Journal of Food Research; Vol. 1, No. 3; 2012
ISSN 1927-0887 E-ISSN 1927-0895
Published by Canadian Center of Science and Education

# Non-wood Forest Products Based on Extractives - A New Opportunity for the Canadian Forest Industry
# Part 1: Hardwood Forest Species

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Received: February 22, 2012 Accepted: March 14, 2012 Online Published: May 28, 2012

doi:10.5539/jfr.v1n3p8 URL: http://dx.doi.org/10.5539/jfr.v1n3p8

**Abstract**

Forest resources are among the most important of Canada (in the case of Québec, nearly 90% of the territory). Innovation represents an essential challenge for the Canadian forest industry, which is presently undergoing major changes towards finding new solutions for recovery. The processing of forest biomass has become increasingly relevant along with the popular concept of biorefineries. This concept should include the development of novel technologies based on forest extractives. Bioactive molecules are readily available through eco-friendly extraction processes using various types of forest residues including barks which are generated in significant quantities by the industry. This literature review offers a glimpse into the hardwood boreal forest with a particular focus on industrial species. We are adopting an ethno-pharmacological approach prior to presenting existing data on bioactive molecules from various sources, along with results from our own laboratory. In conclusion, this paper clearly demonstrates the need for further research on bioactive molecules from Canadian forest species since there remains an important lack of reliable data.

**Keywords:** Canadian forest species, extractives, terpenes, polyphenols, traditional uses, bioactivities

## 1. Introduction

The Canadian forest industry has now for many years gone through a crisis that has seen asignificant decrease both in terms of commissioned sites (1.3% for Québec in 2008) and in demand from the USA and elsewhere in Canada. Downtrends have been observed in production numbers, jobs, exports and profits. In the case of Québec, job figures in the combined forestry and pulp & paper sectors have gone from 370000 in 2004 to 260000 in 2007. The main sub-sectors in the forestry industry include: pulp & paper (48.5% of the sector's production), wood product manufacturing (36.4%) and logging activities (15.0%). A majority of jobs have been saved in the sub-sector of wood product manufacturing. However, some 1300 layoffs were noted in logging, a situation which confirms the irreversible downward tendency recorded in the last five years.

Within this context, Québec's Ministry of Natural Resources and Wildlife in its green paper titled *«La forêt pour construire le Québec de demain»* published in February 2008[i], puts forward an industrial development strategy based on high value-added products, in order (i) to promote an innovating industrial sector, generating wealth and sustainable jobs, and (ii) to encourage wider opportunities in the uses of wood as a renewable raw material.

Innovation is the key for the forestry sector to come up with a novel resource management system, thus leading to original value-added solutions. In Québec, upcoming forest biomass conversion technologies are seen as critical tools in this overall strategy. For instance, the cluster known as «forest extractives» represents a novel path in this value-adding proposition. This will initially require basic work such as the systematic identification of bioactive molecules found in significant amounts in forest residues and notably in bark tissues. The need for further research is clear, and will require a synergistic collaborative framework between industry and academia. The beneficial exploitation of those so-called extractives will allow industry players to access new markets. It is well understood that the forest industry generates large volumes of residues in the majority of its process stages; of those, bark materials are residues found in primary forestry processes. A study undertaken in 2008 by the Québec Wood Export Bureau pointed to the fact that overall, Québec's industrial forestry sector produces roughly 2.9 million tons of residuesper annum (Fortin, 2008). These are mostly burned as supplemental sources of energy but a more original and tentative approach has emerged: indeed, the controlled and optimized extraction of bioactive molecules from such residues prior to their use as combustible material represents an essential path leading to added intrinsic value. Those extracts will find various applications for instance as pharmaceuticals, agri-food additives, cosmeceuticals and nutraceuticals.

### *1.1 Natural Health Products*

Worldwide demand for bioactive molecules of natural origin has progressed sharply in recent years, due to several factors such as new consumer awareness, cultural and societal changes as well as expanded knowledge in energy alternatives and natural raw materials. Increased exposure to "green" trends in the media and in wider distribution networks also contributed to higher growth in those sectors. Despite significant medical progress in the last century, some segments of the population are concerned with decreases in their quality of life as related to one or more of these chronic diseases: type 2 diabetes, cardiovascular problems, cancer, and Alzheimer's. In this respect, eating habits have been singled out as one contributing factor in first world countries. As a consequence, a return to healthy nutrition represents a desirable strategy in the prevention of such diseases. With regards to nutritional products, dietary supplements and vitaminic formulations as well as personal care products represent what is known as the natural health products (NHP) market. The latter has seen remarkable growth in developed countries, and Canada is no exception. A sizeable number of businesses are involved in the production of nutraceuticals, dermo-cosmetics, homeopatics, not to mention the raw materials from which various NHP's are produced[ii]. Results of recent surveys have shown that consumers do indeed favor the use of NHP's as a tool in managing their own health. For instance, a certain percentage of the population willfully substitutes conventional synthetic medications with "natural" formulations.

Based on significant advances in screening techniques for bioactive compounds in the last decade, researchers are currently well positioned to identify and pursue novel biological properties of forest plants and trees. A number of known traditional uses for medicinal plants by First Nations and native groups also represent a readily available dataset for screening and validating potential benefits of Canadian forest species.

The boreal forest - a wide band of softwood and hardwood species - is the main vegetation domain in Canada. Approximately 850 different plant species have been identified on the Québec territory alone, on top of twenty or so wood species. This biodiversity is now viewed as an important reservoir of new therapeutic agents, not to mention cosmetic and agrifood additives as well. A single plant species may harbor more than a hundred different secondary metabolites of various chemical structures; representing a wealth of bioactive extracts and purified molecules. Still, according to some estimates less than 10 % of those plant species have been adequately screened during phytochemical studies.

A key step in the upgrading of plant or forestry residues is the efficient and controlled extraction of the aforementioned secondary metabolites. The main stakeholders in the forestry industry must look at the future with a different view with regards to available co-products. Extractives can be manufactured without any significant reduction in the current uses of those residues – namely energy applications – and clearly represent added value in conversion processes. This value is tied to high margin markets such as cosmeceuticals or cosmetics, pharmaceuticals, human and animal nutraceuticals. For instance, Taxol® remains a success case for a natural product used in contemporary pharmacopeia (Blay, Thibault, Thiberge, Kiecken, Lebrun, & Mercure, 1993). This anticancer agent, first identified in the bark of the Pacific Yew (*Taxus brevifolia*) is also found in most of the yew species including *Taxus canadensis*.

It is therefore imperative to intensify research focusing on the identification of extracts and their bioactive molecules, as this will lead to new markets for industrialists in the forestry sector.

### *1.2 Forest Zones within the QuébecTerritory*

As part of a total land area of 1.7 million km2, Québec's forests cover roughly 761 100 $km^2$, or nearly half of the territory. Citizens of this province are the collective owners of approximately 92 % of the whole territory, with more than half of the latter being forested areas of commercial value. Three main zones are found, created through bioclimatic variations (Figure 1)

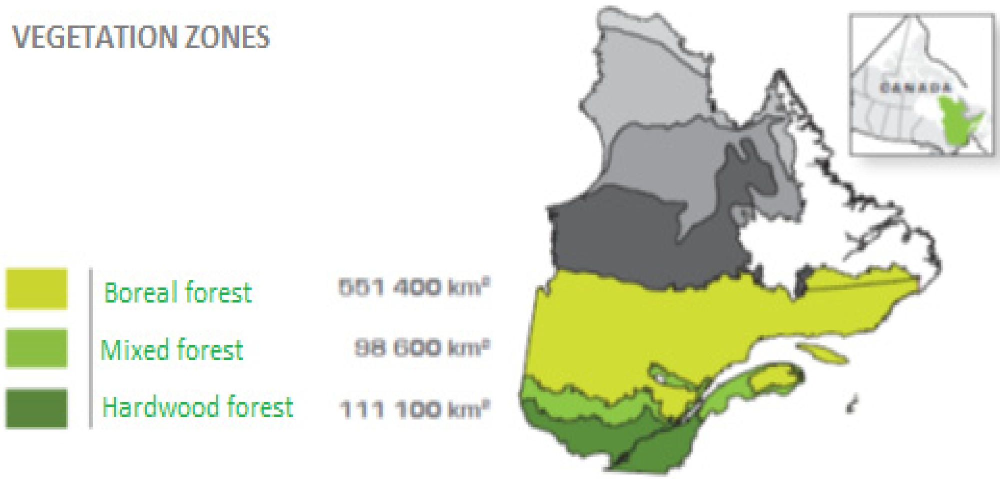


Figure 1. Québec's main distinct vegetation zones[iii]

The equilibrium between vegetation and climate is the main criterion for distinguishing between the actual zones. The boreal forest covers more than 70 % of the overall forested areas of Québec, or roughly 560 000 km$^2$ (Figure 1). Within this zone, one finds mostly evergreen or resinous species, such as black spruce which makes up 80 % of the population; other species include balsam fir, tamarack larch and grey pine. Since this forest extends approximately from the 48th to the 52nd parallel, compositional differences are to be expected. For instance, balsam fir is dominant in the southern part and is found alongside white spruce and white birch. This latter sub-zone is commonly known as «la sapinière à bouleau blanc» or white birch-fir bioclimatic domain. In certain areas - in the southwest essentially - the simultaneous presence of hardwoods such as grey birch, balsam poplar and trembling aspen creates a mixed mosaic. Further north becomes the domain of black spruce (*Picea mariana*), a North American indigenous species (Coulombe, 2004). This type of forest is termed «pessière», and forms dense, nearly pure stands up to the 52nd parallel. Beyond this limit – from the 52nd up to the 55th parallels – densities decrease and eventually one encounters the taïga, mainly composed of black spruce and lichens. Factors such as distances and concurrent high costs preclude feasible commercial forestry operations in that region.

The hardwood and mixed forest zone is found in the southern part of the province. This transition zone between boreal and hardwood forests is defined as "mixed". It has been shown to cover roughly 11.5% of the Québec territory (Gauthier & Saucier, 1999) and is composed of a rich variety of high-value hardwood and softwood species. Three domains are seen from the south upwards, with sugar maple as the dominant species (Gagnon, 2004) and featuring respectively bitternut hickory, linden and yellow birch. The latter domain represents a high commercial value.The maple- bitternut hickory bioclimatic domain is populated by species such as the American beech, (*Fagus grandifolia*), butternut (*Juglans cinerea*), elm, hickories (*Carya cordiformis* and *Carya ovata*), oak, basswoods, ashes (several species) and ironwood (*Ostrya virginana*)[iv] (Rousseau, 1962). A number of conifers are also found in that forest, such as hemlocks or sometimes Eastern white pine. The bioclimatic domain of the maple and hickory forest is spread over the richest soil of the province. The domain of maple with basswood is predominantly composed of sugar maple accompanied by other hardwood species such as basswood, beech, ironwood, and white ash (*Fraxinus americana*). At the more humid sites, elms (especially white elm), walnuts, black ash (*Fraxinus nigra*), balsam fir and eastern white cedar can be found, whereas yellow birch and Eastern hemlock prefer the cooler zones which are situated around the upper part of the slopes (Prévost, Roy, & Raymond, 2003). Finally, red oak and pines are found in drier, acidic soils. The sugar maple-yellow birch bioclimatic domain covers the northern half of the territory which is characterized by the abundance of sugar maple. This domain features variable densities of yellow birch, white (or paper) birch and tamarack, depending on soil quality. The species characteristic to those domains are listed in Table 1.

Table 1. Forest species corresponding to the various vegetation zones and sub-zones in Québec

| Zone | Sub-zone | Tree species |
|---|---|---|
| Temperate nordic | Decidual forest | Sugar maple<br>Yellow birch<br>Linden<br>Bitternut hickory |
| | Mixed forest | Yellow birch<br>Balsam fir<br>White spruce |
| Boreal | Boreal forest | Black spruce<br>Trembling aspen<br>Paper birch<br>White spruce<br>Jack pine<br>Balsam fir |
| | Taiga | Black spruce<br>Jack pine<br>Balsam fir |
| | Tundra forest | Black spruce |
| Arctic | Lower arctic | None |

*1.3 Geographical Distribution – Hardwoods vs Softwoods*

In this review paper, we essentially make use of data presented in the statistical portrait of Québec's forestry sector as published by Québec's Ministry of Natural Resources and Wildlife in January 2009 (Parent, 2009); this document provides a wide encompassing snapshot of the economic status of the forestry sector since 2007. As well it provides a precise overview which becomes useful when forecasting opportunities in terms of volumes, type of species and administrative sectors. The focus here will be on species with commercial value. The main hardwoods in this category are:

- ✓ Genus *Acer*: sugar maple (*Acer saccharum*) and red maple (*Acer rubrum*)
- ✓ Genus *Betula*: white birch (*Betula papyrifera*) and yellow birch (*Betula alleghaniensis*)
- ✓ Genus *Populus*: Jack's aspen (*Populus xjackii*), trembling aspen (*Populus tremuloides*), balsam poplar (*Populus balsamifera*) and eastern poplar (*Populus deltoides*)
- ✓ Genus *Fraxinus*: American ash (*Fraxinus americana*), and Pennsylvania ash (*Fraxinus pennsylvanica*)
- ✓ Genus *Ulmus*: American elm (*Ulmus americana*)
- ✓ Genus *Tilia*: American basswood (*Tillia americanaL.*)
- ✓ Genus *Juglans*: black walnut (*Juglans nigra*)
- ✓ Genus *Carya*: bitternut hickory (*Carya cordiformis*)

The Québec forest is divided into zones[v]each covering several administrative sectors (Table 2). Following steps taken by authorities while reviewing the forest management program, the territory now comprises 74 forest planning units and a northern limit for the allocation of the commercial resource[vi].

For each of those units, the ministry determines an annual capacity for sustainable development and those data provide the guidance for resource allocation. Moreover, the ministry defines various objectives for protection and valorization that may be implemented.

Setting borders for those units[vii]ensures that the resource potential is maximized, based on the targeted region and forestry zone.

Estimates of annual forest biomass production that takes place on public and private lands are in the order of 6 million dry metric tons (dmt)[viii]. Within commercial operations, residues range from stumps and crowns to branches and stems. Primary transformation generates residues such as barks, sawdust, chips and shavings. Secondary transformation yields residues that include chips, shavings, sawdust, pieces of panels, and sanding dust.

Table 2. Division of the Québec forest into administrative sectors

| Forestry zone or MRNF region | *Admininistrative sector* |
|---|---|
| 01: Lower St-Lawrence (boreal zone) | *01: Lower St-Lawrence* |
| 02: Saguenay-Lac-St-Jean (boreal zone) | *02: Saguenay-Lac-St-Jean* |
| 03: National Capital - Chaudière | *03: National Capital* |
| 04: Appalaches- Eastern Townships | *05: Eastern Townships* |
| | *12: Chaudière Appalaches* |
| 05: Mauricie-Central Québec | *04: Mauricie* |
| | *17: Central Québec* |
| 06: Laval-Lanaudière-Laurentians | *06: Montréal* |
| | *13: Laval* |
| | *14: Lanaudière* |
| | *15: Laurentians* |
| | *16: Montérégie* |
| 07: Outaouais | *07: Outaouais* |
| 08: Abitibi-Témiscamingue | *08: Abitibi-Témiscamingue* |
| 09: North Shore | *09: North Shore* |
| 10: Northern Québec (boreal zone) | *10: Northern Québec* |
| 11: Gaspésie-Magdalen Islands | *11: Gaspésie-Magdalen Islands* |

What is designated as biomass includes all those types of residues which contain organic matter, for instance industrial, urban and agricultural wastes, forestry residues and wastes from energy crops such as sugarcane and maize. Biomass used for energy purposes in Québecoriginates mostly from forestry operations such as sawmills and pulp mills. Indeed, the use of forest biomass offers several undeniable advantages: easily set logistics between sawmills and cogeneration units, predictable volumes and quality, materials ready for combustion without pre-processing, an efficient caloric source, and minimal power expenditures during harvesting (Desrochers, 2009). The main benefit of using forest biomass remains the fact that, from an energy source standpoint, wood possesses a neutral carbon cycle. Wood combustion releases a volume of carbon or greenhouse gas that is identical to the amount emanating from the natural decomposition of a similar volume of deadwood in a forest[ix].

In a context where prices of fossil fuels and of electricity are forecast to increase, residual forest biomass thus becomes an option likely to contribute to reducing energy-related costs.

### *1.4 Extraction of Biomolecules, a Logical Step Prior to the Combustion of Residual Forest Biomass to Produce Energy*

By promoting the substitution of fossil fuels with residual forest biomass, it may be possible to reduce greenhouse gas emissions, an objective in direct concordance with Canadian targets within the Kyoto protocol. Nevertheless, combustion is not part of the principles behind sustainable development. Agricultural residues on the other hand are less attractive because of lower availability and a rather high content of silica/alkaline metals (Fortin, 2008; Douville et al., 2006). Extraction of forest residues can thus be regarded as the initial step in the biorefinery concept as applied to wood transformation.

Combustion basically consists of burning solid biomass to generate energy as heat or electricity. Two methods are currently used by industries active in primary wood transformation in Québec: (i) direct combustion which generates heat (for buildings, water, industrial processes) and (ii) cogeneration which produces heat + electricity. The latter method represents roughly 9-10% of Québec's energy production. Currently, the rate for utilization of primary woody residues (bark, sawdust and shavings) for energy purposes is practically 100 % (Gagné, 2007). Closings of numerous sawmills have been reported to cause an undersupply in certain areas, and available volumes have significantly decreased since 2004 (Table 3). The high demand for those by-products has been ascribed to an increased usage rate by various industries which generate added value: for instance, panel manufacturers, granule and briquette makers (high export ratio in 2010), animal bedding producers, users of biomass-fired dryers and finally cogeneration units. Within the wider context of biorefining, forest biomass has prompted numerous integrated research projects: gasification, methanization, nanocellulose production from dissolving pulp, as well as opportunities with industrial lignins from kraft pulp. Those avenues have led to the development of proven technologies for biogas and biofuels, not to mention novel materials containing bio-polymers. The beneficial environmental impact of those technological initiatives is significant, in Canada and in the EEC[x].

Table 3. Co-products from Québec sawmills in 2004-2008 (dmt) (Parent, 2009)

| | 2004 | 2005 | 2006 | 2007 | 2008 |
|---|---|---|---|---|---|
| Chips | 7449 | 7237 | 6502 | 5559 | 5282 |
| Sawdust and shavings | 2119 | 2077 | 1856 | 1578 | 1309 |
| Barks | 2901 | 2750 | 2465 | 2125 | 1772 |
| *Total* | *12469* | *12064* | *10823* | *9263* | *8363* |

Currently, few practical and cost-effective technologies allow for the value-added processing of bark aside from energy production. In this respect, we have previously confirmed that such residues represent attractive sources of bioactive molecules. Indeed, bark generally contains sizeable quantities of extractives (under high yielding extraction conditions), a number of which do possess unique biological and therapeutic properties (Pichette, et al., 2008). Bark contains – among other compounds – polyphenols which represent a class of extractives with beneficial activities such as antioxidant, anticancer, bactericidal, fungicidal, antispasmodic, sedative, analgesic and anti-inflammatory (Cloutier, Blanchet, Koubaa, & Stevanovic, 2008). There is a notable lack of exhaustive studies on the precise biochemical composition of extracts from barks and other forestry residues from species on the Québec territory; this extends to the systematic characterization of biological activities in such extracts. Despite the current situation, worldwide progress on the biopotential of various classes of natural compounds underscores the significant level of interest towards such technologies in the areas of human and animal nutrition, pharmaceuticals and cosmeceuticals, those markets featuring increasingly high demand for nature-derived ingredients.

Within the primary transformation industry, the feasibility of developing this strong potential of bark extractives must be carefully examined in light of modifications required to existing in-house processes. Namely, a simple and rapid extraction step prior to shipping bark to cogeneration centers allows for the recoveryof the desired molecules of interest.

