

# 1

## Organic Materials in Art and Archaeology

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### 1.1 Introduction

Men have always used the natural materials around us to produce functional objects and works of art. Paintings and other objects that are part of our cultural heritage, including textiles, books, sculptures, archaeological objects, furniture and the organic residues found in association with them (e.g. cosmetics, medicines, perfumes, food), contain a wide variety of organic materials from natural to synthetic.

Since ancient times, natural organic materials have been employed as paint binders, adhesives, waterproofing materials and so on, as reported in classical literature by Plinius the Elder and Vitruvius. Archaeological excavations often bring to light a wide variety of objects and materials that have been collected, processed and used by humans over time. Due to their long period underground, some of these materials and objects, especially those of an organic nature, have been partially or totally altered.

Being able to identify natural substances and their degradation products is a challenge. If we manage to do so, we then can shed light on the nature and the origin of the material employed, the artistic techniques used and the state of conservation. Organic materials are more subject to degradation than inorganic ones, so if we can understand their composition then we can ensure that ancient artefacts will remain part of our cultural heritage. This chapter outlines the main organic materials encountered in artistic and archaeological objects, along with their composition, basic behaviour and degradation pathways related to ageing. Table 1.1 summarizes the organic materials and how they were once used.

**Table 1.1** *Category, organic materials and uses*

Category	Organic materials	Uses
Proteins	Egg, milk and casein, animal glue, silk, wool, vegetable proteins (e.g. garlic, beans), human and animal tissues (e.g. mummies)	Paint binders, adhesives, textiles, commodities, parchment
Glycerolipids	Animal fats, vegetable oils (e.g. palm oil, olive oil) including drying oils (e.g. linseed, walnut, poppy seed)	Paint binders, varnishes, illuminants, commodities, ingredients of cosmetic and pharmaceutical preparations
Waxes	Beeswax, spermaceti, Chinese wax, lanolin (animal waxes); carnauba, candelilla, Japan wax, esparto (vegetable waxes); paraffin, ozokerite (fossil waxes)	Paint binders, coatings, sealants, writing tablets, ingredients of cosmetic and pharmaceutical preparations, sculptures
Natural resins	Pine resins, sandarac, copals, mastic, dammar, amber, frankincense, benzoe, styrax, myrrh, (plant resins); shellac (animal resin); tar and pitch (from thermal treatment of plant resins or wood)	Varnishes, coatings, waterproofing materials, paint binders, ingredients of cosmetic and pharmaceutical preparations
Polysaccharide materials	Starch, cellulose, plant gums (arabic gum, tragacanth, karaya, ghatti, guar, locust bean, fruit tree gum)	Paper, paint binders, adhesives
Bituminous materials	Bitumen, asphalt	Moulding materials, adhesive, pigment
Organic dyes	Cochineal, madder, kermes, saffron, purple, indigo, synthetic dyes	Colourants for dyeing textiles, paint materials
Synthetic polymers	Polyacrylates, cellulose nitrate, phenolic resins, polyethylene, poly(vinyl acetate), polystyrene	Paint binders, varnishes, coatings, consolidants, sculptures

## 1.2 Proteins

Proteins are macromolecules made up of one or more unbranched chains of amino acids which are joined together by peptide bonds between the carboxyl and amino groups of adjacent amino acid residues. Several amino acids are commonly found in animal and vegetable proteins: glycine (Gly), alanine (Ala), valine (Val), leucine (Leu), isoleucine (Ile), methionine (Met), proline (Pro), hydroxyproline, (Hyp), threonine (Thr), asparagine (Asn), glutamine (Gln), tyrosine (Tyr), cysteine (Cys), lysine (Lys), arginine (Arg), aspartic acid (Asp), phenylalanine (Phe), tryptophan (Trp), serine (Ser), glutamic acid (Glu), and histidine (His) [1].

The number and the type of amino acids and their sequence determine the surface charge of the protein, its molecular configuration and its unique chemical and physical properties. The function of a protein is dependent on its three-dimensional structure. A number of agents can disrupt this structure thus denaturing it, for example changes in pH, temperature, salt concentration, and the presence of reducing substances.

Both vegetable and animal proteins are encountered in art as textiles, leather and parchment, paint binders, and adhesives, and in archaeological objects as organic residues of commodities, or of human or animal tissues. Aged proteins are denaturalized: as a result of the loss of water and of ageing, the tertiary and quaternary structures change, through the rearrangement of internal bonds between functional groups. Thus, their solubility and reactivity differ from the native ones, whereas in favourable cases the amino acid composition can remain mostly unchanged. Microbic degradation of protein is quite fast in the burial environment, whereas proteins are often present in quite a good state of conservation in the paint layers of paintings.

The determination of the amino acid profile of proteins after hydrolysis of peptide bonds can be used in specific cases for the differentiation and the identification of proteins in paint samples [2–7]. In paintings, animal proteins such as egg, casein and glue, were frequently used as binders for pigments in the tempera technique. Egg was mainly used as whole egg and egg yolk. A whole dry hen egg contains about 45% protein, 41% lipid and 2% cholesterol [2,8]. Milk is an aqueous emulsion of proteins and lipids: dry cow milk contains about 26% protein, 26% lipid, and sugars [2,8]. Casein is obtained by the acidic, enzymatic or thermal treatment of milk, and its main constituents are  $\alpha$ -casein,  $\beta$ -casein,  $\delta$ -casein, and  $\gamma$ -casein. Animal glue was obtained by boiling the skin, bones or cartilaginous parts of mammals and fish. It is made up of collagen, a protein characterised by the presence of a high content of glycine, proline and hydroxyproline [2]. One of the most important vegetable proteins is garlic (*Allium sativum*), a member of the Liliaceae family. Garlic contains 0.1–0.4% volatile oil, carbohydrates (making up 75% of the dry matter), and proteins (15–17% of the dry matter) [9] and was used as an adhesive in gildings [10]. Also plant gums such as arabic gum, which is mainly composed of polysaccharides, contain a minor proteinaceous fraction [11].

Table 1.2 gives the average amino acid composition of some animal and vegetable proteins found in art and archaeology.

During ageing, proteins react with other materials in the historical/archaeological object and, for instance, condensation and cross-linking reactions between proteins and glycerolipids may occur. Amino malonic aldehyde has been identified as a possible product of oxidative degradation of serine, phenylalanine and cysteine [13]. The further oxidation of this compound can lead to the formation of amino malonic acid. This compound has been detected in paint samples, and its presence increases in the course of ageing. Another important factor of protein degradation is pH changes which, in the presence of moisture, can cause the hydrolysis of peptide bonds. As a consequence, the molecular weight may change, and the serine and threonine may dehydrate. Alkaline treatments (commonly used in restoration) can partially hydrolyse proteins and produce cystine and dehydroalanine from cysteine [14]. The formation of oxalate salts on paint surfaces has also been observed, suggesting some kind of photo-oxidation [15]. The reduced solubility of proteins in ancient samples is related to denaturation and cross-linking processes during ageing: cations may act as catalysers for the protein oxidation, thus enhancing this phenomenon. Anaerobic degradation of proteins by micro-organisms may lead to the formation of molecules such as piperidone, benzoic acid and *p*-hydroxyphenylacetate [16].

