Chemical Profiles of Essential Oils and Non-Polar Extractables from Sumac (*Rhus* spp.)

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Abstract

Sumac is the common name for a genus (*Rhus*) with >250 individual species of flowering plants in the family Anacardiaceae. These plants are globally distributed in temperate and tropical regions and can grow on marginal lands, making them strong candidates for renewable bioproduct sources. Despite the extensive historical use of some members of *Rhus* spp. for tannins and other commercial phenolics, little is known about the non-phenolic components of extracts and essentials oils. The current review highlights opportunities available to extend these limited prior studies to other sumac species, and for obtaining value-added compounds to complement already established phenolic extractions in these commercial plant species. To date, a number of individual aldehydes, fatty acids, long chain alcohols, terpenes and terpenoids, and waxes of commercial or bioactive potential in essential oils and non-polar extractables from selected members of the *Rhus* genera have been identified. Additional studies are needed to broaden the phytochemical database from other sumac species, and to better quantify the potential yields of these valuable compounds from the plants under natural and agriculturally managed conditions.

Keywords: Sumac; *Rhus* spp.; Phytochemicals; Non-polar; Hydrodistillation extracts; Oils

Introduction

Sustainable multi-use crops in adaptive systems for food, material, and energy production require plant species that can provide a variety of chemical intermediates for broad-ranging commercial uses. These compounds can include sterols, flavor and aroma compounds, long-chain alcohols, fatty acids, esters, waxes, and terpenes [1-4]. Ideally, these crops would be situated near the processing facilities (i.e., biorefineries) to reduce transportation costs and associated energy and material inputs, and would be indigenous so as to not disrupt local ecosystems [5,6]. To not compete with local food production, the industrial crops should also be suitable for perennial growth without substantial water and nutrient inputs on marginal lands [2,7].

Sumac (*Rhus* spp.) is a potentially suitable and globally distributed species [8] to help meet these sustainability goals. The plants have shallow, spreading root systems that prevent soil erosion, and can grow on poor, eroded soils [8,9]. For example, dwarf sumac (*R. copallina*), white or smooth sumac (*R. glabra*), and staghorn sumac (*R. typhina*) have been successfully used for erosion-control in North America over the past century [10]. Most sumac grown commercially on a global scale is *R. coriaria* in the Mediterranean and Middle East, having been cultivated for several centuries to produce a material of high quality for tanning (from polyphenolics in aqueous leaf extracts), as a food seasoning (from dried fruits), and for the promising bioactivities in various extracts [11-13].

Despite the extensive historical use of *Rhus* spp. (especially *R. coriaria*) for tannins and other commercial phenolics, little is known about the non-phenolic components of extracts and essentials oils. These phytochemicals have a wide range of potential commercial uses, such as medicinals, nutraceuticals, cosmetics, aroma and flavor agents for foods and beverages, pesticides, antimicrobials/antifungals/antivirals, surfactants, lubricants, waxes, and plasticizers, and as starting materials for industrial syntheses [14]. For this reason, the current mini-review has the objective of highlighting opportunities available to extend these studies to other sumac species, and for obtaining value-added compounds to complement already established phenolic extractions in these commercial plant species.

Phytochemicals in essential oils and non-polar extractables from sumac

Limited work has been done on determining the chemical composition of essential oils from sumac species. The few published studies have analyzed compounds in hydrodistillation oils from specific parts of the following small subset of >250 possible sumac species: *R. semialata*, *R. coriaria*, *R. mysurensis*, *R. javanica*, *R. taitensis*, *R. thyrsiflora*, and *R. typhina*. No other members of the *Rhus* genera have been reported on.

Surveys of essential oil compositions of Turkish *R. coriaria* plants using GC and GC-MS analysis have been performed [15,16]. A large number of compounds were tentatively identified in both studies (although details of structural confirmation by authentic standards are lacking, similar to the other two survey reports discussed below), of which the major components are summarized in Table 1. Of note, only two other studies have conducted surveys of non-phenolic phytochemicals in sumac, and are limited to the leaves of *R. typhina* [17] and the leaves and flowers of *R. mysurensis* [18].