*1.5 The Importance of Extractives in the Development of Novel Non-wood Forest Products (NWFP)*

The term "Extractives" comprises a series of biochemical compounds of low molecular weights, found in the porous structure of wood. Easily extracted using mild organic or aqueous solvents, theprocess conditions thus differ from conditions necessary for solubilization of structural wood constituents, e.g. cellulose, hemicelluloses, and lignins. Most extractives are in fact secondary metabolites, that ismolecules not essential to the growth and survival of trees as opposed to primary metabolites. Most extractives are located in the cell lumen – hollow spaces between cells – or within the pores in cell wall structures. A number of extractives are part of a class known as exudates, produced by specialized resiniferous channels in softwoods or by oil cells in some hardwoods (Lauraceae).

Among the various wood species, chemical structures vary little for the three main structural components: cellulose, hemicelluloses and lignins (Hon & Shiraishi, 2001). On the contrary, with regards to molecules present in extractives, strong compositional differences are noted between species. For instance, the yield of a crude extractive may vary anywhere between 2 to over 20%, along with itscompositional profile which is dependent on several factors including: tree species, type of tissue extracted, geographical harvest site, genetics, harvest time... The molecules belonging to extractives are responsible for several wood characteristics such as color (Hon & Shiraishi, 2001; Gierlinger et al., 2004; Aloui, Ayadi, Charrier, & Charrier, 2004), odor, hygroscopic properties (Krutul, 1992), inherent durability (Aloui, Ayadi, Charrier, & Charrier, 2004; Barbosa, Nascimento, & Morais, 2007), other physical and mechanical properties such as dimensional stability (Royer et al., 2010), and acoustical properties (Minato & Sakai, 1997). Additionally, extractives play a role in the quality of wood pulp and the capacity of a type of wood towards glue adhesion (Nussbaum & Sterley, 2002). Wood extracts have been used for centuries as natural remedies because of their unique biological activities (Arnason, Hebda, & Johns, 1981).

#### 1.5.1 Main Classes of Extractives

It is now understood that the molecules present in extractives are specific to each type of tree and despite their low concentration in tissues relative to the three structural polymers, they are responsible for variations in several properties both inter- and intra-species, not to mention among tissues within each species (for instance, radial concentration gradients between bark-sapwood-heartwood) (Mosedale, Feuillat, Baumes, Dupouey, & Puech, 1998; Sjöström & Alén, 1999; Lacandula, 2002). Different families, genera and species harbor characteristic types of extractives. Some of the molecules present in those effectively act as chemotaxons, or markers unique to the family, genus or species. Those chemotaxons allow for the precise identification of plant material (so-called "chemical signatures"). For example, the *Cupressaceae* family is the sole source of tropolones, a group of terpenic derivatives with 7 carbon unsaturated rings, including thujaplicins found in thuja heartwood (Stevanovic & Perrin, 2009). The actual diversity of molecular structures is the basis for their classification into several families (Stevanovic & Perrin, 2009).

Terpenoids (including tropolones), waxes and fats exhibit low polarity and a higher lipophilic character. Compounds with higher polarity including polyphenols (benzenic molecules with several phenolic hydroxyl groups), salts of organic acids, complex carbohydrates and nitrogenous compounds (proteins, alkaloïds) are extractable using polar solvents, with the intrinsic limitation of no single "green" solvent being 100 % specific to a single family of compounds. Most extracts can thus be defined as complex mixtures, which call for advanced separation and fractionation steps in order to achieve high levels of purity of each individual compound for required structural analysis.

Extracts from woods and barks show complex profiles, and their composition is dependent both on the solvent used and the particular extraction conditions (Royer, 2008; Diouf, Stevanovic, & Boutin, 2009). Extractives from woody tissues differ from those obtained from bark. This review will focus mostly on the bark tissue, the most abundant residue from forestry operations. Two classes of extractives have attracted much interest: terpenes and polyphenols. Indeed, those two not only make up the major proportion of constituents in extractives available from Eastern Canadian species, but also offer significant practical opportunities when targeted to such sectors as pharma, nutraceuticals and cosmetics because of their unique physico-chemical and biological properties. The following sections will focus on terpenoids, and polyphenols will be described afterwards.

#### 1.5.2 Terpenes and Terpenoïds

Terpenes represent a wide group of natural hydrocarbon compounds, with as general structure a series of repeating isoprenic units ("IP" or $C_5$). Terpenes include: (i) monoterpenes ($C_{10}$= 2 IP units), (ii) sesquiterpenes ($C_{15}$ = 3 IP units), (iii) diterpenes ($C_{20}$= 4 IP units) including their acidic derivatives as major constituents of resins, (iv) sesterpenes ($C_{25}$= 5 IP units), (v) triterpenes ($C_{30}$= 6 IP units) of varying structures and omnipresent in vascular plants, (vi) tetraterpenic carotenoïds ($C_{40}$= 8 IP units) abundant in our food intake, and finally (vii) polyterpenes (over 8 IP units) that are found in latexes and gutta-percha. The only naturally occurring hemiterpene (C-5) is isoprene *per se*. The term "terpenoids" is used to describe the oxygenated derivatives of those hydrocarbons. The complex chemistry of terpenic compounds includes terpenes, tropolones, sterols and taxanes.

Often implicated in a tree's resistance to disease and microbial attack, their concentration increases following intrusions by predators or parasitic organisms. This phenomenon forms the basis for ecological interactions of forest trees. High concentrations of terpenoids exhibit toxic effects and play a protective role against pathogens and herbivorous animals. Some of those compounds such as volatile monoterpenes are involved in chemo-recognition, act as attractants or deterrents, and often determine the particular "bouquet" of plant material. Along with sesquiterpenes, they form the main constituents of essential oils and of oleoresins volatile fractions.

The vast majority of terpenes exhibit some type of bioactivity, and thus possess therapeutic applications. For instance, several studies have demonstrated the strong potential of triterpenes and of related compounds which make up the aglycon moiety of saponins (Patočka, 2003). Growing interest towards this class of compounds comes mainly from their wide activity spectrum and their related potential applications as preventative agents in human health (Paduch, Kandefer-Szerszen, Trytek, & Fiedurek, 2007). Numerous studies have attributed the following properties to terpenes: antimicrobial (Trombetta et al., 2005; Inouye, Takizawa, & Yamaguchi, 2001), fungicidal (Hammer, Carson, & Riley, 2003), antiviral (Özçelik, Gürbüz, Karaoglu, & Yesilada, 2009), anti-inflammatory (Raju & Sanjay, 2009), cytotoxic (Sivropoulou, Papanikolaou, Nikolaou, Kokkini, Lanaras, & Arsenakis, 1996), anticancer (Gould, 1997; Bowen & Ali, 2007) etc.

1.5.3 Common Applications of Terpenes

Among known applications of this class of compounds, the following are notable: (i) natural rubber is composed of polyterpenes from the latex secretion of *Hevea brasiliensis*; (ii) gem, a mixture of terpenic acids (derived from diterpenes) and volatile monoterpenes, is extracted from pine species, for instance from the maritime pine (*Pinus pinaster*) and was processed in past years to produce turpentine (a volatile fraction with high mono- and sesquiterpenes)and colophony (solid fraction rich in resin acids) that are used as specialty chemicals; (iii) tall oils and turpentine are now available as by-products from kraft pulping, and find uses in solvents, adhesives, polymers, emulsifiers, coatings and modifiers in papermaking; (iv) frankincense, a type of oleoresin from brush species of the *Boswellia* genus (Burseracea family) and myrrh, an exsudate from *Commiphora myrrha* (Burseraceae), both being complex mixtures of polysaccharides and resinous matter composed of sesquiterpenes and triterpenes; (v) amber, a fossilized coniferous resin composed of non-volatile terpenes (diterpenes and higher) and subjected to oxidative polymerization which offers protection from microbial and chemical activity over the years.Essential oils contain mainly monoterpenes, sesquiterpenes and their derivatives, and have been used as key components in perfumes and aromas for centuries; much interest has also arisen from their therapeutic virtues. For instance, wood species that are sources of terpene-based aromatic oils include: (i) camphorwood (*Cinnamomum camphora*, family Lauraceae) of which the essential oil contains mostly camphor, a ketonic monoterpenic derivative; (ii) rosewood (*Aniba duckei,* family Lauraceae) a source of linalool, an alcoholic derivative from a non-cyclic monoterpene; (iii) sandalwood (*Santalum album*, family Santalaceae) which yields santalol, a sesquiterpene-based alcohol derivative.

Terpene extractives have proven their intrinsic value in pharmaceutical science. A key example remains paclitaxel (a diterpene derivative) which is extracted from needles or bark of either the pacific yew (*Taxus brevifolia*) or the Canadian yew (*Taxus canadensis*) and exhibits a well-documented anticancer activity (Witherup, Look, Stasko, Ghiorzi, Muschik, & Cragg, 1990). This compound is marketed under the name Taxol and the molecule is part of the taxans family (complex compounds with structure containing a diterpene). Jubavione is another example, a lipophilic sesquiterpenic extractive from balsam fir (*Abies balsamea*) which acts as juvenile hormone inhibitor in coleopterae (Williams, 1970). The anticancer bioactivities of thetriterpeneslupeol, betulin and betulinic acid, extractable from the bark of white and yellow birches, have also been recognized (Pichette, Legault, & Gauthier, 2008; Krasutsky, 2006).

Currently, there is a critical need for further research and phytochemical analytical work, starting with the main species on the Québec provincial territory. Such an undertaking will allow for the collection and integration of key data leading to product development and novel applications on high-return markets such as pharma and nutraceuticals. Indeed, there remains a treasure trove of bioactive natural principles yet to be discovered from forest extractives (Stevanovic & Perrin, 2009).

1.5.4 Polyphenols: Structures and Properties

Compounds found in the polyphenol group present a wide variety of structures, featuring as their basic element a benzenic nucleus to which are directly attached one or more hydroxyl group(s), either free or linked to specific chemical functions (ether, ester, as aglycon in glycosidic structures, etc.). Over 8000 natural compounds corresponding to those criteria have been isolated and identified (Triaud, 1998). Being grouped into several families (coumarins, lignans, stilbenes, flavonoïds, phenolic acids, tannins, xanthones, quinones etc.), these molecules range from monomers to polymers and include various types of complexes (Table 4). Such a wide variety of structures explains for the most part the impressive range of physico-chemical and biological activities recorded and which comes from their significant chemical reactivity: namely, easily created bonds with other molecules and their capacity to complex mineral cations such as iron and copper. Another key factor with regards to their biopotential is their ability to interact with cellular proteins; in fact, polyphenols can function as activators or inhibitors of numerous cellular enzymes.

Polyphenolic compounds are found in various woody tissues, and in higher concentration in wood and bark.

They are known to play a definite role in the inherent natural durability of certain species, because of synergies created among their various properties (Royer, 2008; Aloui, Ayadi, Charrier, & Charrier, 2004), for instance their ability to scavenge free radicals (strong antioxidant activity), to block enzymatic processes, and to stop fungal growth (Schultz & Darrel, 2000; Schultz & Nicholas, 2002). In particular, the role of stilbenes has been elucidated through several studies, especially with oxyresveratrol. Some of those stilbenes are in essence phytoalexins, produced in high concentrations by a plant as response to pathogenic invasion (Hart, 1981; Woodward & Pearce, 1988). Studies have demonstrated that polyphenols (phenolic acids, condensed tannins, quinones and flavonoids) are responsible for wood coloration because of their chromophoric groups, absorbing light in the visible region of the spectrum (Dellus, Mila, Scalbert, Menard, Michon, & Herve du Penhoat, 1997; Johansson, Saddler, & Beatson, 2000).

Table 4. Main classes of polyphenols

| Class | Sub-class | Typical examples |
|---|---|---|
| Benzoic acids | | Salicylic acid |
| Cinnamic acids | | Ferulic acid, caffeic acid |
| Coumarins | | Aesculetin |
| Flavonoïds | Flavons | Luteolin, apigenin |
| | Isoflavons | Daidzein, genistein |
| | Flavonols | Quercetin, kaempferol |
| | Flavanonols | Dihydroquercetin |
| | Flavanons | Hesperitin, naringenin |
| | Flavan-3-ols | Catechins |
| | Chalcons | Phloridzin, arbutin |
| | Dihydrochalcons | |
| | Anthocyanidins | Cyanidin, delphinidin |
| | Anthocyanins | Glycosids anthocyanidins |
| Tannins | Condensed tannins | Proanthocyanidins, anthocyanidins oligomers |
| | Hydrolysable tannins | Gallotannins, ellagitannins |
| Lignins | | High moleular weight biopolymer based on phenylpropanoids units. |

A number of polyphenols of interest mentioned in the current review are found in forestry extractives and are derived from the same biosynthetic phenylpropanoid pathway as lignins (Stevanovic & Perrin, 2009). Much attention has been devoted to polyphenols in the last 10 years or so, on the part of nutritionists, the agri-food industry and consumers (Stevanovic, Diouf, & Garcia-Perez, 2009). These compounds are responsible for browning reactions, and are implicated in the astringency and bitterness of certain foods. As aromatic and colorful molecules, they play a major role in the organoleptic characteristics of numerous products and also contribute antiseptic, antibacterial and fungicidal properties (Amarowicz, Dykes, & Pegg, 2008; Aslam, Stevenson, Kokubun, & Hall, 2006; Bafi-Yebo, Arnason, Baker, & Smith, 2005; Fukai, Kaitou, & Terada, 2005). They also represent the most abundant antioxidants in our food, with an average daily intake around 1 g which is nearly 10 fold and 100 fold our intake of Vitamin C and of Vitamin E or carotenoidsrespectively. They also have a positive incidence on product preservation be it in cosmetics (Arct & Pytkowska, 2008), foods or pharmaceuticals. Their free-radical scavenging properties coupled with their antioxidant and anti-inflammatory activities are linked to the prevention of certain diseases that implicate oxidative stress and cellular ageing, cardiovascular and degenerative conditions: osteoporosis, cancer, arthritis and type II diabetes (Federico, Morgillo, Tuccillo, Ciardiello, & Loguercio, 2007; Ammar et al., 2009; Atmani et al., 2009; Goetz, 2007; Halliwell, 1996). Within the food industry, the inclusion of natural antioxidant additives is a relatively recent trend. Since the 80's, natural antioxidants have been proposed as alternatives to conventional synthetic ones, as the latter's safety is being questioned both in human and in animal nutrition (Moure et al., 2001). This trend is likely irreversible: consumers now clearly discriminate in favor of natural additives.

#### 1.5.5 Current Health Applications of Polyphenols

Polyphenols make up the active principles in a number of medications. Salicylic acid is the main raw material in the manufacture of aspirin, while rutoside (rutin) which forms the glycosidic moiety of the flavonoïd quercetin (quercetin -3-rutinoside found in several plants - eucalyptus, buckwheat, sophora) is used in the treatment of veinous and capillary weakness. Ginkgo extract (*Ginkgo biloba*) contains the active principle EGb 761 which is high in polyphenols, notably flavonol glycosides (up to 24 % of the extract). In cosmetology, procyanidin oligomers (OPC) isolated from grapeseeds have been widely used to help combat skin ageing and to protect against UV radiations. In agri-food processing, currently used additives include rosemary extracts, tocopherols from vegetable oil processing, and anthocyanins from red cabbage or grape skin; the latter are put to use both for their coloring power and for their free radical-scavenging capacity. Another application in processed foods is as aroma modifiers because of their bitter, astringent or sweet reactions (oak tannins, vanillin, anisaldehyde…). In a totally different context, tannins have been successfully used for centuries in the production of fabric dyes and for tanning hides. The application of condensed tannins as components of wood adhesives is another example of the use of polymeric proanthocyanidins from bark and wood from different species (Stevanovic & Perrin, 2009).

The above examples are but a fraction of the wide applications of polyphenols, and confirm the highly versatile nature of those compounds omnipresent in our daily lives as complexes, extracts, or purified isolates. Their benefits range from curative activity, flavor and color modulating, protection of unsaturated lipids, and others. The significant volumes of some of those compounds present in forest residues, along with their timely extraction and processing will lead to a broad range of value-added natural products, in line with the demand from industrial and consumer markets for bioactive, proven and cost-effective compounds.

## 2. Current Awareness of Forest Extractives

### *2.1 Commercial Hardwood Species*

A literature review focusing on the most important commercial species (Table 5) yields a detailed portrait of their individual potentials.

Table 5. List of hardwood genera described in the current review

| Species | Botanical terminology (Genus) |
|---|---|
| Maple | *Acer* |
| Birch | *Betula* |
| Poplar | *Populus* |
| Oak | *Quercus* |
| Ash | *Fraxinus* |
| Elm | *Ulmus* |
| Limetree | *Tilia* |
| Butternut | *Juglans* |
| Hickory | *Carya* |

### *2.2 Maple: Genus Acer*

#### 2.2.1 The Various Species in Canada

Maples are part of the *Aceraceae* family. Fourteen species are found in Canada:

- ✓ Mountain maple (*Acer spicatum* L.)
- ✓ Manitoba maple (*Acer negundo* L.)
- ✓ Bigleaf maple (*Acer macrophyllum* L.)
- ✓ Sugar maple (*Acer saccharum* L.)

- ✓ Silver maple (*Acer saccharinum* L.)
- ✓ Western mountain maple, Vine maple (*Acer circinatum* L.)
- ✓ Norway maple (*Acer platanoides* L.)
- ✓ Striped maple (*Acer pensylvanicum* L.)
- ✓ Ginnala maple, Amur maple (*Acer ginnala* Maxim.)
- ✓ Douglas maple (*Acer glabrum* Torr.*var. douglasii* (Hook) Dippel)
- ✓ Black maple (*Acer nigrum* L.)
- ✓ Japanese maple (*Acer palmatum* Thunb.)
- ✓ Red maple (*Acer rubrum* L.)
- ✓ Scottish maple (*Acer pseudoplatanus* L.)

Most are indigenous to Canada, but others were introduced and are now fully naturalized (Norway, Ginnala, Japanese, Scottish). Five are found only in the eastern regions (sugar, red, black, silver and striped), three in British Columbia (broadleaf, western mountain, Douglas') and another (Manitoba) mainly in Saskatchewan and Manitoba. The dominant species from a commercial standpoint is the sugar maple, because of the particular hardness of its wood. Still, other maple species find particular uses as well, notably the red and silver maples.

#### 2.2.2 Current Uses of Maple by Québec's Forest Industries

##### 2.2.2.1 Sugar Maple (*Acer saccharum*)

Found in maple groves in Québec's deciduous forests (temperate nordic zone), this tree is highly popular for its unique syrup, its renowned wood quality as well as for its superb fall colors. Also called hard maple, one will find it in many parts of Ontario as well. The sugar maple is an important commercial hardwood, sought for its wood qualities such as hardness, density and pale color. Those qualities have spawned many uses: furniture, flooring, agricultural tools, siding, blocks and other products, not to mention general construction applications. The species also represents a valuable combustible material, because of its high calorific yield and rather slow combustion.

##### 2.2.2.2 Red Maple (*Acer rubrum*)

Also known as the Canada maple, red maple grows mainly in the Acadian peninsula, the Great Lakes area, the St-Lawrence valley and in parts of the Newfoundland boreal forest. Of average height, it can reach 15 to 30 meters (at times over 40 m), diameters from 0.5 to 2 m, and a lifespan from 100 to 200 years - sometimes more. The forest industry considers red maple as an average quality wood, below sugar maple, more difficult to work and more likely to warp during post-mechanical treatment drying. Nevertheless it finds uses in furniture making, wooden pallets, and in pulp manufacturing.

##### 2.2.2.3 Silver Maple (*Acer saccharinum*)

Reaching as high as 30 m, this species is found along the Ottawa and Richelieu rivers, and along the St-Lawrence up to Lac St-Pierre as well as in parts of the Northeastern USA. Often planted in urban areas, its wood is rather soft, very white, with a fine grain; uses include floor planks, furniture, and mechanical parts for pianos. Certain types of plywood may contain selected silver maple cuts.