Proteins are synthesized from L-amino acids. When the living organism has died, they start to spontaneously convert to the D-form through a process called racemization. The extent of racemization is measured by the ratio of D/L isomers and increases as a function of time and temperature, and can be used for geochronology or palaeothermometry. The longer racemization continues, the closer to 1 the ratio between the D- and L-forms

**Table 1.2** *Amino acid composition of proteinaceous materials (w/w %) [2,12]*

Amino acid	Egg white	Egg yolk	Casein	Animal glue (collagen)	Wool (keratin)	Silk (fibroin)	Garlic
Glycine	3.6	3.5	1.7	26.6	6.0	42.8	4.9
Alanine	6.3	5.6	2.7	10.3	3.9	33.5	6.2
Valine	8.3	6.4	7.2	2.5	5.5	3.3	5.8
Leucine	10.3	9.2	9.0	3.7	7.9	0.9	5.8
Isoleucine	6.2	5.1	6.0	1.9	3.8	1.1	3.0
Proline	4.5	4.5	13.2	14.4	6.7	0.5	3.1
Phenylalanine	5.2	3.9	5.1	2.3	3.7	1.3	4.9
Tyrosine	1.4	2.8	5.5	1.0	5.2	11.9	2.1
Serine	5.8	9.1	4.0	4.3	8.4	16.3	10.9
Threonine	3.7	5.6	2.7	2.3	6.6	1.4	—
Cystine	1.9	1.9	0.0	0.0	12.8	0.0	—
Methionine	1.2	2.3	2.3	0.9	0.6	0.0	0.8
Arginine	6.8	5.5	4.0	8.2	9.9	1.0	—
Histidine	2.4	2.4	3.6	0.7	3.0	0.4	—
Lysine	8.0	5.7	6.7	4.0	0.9	0.6	6.1
Aspartic acid	10.5	11.5	6.1	6.9	6.9	2.2	16.7
Glutamic acid	13.9	15.0	20.2	11.2	14.5	1.9	29.3
Hydroxyproline	0.0	0.0	0.0	12.8	0.0	0.0	0.3

becomes. Although it is not an absolute dating method, the extent of amino acid racemization has been used to date organic materials such as well-preserved fossils, teeth, bones, egg and mollusc shells, plants, calcium-rich soil sediments, as well as rock paintings and to evaluate the state of degradation of proteinaceous matter. The racemization of some amino acids can also be used to estimate the age of animals at the time of their death [17–20].

### 1.3 Glycerolipids

Oils and fats are mixtures of triglycerides, also known as triacylglycerols. They are basically esters of glycerol with fatty acids, and contain smaller amounts of other compounds, which include sterols and vitamins.

The physical and chemical properties of individual oils and fats are determined by the nature and proportions of fatty acids that enter into the triglycerides composition. Animal and dairy fat like plant oils are dominated by triacylglycerols, with steroids present as minor components, cholesterol and its esters being the most significant. The triacylglycerols of animal fats differ from plant oils since they contain more of the saturated fatty acids and consequently are solid at room temperature.

The fatty acid percentage composition of some fresh lipids which may be encountered in an archaeological context or in a painting is reported in Table 1.3.

Vegetable oils and dairy and animal fats were used extensively in ancient times in cookery, for lighting, and as ingredients of cosmetics, balms and medications [21–29]. Olive, almond, balanos, castor, coconut, linseed, moringa, palm, poppy, radish, safflower, and sesame oils were well known oleiferous species in the Mediterranean [21,30]. Data on

**Table 1.3** Fatty acid percentage composition of some fresh vegetable oils and of animal lipids

Oil	Palmitic acid (esadecanoic acid)	Stearic acid (octadecanoic acid)	Oleic acid (9-octadecenoic acid)	Linoleic acid (9,12-octadecadienoic acid)	Linolenic acid (9,12,15-octadecatrienoic acid)	Elaeostearic acid (9,11,13-octadecatrienoic acid)	Ricinoleic acid (12-hydroxy-(Z)-9-octadecenoic acid)	Gondoic acid (11-eicosenoic acid)	Erucic acid (13-docosenoic acid)
Linseed	6-8	3-6	14-24	14-19	48-60	—	—	—	—
Walnut	3-7	0.5-3	9-30	57-76	2-16	—	—	—	—
Poppyseed	8-12	2-3	12-17	55-65	3-8	—	—	—	—
Olive	8-18	2-5	56-82	4-19	0.5-1	—	—	—	—
Sunflower	5-6	4-6	17-51	38-74	—	—	—	—	—
Castor	1-2	1-2	3-6	4-7	—	—	83-89	—	—
Tung	3-5	2-4	8-11	12-15	0-3	75-85	—	—	—
Palm	43-46	4-10	35-40	7-10	—	—	—	—	—
Rapeseed	2-6	1-3	20-30	17-22	6-10	—	—	13-16	20-40
Hen's egg	25-27	9-12	38-44	13-15	0-1	—	—	—	—
Lard	20-27	13-19	37-45	7-10	0-1	—	—	—	—

the use of oils are derived from papyri and from texts written by Theophrastus, Dioscorides and Pliny, which help to clarify the identification of plants cultivated for their oily seeds [30]. Lipids radically alter their original chemical composition as a consequence of degradation reactions [29,31,32]. The hydrolysis of triacylglycerols is a common process that leads to the formation of free fatty acids. Monoacylglycerols and diacylglycerols, which are produced by the partial hydrolysis of triacylglycerols, can survive in archaeological samples [32].

Unsaturated and especially polyunsaturated fatty acids in the triacylglycerol molecule are commonly subject to oxidation [33–37] via radical reactions with the inclusion of oxygen in the acyl chain, carbon-carbon bond cleavage, and the formation of lower molecular weight species. This phenomenon causes polymerization and cross-linking processes during the curing of drying oils (linseed oil, poppy seed oil, walnut oil, tung oil), highly polyunsaturated oils widely used as paint binders, varnishes and coatings. It leads to the formation of a polymeric network, generating a solid paint film.

The amount of free fatty acids increases with ageing and reflects the extent of hydrolysis of the triacylglycerols. The uptake of oxygen by double bonds leads to the formation of new oxygen containing functional groups and to the oxidative cleavage of fatty acid hydrocarbon chains. The products of the oxidation processes of lipids are generally  $\alpha,\omega$ -dicarboxylic fatty acids, hydroxycarboxylic acids and dihydroxycarboxylic acids [32,38,39]. Due to their relatively high solubility in water, which facilitates leaching once they have been buried, they are rarely detected in ancient artefacts [32].

Particular conservation conditions such as very arid environments, the absence of percolating water, and controlled storage conditions (e.g. paintings in museums) mean that relatively high amounts of hydroxyacids can be recovered along with dicarboxylic acids and dihydroxycarboxylic acids [29,39,40–42]. Aged drying oil paint films generally contain substantial amounts of dicarboxylic acids such as pimelic (1,7-heptanedioic, 7di), suberic (1,8-octanedioic, 8di), azelaic (1,9-nonanedioic, 9di) and sebacic (1,10-decane-dioic, 10di) acid, with azelaic acid being the most abundant.

The natural degradation processes of lipids can be accelerated or modified if the material is exposed to oxidizing conditions or to high temperatures, which occurs when cooking pottery, with oils used as illuminants, with drying oil prepolymerized by heating before use as paint binders, and with paint layers that are exposed to light and oxygen. Thus, the nature of degradation products depends on the composition of the original material, on the treatment of the material before or during its use, the presence of interacting species in the material, and on the environmental conditions.

It is thus quite difficult to distinguish between different degraded oils and fats on the basis of their fatty acid composition. The similarities in the composition of many vegetable oils used in ancient times and the way they might have been mixed together, means that degraded oils exhibit complex molecular patterns that usually prevent us from identifying the original botanical source.

Nevertheless, there are some vegetable oils that have a very specific composition. For example, castor oil consists of large amounts (83–89%) of 12-hydroxy-(Z)-9-octadecenoic acid (ricinoleic acid) which is not found in other natural lipids [21]. Ricinoleic acid produces a very characteristic oxidation product, 9,12-dihydroxyoctadecanoic acid [43], and both of these compounds can be considered as specific biomarkers for castor oil and have been used to assess its presence in ceramic lamps [43] and mummification balms [23].