Brunke *et al.* [15] identified the following major compounds in *R. coriaria* fruit oils, which gave hydrodistillation yields of 0.02-0.03% for separate samples from six different provinces in Turkey: α-pinene, limonene, octanal, (*E*)-hept-2-enal, nonanal, (*E*)-dec-2-enal, α-/β-humulene, α-terpineol, (*E*)-undec-2-enal, hexahydrofarnesylacetone, pelargonic acid, β-humulene alcohol, carvacrol, heptacosane, palmitic acid, and nonacosane. Together, the saturated and unsaturated aliphatic aldehydes made up about 10% to 40% of the oils, based on relative GC-MS peak areas. The GC-MS analysis of a fatty acid methyl ester fraction obtained by transesterification of extracted *R. coriaria* seed fat showed that the triglycerides consist of significant quantities of oleic and linoleic acids (42% and 31% of total fatty acids, respectively), with lesser amounts of palmitic acid (20%) and stearic acid (2.6%).

Higher yields (0.11% to 0.32%) of essential oils were obtained by hydrodistillation from *R. coriaria* fruits from two regions of Turkey [16]. Geographic variation in the essential oil composition was observed. Comparable oil yields were realized from the hydrodistillation of leaves (0.11% to 0.32%) and branches (0.31% to 0.42%). Similar to the work of Brunke *et al.* [15], Kurucu *et al.* [16] found α-pinene, limonene, octanal, β-humulene, α-terpineol, (*E*)-undec-2-enal, and carvacrol as major compounds in the fruit oils. In contrast, (*E*)-hept-2-enal, (*E*)-dec-2-enal, β-humulene alcohol, heptacosane, palmitic acid, and nonacosane were not observed. Major components of the leaf oil were β-humulene (0.3% to 17.0%) and a sesquiterpene hydrocarbon tentatively identified as patchoulane (3.1% to 23.9%). The major constituents of the branch/bark oil were β-humulene (12.4% to 21.9%) and the newly identified cembrene (**1**; 10.7% to 26.5%).

Work on steam volatile constituents from leaves of *R. typhina* showed that of the monoterpenes, only a small number of alcohols in low concentration were found: *p*-menthadien-7-ol, linalool, terpineol, and geraniol [17]. The main sesquiterpene hydrocarbon characterized was β-humulene, followed by δ-cadinene, γ-cadinene, α-muurolene, α-humulene, α-copaene, and trans-β-bergamotene in order of decreasing concentrations. One of the most abundant components in the leaf oils was the diterpene alcohol phytol, as well as its oxidation product hexahydrofarnesyl acetone. Phytol is particularly of note given recent research showing it is a novel and effective vaccine adjuvant (a pharmacological agent added to a drug to increase or aid its effect) with little toxicity [18]. The authors noted that most of the constituents of *R. typhina* leaf oils seemed to originate from fat metabolism, including the fatty acids dodecanoic, tetradecanoic, pentadecanoic, hexadecanoic, and octadecanoic acids, and almost the complete series of *n*-hydrocarbons from heptane through triacontane. As well, small quantities of the furfural, benzyl salicylate, and the alcohols octanol, tetradecanol, hexadecanol, octadecanol, eicosanol, docosanol were observed.

In the leaf and/or flower (inflorescence) oils of *R. mysurensis*, 55 compounds were identified [19] (Table 1). Two of the major compounds in both oil types were the monoterpenes α-pinene (26.8% in leaf oil and 15.5% in flower oil) and limonene (26.2% in leaf oil and 51.3% in flower oil). The other major components of the two oils were found to be sabinene and α- and β-eudesmol.

More targeted studies on non-phenolic phytochemicals in sumac have isolated and structurally characterized the following compounds: 3α,20-dihydroxy-3β,25-epoxylupane (**2**) from the flowers of *R. typhina* [20]; allobutulin, α-/β-amyrin, campesterol, lupeol, and β-sitosterol from *R. typhina* leaves and branches [21]; rhuslactone (**3**) [22] and semialatic acid (**4**), semialactone (**5**), isofouquierone peroxide (**6**), and fouquierone (**7**) from the bark of *R. javanica* [23]; **2**, 3β,20,25-trihydroxylupane (**8**), 3,25-diacetyl-3β,20,25-trihydroxylupane (**9**), 3β,20-dihydroxylupane (**10**), 20-hydroxylupane-3-one (**11**), and 20,28-dihydroxylupane-3-one (**12**) from the leaves of *R. taitensis* [24] and campesterol from *R. thyrsiflora* leaves [25]. Only two studies have investigated non-phenolic compounds from *R. semialata*, and the works involved isolation of just three compounds. Semialatic acid (**4**) was obtained from leaves [26], and lantabetulic acid and methyl lantabetulate were isolated from the stems [27].