#### 2.2.3 Traditional Uses of Extracts from the Genus *Acer*

A study by Arnason (1981) illustrates the wide range of traditional uses for the Canadian species (Arnason, Hebda, & Johns, 1981). Table 6 lists the data from that author on the genus *Acer*.

The main traditional use that stands out remains the production of sugar from the sap. As well, foodstuffs were produced by using the inner bark, which suggests a low toxicity level for any compound present in that tissue (Kunkel, 1984). Apparently, powdered inner bark was favored as thickening agent in soups and was also mixed with grains during breadmaking. Besides such food applications, red maple recently was included in the list of Québec medicinal vascular plants established as part of a master thesis (Léger, 2008). Other sources indicate that Ojibways used red maple bark for its properties as dewormer, tonic, and as a treatment for sore eyes (Krochmal, Walters, & Doughty, 1969; Wren, 1975). Bark infusion helped to cure cramps and dysentery (Moerman, 1998).

#### 2.2.4 Maple Extractives and Their Biological Properties

A very limited number of studies reported on the composition of bark extracts from Canadian members of the *Acer* genus. This lack of data also applies to any biological effects of those extracts, in stark contrast to exotic species such as the Japanese *Acer nikoense*, for which numerous reports are available (Table 7) (Iizuka, Nagumo, Yotsumoto, Moriyama, & Nagai, 2007; Sato, Goto, Nanjo, Kawai, & Murata, 2000; Morikawa T. , Tao, Ueda, Matsuda, & Yoshikawa, 2003; Akihisa et al., 2006; Morikawa, Tao, Toguchida, Matsuda, & Yoshikawa, 2003; Akazawa, Akihisa, Taguchi, Banno, Yoneima, & Yasukawa, 2006; Morikawa, 2007; Nitta et al., 1999; Satoh, Anzai, & Sakagami, 1998; Sakagami, Anzai, Goto, & Takeda, 1997).

Table 6. Examples of uses of maple species by native populations (Arnason, Hebda, & Johns, 1981)

| Species | First Nation group | Type of use | References |
|---|---|---|---|
| Black maple | Ojibway | Sugar production from sap | Reagan 1929 |
| Red maple | Iroquois | Dried bark, ground and blended with flour for breakmaking | Waugh 1916 |
| | Algonquin | Sugar production from sap | Black 1980 |
| | Abenaki | Sugar production from sap | Rousseau 1947 |
| Silver maple | Iroquois | Dried bark, ground and blended with flour for breakmaking | Waugh 1916 |
| | | Sugar production from sap | |
| | Ojibway | Sugar production from sap | Gilmore 1933 and Reagan 1928 |
| Sugar maple | Ojibway<br>Iroquois<br>Algonquin<br>Micmac and Malecite | Sugar production from sap | Rousseau 1945, Smith 1932, Densmore 1928, Gilmore 1933, Reagan 1928, Hoffman 1891, Black 1980. |

Table 7. Extracts from the Japanese maple: examples of bioactivities

| Genus Acer | Tissue evaluated | *Biological activities* |
|---|---|---|
| Nikoense | Wood | *Vasorelaxant* |
| Nikoense | Wood | *Antifungal* |
| Nikoense | Branch bark | *Anti-allergenic* |
| Nikoense | Branch bark | *Anti-inflammatory*<br>*Antitumoral* |
| Nikoense | Branch bark | *Anti-inflammatory* |
| Nikoense | Bark | *Anti-pigmentary (skin spots)*<br>*Antiradical* |
| Nikoense | Bark | *Anti-inflammatory*<br>*Anti-allergenic* |
| Nikoense | Bark | *Antitumoral*<br>*Anti-leucemic* |
| Nikoense | Bark | *Antiradical*<br>*Activation of ascorbate-mediated apoptosis* |
| Nikoense | Bark | *Improvement of ascorbate cytotoxicity* |
| Nikoense | Branch<br>Leaves | *Anti-inflammatory* |
| Nikoense | Wood<br>Bark<br>Twigs<br>Leaves | *Anticancer*<br>*Antitumoral* |
| Nikoense | Bark | *Osteoprotection* |

This reaffirms the need for systematic phytochemistry work in Canada in this field. Our literature search pointed to a few studies dealing in particular with leaves, and compounds responsible for their toxic or deterrent properties towards certain insects or mammals. A series of polyphenolic compounds were isolated from red maple leaves (gallic acid, methyl gallate, ethyl gallate and derivatives, 1-*O*-galloyl-*β*-D-glucose and 1-*O*-galloyl-*α*-L-rhamnose, glycosylated derivatives of kaempferol and quercetin, (-)-epicatechin, (+)-catechin and ellagic acid) and were shown to play a role in this species' resistance towards the larvae of the forest tent caterpillar moth (Abou-Zaid, Helson, Nozzolillo, & Arnason, 2001; Abou-Zaid & Nozzolillo, 1999). Such molecules are otherwise strong antioxidants of which the activities are now better understood. Other research teams successfully demonstrated the deterrent or toxic properties of maple leaves towards beavers (Müller-Schwarze, Schulte, Sun, Müller-Schwarze, & Müller-Schwarze, 1994) (*Acer rubrum*) or horses (Boyer, Breeden, & Brown, 2002); in the latter case an increase in methaemoglobin was ascribed to polyphenolics present in *Acersaccharinum* and *Acerrubrum* leaves. Besides North American maple sap and syrup, the antitumoral activity of leaves from *Acersaccharinum* (Bailey, Asplund, & Ali, 1986) has been documented. Various extracts (leaves, bark, sap) obtained from *Acer saccharum* and *Acer rubrum* have shown an anticancer effect against colon tumor cells (González-Sarrías, Li, & Seeram, 2011). Work by Hagerman provided data on the high tannin content in leaves of *Acer saccharum* (Hagerman, 1988). Variations in phenolics concentrations in *Acer rubrum* leaves were measured as a function of environmental stress (Muller, Kalisz, & Kimmerer, 1987).

A more recent study established a series of bioactivities (antioxidant, antiradical and antimutagenic) of polyphenols from the sap and syrup of *Acer saccharum* (Thériault, Caillet, Kermasha, & Lacroix, 2006) and also pointed out seasonal variations in activity. An investigation into oxidative spotting of *Acer saccharum* sapwood during storage led to the isolation of scopoletin (Miller, Sutcliffe, & Thauvette, 1990), a phenolic in the coumarin family; similar compounds have shown benefits against hyperthyroïdy, lipid peroxydation and hyperglycemia (Panda & Kar, 2006). Confirmation of the activity of maple syrup against hyperglycaemia came via the identification of the active acertannin molecule (Honma, Koyama, & Yazawa, 2010).

Two different studies established the antimicrobial and antifungal activities of extracts from both the woody tissue and bark of *Acer rubrum*, hinting at potential applications in human health (Ficker, et al., 2003; Omar, et al., 2000); those extracts inhibit several pathogenic bacterial and fungal strains responsible for infectious diseases. The same authors emphasized that the bark extracts show higher antimicrobial potency than those from the woody tissue. In parallel, antibacterial properties were revealed in extracts from the leaves of five different species: *A. platanoides, A. campestre, A. rubrum, A. saccharum* and *A. truncatum* (Wu, Wu, You, Ma, & Tian, 2010). An investigation into the pigmentation of wood from red maple identified catechin and gallic acid in the hot water extracts following acid hydrolysis (Tattar & Rich, 1973). Similar work led to the isolation of (+)-catechin and procyanidins from wood and bark, the dimer in wood and the trimer in bark respectively (Narayanan & Seshadri, 1969; Seshadri, 1973). Interestingly, this bark also contains pyrogallol, possibly from gallic acid thermal degradation during extraction, as well as 6.9% proanthocyanidins which puts it behind that of silver maple (7.8 %) in terms of high tannin content among North American species (Russell, Vanneman, & Waddey, 1942-1945). Hillis (Hillis, 1962) demonstrated the presence of hydrolyzable tannins in barks from certain maple species including *A. rubrum* (6.9%). The same bark apparently also contains suberin of unknown structure, at a concentration of 3.1% (Harun & Labosky, 1985). Finally, a number of novel compounds - gallotannins and phenolic glycosides – were recently identified in the bark of *Acer rubrum* (Yuan, Wan, Liu, & Seerama, 2012) and may be strongly implicated in some observed *α*-glucosidase inhibition by the extract. Those findings confirm the importance of pursuing further investigations into Canadian maple species.

2.2.5 Main Results from Our Research Program

The Red Maple Project which has been ongoing since 2008 in our *Laboratoire de Chimie du Bois* was initiated in order to define scientific steps leading to the development of value-added novel natural products. The targeted applications were the antioxidant benefits in the form of supplements or food additives (human and animal markets) or as actives in cosmetic productformulation. We carried out work with residual materials from red maple processing (*Acer rubrum*) in the Upper Saint-François region – bark, twigs, branches – in order to identify opportunities that would not interfere with the use of such biomass as energy source. In the course of that project, phytochemical analysis of polyphenols as well as screening of bioactivities in the extracts (antiradical, antioxidant, hypoglycemic) were performed in our laboratory.

Results indicated that trunk bark, and to a lesser extent branch bark, are potential novel antioxidant sources with significant polyphenol content. Such natural additives may find niche applications for instance in agri-food processing. Simple extractions using hot water or ethanol confirmed the possibility of adding value to bark biomass. Even more remarkable is the fact that crude*Acer rubrum* extracts, without further fractionation and cleanup, are as potent from an antioxidant standpoint as commercial standardized bark extracts from French maritime pine (*Pinus pinaster*). We thus concluded that as part of an industrial development strategy, hot water extracts are preferable since: (i) water remains the ultimate green solvent, and less expensive than ethanol; (ii) extraction yields are higher than the corresponding ethanolic extracts; (iii) there are no significant differences in antioxidant capacity between the two types of extracts (Tables 8-10) (Royer, Diouf, & Stevanovic, 2011).

Table 8. Red maple extraction yields (basis: % anhydrous raw material) (Royer, Diouf, & Stevanovic, 2011)

| Solvent | Complete branches | Wood from branches | Bark from branches | Bark | Twigs |
|---|---|---|---|---|---|
| Hot water | 14,5 | 7,2 | 23,7 | 21,2 | 16,3 |
| Ethanol | 4,4 | 2,0 | 6,8 | 12,5 | 4,7 |

* two replicates; SD ± 3%.

Table 9. Concentrations of various classes of polyphenols in hot water extracts from red maple bark (Royer, Diouf, & Stevanovic, 2011)

| | Complete branches | Wood from branches | Bark from branches | Bark | Twigs |
|---|---|---|---|---|---|
| Total phenolics [a] | 115.1 | 101.1 | 267.2 | 323.6 | 236.5 |
| Total phenolic acids [b] | 20.8 | 26.4 | 37.0 | 53.9 | 33.9 |
| Total flavonoïds [c] | 1.7 | 3.4 | 3.1 | 3.9 | 12.3 |
| Total tannins [a] | 47.0 | 36.8 | 140.2 | 194.6 | 118.7 |
| Total proanthocyanidins [d] | n.d. | n.d. | 57.6 | 110.9 | 17.9 |

Table 10. Concentrations of various classes of polyphenols in ethanolic extracts from red maple barks (Royer, Diouf, & Stevanovic, 2011)

| | Complete branches | Wood from branches | Bark from branches | Bark | Twigs |
|---|---|---|---|---|---|
| Total phenolics [a] | 196.5 | 124.8 | 232.4 | 494.3 | 188.5 |
| Total phenolic acids [b] | 2.5 | 8.2 | 28.0 | 19.8 | 0.2 |
| Total flavonoïds [c] | 1.9 | 0.5 | 0.7 | 0.6 | 0.7 |
| Total tannins [a] | 132.5 | 61.5 | 133.0 | 307.4 | 116.2 |
| Total proanthocyanidins [d] | 41.5 | 40.3 | 135.2 | 350.7 | 110.5 |

[a] as mg of tannic acid equivalent per g dry matter.

[b] as mg of chlorogenic acid equivalent per g dry matter.

[c] as mg of catechin equivalent per g dry matter.

[d] as mg of black spruce proanthocyanidins equivalent per g dry matter..

n. d. non detected.

* Three replicates; SD ± 4%.

### *2.3 Birch: Genus Betula*

#### 2.3.1 The Various Species Found in Canada

No less than ten birch species are identified across Canada, and most are indigenous except for the weeping species which has been introduced from Europe.

- ✓ Mountain white birch (*Betula cordifolia* Regel)

- ✓ White or Paper birch (*Betula papyrifera* Marsh.)
- ✓ Blue birch (*Betula xcaerulea*)
- ✓ Alaskan paper birch (*Betula neoalaskana* )
- ✓ Black birch (*Betula lenta*)
- ✓ Western or Water birch (*Betula occidentalis* Hook)
- ✓ Gray birch (*Betula populifolia* Marsh.)
- ✓ Yellow birch (*Betula alleghaniensis* Britt.)
- ✓ Kenai (red) birch (*Betula kenaica* W. H. Evans)
- ✓ European white birch (*Betula pendula* Marsh.)

The most commonly observed birch species in Québec are the following: yellow birch (*Betula alleghaniensis*), white birch (*Betula papyfera*) and grey birch (Betula populifolia). Coincidentally, the Québec territory is one of the richest in the world with regards to yellow birch populations. These species can be found mainly in the southern zone of the province.

2.3.2 Current Utilization by Québec's Forest Industries

2.3.2.1 Yellow Birch (*Betula alleghaniensis*)

Sometimes called "cherrywood" this emblematic tree is characteristic of the southern forest. It remains one of the most sought after hardwoods for construction materials. Tight grain and remarkable hardness make it impact-resistant while easily shaped. Woodworkers use it for moldings, doors, and flooring. As a raw material in sheeting and plywood, it also finds uses in the manufacturing of coffins and agricultural instruments. Similarly to maple, it enjoys a fine reputation as quality firewood.

2.3.2.2 White Birch (*Betula papyrifera*)

Reaching as high as 30 m and with a lifespan as long as 200 years, the white birch grows at a fast pace and thus reaches its target workable dimensions at between 15 to 20 years. Because of poor resistance to moisture, the wood from this species is brittle and of low durability. However its low cost (and growth rate not dependent on soil quality) makes it a common firewood, albeit not the most efficient. Occasionally white birch is used in furniture making, and more often for clogs, utensil handles, masks, toothpicks, and also plywood and pulp.

2.3.3 Traditional Uses of Birches

Most contemporary reports on the medicinal properties of birch focus on the European white birch (*Betula pendula* and *Betula verrucosa*). A number of herbal doctors in fact equate this species with the one found locally in eastern Canada. In terms of culinary applications, using the sap and the resulting syrup has been known for a while. The latter tastes differently from its maple-derived equivalent, but is used for identical purposes. The sap also is a raw material to produce birch wine, and a type of beer has been brewed from branches, bark and sap (Hocking, 1963).

2.3.3.1 Yellow Birch (*Betula alleghaniensis*)

The bark from this species is considered medicinal but does ignite easily. Both the bark and the trunk contain a type of essential oil with analgesic, anti-inflammatory and anti-arthritic properties. North American natives made use of this birch to build sweatlodges, and also for therapeutic and spiritual purposes, for instance chewing on twigs to dull certain types of pain. First Nation Algonquins collected and blended birch sap with maple sap to manufacture sugar (Arnason, Hebda, & Johns, 1981). However little data remain available on the use of this species by Québec native populations.

2.3.3.2 White Birch (*Betula papyfera*)

Native North Americans made much use of white birch bark, because of the latter's high resistance to microbial degradation - hence its reputation as "canoe birch". Canadian hunters also used it to build decoys when attracting moose, and also to build various types of containers. The species was still being used in recent years to manufacture a variety of objects: wirespools, broomsticks, and barrels for fish packaging. The inner bark is edible, and may be used to make flour (Arnason, Hebda, & Johns, 1981). As for leaves, despite their mild bitterness, they have been processed into herbal decoctions to alleviate arthritis pain, hydropsia and kidney stones. When applied topically as steamed poultice, the leaves are apparently highly effective against eczema and other skin disorders. Those leaves possess a specific and pleasant aroma, and have been ascribed laxative and tonic properties. Birch oil has been extracted industrially in some northern European countries and used as insecticide and in hand ointments.

2.3.3.3 Grey Birch (*Betula populifolia*)

According to Natural Resources Canada, in past centuries this species was used to manufacture barrel covers, spools and firewood. A search on medical or food applications of tissues or extracts from grey birch yielded no significant data.

2.3.4 Birch Extractives and Their Bioactivities

A limited number of studies have been published on European species of the genus *Betula*, but none on North American birches. Despite the fact that most reports on extractives have dealt with leaves as substrate, we were able to gather information on other tissues, namely wood, twigs and mostly bark (internal and external) which represents the most abundant by-product. The majority of studies focus on *Betula pendula* (Calliste, Trouillas, Allais, Simon, & Duroux, 2001; Willfor et al., 2003; Kähkönen et al., 1999) with a few others on *Betula pubescens* (Kähkönen et al., 1999) and *Betula platyphylla* var *japonica* (Matsuda et al., 1998; Ju, Lee, Hwang, & Kim, 2004). Overall, results clearly confirm that birch extracts do possess therapeutic properties. In fact, the chemotaxons in *Betula* are extractives that belong to both key classes previously described, the terpenes and polyphenols.

A literature review by Krasutsky on birch terpenic extractives revealed that tissues from *Betula* species contain mainly triterpenes and their derivatives (Krasutsky, 2006). Interestingly, the concentrations of extractives in barks from 38 birch species are more or less similar, a fact that would help streamline production management at extraction facilities handling more than a single species. The same review describes the nature of components in bark extracts from three species including white birch (*Betula papyrifera*), a predominant species in Canada (Table 11).

Table 11. Proportions of various triterpenes in bark extracts of three species within the genus Betula (Krasutsky, 2006)

| | *B. pendula*[a] | *B. papyrifera* | *B. neoalaskana* |
|---|---|---|---|
| Betulin | 78.1 | 72.4 | 68.1 |
| Betulinic acid | 4.3 | 5.4 | 12.5 |
| Betulinic aldehyde | 1.2 | 1.3 | 1.4 |
| Lupeol | 7.9 | 5.9 | 2.1 |
| Oleanolic acid | 2.0 | 0.3 | 2.2 |
| Oleanolic acid 3-acetate | — | 1.6 | 3.8 |
| Betulin 3-caffeate | 0.5 | 6.2 | 6.1 |
| Erithrodiol | 2.8 | — | — |
| Other (minor) | 3.2 | 6.9 | 3.8 |

[a] Samples of outer birch bark from Betula neoalaskana were kindly provided for extraction and GC/MS, NMR and HPLC analyses by Dr. Edmond C. Packee (SNRAS Forest Science Department, University of Alaska, Fairbanks).

The proportions of each component vary from one tissue specimen to the other within a single species, and vary also due to other parameters such as harvest time, geographical location, or other environmental conditions. Notably, the contents of betulinic acid and betulin ester (Betulin 3-caffeate) in barks of North American species – including white birch – are significant and those compounds possess demonstrated bioactivities as anticancer and anti-HIV agents. The white pigmentation of *Betula papyfera* bark is due to the presence of betulin filling the peridermal cells (Patočka, 2003; Alakurtti, Mäkelä, Koskimies, & Yli-Kauhaluoma, 2006). Several organic solvents easily solubilize betulin (e.g. chloroform, dichloromethane, acetone, ethanol and others). Practical applications in cosmeticformulations have been investigated, for instance in after-shampoos (Patočka, 2003). Betulin and birch extract are already commercialized as nutraceutical supplements (trademark Betula®) with hepatoprotective activity to prevent or treat acute alcoholic intoxication, and as additive in alcoholic drinks (Krasutsky, 2006). A range of bioactivities have been assigned to pentacyclic triterpenes of « lupane » structure (including betulin): bactericidal, antiviral, anti-inflammatory, cytotoxic and antitumoral (Gauthier C., 2006; O'Connell, Bentley, Campbell, & Cole, 1988; Omar et al., 2000). Within the lupanes series, betulinic acid stands out with its proven antiviral activity towards type I human immunodeficiency virus (HIV) (Fujioka et al., 1994), apart from its selective cytotoxicity towards human melanoma (Pisha et al., 1995). In the mouse model, betulinic acid shows an absence of toxicity even at doses higher than 500 mg/kg of live weight. Such promising results prompted the *National CancerInstitute* (NCI) to include betulinic acid in its so-called *Rapid Access to Intervention Development* (RAID) program.

