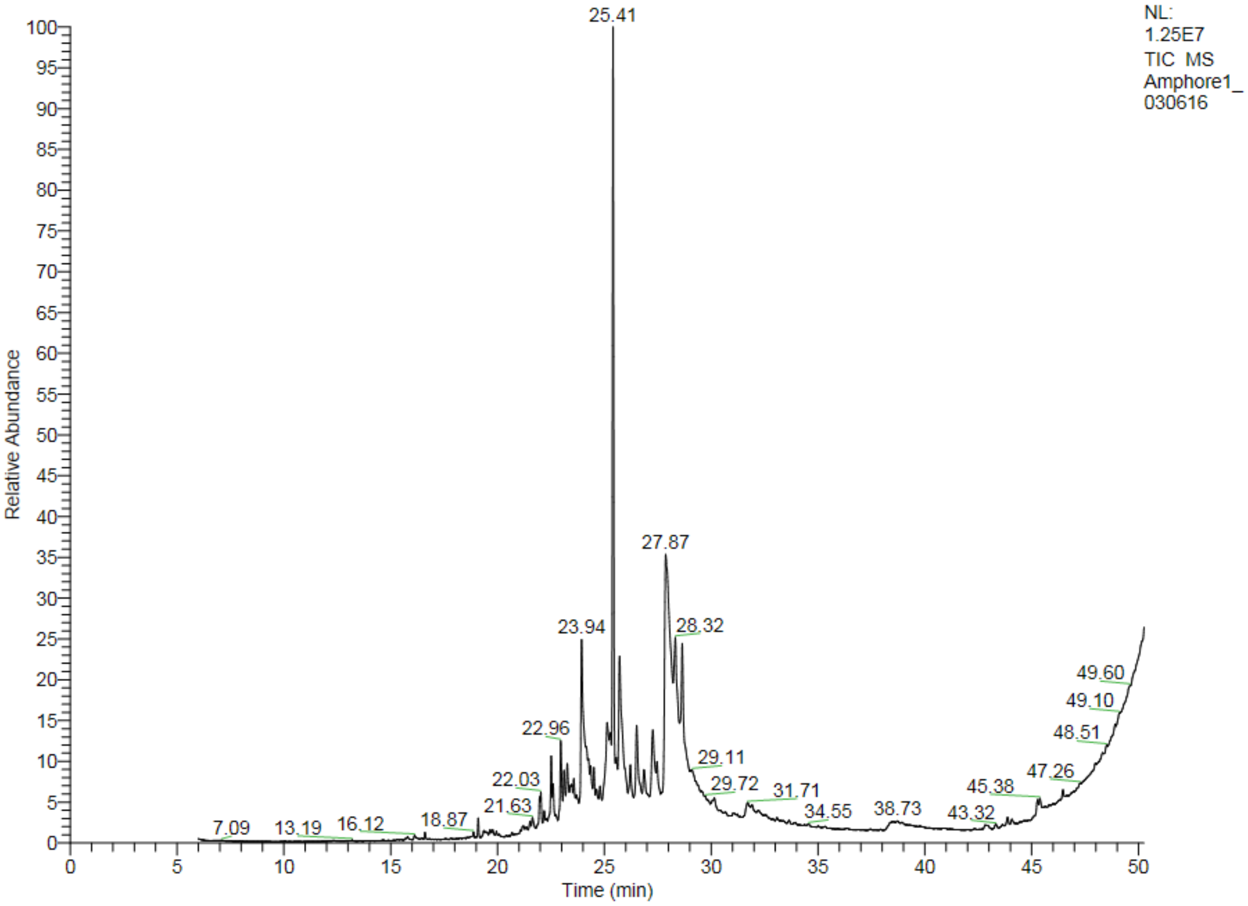
Time (min)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Relative Abundance
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