Other oils show a very distinctive saturated fatty acid profile which in theory could be used for identification purposes in archaeological samples; for example moringa oil, which contains about 8% of long-chain saturated fatty acids (eicosanoic acid and docosanoic acid) which usually survive ageing [21,44], and coconut oil, which mainly consists of saturated triglycerides in which dodecanoic acid (lauric) and tetradecanoic acid (myristic) are the principal fatty acids [21]. All oils obtained from the seeds of Cruciferae such as rapeseed oil, turnip oil and radish oil, which were used in North Africa and in large areas of Europe and Asia [21,45], are characterised by a fatty acid profile showing some distinctive features: 5–15% (Z,Z)-9,12-octadecadienoic acid (linoleic acid), 10–30% (Z)-9-octadecenoic acid (oleic acid), 5–20% (Z)-11-eicosenoic acid (gondoic acid), 20–60% (Z)-13-docosenoic acid (erucic acid), 0.1–3% (Z)-15-tetracosenoic acid (nervonic acid), and about 4% long chain saturated fatty acids (eicosanoic acid, docosanoic acid, tetracosanoic acid) [21,46]. Mid to long chain  $\alpha,\omega$ -dicarboxylic fatty acids together with 11,12-dihydroxyeicosanoic acid and 13,14-dihydroxydocosanoic acid in ceramic vessels and oil lamps from Egypt have been reported [29,43,47]. These works demonstrated that the formation of these  $\alpha,\omega$ -dicarboxylic and dihydroxycarboxylic acids is related to the oxidation of erucic and gondoic acids, susceptible to degradation due to the presence of the double bond, so that a vegetable oil obtained from Brassicaceae seeds was identified.

A particular case is that of lipid materials as paint binders. Over the centuries, painting techniques have restricted the range of materials used to egg and drying oils [2]. The short list of possible candidates means that lipid materials in paint samples can generally be identified on the basis of their fatty acid profile. After ageing, drying oils are characterised by a higher amount of dicarboxylic acids than in egg lipids [40,41,48,49]. Moreover, steroids can survive in their original form or as degraded steroids such as cholesta-3,5-dien-7-one and 7-ketocholesterol [50–53]. Different drying oils can be distinguished on the basis of their palmitic over stearic acid (C16:0/C18:0) ratio [2,40]. This parameter is not significant in the case of mixtures of binders such as in the presence of *tempera grassa* (whole/yolk egg and drying oil) or in the presence of beeswax.

With regard to animal and dairy fats, the ratio of C16:0/C18:0 fatty acids has been used to identify animal fats and distinguish them from plant oils [21,43,54,55]. A content of C16:0 lower than that of C18:0 generally indicates an animal fat. The presence of odd numbered carbon straight chain fatty acids (C15, C17 and C19) and of significant amounts of branched chain fatty acids are considered characteristic of ruminant fats (sheep, cattle, goats, etc.) [56,57]. Ruminant fats also display a complex mixture of positional isomers of octadecenoic acid, resulting from the biohydrogenation of unsaturated dietary fatty acids in the rumen, characterised by double bonds located in various positions. This means a ruminant fat can be distinguished from non-ruminant fats (such as pig), which contain only the C18:1  $\Delta^9$  isomer [56,57].

Lipids from marine products have been studied less frequently. The detection of  $\omega$ -(*o*-alkylphenyl)alkanoic acids with 16, 18 and 20 carbon atoms together with isoprenoid fatty acids (4,8,12-trimethyltetradecanoic acid and phytanic acid) and substantial quantities of bones from fish and molluscs has provided evidence for the processing of marine animal products in vessels [58–60]. C16, C18, and C20  $\omega$ -(*o*-alkylphenyl)alkanoic acids are presumed to be formed during the heating of tri-unsaturated fatty acids (C16:3, C18:3 and C20:3), fatty acyl components of marine lipids, involving alkali isomerization, pericyclic (intermolecular Diels-Alder reaction) and aromatization reactions.

## 1.4 Natural Waxes

Natural waxes are highly heterogeneous lipid materials containing esters of long chain carboxylic acids, which are solid at room temperature and highly hydrophobic. Waxes of animal origin (beeswax, Chinese wax, lanolin, spermaceti wax), vegetable origin (carnauba, candelilla, esparto wax, Japan wax) and fossil waxes (paraffin wax, montan wax, ceresine) [2] have been used for many purposes such as sealants, surface coatings and polishes, casting and modelling materials, ingredients of balms and cosmetics, and lighting candles. Some chemical and physical features of natural waxes are reported in Table 1.4, and more details can be found in Chapter 4. In addition to natural waxes, a wide variety of synthetic waxes are used in restoration such as silicon waxes and polyethylene glycol.

### 1.4.1 Animal Waxes

Beeswax, obtained from the hives of bees, is the most commonly used natural wax for manufacturing works of art. Since prehistory, beeswax has been used as a waterproofing and sealing agent. The Egyptians used it in balms for mummies, in shipbuilding, to polish the surface of paintings, for lighting, and to make statues and writing tablets [2,61–66]. It was used by the Greeks and Romans to waterproof stone surfaces, as a protective agent and as a varnish [67]. Until the Middle Ages beeswax was used as a binder in a painting technique referred to as the encaustic technique [65,67]. Between the seventeenth and twentieth centuries the ceroplastic technique was developed for the realization of anatomical sculptures and botanical models [68].

**Table 1.4** *Chemical and physical features of natural waxes*

Wax	Melting range (°C)	Saponification number <sup>a</sup>	Iodine number <sup>b</sup>
<b>Animal</b>			
Beeswax	66–71	17–21	8–11
Chinese wax	80–83	11–15	1–2
Spermaceti	42–50	1–3	3–4
Lanolin	35–42		18–36
Ambergris	60–80	—	—
<b>Vegetable</b>			
Carnauba	82–86	4–8	12–15
Candelilla	67–79	16	14–37
Japan wax	50–60	206–237	4–13
<b>Mineral</b>			
Ceresin	54–77		7–9
Montan	76–92	23–27	10–16
Paraffin	46–68	—	—

<sup>a</sup>The saponification number is an indication of the number of acidic functionalities, and is the amount of KOH or NaOH (in mg) required to neutralize the acids in 1 g of lipid material.

<sup>b</sup>The iodine number is an indication of the degree of unsaturation of triglycerides, and is the amount of iodine (in mg) required to react with 1 g of lipid material.



The qualitative average composition of beeswax is quite constant and is made up of hydrocarbons (14%), monoesters (35%), diesters (14%), triesters (3%), hydroxymonoesters (4%), hydroxypolyesters (8%), monoacid esters (1%), acid polyesters (2%), free acids (12%) and free alcohols (1%) [2,69–73].

The aliphatic chains of beeswax compounds are mainly saturated and consequently extremely resistant to ageing. However, depending on the treatments undergone by the wax and the conservation conditions, some modifications to the original composition may occur. Since beeswax is solid at room temperature, thermal treatments were very commonly used to obtain a softened material to act as a binding medium or to be mixed with other materials. As a result, partial sublimation of the constituents can occur, leading to a change in the relative amounts of alkanes and esters [61,71,74–77]. Moreover, ambient humidity can cause a partial hydrolysis of beeswax esters, leading to the formation of free palmitic acid and long chain alcohols, which may also partially sublime, leading to changes in the acid and alcohol profiles.

Chinese wax is a white to yellowish-white, gelatinous, crystalline, water-insoluble substance obtained from the secretion of the scaled insect *Coccus ceriferus*, common in China and India. Chinese wax is used chiefly in the manufacture of polishes, sizes, and candles and is traditionally employed in Chinese medicine. It is basically made up of ceryl cerotate (esacosanoyl esacosanoate) and esacosanol [78,79].

Spermaceti wax (ambergris) is obtained from the precious oil in the head cavity of the sperm whale *Physeter macrocephalus*, and was used chiefly in balms, ointments, cosmetic creams, fine wax candles, pomades, textile finishing, and as a fuel for oil burning lamps. Nowadays, due to the current ban on whaling, authentic spermaceti wax is unavailable and the synthetic cetyl esters wax is used as a replacement for the naturally occurring material. The spermaceti wax composition includes cetyl palmitate (esadecanoyl esadecanoate), cetyl myristate, cetyl laurate, octyl stearate, octyl palmitate and cetyl alcohol [80,81]. Ambergris occurs as a biliary secretion of the intestines of the sperm whale and contains 46% cholestanol-type sterols [82].