From a strategic standpoint, the use of white birch (*Betula papyrifera*) in the production of pulp and paper would generate volumes of raw extract from external bark that could yield approximately 15 % of adequately pure betulin, in turn easily oxidized to betulinic acid. According to Krasutsky, an industrial plant would therefore produce annually as much as 1800 tons of betulin, 75 tons of betulinic acid and 150 tons of lupeol. Currently in Québec, birch bark is essentially used as fuel, which would remain its main application after an extraction process. Simple biomass combustion does not qualify as a sustainable option, neither do other alternatives such as landfill or incineration. In a truly sustainable development scheme, an optimized pre-extraction step would add significant value to the bark material and provide a residual combustible biomass / fiber source devoid of the hitherto marketable bioactive molecules.

Several studies have identified polyphenols in birch tissues and determined which biotic or abiotic factors impact their concentrations: high $CO_2$ levels, seasonal changes, ozone, UV-B wavelengths, exposure to microorganisms and mammals, temperatures, etc (Loponen et al., 2001; Kuokkanen, Julkunen-Tiito, Keinanen, Niemela, & Tahvanainen, 2001). For instance, two reports on yellow birch (*Betula alleghanensis*) provided quantitative data ofseasonal effects on the chemical composition of leaves in terms of polymers and polyphenols (Ricklefs & Matthew, 1982; Hoyle, 1969); several polyphenolics were thus isolated from those leaves (Table 12).

Table 12. Selected polyphenols in yellow birch leaves (Keinänen, Julkunen-Tiitto, Rousi, & Tahvanainen, 1999)

| Phenolic compounds | *Concentration ($mg.g^{-1}$ db) in the leaves* |
|---|---|
| (+)-catechin | *4.8* |
| 3-caffeoylquinic acid | *0.56* |
| 3-coumaroylquinic acid | *2.3* |
| quercetin-3-arabinopyranoside | *0.27* |
| kaempferol-3-rhamnoside | *0.33* |
| kaempferol-O-glycosides | *16.55* |
| *apigenin derivative 1* | *0.23* |

Some polyphenols are biosynthesized by plants in order to repel or resist herbivores, mammals and microorganisms. Platyphylloside, a phenolic molecule isolated in several species within the genus *Betula,* was shown *in vitro* to inhibit digestibility in ruminants (Sunnerhein, Palo, Theander, & Knutsson, 1988). Methanolic extraction of the inner bark of white birch, *Betula papyrifera* afforded this compound along with ten polyphenolics (Mshvildadze, Legault, Lavoie, Gauthier, & Pichette, 2007)such as diarylheptanoid glycosides, phenolic glycosides and lignans (all compounds being common to the genus *Betula*). Screening for anticancer activity in each compound - vs lung and colon cancers - revealed a strong potential for methanolic extracts from the inner bark, apparently due to the polyphenol papyrifoside A isolated for the first time. The following four polyphenols are found across the genus *Betula*: (i) (+)-catechin, a well-recognized antioxidant also present in green tea; (ii) salidroside, known for its anxiolytic properties; (iii) (+)-rhododendrin, a rhododendrol glycoside, and (iv) platyphylloside. Rhododendrol was isolated as far back as 1978 from the hydrolyzed extract of yellow birch bark (Santamour & Vettel, 1978). The same author in 1997 measured a rhododendrin content of 0.01% d. b. in bark (Santamour & Lundgren, 1997) whereas in our study (Lavoie & Stevanovic, 2006) we determined the contents of selected polyphenols in extracts from twigs of *Betula alleghanensis.* Results are shown in Table 13.

Lavoie and Stevanovic succeeded in identifying three phenolic molecules in lipophilic extracts from trunk wood and from sawdust of *Betula alleghaniensis*. The choice of a lipophilic solvent – rather than hydrophilic – favored the dissolution of terpenic compounds. Table 14 describes the polyphenolic moleculesidentified in that study.

Optimization work targeting polyphenol-rich extracts would preferably require polar solvents such as methanol, ethanol and/or water.

No phytochemical study is currently available on grey birch (*Betula populifolia*).

Table 13. Polyphenols in stems from yellow birch (Lavoie & Stevanovic, 2006)

| Compound | Concentration (mg/g) in dry twigs |
|---|---|
| (+)-catechin | 1.08 |
| Salidroside | 3.09 |
| Catechin isomer | 0.04 |
| Condensed tannins | 20.0 |

Table 14. Polyphenols in wood and sawdust from yellow birch (Lavoie & Stevanovic, 2006)

| Compound | Molecular weight | Similarity index | Trunk wood (average concentration µg/g) | Sawdust (average concentration µg/g) |
|---|---|---|---|---|
| Syringaldehyde | 182.17 | 0.92 | 4.1 | 2.3 |
| Salidroside | 300.30 | 0.81 | 5.1 | 84.3 |
| Chlorogenic acid | 354.31 | 0.91 | 18.9 | 11 |

2.3.5 Main Results from Our Research Laboratory

Longstanding work conducted at the CRB by Professor Tatjana Stevanovic's team has focused on extractives from various tissues of *Betula alleghanensis*, leading to several papers being published in the last decade.

In 2005, Lavoie and Stevanovic studied the variations in compositional analysis of hexane extracts from leaves of yellow birch (*Betula alleghanensis*) as a function of harvest season and geographical location. The work aimed at defining optimized harvest conditions leading to high concentrations of bioactive compounds. No less than 14 lipophilic extractives were identified, including triterpene derivatives (lupanes) among them betulonic aldehyde (Lavoie & Stevanovic, 2005). The same authors defined the variations in extractive yieldsagainst time, and changes in concentrations for each compound. A 2009 study on segregated parts (external and internal bark, wood, leaves and twigs) of*Betula alleghanensis*demonstrated that ethanolic extracts obtained by maceration and ultrasonic treatment show strong anti-inflammatory activities (Diouf, Stevanovic, & Boutin, 2009). Those results also confirmed that ultrasonic extracts (via a technique developed at the CRB, patent applied for) were less cytotoxicthan extracts obtained by simple maceration; the data support this novel ultrasonic-assisted protocol as an efficient route when compared with conventional methods. Also shown in the work were the advantages of using ethanol as solvent in order to co-extract the bioactive terpenic compounds along with polyphenols. The isolated compounds are listed in Tables 15 and 16.

A related study on yellow birch extractives confirmed the antioxidant capacity of aqueous extracts from twigs (Garcia Perez, Diouf, & Stevanovic, 2008). Meanwhile, bark ethanolic extracts contained a high concentration of total phenolics and showed significant antioxidant activity (García-Pérez, Royer, Duque-Fernandez, Diouf, Stevanovic, & Pouliot, 2010).

We currently run an ongoing comprehensive program in our laboratory, studying extractives from different tissues of this species; concomitantly a parallel study on the characteristics of ethanolic extracts from wood and bark originating from trees of varying health conditions (healthy, attacked by fungi, dying trees) is focusing on the triterpene profiles in the resulting extracts.

Table 15. Terpenic derivatives in several tissues of yellow birch (*Betula alleghanensis*) (Diouf, Stevanovic, & Boutin, 2009)

| Compound | RT (min) | Tissue | Amount (mg/g of dehydrated extract) | |
|---|---|---|---|---|
| | | | MAE | UAE |
| Squalene | 10.42 | foliage | 0.7 ± 0.0 | 0.6 ± 0.0 |
| β-amyrin | 15.17 | foliage | 1.1 ± 0.3 | 1.4 ± 0.1 |
| Lupenone | 15.29 | outer bark | 4.1 ± 0.2 | 4.0 ± 0.0 |
| | | twigs | 0.5 ± 0.1 | 0.5 ± 0.1 |
| Lupeol | 15.56 | inner bark | 3.5 ± 0.1 | 3.6 ± 0.1 |
| | | outer bark | 92.1 ± 2.7 | 83.1 ± 0.4 |
| | | twigs | 12.9 ± 1.3 | 9.2 ± 0.2 |
| Betulonic acid | 17.80 | wood | 50.5 ± 0.3 | 48.3 ± 0.8 |
| | | twigs | 2.4 ± 0.2 | 1.1 ± 0.1 |
| NI triterpene | 18.11 | inner bark | 4.2 ± 0.1 | 5.0 ± 0.1 |
| | | outer bark | 45.9 ± 2.0 | 57.6 ± 0.4 |
| | | twigs | 0.2 ± 0.1 | 0.6± 0.0 |
| Betulone | 18.80 | outer bark | 26.1 ± 0.6 | 25.1 ± 0.4 |
| Betulin | 19.14 | inner bark | 4.8 ± 0.1 | 5.6 ± 0.3 |
| | | outer bark | 10.2 ± 0.3 | 9.2 ± 0.1 |
| | | twigs | 9.9 ± 0.3 | 4.2 ± 0.1 |
| Acetyl methyl betulinate | 20.88 | wood | 19.0 ± 0.4 | 19.8 ± 1.1 |
| | | twig | 2.6 ± 0.4 | - |

Means with different letters in the same row: significantly different at $p<0.05$ (Student's t-test).

Table 16. Contents of total phenolics and flavonoids in various tissues of yellow birch (*Betula alleghanensis*) (Diouf, Stevanovic, & Boutin, 2009)

| Tissue | MAE | | UAE | |
|---|---|---|---|---|
| | TP [a] | TFlav [b] | TP [a] | TFlav [b] |
| Twigs | 58.3 ± 1.5 | 5.7 ± 0.2 | 87.8 ± 1.3 | 5.4 ± 0.2 |
| Wood | 240.1 ± 6.8 | 15.0 ± 1.4 | 205.2 ± 4.7 | 11.8 ± 0.4 |
| Foliage | 70.2 ± 2.5 | 45.1 ± 0.5 | 68.2 ± 2.9 | 43.0 ± 2.1 |
| Inner bark | 313.1 ± 18.0 | 11.2 ± 0.2 | 303.1 ± 10.2 | 10.1 ± 0.3 |
| Outer bark | 170.2 ± 3.0 | 10.6 ± 0.2 | 172.3 ± 1.5 | 10.0 ± 0.1 |

[a] TP: total phenolic content expressed as mg of gallic acid equivalent per g of dehydrated extract.

[b] TFlav: total flavonoid content expressed as mg quercetin equivalent per g of dehydrated extract.

### *2.4 Poplars: Genus Populus*

#### 2.4.1 The Species Found in Canada

No less than 13 poplar species have been identified in Canada, of which 4 were introduced (white, Carolina, Simon's, Italian black).

- ✓ Waxleaf (Lanceleaf) cottonwood (*Populus xacuminata* Rydb.)
- ✓ Narrowleaf balsam poplar (*Populus angustifolia* James)
- ✓ Bigtooth aspen (*Populus grandidentata*Michx.)
- ✓ Balsam poplar (*Populus balsamifera* L.)
- ✓ White poplar (*Populus alba* L.)

- ✓ Canadian poplar (*Populus xcanadensis* Moench.)
- ✓ Western poplar (*Populus trichocarpa* Torr and A. Gray)
- ✓ Simon's poplar (*Populus simonii* Carrière)
- ✓ Eastern poplar (*Populus deltoides* Bartr. Ex Marsh. *ssp. deltoides*)
- ✓ Plains poplar (*Populus deltoides* Bartr. Ex Marsh. *ssp. monilifera*)
- ✓ Trembling aspen (*Populus tremuloides* Michx.)
- ✓ Jack's aspen (*Populus xjackii*)
- ✓ Italian black poplar (*Populus nigra* L.*cv. Italica*)

Among those species, trembling aspen – found in boreal forest – is the most common in North America and the most commercialized species in Québec (Bouchard, Douville, Dupuis, & Boudreault, 2008); this aspen grows in all forested regions. Balsam poplar remains popular as wind breaker and for ornamental purposes. Among the four poplars on the Québec territory – balsam, trembling, eastern, bigtooth – the eastern speciesis the tallest and can be seen along larger rivers of the St-Lawrence valley. Many types of birds and mammals feast on poplar buds, branches and bark. The genus *Populus* in its various representations makes up 8.3 % of all commercial forest species in Québec; several improved or hybrid varieties with high yields in boreal zones are in fact issued from genetic crossings. Physical and mechanical properties of oriented strandboard from hybrid poplar generally qualify as superior to boards manufactured from non-hybrids. Still, in terms of sawtimber quality, no major advantages have been noted for hybrids except for some slight improvements in drying.

The following sections deal mostly with trembling aspen and balsam poplar.

#### 2.4.2 Current Uses by the Forest Industry

##### 2.4.2.1 Trembling Aspen (*Populus tremuloides)*

Well adapted to various environments, this aspen reaches on average between 16 to 20 m with some individuals as tall as 35 m. Its bark collected from various processes (pulping, plywood, match production) is popular as energy source within the industry. Despite known mechanical issues at drying such as warping, key technological developments coupled to the need for cheap fiber in the last decade have seen many sawmills convert to aspen as raw material; the species is now sought by strandboard and pallet manufacturers and in pulping operations(Bouchard, Douville, Dupuis, & Boudreault, 2008; Dupuis, 2009). Fast growth plantations are expected to provide larger volumes of this aspen, which should foster broader applications and novel value-added products. Tension wood often causes important longitudinal shrinkage in this species, 5-7 times that of other hardwoods. Aspen wood is nowadays transformed in sawmills, despite its problematic reputation in the past. Althoughpallet manufacturing remains the most widespread application for aspen, secondary and tertiary processing will help improve operational costs; to this effect, the industry association "Valoritremble" was formed in 2007 to promote innovative avenues with this resource.

##### 2.4.2.2 Balsam Poplar (*Populus balsamifera*)

This fast-growing and aromatic species is second only to trembling aspen in Canada within the genus *Populus* and yet its potential has been undervalued in Québec (Gaussiran & Boileau, 2007). Several factors may explain this lack of interest on the part of industrial users: a lack of wood rigidity, rotting, and high processing costs derived from a high moisture content. To compensate those inadequacies, the Forintek division of FPInnovations carried out a systematic study that confirmed a strong link between processing characteristics and the quality of the growth site. The Abitibi-Temiscamingue area (region 08) now holds a volume of roughly 65 million m³ of poplar timber. Of the three species in that area, balsam represents roughly 1 million m³, or 1.6 % of the overall volume (Table 17).

Table 17. Poplar volumes in region 08 (personnal communication Gaussiran and Boileau, 2007)

| Species | Volumes standing (m3) | Ratio (%) |
|---|---|---|
| Populus balsamifera | 1 054 828 | 1.6 |
| Populus grandidentata | 4 914 652 | 7.6 |
| Populus tremuloides | 59 040 111 | 90.8 |
| Total | 65 009 590 | 100.0 |

Source: Office of the Chief Forester (Northwest Québec div.).

### 2.4.3 Traditional Uses of Poplars in Human Health

Early on, the poplar has been described as «diuretic, uric acid eliminator, anti-infectious in cases of urinary problems, antimicrobial, thinner of bronchial secretions, and tonic».

North American First Nations used trembling aspen as wormicidal in the form of ground bark mixed with sugar (Ritch-Krc, Thomas, Turner, & Towers, 1996); bark as well as leaves helped treat fever while the beneficial properties of leaves were applied for treating cuts and ulcer wounds. Balsam poplar and other species are part of the same botanical family as willows (*Salicaceae*), which explains their high salicylate content. After theingestion of buds, salicylates are hydrolyzed into salicylic acid (the analog of aspirin), hence their activity towards pain. In N. America, buds from balsam poplar have been used for instance to prepare white pine blended syrup, ointments and bandages, and to treat arthritis and rheumatoid pain; bud wine was a popular spring tonic as well. In the realm of native American herbal medicine, barks of various poplar species were deemed efficacious to treat menstrual dysfunction in women. During spring and early summer, the internal bark of balsam poplar appears thick, sweet and juicy, and as such was regularly consumed by native Ojibways (Arnason, Hebda, & Johns, 1981); because of its carbohydrate content, this material is subject to rapid fermentation and was at times processed into intoxicating preparations. One report indicates that in Europe a liquid extract from *P. tremula* leaves (closely related to trembling aspen) was promoted for relieving inflammation caused by prostate hyperplasia (Buck, 1996), and such bioactivity is likely to originate from the salicin-type glycosides present in the leaves.

### 2.4.4 Extractives from Poplars and Their Biological Properties

To this day, a number of studies have been conducted on the genus *Populus* and some compositional data are available for the various tissues of trembling aspen and balsam poplar. It is however obvious that precise information on the exact nature of the components in those extractives is still lacking despite some interest generated by their medicinal uses by First Nations. According to Arnason, balsam poplar deserves more attention based on the therapeutic potential of its extracts (Arnason, Hebda, & Johns, 1981). The latter contain analgesic polyphenolics such as salicin and o-pyrocatechuic acid. A recent report on ethanolic extracts from balsam poplar buds sheds light on the presence of acylglycerides and sterol ethers, along with minor amounts of sesquiterpenoïds and flavonoids (Isaeva, Lozhkina, & Ryazanova, 2010).

A number of investigations on trembling aspen bark were conducted between 1950 and 1970 (Faber Jr, 1960; Pearl & Darling, 1971). The analysis of aqueous bark extracts by Pearl et al. confirmed the presence of phenylglycosides such as salicin, tremuloidin and salireposide (Pearl, et al., 1961). Besidesthose compounds, the authors also noted the co-extraction of various other glycosides featuring with the following aglycone moieties: salicylic alcohol, gentisyl alcohol (2,5-dihydroxybenzyl alcohol - a reagent used in pharmacology to stabilize peptides and radiolabeled proteins), and benzoic acid, along with several simple carbohydrates. More recently, gas chromatography analysis of extracts from trembling aspen heartwood revealed more than forty compounds (Fernandez, Watson, & Breuil, 2001) and further identification of the lipophilic extractives using GC-MS confirmed the presence of triterpenoids and polyphenols including α-tocopherol and several flavonoids.

A study was undertakenon*Populus tremuloides* and *balsimifera*by McCune et al. in order to discriminate between the extracts from either buds, roots or bark in terms of antioxidant (free radical scavenging) and anti-diabetic activities. As it turned out, extracts from the bark showed higher antioxidative activity than those of buds that were used in native American practices (McCune & Johns, 2002; McCune & Johns, 2007). Meanwhile, ethanolic extracts from buds of *Populus tremuloides*, containing mostly phenolic compounds, demonstrated some cytotoxic activity against human lung carcinoma and adenocarcinoma cells (Pichette, Eftekhari, Georges, Lavoie, Mshvildadze, & Legault, 2010). Propolis is known as a resinous substance exuding from the buds of certain plant species, including some within the genus *Populus*; many types of bees collect this resin which contains over 300 different chemical constituents among which phenolics and terpenes may be responsible for its reported bioactivities (antibacterial, antiviral, fungicidal etc.) (Vardar-Unlu, Silici, & Ulu, 2008; Silici & Kutluca, 2005). In the specific case of propolis originating from trembling aspen, chrysophanol – a polyphenolic derivative of anthraquinone – was successfully identified and shown to possess antimicrobial activity against *Bacillus subtilis* and *Staphylococcus aureus* (Garcia-Sosa, Villareal-Alvarez, Lübben, & Pena-Rodriguez, 2006). The compound in trembling aspen branches that attracts beavers was determined to be a mixture of salicin and tremuloïdin (Müller-Schwarze, Schulte, Sun, Müller-Schwarze, & Müller-Schwarze, 1994). Another study was conducted on the leaf extracts of red maple and trembling aspen to determine their insecticidal effects (Abou-Zaid, Helson, Nozzolillo, & Arnason, 2001). Finally, an investigation into leaf extracts from the same species determined that their anti-inflammatory properties were due to the co-presence of flavonol glycosides and salicin derivatives (Albrecht, Nahrstedt, Luepke, Theisen, & Baron, 1990).