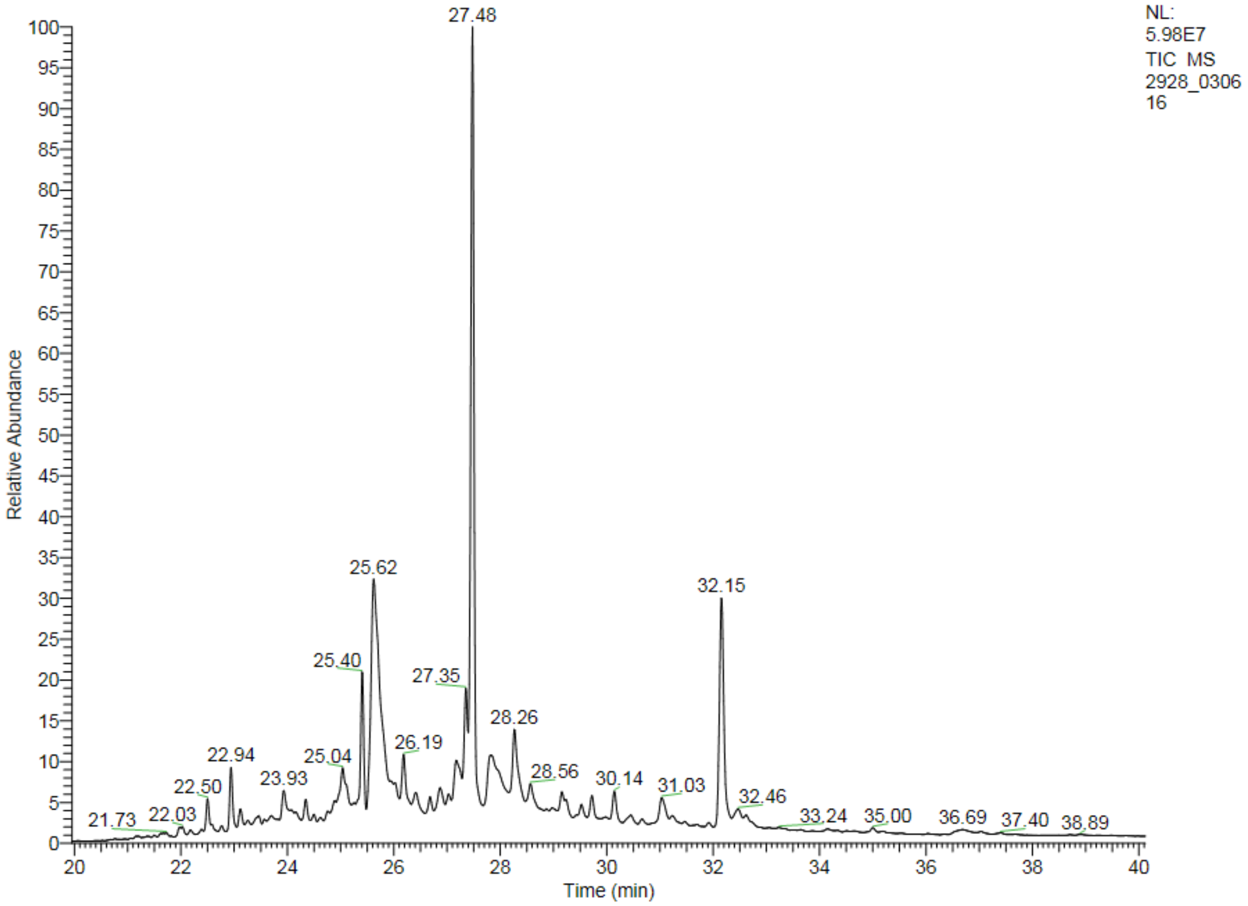
Time (min)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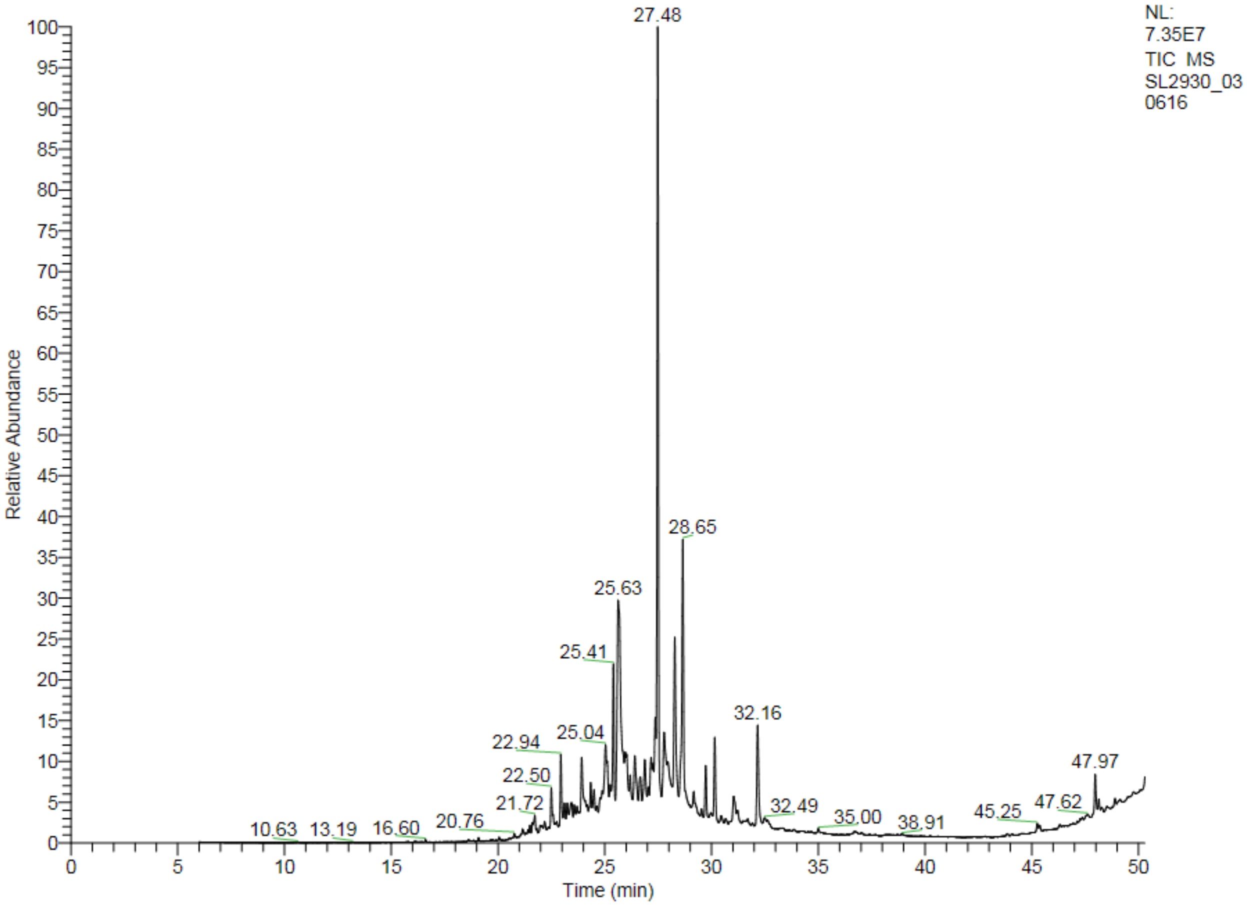