Lanolin is a wax secreted by the sebaceous glands of sheep; it is obtained from wool and it has been used as a lubricant and as an ingredient in pharmaceutical preparations. It contains esters of long chain alkanolic acids, both linear and branched, and of hydroxyacids, cholesterol and lanosterol [2,83].

#### 1.4.2 Plant Waxes

These waxes are biosynthesized from plants and mainly contain esters made from long chain alcohols ( $C_{22}$ – $C_{34}$ ) and fatty acids with even carbon numbers.

Carnauba wax is obtained from the leaves of several species of palm trees in South America, such as *Copernicia cerifera* which grows in Brazil. It is made up of esters of long chain alcohols and acids with high carbon number, high molecular weight polyesters of hydroxyacids, and derivatives of *p*-hydroxy- and *p*-methoxycinnamic acid [84].

Ouricuri wax is an exudate on the underside of the leaves of the *Syagrus coronata* palm in northeastern Brazil and has similar properties and composition to Carnauba wax. Ouricouri wax is used in the manufacture of carbon paper, mould release agents and inks.

Candelilla wax is extracted from *Euphorbia cerifera* and *Euphorbia antisyphilitica*, which grow mainly in Mexico. The wax is collected from the root surface where the wax

acts as a protective coating. It is a dark yellow, hard and fragile solid, and it has been used to harden other waxes such as beeswax. Candelilla wax is used as a polishing material and in the manufacture of candles and sealing paper. Its main constituents are hydrocarbons (about 50%, between C29 and C33), esters (28–29%), alcohols, free fatty acids (7–9%) and triterpenoid esters (12–14%). Entriacontane and miricylic alcohol [ $\text{CH}_3(\text{CH}_2)_{28}\text{CH}_2\text{OH}$ ] are the most abundant and characteristic compounds.

Many other plant waxes have also been exploited for various uses, including esparto wax, from esparto grass *Stipa tenacissima*, and Japan wax, from plants of the *Rhus* species.

### 1.4.3 Fossil Waxes

Ceresine is the white end-product of the purification of the fossil wax ozokerite, which is found in Miocene lignite deposits at considerable depths, by the separation of foreign and resinous matter and decolorisation by active agents. It is harder than paraffin wax, and has linear and cyclic hydrocarbons with high molecular weight [2]. It is used for waterproofing and oil absorption.

Paraffin waxes are also considered of mineral origin and are obtained from petroleum. The petroleum is distilled and the white colour of the wax is obtained by acid washing and purification. It has a typical melting point between about 47 °C and 64 °C. Its uses include candle making, casting and as a solidifier/stabilizer. The wax is composed of C20–C36 n-alkanes (40–90%), isoalkanes and cycloalkanes.

Montan wax is obtained by solvent extraction of certain types of lignite or brown coal. It has a dark colour when not treated, but it is lighter when refined. Its chemical composition includes esters of C22–C32 acids (53%), free acids (17%), free alcohols (1–2%), ketones (3–6%) and terpenoids (20–23%) [85].

Microcrystalline wax is found worldwide as a constituent of crude oil. It is removed by solvent extraction and distillation. The colour varies, depending on grade, from white to brown–black. It has many uses, including waterproofing paper and textiles, and as a sealant. This wax consists of a mixture of long chain (C41–C57) unsaturated hydrocarbons with an average molecular weight of 500–800.

## 1.5 Natural Resins

Plant resins are lipid-soluble mixtures of volatile and nonvolatile terpenoid and/or phenolic secondary compounds that are usually secreted in specialized structures located either internally or on the surface of the plant. Although terpenoid resins constitute the majority of the resins produced and used, some other important resins are phenolic. Phenolic resin components, which occur on the surfaces of plant organs, have been used particularly in medicines [86].

Natural terpenoid resins and resinous materials played a prominent role in ancient times – their intrinsic properties meant that they were used as adhesives, hydro-repellents, and coating and sealing agents [87–92]. They produced incense when burnt [92] and due to their antitoxic and antioxidant properties, they were also added to wine. In ancient Egypt, vegetable resins along with other natural organic compounds such as waxes, gums, oils and bitumen, were used to prepare mummification balms [23,88,93–97]. Resins and wood

from birch, pine and firs were used to produce tar and pitch in various regions of Europe and the Mediterranean.

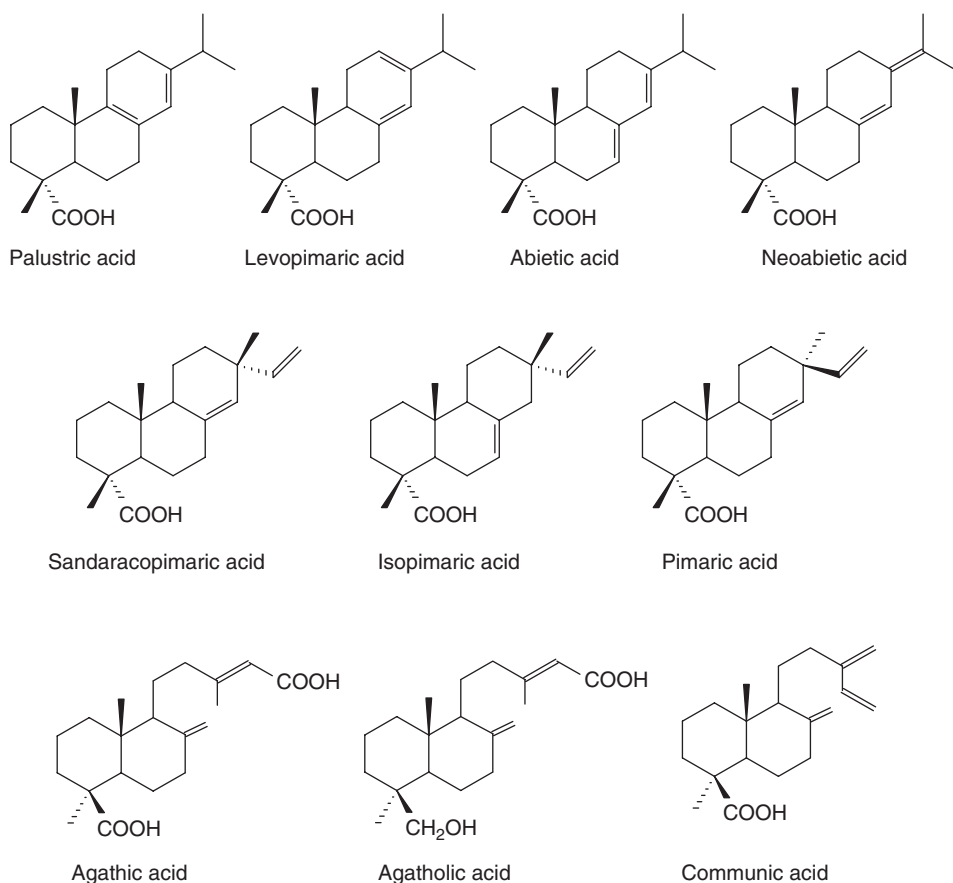
Natural resins are substances with a high viscosity, semisolids or solid and insoluble in water. They are formed in the so-called 'resiniferous canals' of several trees. Many varieties of plants spontaneously exude resins as a product of their metabolism, to protect themselves against excessive loss of water and attack from micro-organisms.

From a chemical point of view, vegetable resins are a complex mixture of mono-, sesqui-, di- and triterpenes, which have, respectively, 10, 15, 20 and 30 carbon atoms per molecule. The mono- and sesquiterpenes are both present in most resins. The di- and triterpenes are rarely found together in the same resin, which means that terpenic resins can be divided into two main classes. Table 1.5 lists the botanical origin and the kind of terpenoid compounds of some natural resins.