With regards to balsam poplars, buds were also the tissue in which several compounds – sesquiterpenes and phenolic acids – were identified (Isidorov & Vinogorova, 2003). A recent reportfocusing on those extracts established their minimum inhibitory concentration towards tumor cells during cancer treatment (Mazzio & Soliman, 2009). Hot water extracts of the bark also yielded the following critical information (Pearl & Darling, 1968; Pearl & Darling, 1968): a first investigation identified a number of phenolic compounds, namely salicin, salicylic acid, pyrocatechol, 2,6-dimethoxy-p-benzoquinone, trichocarpine, salireposide, cinnamic acid and azelaic acid. A second study revealed the presence of trichoside and gentisylic alcohol in bark extracts, both compounds also found in trembling aspen. The recent screening of medicinal properties of certain plants used by First Nation Creesshowedsome slight antidiabetic activity in unspecified tissues of balsam poplar (Tam et al., 2009). Finally, interesting anti-adipogenic properties were noted in ethanolic bark extracts from this species, suggesting some potential in the treatment of obesity (Martineau et al., 2010; Martineau et al., 2010).

2.4.5 Main Results from Our Research Activities

Our laboratory work has focused specifically on extractives from *Populus tremuloides*, and in particular the antioxidant capacity of aqueous bark extracts (Diouf, Stevanovic, & Cloutier, 2009). Several polyphenolic fractions were segregated and significant antioxidant activity measured in the crude extract as well as in individual fractions; in all cases, results exceeded the activity of the control BHT – a commercial synthetic antioxidant. Notably, the less polar fractions exhibited the strongest bioactivity. While comparing concentrations of total phenolics and of flavonoids, we concluded that the antioxidant activity was related to non-flavonoid polyphenolics. Table 18 lists assay results on (i) the crude aqueous extract and (ii) the various fractions.

Table 18. Total phenolics in aqueous extracts from trembling aspen bark and its various fractions (Diouf, Stevanovic, & Cloutier, 2009)

| Extract or fraction | Yield [a] | Total phenolics [b] | Total flavonoids [c] | Total flavanols [d] |
|---|---|---|---|---|
| CHWE | 140.1 | 113.5 ± 6.1 | 11.5 ± 0.2 | 10.2 ± 0.4 |
| TBME | 15.3 | 218.0 ± 7.6 | 12.5 ± 0.2 | 18.3 ± 0.5 |
| EtOAc | 20.1 | 159.9 ± 6.9 | 9.3 ± 0.0 | 9.7 ± 0.1 |
| BuOH | 28.3 | 139.1 ± 5.4 | 10.0 ± 0.1 | 9.1 ± 0.3 |
| $H^2O$ | 76.3 | 21.1 ± 0.2 | 9.9 ± 0.0 | 5.2 ± 0.1 |

CHWE, crude hot water extract; TBME, tert-butyl methyl ether fraction; EtOAc, ethyl acetate fraction; BuOH, butanolic fraction; $H_2O$, aqueous extract.

[a] Yields expressed as mg of dehydrated extract per g of dry bark material.

[b] expressed as mg gallic acid equivalents per g dry extract.

[c] expressed as mg quercetin equivalents per g dry extract.

[d] expressed as mg catechin equivalents per g dry extract.

*2.5 Oak: Genus Quercus*

2.5.1 The Species Found in Canada

Overall, 15 oak species have been inventoried and most are indigenous, with others introduced such as the chestnut, scarlet and English species. The latter is ubiquitous in Europe and nowadays fully naturalized on the Canadian territory. By contrast, the American red oak was introduced on the European continent during the 1970-80 decade mainly as part of reforestation programs (Lanier, Keller, & Kremer, 1980).

- ✓ Bur oak (*Quercus macrocarpa*Michaux.)
- ✓ Bebb's oak (*Quercus bebbiana*C.K. Schneid)
- ✓ Swamp white oak (*Quercus* bicolor Willd.r)
- ✓ Eastern white oak (*Quercus alba* L.)
- ✓ Mountain chestnut oak (*Quercus montana* Willdenow,)

- ✓ Oregon (Garry) White oak (*Quercus garryana* Dougl.ex Hook)
- ✓ Swamp red (Shumard) oak (*Quercus shumardii* Buckl.)
- ✓ Swamp oak (*Quercus palustris* Muenchh.)
- ✓ Scarlet oak (*Quercus coccinea* Muenchh)
- ✓ Hill's oak - Northernpin oak (*Quercus ellipsoidalis* E.J. Hill.)
- ✓ Yellow chestnut oak (*Quercus muehlenbergii* Engelm.)
- ✓ Dwarf chinquapin oak (*Quercus prinoides* Willd.)
- ✓ Black oak (*Quercus velutina* Lam.*)*
- ✓ English oak (*Quercus robur* L.)
- ✓ Red oak (*Quercus rubra* L.)

Among those, both the red and white oaks – part of the Fagaceae family, along with beech - are those most commonly used inQuébec's forestry industry. *Quercus rubra* comes as three varieties: *borealis* (American red oak), *rubra* and *ambigua*.A few centuries ago, oak forests were cleared in order to supply shipbuilding timber for the Queen of England and for flooring inside homes of the English noble class. Nowadays, a few private oak stands have endured, especially in Western and Southern Québec, far from the northern cold. Thankfully, intensive oak planting in the last few decades offers the possibility of harvesting four or five year old bark.

2.5.2 Current Uses by the Forest Industry

2.5.2.1 Red Oak (*Quercus rubra*)

The wood from *Quercus rubra* var *borealis* comes across as dense, with tight grain, with a brown-reddish hue. Popular in framework, barrelmaking (for dry goods only), carpentry and cabinetwork, red oak wood is known as less durable than other European species from the same genus. Thanks to a fast juvenile growth phase, the American red oak is often used for reforestation purposes, despite the risk of mismanaging its ecological traits and especially its limiting characteristics (Timbal, 1990).

2.5.2.2 White Oak (*Quercus alba*)

Found in the southern part of the province, white oak yields a hard, heavy and durable type of wood, with tight grain and a pale brown hue. Uses include sculptures, cabinetwork and carpentry. In commercial trading, its timber is often confused with that of the bur oak, both providing most of the oak wood used in shipyards. With its solid dimensional stability, white oakwood remains much in demand for bodywork, agricultural tools, luxury paneling and boards. Its unique elasticity allows curving to nearly 90 degrees. Trade was brisk in the past between some tropical countries and Québec, the former importing large volumes of mostly *Q. macrocarpa* from the Richelieu valley, where this species is sparsely found nowadays.

2.5.3 Traditional Uses in Human Health

Several reports have described the virtues of the oak inner bark, with that of *Quercus robur* being mostly used in Europe while in North America the First Nations were taking equally advantage of the various available species. According to Arnason (Arnason, Hebda, & Johns, 1981) who reported on this subject, Ojibways were preparing infusions and poultices from the inner barksof *Quercus alba*, *Quercus macrocarpa*, *Quercus rubra* and *Quercus muehlenbergii*, those applications likely based on the particular astringency of the extracts. In contemporary medicine, astringent compounds have many known uses, for example to control the flow of physiological serum or of mucosal secretions. Other indications include: cases of hemorraghia, diarrhea or gastro-duodenal ulcers. Astringent solutions contain molecules that are efficaceous in the treatment of surface lesions or insect bites; such compounds, through their vasoconstrictive effect on skin tissues, decrease sebum secretion. Ethnopharmacological data retrieved by Arnason states that the First Nation Ojibways were using oak bark extracts as treatment for diarrhea, vomiting, hemorrhage and sore throat; when applied topically, inner bark was known to cure eczema and other skin diseases (Meletis & Wagner, 2002) while causing no irritation. Other indications included ocular inflammation, hemorrhoids, frostbites etc. (Neves, Matos, Moutinho, Queiroz, & Gomes, 2009). Bark extracts were also applied at high doses to inhibit infectious gangrene growth. Wood and bark from *Quercus rubra* were used by the Ojibways to treat heart problems (McCune & Johns, 2003) while the bark of *Quercus alba* was recommended by American Indians for its tonic effect on muscles and the body in general (Moerman, 1998).

2.5.4 Extractives from Oaks and Their Biological Properties

In studies devoted to extractives from the genus *Quercus*, European species such as *Quercus robur* are most frequently cited. Tannins from oakwood have been identified as being responsible for changes in color and taste during wine ageing in oak barrels (Gonalves & Jordao, 2009; Del Alamo, Bernal, & Gomez-Cordoves, 2000). The actual content of extractives in oak varies significantly depending on factors such as the specimen's geographical origin, oak species, growth environment etc. Wood from white oak contains lesser amounts of ellagic (hydrolyzable) tannins than European species (Chatonnet & Dubourdieu, 1998). This group of compounds includes roburin A, B, C, D, E, vescalagin, castalagin and grandinin (Prida & Puech, 2006). The monomer, ellagic acid, has been reported in concentrations of 41 mg/g in wood from *Quercus alba* (Bianco, Handaji, & Savolainen, 1998). Interestingly, modern medicine has confirmed that ellagitannins from oakwood play a role (along with grape polyphenols) in the observed benefits towards cardiovascular problems of a moderate consumption of wine (Stevanovic, Diouf, & Garcia-Perez, 2009). This is a remarkable yet understated example of woody components being applied in human nutrition. Ellagitannins have also been shown to prevent colon cancer (Fridrich, Glabasnia, & Fritz, 2008). Other minor aromatic components of white oak which modulate wine bouquet include β-methyl-α-octalactone and an aromatic carotenoid derivative, 3-oxo-retro-α-ionol. Other volatile molecules from oakwood (European and American) such as vanillin, eugenol, guaiacol, syringaldehyde and coniferaldehyde play a key role in wine taste and aroma; however, a high variability in the concentrations of those molecules has been observed in both European and American species, in particular*Quercus alba* (Fernandez De Simon, Cadahia, & Jalocha, 2003). Chemotaxons such as scopoletin (a polyphenolic in the coumarin class, used in modern medicine to regulate bloodflow and also against inflammation during acute bronchitis) and norisoprenoids derived from carotenoids, both allow for the clear distinction between American and European oaks. On a biofuels-related note, the demonstrated yeast-inhibitory effect of extractives from red and white oaks during ethanolic fermentations with *Saccharomyces* sp. confirms the importance of extracting those active principles prior to biomass fermentation (Ranatunga, Jervis, Helm, McMillan, & Hatzis, 1997). Such a recommendation may extend to other woody species as well.

Whereas oakwood contains high amounts of hydrolysable ellagitannins, in contrast the inner and outer barks yield high percentages of condensed tannins, also known as catechin polymers or proanthocyanidins. Bark remains the most sought after tissue based on its medicinal properties, either as astringent or as antiseptic. The following polyphenols have been identified in American oak bark (Rowe & Conner, 1979): (+)-catechin, (+)-gallocatechin, leucopelargonidin, leucocyanidin, leucodelphinidin, and gallic acid. Bark from white oak, *Quercus alba* was valued for its tonic character likely related to its antioxidant content in the form of vitamins (such as ascorbic acid or vitamin C) (McCune & Johns, 2003). It has been pointed out that the methanolic bark extract from *Quercus alba* registers a level of antioxidant/antiradical activity similar to that of green tea (McCune & Johns, 2002), the latter's antioxidant activity being directly related to the presence of catechin and other flavonoïds. With regards to terpenic compounds in oak tissues, published data only deal with the phenomenon of atmospheric losses of monoterpenes and isoprene in red oak, *Quercus rubra* (Isebrands et al., 1999).

Considering the wide range of medicinal properties reported for bark extracts from *Quercus rubra* and *Quercus alba*, further investigations into isolation conditions and characterization of resulting extractives are no doubt justified. The number of studies available up to now on the Canadian species is clearly insufficient.

#### 2.5.5 Results from Our Laboratory

A previous review from this laboratory cites several references dealing with the unique properties of polyphenols from the genus *Quercus* and their applications in the agri-food or nutraceutical sectors (Stevanovic, Diouf, & Garcia-Perez, 2009).

Within Québec, volumes of hardwood species are higher in areas such as the Outaouais and the Laurentians. Yellow birch dominates in those forests, alongside sugar maple and balsam fir. Therefore a number of local sawmills may potentially benefit from proper evaluation of the feasibility of pilot extraction units designed to process yellow birch bark into crude bioactive extracts; such minor plant modifications would likely add significant value to the bottom line of their sawmilling operations. Those extracts possess well documented properties and would find applications in various technological markets (pharmaceuticals, cosmetics, nutraceuticals and agri-food). Another area of interest is Abitibi-Temiscamingue, where mixed forest would allow similar upgrading of softwood species as well (Parent, 2009); in that particular area, 80% of jobs are tied to the forestry industry (pulp and paper mills, sawmills, etc.) and close to 11% of overall employment is related to the harvest of commercial species. The conversion ratio used with hardwoods to obtain the metric tonnage of bark per cubic meter of processed wood is 0.095. Consequently a comprehensive research program is advisable in order to fully determine the exact chemical nature and biological properties of the species available in those regions, for instance a program sustaining permanent academic research and spurring related commercial ventures as well.

*2.6 Notes on Extractives from Secondary Hardwoods Species in Québec*

The biodiversity of Québec's forests is such that we have narrowed our review down to those species that are commercially dominant. The following section will provide brief descriptions of the potential for five other local genera: *Fraxinus*, *Ulmus*, *Tillia, Juglans* and *Carya.* Several of those secondary species have attracted scientific and commercial interest. Once again, markets would include pharmaceuticals, cosmeceuticals, agri-food and nutraceuticals.

2.6.1 Ash: Genus *Fraxinus*

Within this genus, three species can be observed in most Québec forests: white (American) ash (*Fraxinus americana* L.), red ash (*Fraxinus pennsylvanica* Marshall) and black ash (*Fraxinus nigra* Marshall). Only the latter is sufficiently hardy to grow in northern areas.

The white ash, a member of the *Oleaceae* family, is the *Fraxinus* species most widespread in North America and in Québec's forests. Always handy when a solid material is required such as for sports items and various handles, its highly resistant wood remains one of the most precious in North America especially for cabinetmaking and production of wood turnings. Lesser known is the fact that its bark yields a yellow-beige natural dye. From a health standpoint, the inner bark comes highly recommended for treating dysmenorrhea and rheumatoid pain, with the leaves also indicated in the latter condition (Frendo, 2004).

Extractives have been prepared from American ash tissues, and a 1997 study on bark polyphenolics revealed some antioxidant and enzyme-inhibitory activities in extracts that contained among others, acteoside, 10-hydroxyligstroside, ligstroside and syringin (Nishibe et al., 1997). Other groups revealed various bioactivities for the compound acteoside: modulation of hypertension (Mansoor A., 1995), inhibition of leukemial cell proliferation (Lee et al., 2007) and antimetastatic effects towards cancerous cells (Ohno, Inoue, Ogihara, & Saracoglu, 2002). Ligstroside, another complex phenolic in the extract, has been previously identified in olive oil (Tripoli, Giammanco, Tabacchi, Di Majo, Giammanco, & La Guardia, 2005). In 2000, Takenaka et al. successfully isolated several secoiridoïd glycosides from alcoholic leaf extracts (Takenaka, Tanahashi, Shintaku, Sakai, Nagakura, & Parida, 2000); this type of compound plays a repellent role towards insects. More recently, phloem extractives both from the white and red species yielded several phenolic constituents (Eyles et al., 2007) as follows: from white ash the list includes previously known molecules but also quercetin, pinoresinol-derived hexosides (insecticidal aglycone), lariciresinol and apigenin. A similar compositional profile was noted for red ash phloem, with the additional presence of tyrosol-derived hexosides.

Omar et al. in their investigation of red ash bark (*Fraxinus pennsylvanica*) detected antimicrobial activity towards *Staphylococcus aureus* bacteria and very weak inhibition towards a series of fungal strains (Omar et al., 2000).

This brief account illustrates the potential of bioactive oak extracts and their complex polyphenols; nevertheless the depth of available information needs to be addressed.

2.6.2 Elm: Genus *Ulmus*

The Québec territory features three distinct indigenous elm species: American (*Ulmus americana* L.), cork (*Ulmus thomasii* Sargent) and red (*Ulmus rubra* Muhl.). The American elm is the most common.

This species can be found in all the southern areas, but remains highly susceptible to Elm Dutch disease, caused by two related microfungi (*Ophiostoma ulmi* (Buisman) Nannf. and *Ophiostoma novo-ulmi* Brasier, the most devastating)[xi].In terms of mechanical characteristics, elm wood is considered hard, tough to split, coarse grained and of poor durability. Large specimens with rotten, hollow lengthwise cores are often observed. Nevertheless, this timber finds applications in shipbuilding (being stable underwater), cabinetmaking and barrelmaking. First Nation Iroquois used elm bark in emergency cases (Arnason, Hebda, & Johns, 1981) in the form of a mixed infusion with oak bark to heal hernias. In traditional medicine, red elm has been reportedly used by Ojibways as decoctions to treat sore throat and by Montagnais to heal wounds and hemorrhage.

Earlier studies describing *Ulmus americana* extractives mention the stimulating properties of twig bark benzenic extracts when tested on beetles (*Scolytus multistriatus*), an insect known to consume this bark from its host species (Gilbert & Norris, 1968; Norris & Baker, 1967). A series of sesquiterpene quinones (mansonones) were later isolated from branch extracts following fungal infestation (Dumas, Strunz, Hubbes, & Jeng, 1983); the authors concluded that those antifungal molecules were synthesized by the American elm in response to the pathogenic invasion. The same extracts also yielded β-sitosterol and scopoletin, a potent analgesic. More recently, Omar et al. noted that UV exposure significantly increased the subsequent antimicrobial activity of the bark extracts (Omar, et al., 2000), this species produces phytoalexins in order to combat environmental stress and ward off microbial attacks.

2.6.3 Basswood: Genus *Tilia*

The American basswood (*Tilia americana* L or *Tilia glabra*) represents the sole indigenous species in Québec and has long been locally known as "white wood" no doubt because of its value to cabinetmakers, sculptors and string instrument makers. Traditionally, linden flowers were recommended for conditions as diverse as spasms, digestive troubles, insomnia, neurosis and atherosclerosis – due to their action on blood hyperviscosity and hypercoagulation (Sousa et al., 2008); more recently it was noted that those flowers increased non-specific resistance in the human body and thus qualified as an excellent remedy against the flu and colds – particularly in children. The famed ecologist Brother Marie-Victorin in his well-known treatise *Flore Laurentienne* mentioned the antispasmodic and diaphoretic properties of those flowers. In recent years, systematic studies using hexane and methanol extracts successfully demonstrated sedative effects in the mouse model, through measurements of anxiolytic levels and ambulatory activity (impact on motor equilibria)(Aguirre-Hernández, Martínez, González-Trujano, Moreno, Vibrans, & Soto-Hernández, 2007). Research in Mexico identified β-sitosterol and several fatty acids along with a specific triterpene in hexane extracts from the flowers (Aguirre-Hernández, Rosas-Acevedo, Soto-Hernández, Martínez, Moreno, & González-Trujano, 2007) and the same team also observed some anxiolytic activity of the aqueous extracts. Extensive phytochemical studies on polar extracts within this genus revealed the recurrent presence of polyphenols including several flavonoids: quercitrin and isoquercitrin, kaempferol, astragalin, hyperoside, tiliroside, quercetin-3,7-*O*-dirhamnoside and kaempferol-3,7-*O*-dirhamnoside. Meanwhile quercetin and kaempferol derivatives were successfully identified in aqueous flower extracts (Pérez-Ortega, et al., 2008). Further work on the fractionation of hexane extracts indicated that compounds soluble in methanol were most active; therefore this fraction contains the sedative and anxiolytic molecules of interest. These include tiliroside, quercitrin, rutin, kaempferol and quercetin. The latter molecule – already known for its anti-inflammatory properties – may play a key role in the observed analgesic activity of the aqueous extract, as this extract appears more active than its hexane and methanol counterparts; aqueous extract from basswood flowers may represent an option when dealing with arthritic pain (Martínez, González-Trujano, Aguirre-Hernández, Moreno, Soto-Hernández, & López-Muñoz, 2009).