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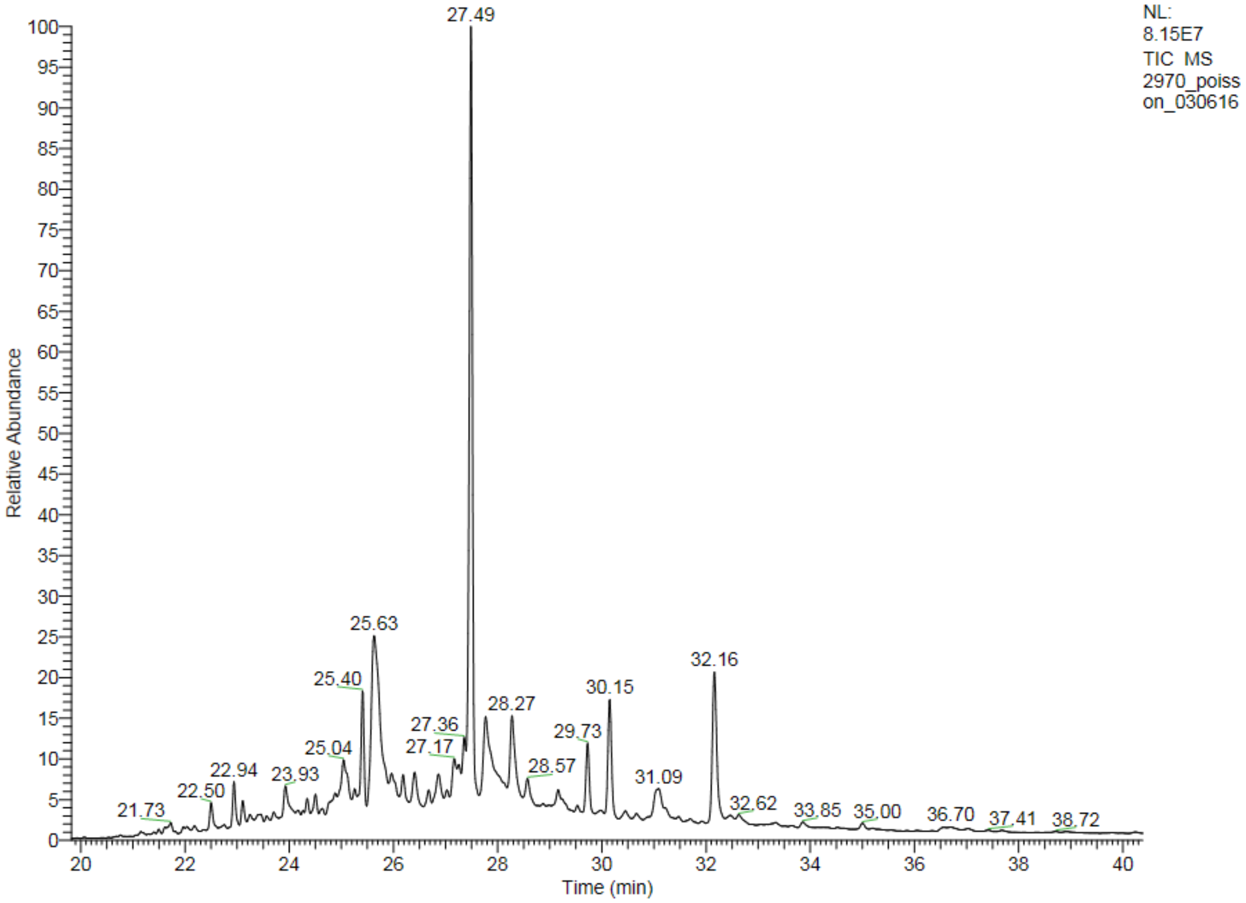
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Relative Abundance
Time (min)