Mono- and sesquiterpenoids are of limited use for the identification and classification of aged resins. Due to their volatility, they are rarely found in ancient samples except when they have been conserved in very particular conditions [88,98]. On the other hand, the di- and triterpenoids enable us to identify resins thereby identifying their botanical origin [2,99]. Figures 1.1 and 1.2 show the main diterpenoid and triterpenoid structures.

**Table 1.5** Botanical origin and chemical composition of terpenic resins

Class	Family	Genus (type of resin)	Composition
Coniferales	Pinaceae	<i>Pinus</i> (pine resin, colophony)	Abietadienic acids, pimaradienic acids
		<i>Abies</i> (Strasbourg turpentine)	Abietadienic acids, pimaradienic acids, <i>cis</i> -abienol
		<i>Larix</i> (Venice turpentine)	Abietadienic acids, pimaradienic acids, epimanol, larixol, larixyl acetate
	Cupressaceae	<i>Juniper</i> , <i>Cupressus</i> , <i>Tetraclinis articulata</i> (sandarac)	Pimaradienic acids (sandaracopimaric acid), communic acid, totarol
Guttiferales	Dipterocarpaceae	<i>Hopea</i> (dammar)	Dammaranes (hydroxydammarenone, dammaradienol), ursanes (ursonic acid, ursonaldehyde)
Terebinthales	Anacardiaceae	<i>Pistacia</i> (mastic)	Euphanes (masticadienonic acid, isomasticadienonic acid), oleananes (oleanonic acid, moronic acid), dammaranes
	Bursaceae	<i>Commiphora</i> (myrrh)	$\alpha$ - and $\beta$ -amyrin, euphanes, oleananes
		<i>Boswellia</i> (olibanum or frankincense) <i>Canarium</i> (elemi)	



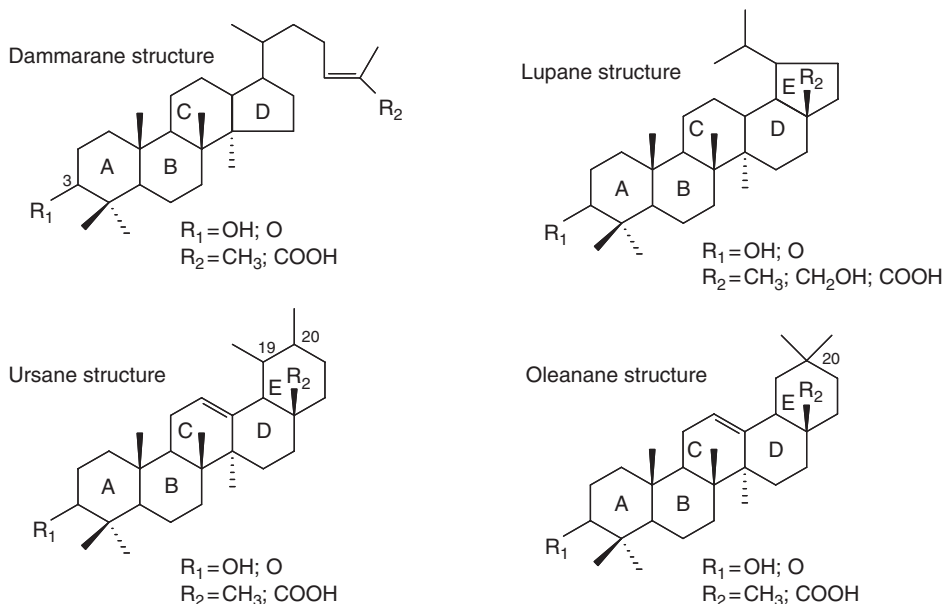
**Figure 1.1** Characteristic diterpenoid compounds of Pinaceae and Cupressaceae resins

Diterpenoid and triterpenoids in natural resins generally lead to one, two or three oxygen atoms in the form of acidic, carboxylic or alcoholic functionality and a variable degree of unsaturation.

### 1.5.1 Diterpenoid Resins

The plants that exude diterpenoid resins belong to the order of conifers. Pine resins (from the *Pinus* genus), Strasburg turpentine (from the *Abies* genus), Venice turpentine (from *Larix decidua*) were extracted from Pinaceae. Sandarac, juniper and cypress resins were extracted from trees of the Cupressaceae family: *Tetraclinis articulata*, *Juniperus* spp. and *Cupressus sempervirens*, respectively. Moreover, labdanum resin from the Cistaceae family (*Cistus* spp.) also belongs to the diterpenoid resins.

Pine resin, namely rosin or colophony, is one of the most widespread diterpenoid resins and has been used for waterproofing, for treating wood and paper, as varnish, as incense and as an ingredient in scented ointments. The main compounds present in fresh Pinaceae resins



**Figure 1.2** General molecular formulae of triterpenes present in triterpenoid resins

are diterpenoid acids with either abietane or pimarane type skeletons (see Figure 1.1). Both kinds of acids are tricyclic: the abietadienic acids contain a conjugated double bond, whereas pimaradienic acids lack this conjugation, since a quaternary carbon separates the two double bonds. The absence of the conjugated double bond makes them more stable to oxidation processes than abietadienes [31]. Conifer resins, such as those of the pine family (Pinaceae), are characterised by a large volatile fraction (20–50%) with monoterpenes predominating over sesquiterpenes. Both classes most commonly occur as hydrocarbons with a few oxidized forms, often as trace components. Under natural conditions, monoterpenes volatilize with varying rapidity, providing, for example, the fragrant aromas in conifer forests during warm weather [86].

However, in many archaeological samples pimarane diterpenoids are often absent, and of the abietane compounds only dehydroabietic acid remains. In fact, dehydroabietic acid is present as a minor component in the fresh resins, but its abundance increases on ageing at the expense of the abietadienic acids since the latter undergo oxidative dehydrogenation to the more stable aromatic triene, dehydroabietic acid [2,18]. If oxygen is available, dehydroabietic acid can be oxidized to 7-oxodehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid. Since these diterpenoid compounds are often the dominant components in archaeological samples [95,97], they are considered characteristic for the presence of Pinaceae resins.

Of the Cupressaceae family, sandarac (from *Tetraclinis articulata*) has frequently been used as a paint varnish. It contains labdane compounds that account for the polymeric fraction of the resin (about 70%) [31]. The main monomeric diterpenoid present is sandaracopimaric acid, together with smaller amounts of 12-acetoxysandaracopimaric acid. Phenols, including totarol, are also present [31].

Labdanum resin (from the Cistaceae family) contains diterpenoid compounds with a labdane-type structure, namely laurifolic, cistenolic and labdanolic acids [100–103].

### 1.5.2 Triterpenoid Resins

Triterpenoid resins include gum resins from the Burseraceae family including myrrh and frankincense, and mastic resins (from *Pistacia* genus) [88]. Triterpenoid resins consist of mixtures of triterpenoid molecules with mainly pentacyclic and tetracyclic skeletons (see Figure 1.2). Tetracyclic triterpenes include dammarane and lanostane structures, characterised by the presence of a hydroxy or a keto group at position 3 and of a lateral chain bearing a double bond. Further possible functional groups are also usually present. Lanostane type molecules can be distinguished from dammarane molecules by the presence of a second double bond at position 7 or 8. Pentacyclic triterpenes can be divided into four main groups: ursane, oleanane, lupane and hopane. Ursane and oleanane triterpenes differ only in the position of one methyl group. The ursane type molecules bear one methyl group at position 20 and the other at position 19, while the oleanane ones bear the two methyl groups at position 20. The triterpenes with lupane and hopane skeletons have four six-membered rings and one five-membered ring (E) (Figure 1.2).

Frankincense, also known as olibanum, is obtained from trees belonging to the genus *Boswellia* (Burseraceae family). It is one of the best-known ancient plant resins. The ancient Egyptians were the first to use it as incense in embalming practices and in the preparation of medicines, cosmetics and perfumes, and today it is still used therapeutically. It contains pentacyclic triterpenoids belonging to oleanane, ursane or lupane type molecules and in particular of  $\alpha$ - and  $\beta$ -boswellic acids, and their *O*-acetates [104–111]. 11-Oxo- $\beta$ -boswellic acid and its acetyl derivative, identified in several *Boswellia* species, are also diagnostic for frankincense [112].