In the course of his extensive ethnopharmacological study, Arnason noted that First Nation Iroquois were using basswood bark as twig tea prior to delivery and also to treat wounds. The screening of a number of species (Omar, et al., 2000) for their antimicrobial activities also revealed that basswood extracts effectively inhibited *Bacillussubtilis*sporulating Gram+ bacteria and this activity becomes more pronounced following UV exposure; the absence of antifungal properties was also reported. There appears to be no published data on basswood bark extracts.

2.6.4 Walnut: Genus *Juglans*

Several indigenous walnut species can be observed in Canada, among those Eastern black walnut (*Juglans nigra* L.), butternut or white walnut (*Juglans cinerea* L) as well as Japanese walnut (*Juglans ailantifolia*).

Black walnut grows in its natural state only in southern Ontario, and is found in southern Québec as an ornamental – also on experimental plots – and grown for the production of high-quality specialty woods.

The sole species indigenous to Québec, *Juglans cinerea* remains undercommercialized relative to the other species despite its fine nut and wood qualities. This walnut has become near extinction following the infective devastation known as butternut canker, caused by the *Sirococcus* sp. fungus. Wood from the white walnut or butternut is known as light, soft and weak, coarse grained, with its pale brown hue quickly turning dark upon exposure to air; it is often used in cabinetmaking and interior home decoration. For many years, cathartic properties have been assigned to the bark inner layers, for instance a blend of bark extract with honey permitted to operate on a patient without causing pain or irritation. Other notable uses included the treatment of dysentery, of inflammatory ophthalmia, and for toothache by applying a small wetted piece of bark on the nape of the neck.

The majority of studies on walnut extractives have focused on *Juglans nigra* and on all parts of the tree. Most recent work has dealt with the fruits, but the following information relates to the properties of barks from a limited number of species. The black and white walnut are part of the *Juglandaceae* family. Juglone, a naphtoquinone derivative, represents the best known bark compound in this family (Rowe & Conner, 1979), and exhibits a wide spectrum of bioactivities (Alice, Tannis, & Charles, 1990; Gîrzu, Carnat, Privat, Fialip, Carnat, & Lamaison, 1998; Auyong, Westfall, & Russell, 1963): antimicrobial, antitumoral, sedative, antioxidant, fungicidal. Other properties include a type of cytotoxicity that deactivates the body's enzymatic system which protects against oxidative stress (Inbaraj & Chignell, 2003). Juglone from *Juglans nigra* may also cause skin damage by direct contact, and it has nevertheless been used as purgative and laxative. The same compound was proposed as contributor to the allelopathic characteristics of extracts used in natural herbicides (Shrestha, 2009). This molecule may therefore have a bright future in terms of applications. Qualitywise, *Juglans nigra* wood is recognized as highly resistant to biodegradation. Gupta et al. (1972) successfully identified a series of polyphenols in black butternut bark extract (Gupta, Ravindranath, & Seshadri, 1972): four flavonoids –myricetin, myricitrin (myricetin-3-rhamnoside), sakuranetin and sakurenin (sakuranetin-5-glucoside) – as well as the chalcone glycoside neosakuranin and juglone and its derivative dihydrojuglone-4-glycoside.

Bark extracts from *Juglans cinerea* demonstrated a wide spectrum of activities against a number of Gram+ and Gram- bacteria and also fungi; those activities increase following exposure to UV wavelengths as observed elsewhere (Omar et al., 2000). No detailed studies appear to be available on the topic white butternut bark. The potential of extractives from those species deserves more attention, particularly with regards to their applications in various areas such as pesticides, herbicides, medicines, and cosmetics.

#### 2.6.5 Hickory: Genus *Carya*

Records indicate the presence of five indigenous species of hickory in Canada. In Québec, bitternut hickory (*Carya cordiformis* (Wangenh) K. Koch) and shellbark hickory (*Carya ovata* Michx. F.) dominate the bioclimatic areas known as hickory maple stands (Lupien, 2009). Those species produce edible nuts as well, as do other relatives from the nut tree family *Juglandaceae*.

The name hickory originates from the Algonquin language. *Carya cordiformis*, or ”northernmost one”, and the tree turns out round highly bitter nuts that some animals will consume; humans are generally repulsed by their high tannin content and extreme unpalatability. Early settlers found ways to press the oil out of the nuts to light their lamps, and apparently believed this oil could cure rheumatisms. First Nation Iroquois were known to blend the oil with bear fat to manufacture an insect repellent; they also made use of the bark to build furniture and snowshoes. Hickory has long been favored as firewood, as it will burn evenly and generate long hours of heat. Charcoal from this species imparts a delightfully smoky aroma to foods. Unregulated felling for the firewood market is at the root of its dwindling population in many forested areas.

Wood from shellbark hickory is considered as superior within this species. It remains highly prized by cabinetmakers – despite its poor availability – on the basis of its hardness, strength, resistance and porosity. Nuts from this species, in contrast to *Carya cordiformis*, are sweet and pleasantly tasty.

Bark extracts from both species have been tested against a series of bacterial and fungal strains. The *C.cordiformis* extract inhibited *Staphylococcus aureus* bacteria whereas no effect was observed when using the *C. ovata* extract. Overall, hickory bark extracts exhibited lower antimicrobial activities than other species according to the work of Omar et al (Omar, et al., 2000). Notably, bark from the *C. ovata* species contains mostly juglone, a naphtoquinone previously described in this article, and shown in a 1967 study to be responsible for the extract’s insect-repelling effect (Gilbert, Baker, & Norris, 1967).

There appears to be no other phytochemical investigations on hickory bark extracts in the literature.

## 3. Conclusion: The Commercial Potential of Extractives from Hardwood Species

This review underlines the need to pursue targeted research on the phytochemical analysis and biological properties of extractives from Boreal forest wood species and North American wood species in general. A clear lack of reliable data on North American hardwoods emerges when comparing with information available on European species from the same genera. Ethnopharmacological data are a useful guide for researchers focusing on wood species of high biological potential. This will help for instance in defining the equivalence factors between on one hand, traditional medicinal uses and on the other hand recent scientific observations on similar extracts. In most known cases, First Nations individuals were consuming various molecules originating from forest biomass, without reports of toxic episodes.

Hardwood species in Québec represent considerable sources of extractives with multiple biological properties, which could lead to the design and formulation of high value-added products. This includes triterpenes betulinic acid from white birch (anticancer, anti-HIV), lupeol from yellow birch bark (anti-inflammatory), red oak tannins (astringent, antioxidant), polyphenols such as poplar salicylates (analgesic, antioxidant, tonic) and others.

In light of this overall assessment, it becomes clear that tree bark is a renewable source of bioactive molecules but this tissue has been studied to a lesser extent than other aerial tissues such as leaves, flowers, branches, and buds. Therefore, in order to create value propositions for residual bark biomass generated in large quantities by the forest industry, screening programs will be required that will accurately link the biochemical composition of bark extractives with their biomedical benefits. Other considerations such as the distinction between outer and inner bark tissues will be important since their respective compositional profiles may vary significantly and thus harbor quite different bioactivities. There is also a pressing need to study the various types of bark on the basis of factors such as regional distribution and long term availability. Data available on First Nations traditional uses represent an excellent starting point and illustrate intricate differences between species and their therapeutic applications. It is now our turn to draw inspiration from this rich empirical knowledge, the result of centuries of First Nations traditions.

**Reference**

Abou-Zaid, M., & Nozzolillo, C. (1999). 1-O-galloyl-[alpha]--rhamnose from Acer rubrum. *Phytochemistry, 52*(8), 1629-1631. http://dx.doi.org/10.1016/S0031-9422(99)00236-8

Abou-Zaid, M., Helson, B., Nozzolillo, C., & Arnason, J. (2001). Ethyl m-Digallate from Red Maple, Acer rubrum L., as the Major Resistance Factor to Forest Tent Caterpillar, Malacosoma disstria Hbn. *Journal of Chemical Ecology, 27*(12), 2517-2527. http://dx.doi.org/10.1023/A:1013683600211

Aguirre-Hernández, E., Martínez, A., González-Trujano, M., Moreno, J., Vibrans, H., & Soto-Hernández, M. (2007). Pharmacological evaluation of the anxiolytic and sedative effects of Tilia americana L. var. mexicana in mice. *Journal of Ethnopharmacology, 109*(1), 140-145.

Aguirre-Hernández, E., Rosas-Acevedo, H., Soto-Hernández, M., Martínez, A., Moreno, J., & González-Trujano, M. (2007). Bioactivity-Guided isolation of Î²-Sitosterol and Some Fatty Acids as Active Compounds in the Anxiolytic and Sedative Effects of Tilia americana var. mexicana inflorescences used traditionally by communities of State of Michoacan, Mexico. *Journal of Ethnopharmacology, 116*(3), 461-468. http://dx.doi.org/10.1016/j.jep.2006.07.017

Akazawa, H., Akihisa, T., Taguchi, Y., Banno, N., Yoneima, R., & Yasukawa, K. (2006). Melanogenesis Inhibitory and Free Radical Scavenging Activities of Diarylheptanoids and Other Phenolic Compounds from the Bark of Acer nikoense. *Biological and Pharmaceutical Bulletin, 29*(9), 1970-1972. http://dx.doi.org/10.1248/bpb.29.1970

Akihisa, T., Tagushi, Y., Yasukawa, K., Tokuda, H., Akazawa, H., Suzuki, T., et al. (2006). Acerogenin M, a cyclic diarylheptanoid, and other phenolic compounds from Acer nikoense and their anti-inflammatory and anti-tumor-promoting effects. *Chemical Pharmaceutical Bulletin, 54*(5), 735-739. http://dx.doi.org/10.1248/cpb.54.735

Alakurtti, S., Mäkelä, T., Koskimies, S., & Yli-Kauhaluoma, J. (2006). Pharmacological properties of the ubiquitous natural product betulin. *European Journal of Pharmaceutical Sciences, 29*(1), 1-13. http://dx.doi.org/10.1016/j.ejps.2006.04.006

Albrecht, M., Nahrstedt, A., Luepke, N., Theisen, N., & Baron, G. (1990). Anti-inflammatory activity of flavonol glycosides and salicin derivatives from the leaves of Populus tremuloides. *Planta Medica, 56*(6), 660. http://dx.doi.org/10.1055/s-2006-961318

Alice, M., Tannis, M., & Charles, D. (1990). Antimicrobial activity of juglone. *Phytotherapy Research, 4*(1), 11-14. http://dx.doi.org/10.1002/ptr.2650040104

Aloui, F., Ayadi, N., Charrier, F., & Charrier, B. (2004). Durability of European oak (Quercus petraea and Quercus robur) against white rot fungi (Coriolus versicolor): relations with phenol extractives. *Holz Roh Werkst, 62*(4), 286-290. http://dx.doi.org/10.1007/s00107-004-0489-7

Amarowicz, R., Dykes, G., & Pegg, R. (2008). Antibacterial activity of tannin constituents from Phaseolus vulgaris, Fagoypyrum esculentum, Corylus avellana and Juglans nigra. *Fitoterapia, 79*(3), 217-219. http://dx.doi.org/10.1016/j.fitote.2007.11.019

Ammar, R., Bhouri, W., Sghaier, M., Boubaker, J., Skandrani, I., Neffati, A., et al. (2009). Antioxidant and free radical-scavenging properties of three flavonoids isolated from the leaves of Rhamnus alaternus L. (Rhamnaceae): A structure-activity relationship study. *Food Chemistry, 116*(1), 258-264. http://dx.doi.org/10.1016/j.foodchem.2009.02.043

Arct, J., & Pytkowska, K. (2008). Flavonoids as components of biologically active cosmeceuticals. *Clinics in Dermatology, 26*(4), 347-357. http://dx.doi.org/10.1016/j.clindermatol.2008.01.004

Arnason, T., Hebda, R., & Johns, T. (1981). Use of plants for food and medicine by Native Peoples of eastern Canada. *Canadian Journal of Botany, 59*, 2189-2325. http://dx.doi.org/10.1139/b81-287

Aslam, S., Stevenson, P., Kokubun, T., & Hall, D. (2006). Antibacterial and antifungal activity of cicerfuran and related 2-arylbenzofurans and stilbenes. *Microbiology research, 164*(2), 191-195. http://dx.doi.org/10.1016/j.micres.2006.11.012

Atmani, D., Chaher, N., Berboucha, M., Ayouni, K., Lounis, H., Boudaoud, H., et al. (2009). Antioxidant capacity and phenol content of selected Algerian medicinal plants. *Food Chemistry, 112*(2), 303-309. http://dx.doi.org/10.1016/j.foodchem.2008.05.077

Auyong, T., Westfall, B., & Russell, R. (1963). Pharmacological aspects of juglone. *Toxicon, 1*(4), 235-239. http://dx.doi.org/10.1016/0041-0101(63)90005-9

Bafi-Yebo, N., Arnason, J., Baker, J., & Smith, M. (2005). Antifungal constituents of Northern prickly ash, Zanthoxylum americanum Mill. *Phytomedicine, 12*, 370–377. http://dx.doi.org/10.1016/j.phymed.2003.12.005

Bailey, A., Asplund, R., & Ali, M. (1986). Isolation of methyl gallate as the antitumor principle of Acer saccharinum. *Journal of Natural Products, 49*(6), 1149-1150. http://dx.doi.org/10.1021/np50048a040

Barbosa, A., Nascimento, C., & Morais, J. (2007). Studies on the antitermitic properties of wood and bark crude extracts of forest species from Central Amazonian. *Brazil. Acta Amazonica, 37*(2), 213-218.

Bianco, M., Handaji, A., & Savolainen, H. (1998). Quantitative analysis of ellagic acid in hardwood samples. *Science of the Total Environment, 222*(1-2), 123-126. http://dx.doi.org/10.1016/S0048-9697(98)00294-0

Blay, P., Thibault, P., Thiberge, N., Kiecken, B., Lebrun, A., & Mercure, C. (1993). Analysis of taxol and related taxanes from taxus canadensis using liquid chromatography combined with mass spectrometry or tandem mass spectrometry. *Rapid Communications in Mass Spectrometry, 7*(7), 626-634. http://dx.doi.org/10.1002/rcm.1290070715

Bouchard, M., Douville, G., Dupuis, J., & Boudreault, A. (2008). *Profil des produits forestiers. Première transformation. Bois de sciage de Peuplier faux-tremble. Centre de Recherche Industrielle Québec.* Québec: Ministère des Ressources Naturelles et de la faune.

Bowen, I., & Ali, A. (2007). *Anti-tumor terpene compounds.* Compton Developments LTD. C. D., application number, US 2007/0259056A1.

Boyer, J., Breeden, D., & Brown, D. (2002). Isolation, identification, and characterization of compounds from Acer rubrum capable of oxidizing equine erythrocytes. *American Journal of Veterinary Research, 63*(4), 604–610. http://dx.doi.org/10.2460/ajvr.2002.63.604

Buck, A. (1996). Phytotherapy for the prostate. *British Journal of Urology, 78*(3), 325-336. http://dx.doi.org/10.1046/j.1464-410X.1996.00104.x

Calliste, C.-A., Trouillas, P., Allais, D.-P., Simon, A., & Duroux, J.-L. (2001). Free Radical Scavenging Activities Measured by Electron Spin Resonance Spectroscopy and B16 Cell Antiproliferative Behaviors of Seven Plants. *Journal of Agricultural and Food Chemistry, 49*(7), 3321-3327. http://dx.doi.org/10.1021/jf010086v

Chatonnet, P., & Dubourdieu, D. (1998). Comparative Study of the Characteristics of American White Oak (Quercus alba) and European Oak (Quercus petraea and Q. robur) for Production of Barrels Used in Barrel Aging of Wines. *American Journal of Enology and Viticulture, 49*, 79-85.

Cloutier, A., Blanchet, P., Koubaa, A., & Stevanovic, T. (2008). *Valorisation de l'écorce d'épinette noire et de peuplier faux-tremble, Projet financé dans le cadre de l'Action concertée Fonds Nature et Technologies – FRF-02. Programme de recherche sur la forêt boréale et son écologie au Saguenay.*

Coulombe, G. (2004). *Commission d'étude sur la gestion de la forêt publique québécoise.*ISBN 2-550-43626-1.

Del Alamo, M., Bernal, J., & Gomez-Cordoves, C. (2000). Behavior of monosaccharides, phenolic compounds, and color of red wines aged in used oak barrels and in the bottle. *Journal of Agriculture and Food Chemistry, 48*(10), 4613-4618. http://dx.doi.org/10.1021/jf9909050

Dellus, V., Mila, I., Scalbert, A., Menard, C., Michon, V., & Herve du Penhoat, C. (1997). Douglas-fir polyphenols and heartwood formation. *Phytochemistry, 45*(8), 1573-1578. http://dx.doi.org/10.1016/S0031-9422(97)00245-8

Desrochers, L. (2009). *10 éléments pour assurer le succès d'une opération de récupération de la biomasse forestière.* FP INNOVATIONS, FERIC, créer des solutions pour le secteur forestier.

Diouf, P., Stevanovic, T., & Boutin, Y. (2009). The effect of extraction process on polyphenol content, triterpene composition and bioactivity of yellow birch (Betula alleghaniensis Britton) extracts. *Industrial Crops and Products, 30*(2), 297-303. http://dx.doi.org/10.1007/s00226-009-0240-y

Diouf, P., Stevanovic, T., & Cloutier, A. (2009). Antioxidant properties and polyphenol contents of trembling aspen bark extracts. *Wood Science and Technology, 43*(5-6), 457-470. http://dx.doi.org/10.1016/j.indcrop.2009.05.008

Douville, G., Vallée, V., Proulx, A., Bouchard, M., Brulotte, F., Baribeault, J., et al. (2006). *Inventaires des méthodes et équipements de récupération ainsi que des systèmes de combustion les plus courants. Profil des produits forestiers, Première transformation, Biomasse forestière résiduelle.* Québec: CRIQ.

Dumas, M., Strunz, G., Hubbes, M., & Jeng, R. (1983). Isolation and identification of six mansonones fromUlmus americana infected with Ceratocystis ulmi. *Cellular and Molecular Life Sciences, 39*(10), 1089-1090. http://dx.doi.org/10.1007/BF01943121

Dupuis, J. (2009). *Détermination du potentiel de croissance du peuplier faux-tremble (Populus tremuloides Micihx.) à l'échelle de l'unité d'aménagement forestier en Haute-Mauricie, Québec, Canada. Mémoire de Maîtrise en géographie.* Montreal: Université du Québec.

Eyles, A., Jones, W., Riedl, K., Cipollini, D., Schwartz, S., Chan, K., et al. (2007). Comparative phloem chemistry of manchurian (Fraxinus mandshurica) and two North American ash species (Fraxinus americana and Fraxinus pennsylvanica). *Journal of Chemical Ecology, 33*(7), 1430-1448. http://dx.doi.org/10.1007/s10886-007-9312-3

Faber Jr, H. (1960). The methanol extractable aromatic materials in the inner bark of P. tremuloides. *Tappi, 43*, 406-413.