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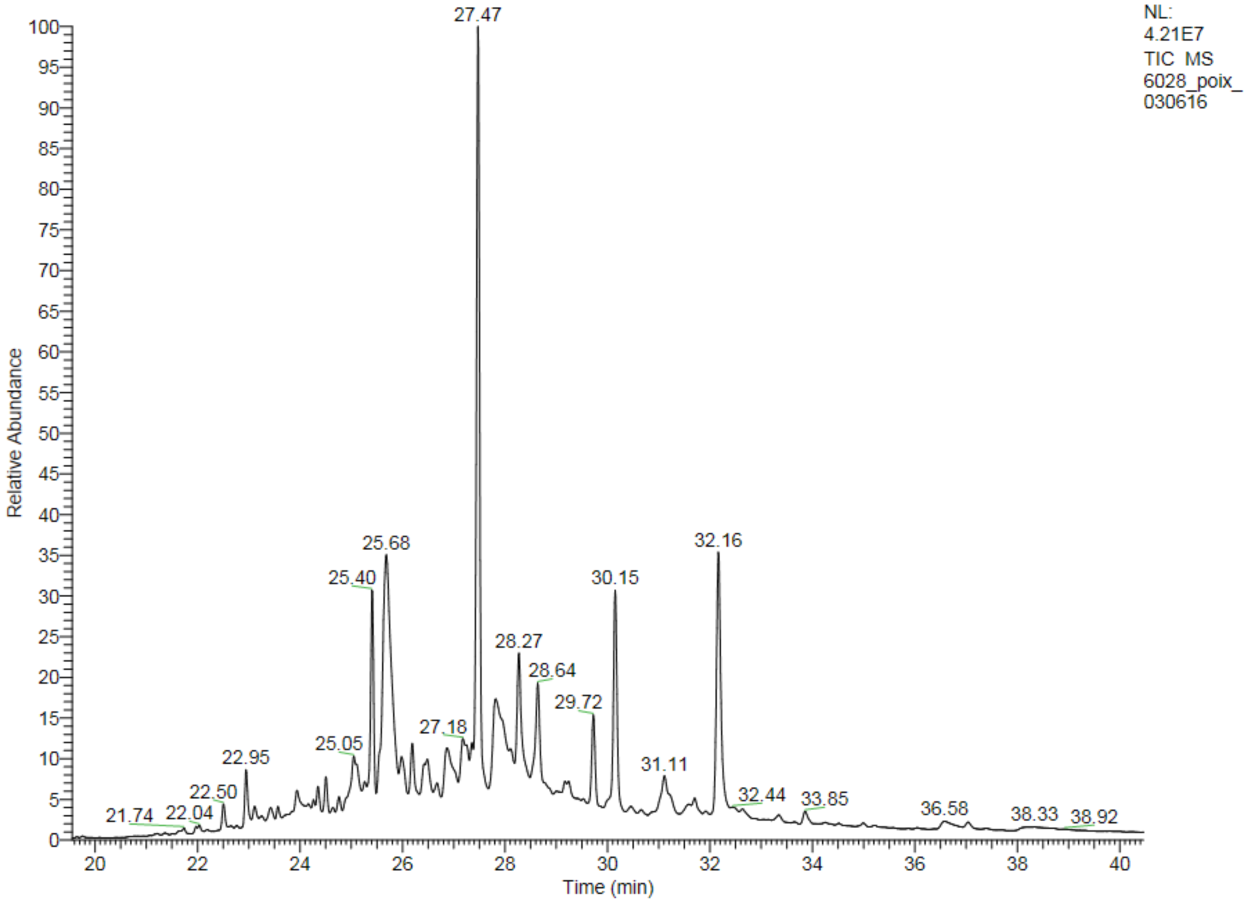
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38.92
Relative Abundance