Concluding remarks

To date, a number of individual aldehydes, fatty acids, long chain alcohols, terpenes and terpenoids, and waxes of commercial or bioactive potential in essential oils and non-polar extractables from selected members of the *Rhus* genera have been identified. Additional studies are needed to broaden the phytochemical database from other sumac species, and to better quantify the potential yields of these valuable compounds from the plants under natural and agriculturally managed conditions. A biorefinery concept applied to various sumac species could have leaves, stems and fruits extracted first with a non-polar solvent (e.g., hexane, supercritical CO_2) to recover valuable fats, waxes, oils, sterols, terpenes, and other high-value phytochemicals, followed by an aqueous/alcoholic extraction to recover tannins, and any subsequent processing to utilize the lignocellulosic residues.

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Table 1. Reported major constituents of essential oils obtained by hydrodistillation from *Rhus* spp. Values are ranges observed and represent percent of total peak area as determined by gas chromatography with flame ionization or mass spectrometric detection. A search of the Merck Index (http://themerckindex.cambridgesoft.com/TheMerckIndex/), the Combined Chemical Dictionary (http://ccd.chemnetbase.com/), and the National Center for Biotechnology Information PubChem for information on the biological activities of small molecules (http://pubchem.ncbi.nlm.nih.gov/) was conducted to determine the industrial uses and bioactivities of compounds identified in the sumac extracts.

Species	*R. coriaria*				*R. mysurensis*		*R. typhina*		
Plant portion	fruits	fruits	leaves	branches	leaves	flowers	leaves		
Reference	[15]	[16]			[19]		[17]	Industrial uses	Bioactivities
Aldehydes									
(*E,E*)-2,4-decadienal	1.0-5.8	1.3-7.0	<mdl	<mdl-0.1	nr	nr	nr		
(*E,Z*)-2,4-decadienal	0.6-2.4	0.4-1.7	<mdl	<mdl	nr	nr	nr		
(*E*)-dec-2-enal	2.9-22.2	nr	nr	nr	nr	nr	nr		
(*Z*)-dec-2-enal	nr	9.9-42.4	0.2-0.4	<mdl	nr	nr	nr		
(*E*)-hept-2-enal	0.4-4.4	1.9-2.5	0.1-0.2	0.05	nr	nr	nr		
hexanal	0.2-2.4	0.1-1.3	0.1-0.2	0.2-0.6	nr	nr	nr	Used in fruit flavours and in perfumery.	Antifungal agents, insecticide.
(*E*)-hex-2-enal	<mdl[a]-0.2	0.02-0.1	0.03-4.4	<mdl	nr	nr	nr		
nonanal	3.0-11.5	10.8-13.1	0.2-0.3	0.3-0.4	nr	nr	1.3	Perfumery ingredient. Flavouring ingredient.	Acts as an insect pheromone and may also be a pheromone in humans.
(*E*)-non-2-enal	0.5-1.6	nr	nr	nr	nr	nr	nr		
(*Z*)-non-2-enal	nr[b]	1.1-1.2	0.1	0.1	nr	nr	nr		
octanal	0.2-1.1	0.8-1.3	<mdl	0.05-0.1	nr	nr	nr	Flavouring agent, used in eau-de-cologne and artificial citrus formulations.	
(*E*)-oct-2-enal	0.5-1.1	1.0-1.3	0.1	0.1	nr	nr	nr		
(*E*)-undec-2-enal	0.3-2.3	1.3-1.6	<mdl	0.1	nr	nr	nr		
Esters	nr	nr	nr	nr	nr	nr	nr		
Fatty acids									
palmitic acid	0.8-5.1	nr	nr	nr	nr	nr	11.1	Food additives. Used in manufacture of surfactants, soaps, plasticizers, polishing compounds, and thickening lubricating oils. Emulsifying agents in foods and pharmaceuticals. Used for waterproofing textiles.	Skin penetrants. Enzyme inhibitors. Herbicides, insecticides, and fungicides.
pelargonic acid	0.1-2.6	nr	nr	nr	nr	nr	nr		
myristic acid	nr	nr	nr	nr	nr	nr	3.2		
Long chain alcohols									
eicosanol	nr	nr	nr	nr	nr	nr	3.6		
octanol	0.2-0.6	0.7-1.9	0.1-0.3	<mdl	nr	nr	0.1	Used as a defoaming or wetting agent. Also used as a solvent for protective coatings, waxes, and oils, and as a raw material for plasticizers.	
Sterols	nr	nr	nr	nr	nr	nr	nr		
Terpenes and terpenoids									
trans-anethole	<mdl-2.4	nr	nr	nr	nr	nr	nr	Extensively used in flavour industry.	Possesses carminative, expectorant, and insecticide properties. Gastric stimulant.
δ-cadinene	nr	0.4-0.7	0.5-1.3	1.4-6.7	1.2	0.2	2.1		
δ-cadinol	nr	nr	nr	nr	1.2	0.2	nr		Shows cytotoxic activity.
carvacrol	0.2-10.4	<mdl	0.4-2.2	<mdl	0.2	0.2	nr	Flavouring agent.	Antiseptic. Shows antimicrobial activity.
carvone	0.2-2.0	nr	nr	nr	nr	nr	nr	Flavouring ingredient.	Antineoplastic agent, phytogenic. CNS stimulant, carminative agent, insecticide. Under development as a potato sprout inhibitor.
cembrene	1.5-15.4	<mdl-6.4	1.2-7.8	10.7-26.5	nr	nr	nr		
α-eudesmol	nr	nr	nr	nr	4.6	2.2	nr		
β-eudesmol	nr	nr	nr	nr	3.2	2.2	nr		