Federico, A., Morgillo, F., Tuccillo, C., Ciardiello, F., & Loguercio, C. (2007). Chronic inflammation and oxidative stress in human carcinogenesis. *International Journal of Cancer, 121*(11), 2381-2386. http://dx.doi.org/10.1002/ijc.23192

Fernandez De Simon, B., Cadahia, E., & Jalocha, J. (2003). Volatile Compounds in a Spanish Red Wine Aged in Barrels Made of Spanish, French, and American Oak Wood. *Journal of Agriculture and Food Chemistry, 51*(26), 7671-7678. http://dx.doi.org/10.1021/jf030287u

Fernandez, M., Watson, P., & Breuil, C. (2001). Gas chromatography-mass spectrometry method for the simultaneous determination of wood extractive compounds in quaking aspen. *Journal of Chromatography A, 922*(1-2), 225-233. http://dx.doi.org/10.1016/S0021-9673(01)00948-7

Ficker, C., Arnason, J., Vindas, P., Alvarez, L., Akpagana, K., GbÃassor, M., et al. (2003). Inhibition of human pathogenic fungi by ethnobotanically selected plant extracts. *Mycoses, 46*(1-2), 29-37. http://dx.doi.org/10.1046/j.1439-0507.2003.00838.x

Fortin, F. (2008). Estimation de la disponibilité de la biomasse forestière 2007-2008. *Conférence présenté au 2ième symposium sur la valorisation de la biomasse forestière et des résidus de transformation de QWEB.*

Frendo, R. (2004). Fraxinus Americana-Observation Clinique-Matière médicale-Etude thématique. *Societas Regalis Homeopathica Belgica. MDCCCLXXII, Revue, 43*(22).

Fridrich, D., Glabasnia, A., & Fritz, J. (2008). Oak ellagitannins suppress the phosphorylation of the epidermal growth factor receptor in human colon carcinonma cells. *Journal of Agriculture and Food Chemistry, 56*, 3010-3015. http://dx.doi.org/10.1021/jf073427z

Fujioka, T., Kashiwada, Y., Kilkuskie, R. E., Cosentino, L. M., Bailas, L. M., Jiang, J. B., et al. (1994). Anti-AIDS agents. 11. Betulinic acid and piatanic acid as anti-HIV principles from Syzigium claviflorum, and the anti-HIV activity of structurally related triterpenes. *Journal of Natural Products, 57*, 243-247. http://dx.doi.org/10.1021/np50104a008

Fukai, T., Kaitou, K., & Terada, S. (2005). Antimicrobial activity of 2-arylbenzofurans fromMorus species against methicillin-resistant Staphylococcus aureus. *Fitoterapia, 76*, 708-711. http://dx.doi.org/10.1016/j.fitote.2005.06.012

Gagné, E. (2007). *La récolte de la biomasse forestière-Excellente occasion de développement. Fédération Québécoise des coopératives forestières.*

Gagnon, D. (2004). *La forêt naturelle du Québec, un survol. Rapport présenté pour la Commission d'étude sur la gestion de la forêt publique québécoise.* Université du Québec, Montréal.

Garcia Perez, M.-E., Diouf, P., & Stevanovic, T. (2008). Comparative study of antioxidant capacity of yellow birch twigs extracts at ambient and high temperatures. *Food Chemistry, 107*(1), 344-351. http://dx.doi.org/10.1016/j.foodchem.2007.08.026

García-Pérez, M., Royer, M., Duque-Fernandez, A., Diouf, P., Stevanovic, T., & Pouliot, R. (2010). Antioxidant, toxicological and antiproliferative properties of Canadian polyphenolic extracts on normal and psoriatic keratinocytes. *Journal of Ethnopharmacology, 132*, 251-258. http://dx.doi.org/10.1016/j.jep.2010.08.030

Garcia-Sosa, K., Villareal-Alvarez, N., Lübben, P., & Pena-Rodriguez, L. (2006). Chrysophanol, an antimicrobial anthrquinone from the root extract of Colubrina greggii. *Journal of Mexican Chemical Society, 50*(2), 76-78.

Gaussiran, S., & Boileau, E. (2007). *Le liard…Une essence qui gagne à être connu. Le couvert boréal.* Québec: Partenariat Innovation Forêt.

Gauthier, C. (2006). *Glycosidation de terpènes pentacycliques de type lupane et évaluation in vitro de leur potentiel anticancéreux.* Chicoutimi: Université du Québec à Chicoutimi.

Gauthier, G., & Saucier, J. (1999). L'aménagement forestier du Québec. *Revue forestière Française LI, Numéro spécial*.

Gierlinger, N., Jacques, D., Grabner, M., Wimmer, R., Schwanninger, M., Rozenberg, P., et al. (2004). Colour of larch heartwood and relationships to extractives and brown-rot decay resistance. *Trees, 18*, 102-108. http://dx.doi.org/10.1007/s00468-003-0290-y

Gilbert, B., & Norris, D. (1968). A chemical basis for bark beetle (Scolytus) distinction between host and non-host trees. *Journal of Insect Physiology, 14*(8), 1063-1066. http://dx.doi.org/10.1016/0022-1910(68)90044-9

Gilbert, B., Baker, J., & Norris, D. (1967). Juglone (5-hydroxy-1,4-naphthoquinone) from Carya ovata, a deterrent to feeding by Scolytus multistriatus. *Journal of Insect Physiology, 13*(10), 1453-1454. http://dx.doi.org/10.1016/0022-1910(67)90170-9

Gîrzu, M., Carnat, A., Privat, A., Fialip, J., Carnat, A., & Lamaison, J. (1998). Sedative Effect of Walnut Leaf Extract and Juglone, an Isolated Constituent. *Pharmaceutical Biology, 36*(4), 280-286. http://dx.doi.org/10.1076/phbi.36.4.280.4580

Goetz, P. (2007). Phytothérapie du diabète. *Phytothérapie, 5*, 212-217. http://dx.doi.org/10.1007/s10298-007-0255-1

Gonalves, F., & Jordao, A. (2009). Changes in antioxidant activity and the proanthocyanidin fraction of red wine aged in contact with portuguese (Quercus Pyrenaica Willd.) and American (Quercus Alba L.) oak wood chips. *Italian Journal of Food Science, 21*(1), 51-64.

González-Sarrías, A., Li, L., & Seeram, N. P. (2011). Effects of Maple (Acer) Plant Part Extracts on of Human Tumorigenic and Non-tumorigenic Colon Cells. *Phytotherapy Research*, in Press.

Gould, M. (1997). Cancer chemoprevention and therapy by monoterpenes. *Environmental Health Perspectives, 105*(4), 977-979. http://dx.doi.org/10.1289/ehp.97105s4977

Gupta, S., Ravindranath, B., & Seshadri, T. (1972). Polyphenols of Juglans nigra. *Phytochemistry, 11*(8), 2634-2636. http://dx.doi.org/10.1016/S0031-9422(00)88569-6

Hagerman, A. (1988). Extraction of tannin from fresh and preserved leaves. *Journal of Chemical Ecology, 14*(2), 453-461. http://dx.doi.org/10.1007/BF01013897

Halliwell, B. (1996). Antioxidants in human health and disease. *Annual Review of Nutrition*, 33-50. http://dx.doi.org/10.1146/annurev.nu.16.070196.000341

Hammer, K., Carson, C., & Riley, T. (2003). Antifungal activity of the components of Melaleuca alternifolia (tea tree) oil. *Journal of Antimicrobial Chemotherapy, 53*, 853-860.

Hart, J. (1981). Role of Phytostilbenes in Decay and Disease Resistance. *Annual Review of Phytopathology, 19*, 437-458. http://dx.doi.org/10.1146/annurev.py.19.090181.002253

Harun, J., & Labosky, P. (1985). Chemical constituents of five northeastern barks. *Wood and Fiber Science, 17*(2), 274-280.

Hillis, W. (1962). *Wood extractives and their significance to the pulp and paper industrie.* New York: Academic Press, 512.

Hocking, G. (1963). Betula Species. *Pharmaceutical Biology, 3*(1), 351-357. http://dx.doi.org/10.3109/13880206309102228

Hon, D., & Shiraishi, N. (2001). *Wood and cellulosic chemistry.* New York: Marcel Dekker, Inc. 914 p.

Honma, A., Koyama, T., & Yazawa, K. (2010). Anti-hyperglycemic effects of sugar maple Acer saccharum and its constituent acertannin. *Food Chemistry, 123*, 390–394. http://dx.doi.org/10.1016/j.foodchem.2010.04.052

Hoyle, M. (1969). Variation in Content of Microelements in Yellow Birch Foliage Due to Season and Soil Drainage. *Soil Science Society of America Journal, 33*, 458-459. http://dx.doi.org/10.2136/sssaj1969.03615995003300030034x

Iizuka, T., Nagumo, S., Yotsumoto, H., Moriyama, H., & Nagai, M. (2007). Vasorelaxant effects of Acer nikoense extract and isolated coumarinolignans on rat aortic rings. *Biological and Pharmaceutical Bulletin, 30*(6), 1164-1166. http://dx.doi.org/10.1248/bpb.30.1164

Inbaraj, J., & Chignell, C. (2003). Cytotoxic Action of Juglone and Plumbagin: A Mechanistic Study Using HaCaT Keratinocytes. *Chemical Research in Toxicology, 17*(1), 55-62. http://dx.doi.org/10.1021/tx034132s

Inouye, S., Takizawa, T., & Yamaguchi, H. (2001). Antibacterial activity of essential oils and their major constituents against respiratory tract pathogens by gaseous contact. *Journal of Antimicrobial Chemotherapy, 47*, 565-573. http://dx.doi.org/10.1093/jac/47.5.565

Isaeva, E. V., Lozhkina, G. A., & Ryazanova, T. (2010). A Study of the Alcohol Extract from Balsam Poplar Buds. *Russian Journal of Bioorganic Chemistry, 36*(7), 929–933. http://dx.doi.org/10.1134/S1068162010070228

Isebrands, J., Guenther, A., Harley, P., Helmig, D., Klinger, L., Vierling, L., et al. (1999). Volatile organic compound emission rates from mixed deciduous and coniferous forests in Northern Wisconsin, USA. *Atmospheric Environment, 33*(16), 2527-2536. http://dx.doi.org/10.1016/S1352-2310(98)00250-7

Isidorov, V., & Vinogorova, V. (2003). GC-MS analysis of compounds extracted from buds of Populus balsamifera and Populus nigra. *Z. Naturforsch., 58*, 355-360.

Johansson, C., Saddler, J., & Beatson, R. (2000). Characterization of the Polyphenolics related to the colour of Western Red Cedar (Thuja plicata Donn.) heartwood. *Holzforschung, 54*(3), 246-254. http://dx.doi.org/10.1515/HF.2000.042

Ju, E., Lee, S., Hwang, H., & Kim, J. (2004). Antioxidant and anticancer activity of extract from Betula platyphylla var. japonica. *Life Sciences, 74*(8), 1013-1026. http://dx.doi.org/10.1016/j.lfs.2003.07.025

Julkunen-Tiito, R., Rousi, M., Bryant, J., Sorsa, S., Keinanen, M., & Sikanen, H. (1996). Chemical diversity of several Betulaceae species: comparison of phenolics and terpenoids in northern birch stems. *Trees, 11*, 16-22. http://dx.doi.org/10.1007/s004680050053

Kähkönen, M., Hopia, A., Vuorela, H., Rauha, J., Pihlaja, K., Kulaja, T., et al. (1999). Antioxydant activity of plant extracts containing phenolic compounds. *Journal of agricultural and food chemistry, 47*, 3954-3962. http://dx.doi.org/10.1021/jf990146l

Keinänen, M., Julkunen-Tiitto, R., Rousi, M., & Tahvanainen, J. (1999). Taxonomic implications of phenolic variation in leaves of birch (Betula L.) species. *Biochemical Systematics and Ecology, 27*, 243-254. http://dx.doi.org/10.1016/S0305-1978(98)00086-6

Krasutsky, P. (2006). Birch bark research and development. *Natural Products Report, 23*, 919-942. http://dx.doi.org/10.1039/b606816b

Krochmal, A., Walters, R., & Doughty, R. (1969). *A guide to medicinal plants of Appalachia.* USDA For. Serv. Res. Pap. NE-138, Northeast. Forest Exp. Sta., Upper Darby, Pa.

Krutul, D. (1992). The effect of extractives substances soluble in the alcohol-benzene mixture and in alkalies on some hygroscopic properties of birch wood. *Forestry and Wood Technology, 43*, 93-99.

Kunkel, G. (1984). *Plants for human consumption.* Koenigatein: Koeltz Scientific Books, pp. 393.

Kuokkanen, K., Julkunen-Tiito, R., Keinanen, M., Niemela, P., & Tahvanainen, J. (2001). The effect of elevated CO2 and temperature on the secondary chemistry of Betula pendula seedlings. *Trees, 15*, 378-384. http://dx.doi.org/10.1007/s004680100108

Lacandula, J. (2002). Variations in the physics of wood of selected Philippine tree species as a function Of extractive content. *CMU Journal of Science, 10*(1), 69-111.

Lanier, L., Keller, R., & Kremer, A. (1980). *Le Chêne rouge (Quercus rubra L.) en France. Extrait de : The Silva of North America.* USA: Ed, SARGENT.

Lavoie, J., & Stevanovic, T. (2005). Variation of chemical composition of the lipophilic extracts from yellow birch (Betula alleghaniensis) foliage. *Journal of Agriculture and Food Chemistry, 53*(12), 4747-4756. http://dx.doi.org/10.1021/jf050301y

Lavoie, J., & Stevanovic, T. (2006). Yield and composition of lipophylic extracts of yellow birch (Betula alleghaniensis Britton) as a function of wood age and aging under industrial conditions. *Holzforschung, 60*, 184-189. http://dx.doi.org/10.1515/HF.2006.030

Lee, K.-W., Kim, H., Lee, Y., Park, H.-J., Choi, J.-W., Ha, J., et al. (2007). Acteoside inhibits human promyelocytic HL-60 leukemia cell proliferation via inducing cell cycle arrest at G0/G1 phase and differentiation into monocyte. *Carcinogenesis, 28*(9), 1928-1936. http://dx.doi.org/10.1093/carcin/bgm126

Léger, A. (2008). *Biodiversité des plantes médicinales québécoise et dispositifs de protection de la biodiversité et de l'environnement. Thèse de maitrise en science de l'environnement.* Montréal: Université du Québec.

Loponen, J., Lempa, K., Ossipov, V., Kozlov, M., Girs, A., Hangasmaa, K., et al. (2001). Patterns in content of phenolic compounds in leaves of mountain birches along a strong pollution gradient. *Chemosphere, 45*, 291-301. http://dx.doi.org/10.1016/S0045-6535(00)00545-2

Lupien, P. (2009). *Espèces arborescentes indigènes compagnes. Consultation sur les guides sylvicoles.*

Mansoor A., G. H. (1995). Acteoside: A new antihypertensive drug. *Phytotherapy Research, 9*(7), 525-527. http://dx.doi.org/10.1002/ptr.2650090713

Martineau, L., Hervé, J., Muhamad, A., Saleem, A., Harris, C., Arnason, J., et al. (2010). Anti-adipogenic Activities of Alnus incana and Populus balsamifera Bark Extracts, Part I: Sites and Mechanisms of Action. *Planta Medica, 76*, 1439–1446. http://dx.doi.org/10.1055/s-0029-1240941

Martineau, L., Muhamad, A., Saleem, A., Hervé, J., Harris, C., Arnason, J., et al. (2010). Anti-adipogenic Activities of Alnus incana and Populus balsamifera Bark Extracts, Part II: Bioassay-guided Identification of Actives Salicortin and Oregonin. *Planta Medica, 76*, 1519–1524. http://dx.doi.org/10.1055/s-0029-1240991

Martínez, A., González-Trujano, M., Aguirre-Hernández, E., Moreno, J., Soto-Hernández, M., & López-Muñoz, F. (2009). Antinociceptive activity of Tilia americana var. mexicana inflorescences and quercetin in the formalin test and in an arthritic pain model in rats. *Neuropharmacology, 56*, 564-571. http://dx.doi.org/10.1016/j.neuropharm.2008.10.010

Matsuda, H., Ishikado, A., Nishida, N., Ninomiya, K., Fujiwara, H., Kobayashi, Y., et al. (1998). Hepatoprotective, superoxide scavenging, and antioxidative activities of aromatic constituents from the bark of Betula platyphylla var. japonica. *Bioorganic & medicinal chemistry letters, 8*(21), 2939-2944. http://dx.doi.org/10.1016/S0960-894X(98)00528-9

Mazzio, E., & Soliman, K. (2009). In vitro screening for the tumoricidal properties of international medicinal herbs. *Phytotherapy Research, 23*(3), 385-398. http://dx.doi.org/10.1002/ptr.2636

McCune, L., & Johns, T. (2002). Antioxidant activity in medicinal plants associated with the symptoms of diabetes mellitus used by the Indigenous Peoples of the North American boreal forest. *Journal of Ethnopharmacology, 82*(2-3), 197-205. http://dx.doi.org/10.1016/S0378-8741(02)00180-0

McCune, L., & Johns, T. (2003). Symptom-specific antioxidant activity of boreal diabetes treatments. *Pharmaceutical Biology, 41*(5), 362-370. http://dx.doi.org/10.1076/phbi.41.5.362.15942

McCune, L., & Johns, T. (2007). Antioxidant activity relates to plant part, life form and growing condition in some diabetes remedies. *Journal of Ethnopharmacology, 112*(3), 461-469. http://dx.doi.org/10.1016/j.jep.2007.04.006

Meletis, C., & Wagner, E. (2002). Natural remedies for promoting skin health. *Alternative and Complementary Therapies, 8*(3), 186-190. http://dx.doi.org/10.1089/107628002760091047

Miller, D., Sutcliffe, R., & Thauvette, J. (1990). Sticker stain formation in hardwoods: Isolation of scopoletin from sugar maple (Acer saccharum Marsh.). *Wood Science and Technology, 24*(4), 339-344. http://dx.doi.org/10.1007/BF00227054

Minato, K., & Sakai, K. (1997). The vibrational properties of wood impregnated with extractives of some species of Leguminosae. *Mokuzai Gakkaishi, 43*(12), 1035-1037.

Moerman, D. (1998). *Native American ethnobotany.* Oregon: Timber Press, 927pp.

Morikawa, T. (2007). Search for bioactive constituents from several medicinal foods: hepatoprotective, antidiabetic, and antiallergic activities. *Journal of Natural Medicine, 61*, 112-126. http://dx.doi.org/10.1007/s11418-006-0105-8

Morikawa, T., Tao, J., Toguchida, I., Matsuda, H., & Yoshikawa, M. (2003). Structures of new cyclic diarylheptanoids and inhibitors of nitric oxide production from Japanese folk medicine Acer nikoense. *Journal of Natural Products, 66*(1), 86-91. http://dx.doi.org/10.1021/np020351m

Morikawa, T., Tao, J., Ueda, K., Matsuda, H., & Yoshikawa, M. (2003). Medicinal foodstuffs. XXXI. 1) Structures of new aromatic constituents and inhibitors of degranulation in RBL-2H3 cells from a Japanese folk medicine, the stem bark of Acer nikoense. *Chemical Pharmaceutical Bulletin, 51*(1), 62-67. http://dx.doi.org/10.1248/cpb.51.62

Mosedale, J., Feuillat, F., Baumes, R., Dupouey, J., & Puech, J. (1998). Variability of wood extractives among Quercus robur and Quercus petraea trees from mixed stands and their relation to wood anatomy and leaf morphology. *Canadian Journal of Forest Research, 28*(7), 994-1006.