The survival of  $\alpha$ -boswellic acid,  $\beta$ -boswellic acid and their *O*-acetates, which have been isolated only from frankincense, has been demonstrated in archaeological samples [99,107,113]. These compounds are considered as very useful specific chemical markers for the identification of frankincense in resinous archaeological materials.

Mastic resin is derived from the genus *Pistacia* (Anacardiaceae family, four Mediterranean species: *P. atlantica*, *P. khinjuk*, *P. lentiscus* and *P. terebinthus*) and has been used as incense, as an adhesive and as varnish. Together with dammar resin and sandarac, it is one of the most commonly encountered resins in the formulation of varnishes for easel paintings. For this use, mastic was often applied in a mixture with linseed oil, giving an oleoresins varnish which suffered from yellowing and craquelures.

Mastic resins have many components in common with dammar and elemi. The main neutral triterpenoids are nor- $\alpha$ -amyrone, 28-norolean-17-en-3-one, hydroxydammarenone, oleanonic aldehyde together with triterpenoid acids (oleanonic, moronic, isomasticadienonic and masticadienonic) [92,114–122]. Unlike dammar resin, it does not contain ursanes, and contains a relatively higher amount of oleanic species.

Moronic, isomasticadienonic and masticadienonic acids are considered as characteristic and diagnostic molecules for assessing the presence of mastic resin in ancient samples [2,88,94,123,124].

It is also well known that during ageing, new compounds are formed by oxidation reactions. In fact, the presence of 20,24-epoxy-25-hydroxy-dammaren-3-one and 3-oxo-trisnor-

dammarano-20,24-lactone has been highlighted in several aged samples [125–127]. The first compound is produced via the cyclization of the lateral chain of the hydroxydammarone, which then leads to the formation of a tetrahydrofuranic ring. The second is formed from 20,24-epoxy-25-hydroxy-dammarene-3-one by further oxidation reactions involving the formation of a lactone derivative.

In archaeological findings the occurrence of a high abundance of 28-norolean-17-en-3-one has been correlated to smouldering or burning processes undergone by *Pistacia* resins [94,123,124]. Mastic also contains a polymeric fraction (15–20%) identified as *cis*-1,4-poly- $\beta$ -myrcene [128].

Dammar resin was introduced into Europe in the nineteenth century, mainly as a paint varnish. It is still used today since it has good optical properties and low acidity. It is derived from various species (the genus *Hopea* and *Shorea* of the Dipterocarpaceae family). It is characterised by tetracyclic triterpenoids of the dammarane series and contains minor amounts of pentacyclic triterpenoids of the series of oleanane, ursane and hopane. It also contains a polymeric fraction named polycadinene or  $\beta$ -resene. Dammar resin triterpenoids undergo oxidation with ageing, as described for the components of mastic resin.

### 1.5.3 Phenolic Resins

Phenolic resins are mainly composed of aromatic esters: benzoe and storax were the most common in the Mediterranean [86].

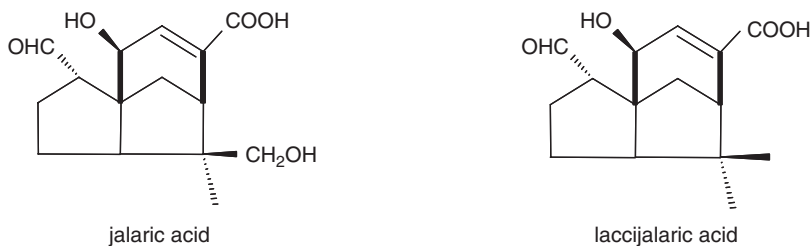
Benzoe resin (also known as benzoin) comes from *Styrax* spp. (Styraceae family). In the *Styrax* genus the only species that occurs in the Mediterranean is *Styrax officinalis*, so this was probably the source of the resin in ancient times in that area. Benzoe mainly contains free cinnamic and benzoic acids, and their corresponding esters with cinnamyl, *p*-coumaryl and coniferyl alcohols. The amounts of these compounds are quite variable and depend on which species the resin was obtained from [129].

Storax resin is extracted from *Liquidambar orientalis* (Hamamelidiaceae) and *Altingia* and its major components are cinnamyl cinnamate and 3-phenylpropanyl cinnamate, with significant amounts of benzoic and cinnamic acids, and 3-phenylpropanol and cinnamyl alcohols [130,131]. The volatile content is very low and triterpenes (oleanonic and 3-epioleanolic acids and liquid ambronic acid) have also been observed [130,132].

### 1.5.4 Animal Resin

The resin of animal origin most used in the field of cultural heritage is shellac. It is a natural resin produced from the glandular secretion of an Indian scaled insect (*Laccifer lacca* Kerr, also known as *Kerria lacca*), which infests branches of numerous trees from the East Indies [133]. It began to be used in Europe towards the end of the sixteenth century [85] mainly as a varnish, known as 'French polish', for wooden objects, musical instruments, gildings, paintings, as an insulating material and as an adhesive in the restoration of pottery.

Shellac is a complex mixture made of mono- and polyesters of hydroxy-aliphatic and sesquiterpene acids, which can be separated into two fractions: the soft resin, soluble in ether, mainly consisting of monoesters [134], constituting about 30% of the total resin; and the hard resin, ether insoluble, which has quite a complex polyester composition, and

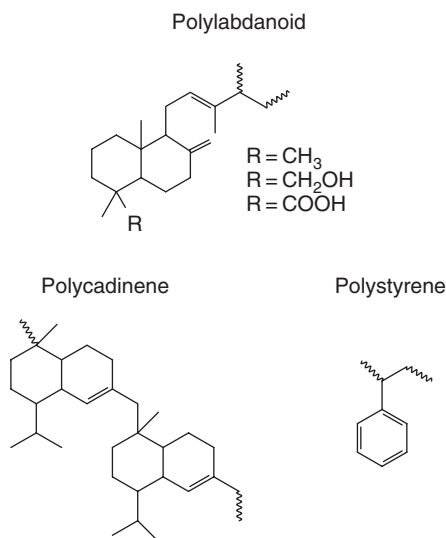


**Figure 1.3** Structures of the main sesquiterpenoid shellac compounds

accounts for the other 70% [135]. The main ester components of shellac are jalaric and laccijalaric acids (Figure 1.3), 9,10,16-trihydroxyhexadecanoic (aleuritic acid) and 6-hydroxytetradecanoic acids (butolic acid) [136–140].

### 1.5.5 Fossil Resins

Resins older than 40 000 years are considered to be fossil resins. The fossilization of resins begins with polymerisation and forms ambers and copals. Most of the ambers are derived from components of diterpenoid resins with a labdanoid structure; other ambers are based on polymers of sesquiterpene hydrocarbons such as cadinene, and may include triterpenoids; less common ambers from phenolic resins derive from polymers of styrene. Figure 1.4 shows the skeletal structures of the components which make up the polymers occurring in fossil resins [141].



**Figure 1.4** Main structures of polymeric fossil resins



Amber deriving from the extinct species *Pinus succinifera* is known as Baltic amber or succinite and consists of dimers of abietic acids and copolymers of communol and communic acid. Amber is less soluble than the other resins, but partially soluble in hot oil, so it has been used as an ingredient in varnish.

Copals, sometimes referred to as immature amber, originate from Africa, Asia or central American countries and derive from the Araucariaceae and Leguminosae families. Polymerised communic acid and agathic acid are found as the main compounds in these fossil resins. The extreme hardness of copal results from polymers of resin acids such as ozoic acid, an enantiomer of communic acid that can polymerize and thus enable fossilization [86]. They are still commonly used today for varnishing and protecting wood.

### 1.5.6 Pitch and Tar

Natural resins and resinous wood were not only used in their natural form but were often subjected to hard-heating treatments and to distillation-type processes. This led to denser and stickier materials, referred to as tar or pitch [87,88].