(*E,E*)-α-farnesene	nr	nr	nr	nr	1.1	0.4	nr		
farnesyl acetone	0.4-1.0	<mdl-0.5	2.6-3.2	1.8-4.9	nr	nr	nr		
geranyl acetone	nr	1.4-1.9	1.7-2.0	0.2-0.4	nr	nr	nr		
phytone	0.5-2.8	<mdl-0.9	0.6-3.0	<mdl-0.2	nr	nr	0.4		
α-humulene	0.8-1.5	<mdl-0.4	0.2-1.4	1.3-2.0	1.2	1.8	0.1	Perfumery	
β-humulene	4.0-13.8	0.3-2.8	0.3-17.0	12.4-21.9	6.6	9.4	6.3	Fragrance and flavouring agent. Starting material for synthesis of other terpenoids.	Active principle of extract of lemon balm. Used for its sedative and antibacterial properties. Non-steroidal anti-inflammatory agent.
β-humulene alcohol	<mdl-2.9	nr	nr	nr	nr	nr	nr		
α-/β-humulene oxide	0.4-3.1	nr	nr	nr	nr	nr	nr		
limonene	0.4-1.1	0.2-9.5	2.1-3.7	1.4-1.8	26.2	51.3	nr	Extensively used in the perfumery and flavour industries and in manufacturing of polymers and adhesives.	
myrcene	nr	nr	nr	nr	2.1	2.4	nr	Flavouring agent.	
(*Z*)-β-ocimene	nr	nr	nr	nr	6.9	3.0	nr		
(*E*)-β-ocimene	nr	nr	nr	nr	2.2	1.8	nr		
patchoulane	nr	0.4-1.8	3.1-23.9	4.9-8.4	nr	nr	nr		
phytol	nr	nr	nr	nr	nr	nr	31.9	Preparation of vitamins E and K_1.	Anticancer agent (colon and gastric cancer).
α-pinene	1.1-3.8	0.03-1.9	0.3-3.6	3.8-17.7	26.8	15.5	nr		
β-pinene	nr	0.03-0.4	0.1-0.4	0.4-2.7	0.1	<mdl	nr		
sabinene	nr	nr	nr	nr	3.8	4.1	nr		
α-terpineol	0.5-2.4	0.5-1.1	0.5-1.1	0.4-1.6	0.1	0.1	nr		
Waxes									
heptacosane	0.9-5.7	nr	nr	nr	nr	nr	1.1	Lubricants and waxes.	
pentacosane	0.4-1.3	nr	nr	nr	nr	nr	2.0		
nonacosane	<mdl-4.0	nr	nr	nr	nr	nr	nr		

[a] <mdl=below the unspecified method detection limit. [b] nr=not reported.