Time (min)
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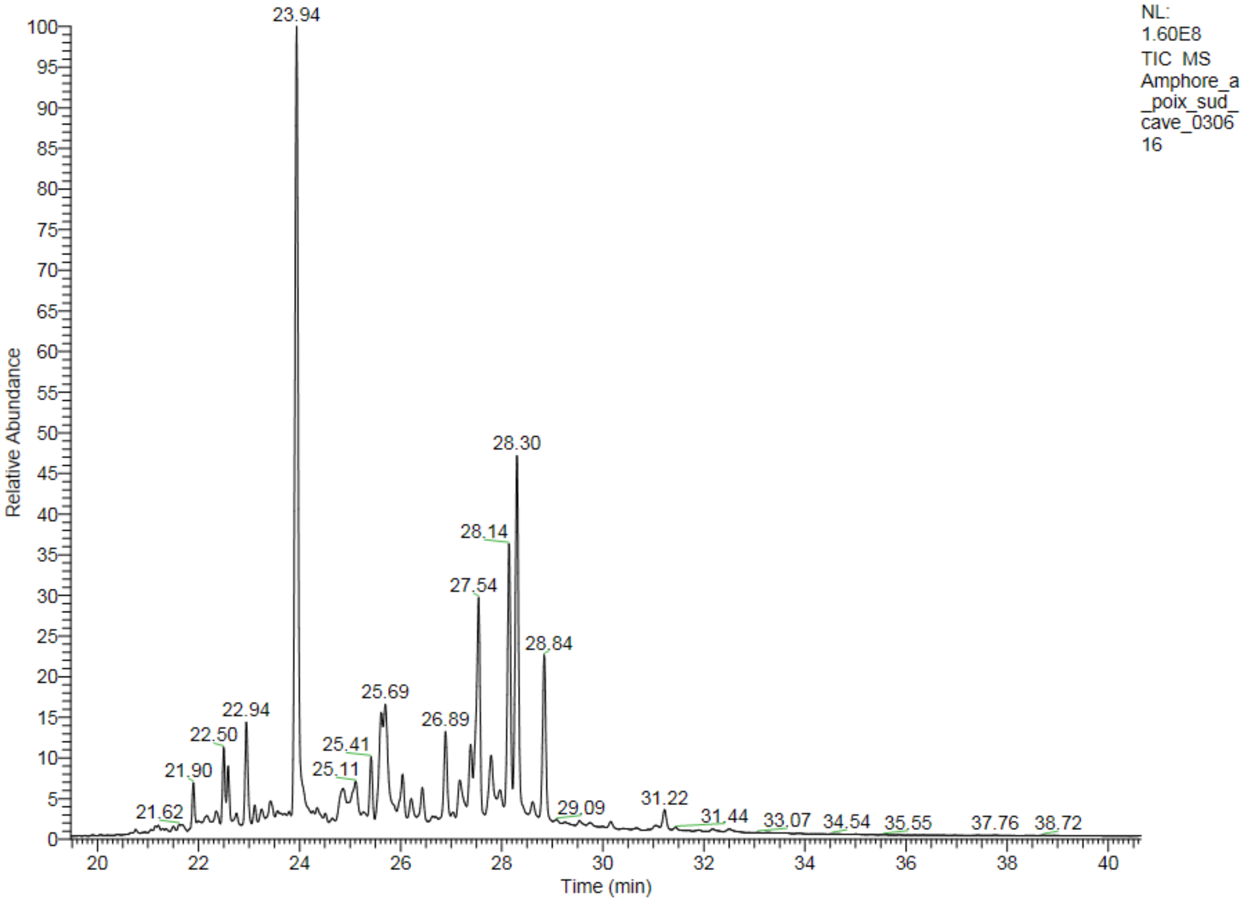
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