Resins and wood from birch, pine and fir were used to produce tar and pitch in various regions of Europe and the Mediterranean [87–92,142–148], both for the production of adhesives and of hydro-repellents and coatings.

In Roman times tar and pitch from Pinaceae resinous wood were used to treat the inner surface of amphorae to store fluids such as wine [145,149] and to seal ship planks [89,144].

Heating treatments applied to natural resins and resinous wood profoundly modify the chemical composition of the original material. Diterpenoid compounds undergo aromatization, demethylation and decarboxylation reactions, with the formation of new compounds of a lower molecular weight that show a high degree of aromatisation [87,88]. In tar and pitch produced from Pinaceae resin and woods, retene is considered as a stable end product of these reaction pathways and nor-abietatrienes, simonellite and tetrahydroretene represent the intermediates of these reactions [87,89,150].

Birch bark was also used to produce pitch and tar. The pitch from Betulaceae bark has been found on arrowheads and flint tools from prehistoric ages and the pitch was probably a residue of the original adhesive [92,151,152]. Birch-bark pitch has also been identified in ceramic artefacts as an adhesive to coat, seal, or repair the inner surfaces of the vessels [90].

Betulin and lupeol, together with low amounts of lupenone, betulone and betulinic acid, are characteristic of birch bark [87,153–157]. All these compounds are pentacyclic triterpenoids with a lupane skeleton. In addition to triterpenoids, birch bark contains high amounts of a lipid material, called suberin [158].

## 1.6 Asphalt and Bitumen

Bitumen, asphalt, and other fossil organic materials such as coal, lignite and peat are found as natural deposits and have practically always been used in arts and handicrafts. Bitumen and asphalt were used in medicines and cosmetics, as pigments, as adhesives and in mummification balms in ancient Egypt [2,159,160].

These materials are chemically very complex and the composition of fossil organic matter depends on the kind of organism from which the deposit has formed [2].

Bitumen contains a solvent-soluble fraction referred to as maltenes, and an insoluble fraction called asphaltenes. The word bitumen is in some cases also used to indicate the residue of the distillation of petroleum.

Asphalt and bitumen contain isoprenoid compounds that derive from phytosterols, triterpenoids, and diterpenoids, which have defunctionalized and fragmented with a consequent loss of side chains. They mainly contain saturated compounds such as hopanes and steranes, but also small amounts of unsaturated and aromatized compounds. Bitumen generally contains a complete range of homologous series of n-alkanes, and the isoprenes pristane and phytane. The hopanes are biomarker compounds which can be related to their original biogenic precursors. Their ubiquity in sedimentary organic matter indicates that they are formed by the bacterial transformation of biological remains [2]. The identification, origin, uses and trade of bitumen has been widely described [161,162].

## 1.7 Polysaccharide Materials

Polysaccharides are polymers made up of many monosaccharides joined together by glycoside bonds, and include cellulose, starch, vegetable mucilage and plant gums.

Cellulose is a high molecular weight polymer of D-glucose with  $\beta(1-4)$ -glycosidic bonds, found in plant fibres; it is the major component of most plant tissues. Starch is another common polysaccharide, containing two polymers of glucose, amylose and amylopectin. It was used in some paint preparations and in the production of paper. Acid treatment of starch produces dextrans, which are used as adhesives and additives in water colour paintings.

Plant gums are naturally occurring polysaccharide exudates from several species of plants or extracted from the endosperm of some seeds. The polymers consist of aldopentoses, aldohexoses and uronic acids joined together by glycosidic bonds. Since ancient times, several plant gums have widely been used as paint media and sizing agents. The gums traditionally employed were Arabic gum (exuded by *Acacia senegal* and *Acacia seyal*), tragacanth gum (exuded by *Astragalus*) and fruit tree gum (obtained mainly from cherry, apricot, peach and plum trees). Locust bean, extracted from the kernels of the carob tree (*Ceratonia siliqua*), guar (from *Cyanoposis tetragonolobus*, Leguminosae), ghatti (from *Anogeissus latifolia*, Combretaceae) and karaya gum (from *Sterculia urens*, Sterculiaceae) were important materials mainly used in the Indian subcontinent. Natural gums present variable distributions in mean molecular mass of polymeric molecules, whereas the composition of the constituent sugar percentages remains reasonably constant and depends on the specie of the plant. The composition of monosaccharide differs from gum to gum and can thus be exploited for their identification [163,164]. Fucose, for example, is considered a marker for the recognition of tragacanth gum, since this sugar is absent in the other gums. Table 1.6 gives the saccharide composition of the most widespread gums.

**Table 1.6** *Percentage composition of plant gums and honey*

	Xylose	Arabinose	Ramnhose	Fucose	Galacturonic acid	Glucuronic acid	Glucose	Mannose	Galactose	Fructose
Arabic	—	37	11	—	—	7	—	—	45	—
Fruit tree	6	35	3	—	—	13	—	5	37	—
Locust bean	—	1	—	—	—	—	—	81	17	—
Karaya	—	—	25	—	7	4	—	—	64	—
Tragacanth	15	35	3	7	14	4	11	—	10	—
Guar	—	2	—	—	—	—	—	63	34	—
Ghatti	—	47	3	—	—	11	—	2	36	—
Honey	—	—	—	—	—	—	40	—	—	49

Gums are hydrophilic materials that easily undergo chemical hydrolysis with depolymerization, oxidation and microbiological attack. Leaching is a well-known phenomenon, and the inversion between arabinose and xylose content has been reported [164,165].

## 1.8 Organic Dyes

Natural organic colouring materials have been widely used to dye textiles and as pigments in paintings [165–168]. Investigation into natural colourants of historic importance mean that we gain a clearer idea of how the use and trade of pigments, dyestuff, dyed artefacts, and of dyeing technologies, differed from one geographical area to another. In the nineteenth century synthetic dyes began to replace natural ones, starting with the production of mauvein in 1856.

Organic dyes are fixed to the support by dispersion in a binder or by direct adsorption. Many organic dyes are used after precipitation with metal salts or metal hydroxides (mordants) as alum  $K_2(SO_4)_2 \cdot Al_2(SO_4)_3 \cdot 24H_2O$  or potassium tartrate.

The chromophores contained in natural dyes are mainly flavonoids, anthrachinoids, indigoids and gallotannins. Other molecular types include carotenoids, benzochinons and anthocyanidins.

The most commonly used yellow dyes contain flavonoids (flavones and flavonols) and occur in plants as sugar derivatives. Weld (*Reseda luteola* L.), young fustic (*Cotinus coggyria* Scop.), dyer's broom (*Genista tinctoria* L.), sawwort (*Serratula tinctoria* L.), the berries of some species of rhamnus, old fustic (*Chlorophora tinctoria* L.), and quercitron bark (*Quercus velutina* L.) are the most common vegetable materials from which yellow dyes are extracted. After hydrolysis in the dye-bath to the parent aglycone, flavonoids bind to the fibre through a metal complex with the mordant via the carbonyl group and the adjacent phenolic group. Since many plants are rich in flavonoids, no individual source of yellow dye has become predominant – as did, for example, the red dyes madder and cochineal – and many different and local sources were in use at the same time.

All dyes are prone to fading caused mainly by chemical oxidation when exposed to light. The formation of low molecular mass products has been evidenced, such as 2,4-dihydroxybenzoic acid and 2,4,6-trihydroxybenzoic acid from morin degradation, in old fustic dyed samples [169] and from luteolin in weld and dyer's broom [170].

Debromination with ageing has been observed in the indigoid components of purple [171,172], and photochemical breakdown patterns of the three anthocyanidins contained in *Arrabidaea chica* red dye, produced by Andean Indian cultures in the tenth to fifteenth centuries, have been hypothesized [173]. Although identifying dye sources in ancient artefacts is quite difficult, it is helped considerably by understanding the fading and degradation mechanisms.