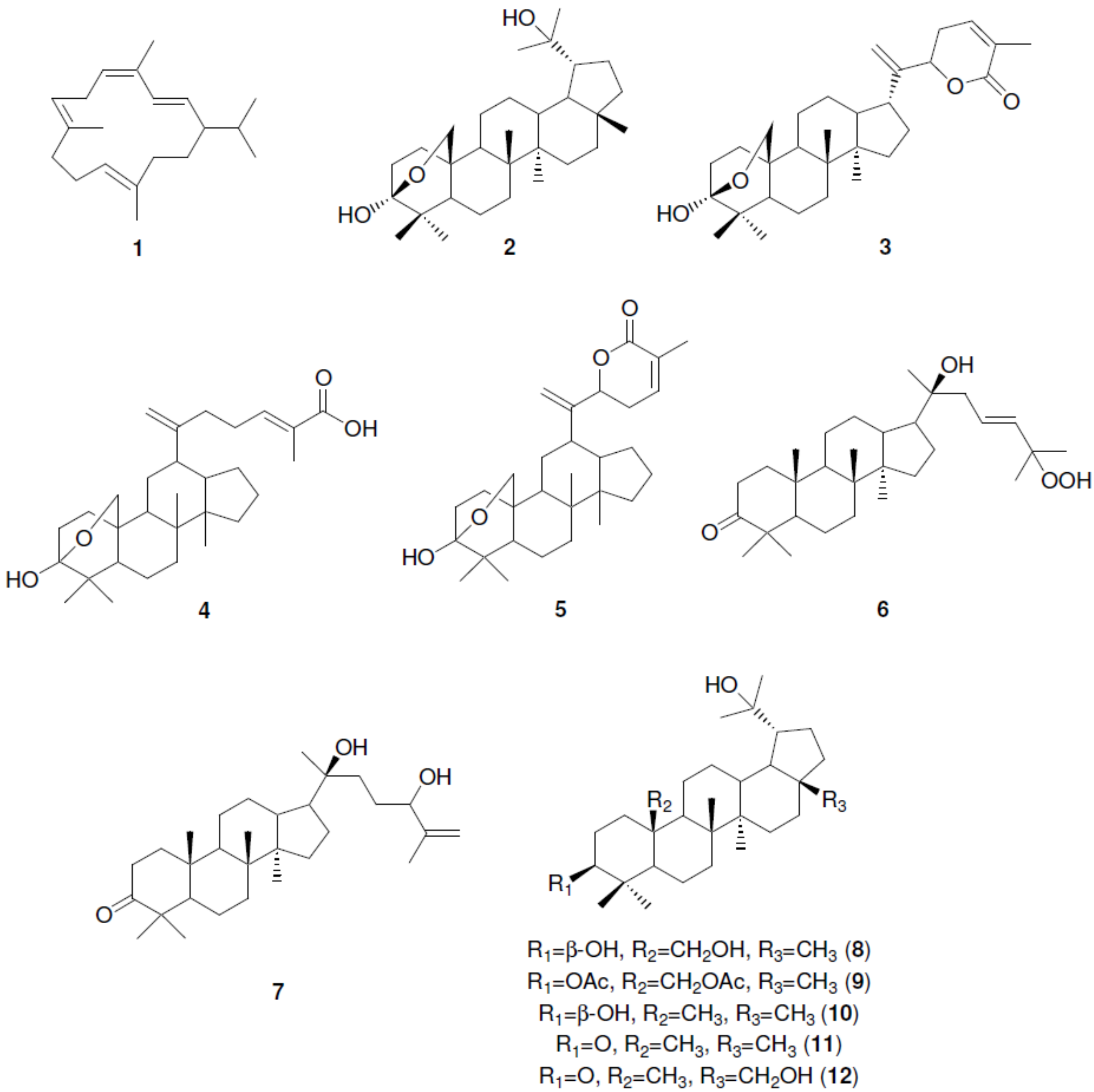

Figure 1. Chemical structures for sumac-derived compounds referred to in the text.