Moure, A., Cruz, J., Franco, D., Manuel Domínguez, J., Sineiro, J., Domínguez, H., et al. (2001). Natural antioxidants from residual sources. *Food Chemistry, 72*(2), 145-171. http://dx.doi.org/10.1016/S0308-8146(00)00223-5

Mshvildadze, V., Legault, J., Lavoie, S., Gauthier, C., & Pichette, A. (2007). Anticancer diarylheptanoid glycosides from the inner bark of Betula papyrifera. *Phytochemistry, 68*(20), 2531-2536. http://dx.doi.org/10.1016/j.phytochem.2007.05.018

Muller, R., Kalisz, P., & Kimmerer, T. (1987). Intraspecific Variation in Production of Astringent Phenolics over a Vegetation-Resource Availability Gradient. *Oecologia, 72*(2), 211-215. http://dx.doi.org/10.1007/BF00379270

Müller-Schwarze, D., Schulte, B., Sun, L., Müller-Schwarze, A., & Müller-Schwarze, C. (1994). Red maple (Acer rubrum) inhibits feeding by beaver (Castor canadensis). *Journal of Chemical Ecology, 20*(8), 2021-2034. http://dx.doi.org/10.1007/BF02066240

Müller-Schwarze, D., Schulte, B., Sun, L., Müller-Schwarze, A., & Müller-Schwarze, C. (1994). Red maple (Acer rubrum) inhibits feeding by beaver (Castor canadensis). *Journal of Chemical Ecology, 20*(8), 2021-2034. http://dx.doi.org/10.1007/BF02066240

Narayanan, V., & Seshadri, T. (1969). Chemical components of Acer rubrum wood and bark: Occurrence of procyanidin dimer and trimer. *Indian Journal of Chemistry, 7*, 213-214.

Neves, J., Matos, C., Moutinho, C., Queiroz, G., & Gomes, L. (2009). Ethnopharmacological notes about ancient uses of medicinal plants in Tras-os-Montes (northern of Portugal). *Journal of Ethnopharmacology, 124*(2), 270-283. http://dx.doi.org/10.1016/j.jep.2009.04.041

Nishibe, S., Sardari, S., Kodama, A., Horita, K., Kudo, M., Koike, K., et al. (1997). Constituents of bark of Fraxinus americana. *Natural Medicines, 51*(5), 482-485.

Nitta, K., Ogawa, Y., Negishi, F., Takahashi, T., Ito, A., Hosono, M., et al. (1999). Hot water extract of nikko maple (Acer nikoense) induces apoptosis in leukemia cells. *Biological and Pharmaceutical Bulletin, 22*(4), 378-381. http://dx.doi.org/10.1248/bpb.22.378

Norris, D., & Baker, J. (1967). Feeding responses of the beetle Scolytus to chemical stimuli in the bark of Ulmus. *Journal of Insect Physiology, 13*(6), 955-958. http://dx.doi.org/10.1016/0022-1910(67)90058-3

Nussbaum, R., & Sterley, M. (2002). The effect of wood extractive content on glue adhesion and surface wettability of wood. *Wood and Fiber Science, 34*(1), 57-71.

O'Connell, M., Bentley, M., Campbell, C., & Cole, B. (1988). Betulin and lupeol in bark from four white-barked birches. *Phytochemistry, 27*(7), 2175-2176. http://dx.doi.org/10.1016/0031-9422(88)80120-1

Ohno, T., Inoue, M., Ogihara, Y., & Saracoglu, I. (2002). Antimetastatic Activity of Acteoside, a Phenylethanoid Glycoside. *Biological & Pharmaceutical Bulletin, 25*(5), 666-668. http://dx.doi.org/10.1248/bpb.25.666

Omar, S., Lemonnier, B., Jones, N., Ficker, C., Smith, M., Neema, C., et al. (2000). Antimicrobial activity of extracts of eastern North American hardwood trees and relation to traditional medicine. *Journal of Ethnopharmacology, 73*(1-2), 161-170. http://dx.doi.org/10.1016/S0378-8741(00)00294-4

Özçelik, B., Gürbüz, I., Karaoglu, T., & Yesilada, E. (2009). Antiviral and antimicrobial activities of three sesquiterpene lactones from Centaurea solstitialis L. ssp. solstitialis. *Microbiology Research, 164*(5), 545-552. http://dx.doi.org/10.1016/j.micres.2007.05.006

Paduch, R., Kandefer-Szerszen, M., Trytek, M., & Fiedurek, J. (2007). Terpenes: substances useful in human healthcare. *Archivum Immunologiae et Therapiae Experimentalis, 55*, 315-327. http://dx.doi.org/10.1007/s00005-007-0039-1

Panda, S., & Kar, A. (2006). Evaluation of the antithyroid, antioxidative and antihyperglycemic activity of scopoletin from Aegle marmelos leaves in hyperthyroid rats. *Phytotherapy Research, 20*(12), 1103-1105. http://dx.doi.org/10.1002/ptr.2014

Parent, B. (2009). *Ressources et Industries forestières, Portrait statistique, MRNF.*Québec.

Patočka, J. (2003). Biologically active pentacyclic triterpenes and their current medicine signification. *Journal of applied Biomedicine, 1*, 7-12.

Pearl, I., & Darling, S. (1968). Studies on the barks of the family salicaceae-XIX. Continued studies on the hot water extractives of Populus balsamifera bark. *Phytochemistry, 7*(10), 1851-1853. http://dx.doi.org/10.1016/S0031-9422(00)86658-3

Pearl, I., & Darling, S. (1968). Studies on the barks of the family salicaceae-XX. Variations in the hot water extractives of populus balsamifera bark. *Phytochemistry, 7*(10), 1855-1860. http://dx.doi.org/10.1016/S0031-9422(00)86659-5

Pearl, I., & Darling, S. (1971). Studies on barks of family of salicaceae.27. Hot water phenolic extractives of bark and leaves of diploid Populus tremuloides. *Phytochemistry, 10*, 483–484. http://dx.doi.org/10.1016/S0031-9422(00)94089-5

Pearl, I., Darling, S., De Haas, H., Loving, B., Scott, D., Turley, R., et al. (1961). Preliminary evaluation for glycosides of barks of several species of the genus Populus. *Tappi, 44*, 475–478.

Pérez-Ortega, G., Guevara-Fefer, P., Chávez, M., Herrera, J., Martínez, A., Martínez, A., et al. (2008). Sedative and anxiolytic efficacy of Tilia americana var. mexicana inflorescences used traditionally by communities of State of Michoacan, Mexico. *Journal of Ethnopharmacology, 116*(3), 461-468. http://dx.doi.org/10.1016/j.jep.2007.12.007

Pichette, A., Eftekhari, A., Georges, P., Lavoie, S., Mshvildadze, V., & Legault, J. (2010). Cytotoxic phenolics compounds in leaf buds of Populus tremuloides. *Canadian Journal of Chemistry, 88*, 104-110. http://dx.doi.org/10.1139/V09-151

Pichette, A., Legault, J., & Gauthier, C. (2008). *Triterpenes derivatives and uses thereof as antitumor agents or anti-inflammatory agents.*College M. (Ed.).

Pichette, A., Legault, J., Lavoie, S., Dufour, D., Côté, P., Caron, J., et al. (2008). *Valorisation des produits naturels présents dans les résidus d'écorces d'essences ligneuses du Québec par le développement d'utilisations dans le domaine des adhésifs et de l'agriculture.*Québec: FQRNT.

Pisha, E., Chai, H., Lee, I.-S., Chagwedera, T. E., Farnsworth, N. R., Cordell, G. A., et al. (1995). Discovery of betulinic acid as a selective inhibitor of human melanoma that functions by induction of apoptosis. *Natural Medicine, 1*, 1046-1051. http://dx.doi.org/10.1038/nm1095-1046

Prévost, M., Roy, V., & Raymond, P. (2003). *Sylviculture et régénération des forêts mixtes du Québec (Canada) : une approche qui respecte la dynamique naturelle des peuplements.* Québec: Note recherche n° 125, Direction de la recherche forestière.

Prida, A., & Puech, J.-L. (2006). Influence of Geographical Origin and Botanical Species on the Content of Extractives in American, French, and East European Oak Woods. *Journal of Agriculture and Food Chemistry, 54*(21), 8115-8126. http://dx.doi.org/10.1021/jf0616098

Raju, G., & Sanjay, M. (2009). Recent developments in anti-inflammatory natural products. *Medicinal Research Reviews, 5*, 767-820.

Ranatunga, T., Jervis, J., Helm, R., McMillan, J., & Hatzis, C. (1997). Toxicity of hardwood extractives toward Saccharomyces cerevisiae glucose fermentation. *Biotechnology Letters, 19*(11), 1125-1127. http://dx.doi.org/10.1023/A:1018400912828

Ricklefs, R., & Matthew, K. (1982). Chemical characteristics of the foliage of some deciduous trees in southeastern Ontario. *Canadian Journal of Botany, 60*(10), 2037-2045. http://dx.doi.org/10.1139/b82-251

Ritch-Krc, E., Thomas, S., Turner, N., & Towers, G. (1996). Carrier herbal medicine: Traditional and contemporary plant use. *Journal of Ethnopharmacology, 52*(2), 85-94. http://dx.doi.org/10.1016/0378-8741(96)01392-X

Rousseau, J. (1962). La forêt mixte du Québec dans la perspective historique. *Cahiers de géographie du Québec, 7*(13), 111-120.

Rowe, J., & Conner, A. (1979). *Extractives in Eastern Hardwood.*MADISON, WISCONSIN: 18 G. t. r.-F. (Ed.).

Royer, M. (2008). Les molécules responsables de la stabilité des bois : cas des bois tropicaux de Guyane Française. Cayenne, pp. 242: Unité Mixte de Recherche Ecologie des forêts de Guyane, Université des Antilles et de la Guyane.

Royer, M., Diouf, P., & Stevanovic, T. (2011). Polyphenol contents and radical scavenging capacities of Red Maple (Acer rubrum L.) extracts. *Food and Chemical Toxicology, 49*, 2180–2188. http://dx.doi.org/10.1016/j.fct.2011.06.003

Royer, M., Stien, D., Beauchêne, J., Herbette, G., McLean, J., Thibaut, A., et al. (2010). Extractives of the tropical wood wallaba (Eperua falcata Aubl.) as natural anti-swelling agent. *Holzforschung, 64*(2), 211-215. http://dx.doi.org/10.1515/hf.2010.034

Russell, A., Vanneman, C., & Waddey, W. (1942-1945). Natural tanning materials of the Southeastern United States. Parts IVIII. *Journal of American Leather Chemists Association, 37:340-356; 38:30-34, 144-148, 235-238, 355-358; 39:173-178; 40:110-121, 422-426.*

Sakagami, H., Anzai, S., Goto, S., & Takeda, M. (1997). Enhancement of cytotoxic activity of ascorbate by Acer nikoense maxim. extracts. *Anticancer Res, 17*(6D), 4453-4456.

Santamour, F., & Lundgren, L. (1997). Rhododendrin in Betula: a reappraisal. *Biochemical Systematics and Ecology, 25*(4), 335-341. http://dx.doi.org/10.1016/S0305-1978(97)83745-3

Santamour, F., & Vettel, H. (1978). The distribution of rhododendrin in birch (Betula) species. *Biochemical Systematics and Ecology, 6*, 107-108. http://dx.doi.org/10.1016/0305-1978(78)90034-0

Sato, J., Goto, K., Nanjo, F., Kawai, S., & Murata, K. (2000). Antifungal activity of plant extracts against Arthrinium sacchari and Chaetomium funicola. *Journal of Bioscience and Bioengineering, 90*(4), 442-446.

Satoh, K., Anzai, S., & Sakagami, H. (1998). Radical scavenging activity of Acer nikoense maxim. *Anticancer Research, 18*(2A), 833-837.

Schultz, P., & Darrel, D. (2000). Naturally durable heartwood: evidence for a proposed dual defensive function of the extractives. *Phytochemistry, 54*, 47-52. http://dx.doi.org/10.1016/S0031-9422(99)00622-6

Schultz, T., & Nicholas, D. (2002). Development of environmentally-benign wood preservatives based on the combination of organic biocides with antioxidants and metal chelators. *Phytochemistry, 61*(5), 555-560. http://dx.doi.org/10.1016/S0031-9422(02)00267-4

Seshadri, T. (1973). *An investigation of the phenolic constituents of certain woods and barks, including North American species and representatives of genera common to North America and India.* (J. W. Rowe, USDA PL-480 Proj. FG-In-425, Forest Prod. Lab., Madison, Wis.

Shrestha, A. (2009). Potential of a black walnut (Juglans nigra) extract product (NatureCur®) as a pre- and post-emergence bioherbicide. *Journal of Sustainable Agriculture, 33*(8), 810-822. http://dx.doi.org/10.1080/10440040903303397

Silici, S., & Kutluca, S. (2005). Chemical composition and antibacterial activity of propolis collected by three different races of honeybees in the same region. *Journal of Ethnopharmacology, 99*(1), 69-73. http://dx.doi.org/10.1016/j.jep.2005.01.046

Sivropoulou, A., Papanikolaou, E., Nikolaou, C., Kokkini, S., Lanaras, T., & Arsenakis, M. (1996). Antimicrobial and Cytotoxic Activities of Origanum Essential Oils. *Journal of Agriculture and Food Chemistry, 44*(5), 1202-1205. http://dx.doi.org/10.1021/jf950540t

Sjöström, E., & Alén, R. (1999). *Analytical methods in wood chemistry, pulping, and papermaking.* Berlin: Springer.

Sousa, F., Melo, C., Citó, M., Félix, F., Vasconcelos, S., Fonteles, M., et al. (2008). Medicinal plants and their bioactive constituents:A scientific review of bioactivity and potential benefits in the anxiety disorders in animal models. *Revista Brasileira de Farmacognosia, 18*(4), 642-654. http://dx.doi.org/10.1590/S0102-695X2008000400023

Stevanovic, T., & Perrin, D. (2009). *Chimie du bois.* Nancy, 241 p: Presses polytechniques et universitaires romandes.

Stevanovic, T., Diouf, P., & Garcia-Perez, M. (2009). Bioactive polyphenols from healthy diets and forest biomass. *Current Nutrition and Food Science, 5*(4), 264-295. http://dx.doi.org/10.2174/157340109790218067

Sunnerhein, K., Palo, T., Theander, O., & Knutsson, P. (1988). Chemical defense in birch. Platyphylloside: A phenol from Betula pendula inhibiting digestibility. *Journal of Chemical Ecology, 14*(2), 549-559. http://dx.doi.org/10.1007/BF01013906

Takenaka, Y., Tanahashi, T., Shintaku, M., Sakai, T., Nagakura, N., & Parida. (2000). Secoiridoid glucosides from Fraxinus americana. *Phytochemistry, 55*(3), 275-284. http://dx.doi.org/10.1016/S0031-9422(00)00319-8

Tam, T., Liu, R., Arnason, J., Krantis, A., Staines, W., Haddad, P., et al. (2009). Actions of ethnobotanically selected Cree anti-diabetic plants on human cytochrome P450 isoforms and flavin-containing monooxygenase 3. *Journal of Ethnopharmacology, 126*(1), 119-126. http://dx.doi.org/10.1016/j.jep.2009.07.036

Tattar, T., & Rich, A. (1973). Extractable phenols in clear, discolored and decayed woody tissues and bark of sugar maple and red maple. *Phytopathology, 63*(1), 167-169. http://dx.doi.org/10.1094/Phyto-63-167

Thériault, M., Caillet, S., Kermasha, S., & Lacroix, M. (2006). Antioxidant, antiradical and antimutagenic activities of phenolic compounds present in maple products. *Food Chemistry, 98*(3), 490-501. http://dx.doi.org/10.1016/j.foodchem.2005.05.079

Timbal, J. (1990). Le chêne rouge d'Amérique. Ecologie et Facteurs limitant. *Revue forestière française XLII.*

Triaud, J. (1998). Polyphenols 96: 18th International Conference on Polyphenols. Bordeaux.

Tripoli, E., Giammanco, M., Tabacchi, G., Di Majo, D., Giammanco, S., & La Guardia, M. (2005). The phenolic compounds of olive oil: structure, biological activity and beneficial effects on human health. *Cambridge Journals Online*, 98-112.

Trombetta, D., Castelli, F., Sarpietro, M., Venuti, V., Cristani, M., Daniele, C., et al. (2005). Mechanisms of Antibacterial Action of Three Monoterpenes. *Antimicrobial Agents and Chemotherapy, 49*(6), 2474-2478. http://dx.doi.org/10.1128/AAC.49.6.2474-2478.2005

Vardar-Unlu, G., Silici, S., & Ulu, M. (2008). Composition and in vitro antimicrobial activity of Populus buds and poplar-type propolis. *World Journal of Microbiology and Biotechnology, 24*(7), 1011-1017. http://dx.doi.org/10.1007/s11274-007-9566-5

Willfor, S., Ahotupa, M., Hemming, J., Reunanen, M., Eklund, P., Sjoholm, R., et al. (2003). Antioxidant activity of knotwood extractives and phenolic compounds of selected tree species. *Journal of agricultural and food chemistry, 51*(26), 7600-7606. http://dx.doi.org/10.1021/jf030445h

Williams, C. (1970). *Hormonal interactions between plants and insects.* New York: Chemical Ecology, Sondheimer E. and Simeone J.B. eds., Academic press pp. 79-87.

Witherup, K., Look, S., Stasko, M., Ghiorzi, T., Muschik, G., & Cragg, G. (1990). Taxus spp. Needles Contain Amounts of Taxol Comparable to the Bark of Taxus brevifolia: Analysis and Isolation. *Journal of Natural Products, 53*(5), 1249-1255. http://dx.doi.org/10.1021/np50071a017

Woodward, S., & Pearce, R. (1988). The role of stilbenes in resistance of Sitka spruce (Picea sitchensis (Bong.) Carr.) to entry of fungal pathogens. *Physiological and Molecular Plant Pathology, 33*(1), 127-149. http://dx.doi.org/10.1016/0885-5765(88)90049-5

Wren, R. (1975). *Potter's New Cyclopaedia of Botanical Drugs and Preparations.* Bradford: Re-edited and enlarged by Wren RW. Health Science Press, pp. 400.

Wu, D., Wu, X., You, X., Ma, X., & Tian, W. (2010). Inhibitory Effects on Bacterial Growth and b-Ketoacyl-ACP Reductase by Different Species of Maple Leaf Extracts and Tannic Acid. *Phytotherapy Research, 24*, 35-41. http://dx.doi.org/10.1002/ptr.2873

Yuan, T., Wan, C., Liu, K., & Seerama, N. P. (2012). New maplexins F-I and phenolic glycosides from red maple (Acer rubrum) bark. *Tetrahedron, 68*, 959-964. http://dx.doi.org/10.1016/j.tet.2011.11.062

**Notes**

[i] Ministère des Ressources Naturelles et de la Faune. (2008). *Document synthèse du Livre vert « La forêt pour construire le Québec de demain ».* Québec.

[ii] Ministère du Développement économique, Innovation et Exportation. (2005). *L'industrie des Produits de Santé Naturel, Profil Industriel, Développement générale de l'industrie et du commerce économique.* Québec.

[iii] Ministère des Ressources Naturelles et de la Faune. (2009). *Chiffres clés du Québec forestier 2009*[iv] Ressources naturelles du Canada; http://foretscanada.rncan.gc.ca.

[v] Portionsof apublicforest landthat is the subjectof a calculationofallowableandcommon areas.

[vi] Ministère des Ressources Naturelles et de la Faune. (2002). *Délimitation des unités d'aménagement forestier et de la limite Nord des attributions commerciales.* Québec.

[vii] Portions of apublic forest landon whichone or more beneficiariesofforest management agreements(CAAF) are authorized toconduct amanagement activityandto harvestacertain volume of timber.

[viii] Ministère des Ressources Naturelles et de la Faune. (2009). *Estimés de la disponibilité de la biomasse forestière par région administrative du Québec en 2007-2008, forêts publiques et privées.*

[ix] Ministère des Ressources Naturelles et de la Faune. (2009). *Vers la valorisation de la biomasse forestière, Plan d'action. Direction du développement de l'industrie des produits forestiers.* Québec.

[x] Conseil de l'Industrie forestière du Québec. (2008). *Mémoire sur la gestion des matières résiduelles présenté dans le cadre des consultations publiques de la commission des transports et de l'environnement de l'Assemblée Nationale.* Québec.

[x i] http://www.mrnfp.gouv.qc.ca/forets/fimaq/insectes/fimaq-insectes-maladies-hollandaise.jsp