Table 1.7 lists the most widely used natural dyeing materials and their chemical composition.



**Table 1.7** (continued)

Common name	Botanic name	Main chromophores								
Indigo carmine	<i>Indigofera tinctoria</i>	—	—	—	—	—	—	—	Indigocarmine	
Purple	<i>Muricidae</i> and <i>Rapariniae</i>	+	—	+	+	—	—	—	—	
Orchil	<i>Rocella</i> and <i>Ochrolechia</i>	—	—	—	—	—	—	—	Orcein	
<b>Flavonoid dyes</b>										
Young fustic	<i>Cotinus coggia</i> Scop.	+	—	—	—	—	—	—	—	Other Compounds Fustin, Sulfuretin
Old fustic	<i>Clorophora tinctoria</i> L.	—	+	+	+	—	—	—	—	—
Quercitron bark	<i>Quercus velutina</i> L.	—	—	—	—	—	—	—	+	Quercitrin
Persian berries	Rhamnus family	—	—	—	—	—	—	—	+	Rhamnetin
Weld	<i>Reseda luteola</i> L.	+	Luteolin	Apigenin	Genistein	3-Methylquercetin				
Dyer's broom	<i>Genista tinctoria</i> L.	+	+	—	+	—	—	—	—	—
Rhamnus bark	<i>Rhamnus frangula</i> (cortex)	—	—	—	—	—	—	—	—	Glucofrangulin A and B, Franguline, Emodin
Sawwort	<i>Serratula tinctoria</i> L.	+	+	—	—	—	—	—	+	—

	Brazilin	Brazilin	Hematoxylin	Hematein
Brazilwood	+	+	+	+
Logwood	—	—	+	+

### Tannin based dyes

Black alder	Gallic acid, quercetin, emodin			
Sumac	Gallic acid, ellagic acid, quercitrin, kaempferol			
Black walnut	Juglon			
Walnut galls	Tannins			
Silver birch	Tannins			

### Other dyes

Henna	Lawsonia inermis	Lawson		
Sandalwood	Pterocarpus santalinus	Santalin A, Santalin B		
Safflower	Carthamus tinctorius L.	Carthamina, Safflower Yellow A and B		
Annatto	Bixa orellana L.	Bixin		
Barberry	Berberis vulgaris L.	Berberin		
Saffron	Crocus sativus L.	Crocin, crocetin		
Turmeric	Curcuma longa	Curcumin, demethoxycurcumin, bisdemethoxycurcumin		

## 1.9 Synthetic Polymers

Since the earliest production of synthetic materials in the mid nineteenth century, artists and restorers have explored their possibilities. After 1900 many artists became familiar with the new and modern materials such as cellulose nitrate and cellulose acetate. Thus modern artists replaced the traditional moulding in wax, casting in gypsum and expensive bronze with the newly available materials. The use of plastic in art objects occurred gradually: 1915 saw the first use of celluloid in sculptures, and after 1943 Plexiglas or Perspex [poly(methyl methacrylate), PMMA] was employed on account of its good resistance to ageing. In paintings, in addition to traditional materials such as drying oils and proteinaceous tempera, a range of synthetic polymers have been experimented with poly(vinyl acetate)s, alkyd resins and acrylic resins as the materials most used in the twentieth century [2,174,175].

Nearly all the polymers that industry has made available have been used in art or conservation [176]. Synthetic resins have been used as solidifiers, varnishes, coatings, paint binders, moulding and casting materials, clothing, jewellery, furniture and as materials for the display, support and storage of art objects.

The range of possible materials is very wide and depending on the function required they can be applied in many ways, for example:

- polymer solutions in a solvent, followed by evaporation of the solvent;
- emulsions or dispersions, usually in water;
- liquid pre-polymers which by chemical reaction form a polymer;
- liquid adhesives which remain as liquids;
- molten liquids which cool and form a solid.

As yet we are not fully aware of the chemical and physical behaviour of modern synthetic materials so this makes it difficult to characterise and conserve them. This is particularly true with regard to interactions with the components in art objects, interactions with additives (e.g. fillers, plasticizers, colourants), and changes in their properties during ageing. Since synthetic polymers are commercial products, the materials used in the past may significantly differ from modern materials of nominally the same composition, thus hampering characterisation and comparisons. Various types of degradation in plastics have been reported, the most commonly known being discoloration, deformation, embrittlement, cracking and crumbling, which are caused by moisture, heat and light.

Table 1.8 lists some synthetic materials and their use in art.

Synthetic coatings and varnishes, which are transparent and give colourless protective films, have for the most part replaced traditional natural paint varnishes (dammar resin, mastic resin, copals or colophony). The modern polymers used for this purpose include ketonic resins, acrylic and metacrylic resins, which have been employed due to their good refraction index, resistance to yellowing, and high transition temperature. Low glass transition temperatures lead, with time, to the inglobation of particulate in the coating layer, with a loss of transparency and gloss. One of the most widely used acrylic polymers is Paraloid B72, an ethyl-methyl methacrylate copolymer, which shows low tendency to reticulation with ageing and in fact remains quite soluble.



**Table 1.8** Some synthetic materials and their use in art

Material	Year of production	Main use	Added plasticizer	Notes
Cellulose nitrate (Celluloid)	1850	Moulding material, paints, glues, coatings, photographic films, varnishes	Camphor, phthalate esters	High flammability and degradability, with production of nitrogen dioxide
Cellulose acetate	1910	Moulding and extruding materials, fibres, photographic films		Degrades with hydrolysis of the acetate group and production of free acetic acid
Phenol-formaldehyde resin (Bakelite)	1906–1909	Enamels, moulding materials, jewellery, paints, consolidants	Wood flour	
Polyamides (nylons)	1934	Fibres, textiles, paint fixatives (Calaton)		No longer used as fixative due to the inclusion of dust
Vinyl polymers [polystyrene, PVC, polyethylene, polypropylene, poly(vinyl acetate), poly(vinyl alcohol), polyacrylonitrile]	~1920	Packaging, tubing, household goods, records, carpets, toys, water-based paint, adhesives, varnishes	Phthalate esters, poly(vinyl alcohol)	
Acrylic resins (Perspex, PMMA, Paraloid)	~1930	Varnishes, adhesives, glazing, sculptures, paint media		Sensitivity to sunlight. Methacrylates are subjected to bond cleavage. Acrylates undergo cross-linking reactions
Alkyd resins		Paints, varnishes	Drying oils	Very low solubility: the product becomes irremovable with ageing
Polyurethanes	1937	Foams, fibres, adhesives, coatings, sculptures, decorations		Tendency to yellowing, depolymerisation. Toxicity of isocyanates
Poly(ethylene glycol)s		Consolidants		Water soluble
Ketonic resins (Laropal K 80®, MS2A)	~1930	Varnishes	Seed oils	Quite stable with ageing with a low tendency to yellowing
Epoxy resins	1936	Adhesives, especially for glass repair		Resistant to acid, alkali and organic solvents. Tendency to yellowing with ageing

At the same time, natural adhesives such as casein glues, animal glue and polysaccharide gums have gradually been replaced by synthetic adhesives: vinyl thermoplastic adhesives [poly(vinyl acetate)], adhesives obtained by reticulation *in situ* of two components (as epoxy resins), represent very important materials in this field.

Thermoplastic synthetic resins as consolidants in restoration are now common. For example, poly(ethylene glycol)s with various molecular weights have been used to consolidate archaeological imbibed wood [177]. Normally materials that maintain a degree of solubility over time are preferred. In theory they can be removed, thus guaranteeing a certain reversibility of the intervention. These include vinyl resins and acrylic resins. Of the vinyl polymers, poly(vinyl acetate) shows good stability towards ageing and photooxidation. However with ageing it undergoes reticulation, and it consequently loses solubility and is difficult to remove. The commercial acrylic products that have found major application as consolidants are Paraloid B72 and Plexisol, which are characterised by less polarity and consequently by a better solubility in non-aggressive solvents.

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