ChemPubSoc Europe

DOI: 10.1002/slct.201700095

Chemistry SELECT Full Papers

Sustainable Chemistry

Extractives fom *Cedar Deodara* and *Alnus Cordata* in the Presence of Molybdenum Catalysts

Marisabel Mecca,[b] Luigi Todaro,[c] and Maurizio D'Auria*[a]

Soxhlet extraction of cedar wood with ethanol/toluene mixture in the presence of molybdenum catalysts can increase the amount of extracts. The treatment of cedar wood in the presence of $H_3PMo_{12}O_{40}$ gave 7.9% extractives. In the presence of silica supported MoO_3, the amount of extractives was 17.0%. The extractives were partially soluble in chloroform (76.5% with silica supported MoO_3 and 33% by using $H_3PMo_{12}O_{40}$). The extracts of cedar can be a source of fatty acids for biodiesel production and simple carbohydrates. The analysis of the chloroform soluble fraction showed that cedar wood gave a mixture of 2-hydroxy-1-(hydroxymethyl)ethyl hexadecanoate and 2,3-dihydroxypropyl octadecanoate. GC-MS of water soluble fraction showed the presence of some simple carbohydrates. The treatment of alder in the same conditions gave 3.5% (37.6% soluble in chloroform) extractives when silica supported MoO_3 was used and 15.5% (6.1% soluble in chloroform) extractives when $H_3PMo_{12}O_{40}$ was the catalyst. The soluble fraction is a source of fatty acid derivatives, while in the insoluble fraction ribose, glucose and myo-inositol were recovered.

Introduction

The extractives in wood represent an important wood constituent allowing us to classify a wood on the basis of its chemotaxonomy. Extractives are responsible for the color, smell, and durability of the wood.[1] Furthermore, extractives can represent a source of valuable fine chemicals such as fatty acids, terpenes and phenols. Therefore, the extractives can be used for their properties in chemical industry, in cosmetic industry or for their biological antioxidant properties in pharmaceutical and nutraceutical industry.

Recently, several efforts have been reported related to the lignin degradation to obtain fine chemicals.[2] This type of study was strictly related to our previous results obtained by using oxidative conditions in lignin degradation.[3] On the basis of these results, we tested the possible use of some oxidants of Mo(VI) to induce chemical degradation of wood. The selection of this type of oxidant species is due to our intention, in one hand, to reevaluate the work of an ancient chemist, Francesco Mauro, a chemist able to synthesize several Mo(V) and Mo(VI) derivatives, born in Basilicata, and coworker of Stanislao Canizzaro,[4] and, on the other hand, on the basis of the green properties of this type of catalysts.[5]

In this article we report the effect on the ethanol-toluene extractives composition if this extraction is performed in the presence of catalytic amounts of two different oxidants of Mo (VI). For these experiments we used both a softwood (cedar) and a hardwood (alnus) species.

The extracts of cedar wood (*Thuja plicata*) had been analyzed in the past in order to quantify the presence of lignans in the extracts.[6] In our knowledge, the composition of extracts of *Cedrus deodara* Roxb. is not known. The extracts of alder wood had been determined in the case of *Alnus incana*,[7] *Alnus glutinosa*,[7b,c] and *Alnus japonica* (Kuroyanagi et al. 2005).[8] No data are available for *Alnus cordata* Loisel.

Results and Discussion

Deodar cedar, Italian cedar, and alder were used in this study. The chemical components of wood, comprising of extractives, lignin and holocellulose, are reported in Table 1.

Table 1. Chemical composition of cedar and alder wood.

Wood	Extractives [%]	Lignin [%]	Holocellulose [%]
Cedar	8.6	29.0	62.4
Alder	3.2	25.1	71.7

Using cedar, 57.8% of the extractives were soluble in chloroform. This fraction was chromatographed on silica gel and the main components found are reported in Table 2.

In the insoluble fraction, after derivatization process in acetic anhydride and pyridine, α-D-ribopyranose, β-D-glucopyranose, and β-D-mannpyranose were found.

Alder wood showed a different behavior. The extractives are not soluble in chloroform but they can be analyzed by CG-

[a] *Prof. M. D'Auria*
Department of Science, Università della Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy
E-mail: maurizio.dauria@unibas.it
[b] *Dr. M. Mecca*
Department of Science, Università della Basilicata, Via dell'Ateneo Lucano 10, 85100 Potenza, Italy
[c] *Dr. L. Todaro*
School of Agricultural Forestry, Food, and Environmental Science, Università della Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/slct.201700095

Table 2. Main chemical components found in cedar wood extractives.

Compound	r.t. [min]	KI	Lit KI
Vanillin	8.53	1415	1410
Longifolene	8.68	1422	1416
8,9-Dihydroneoisolongifolene	10.04	1653	
6,6-Dimethylhepta-2,4-diene	10.42	1700	
1,5-Diethenyl-2,3-dimethylcyclohexane	10.75	1778	
4-Acetyl-3-carene	11.02	1828	
Methyl β-ionone	11.05	1834	
Methyl hexadecanoate	11.54	1927	1927
7,9-Di-*t*-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	11.60	1938	
t-Butylhydroquinone	11.66	1950	
(*E*)-2-Isopropyl-5-methylphenyl 2-methylbut-2-enoate	12.05	2005	
5-Methyl-1-(2,6,6-trimethyl-2,4-cyclohexadien-1-yl)-1,4-hexadien-3-one	12.11	2033	
Methyl stearate	12.44	2090	2088
(*Z*)-8-dodecen-1-ol	12.49	2098	
1,15-Hexadecadiene	12.55	2107	
Octadecanoic acid	12.77	2140	2124
Ergosta-4,6-22-trien-3-ol	13.26	2201	
Butyl citrate	13.71	2203	2150
Butyl octadecanoate	14.79	2383	2388
Methyl docosanoate	16.66	2608	2510
Methyl pseudoecgonine	16.73	2703	
Octadecyl 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene propanoate	17.40	2765	
2-Hydroxy-1-(hydroxymethyl)ethyl hexadecanoate	17.76	2799	
Glicerol 1-palmitate	18.12	2830	
4-Methoxy-4′,5′-methylenedioxobiphenyl-2-carboxylic acid	19.18	2874	
1,2,3,4-tetrahydro-1-naphthalenol acetate	19.53	2889	

MS only after derivatization. In this case, the main components of the extractives were β-D-arabinopyranose, β-D-deoxyribopyranose, α-D-glucopyranose, and myo-inositol.

When the extraction of cedar wood is performed in the presence of silica supported MoO_3 the amount of extractives decreased (7.9%): however, the chloroform soluble fraction increased (76.5%). The analysis of this fraction, after TLC purification, gave mainly 2-hydroxy-1-(hydroxymethyl)ethyl hexadecanoate and 2,3-dihydroxypropyl octadecanoate. The insoluble fraction, after derivatization, was found to be composed by β-D-ribopyranose, α-D-glucopyranose, hexadecanoic acid and octadecanoic acid.

Cedar wood extracted in the presence of the polyoxometalated compound gave an increased amount of the extractives (17.0%). However, only 33% of these extractives were soluble in chloroform. The analysis of the soluble fraction gave mainly 2-hydroxy-1-(hydroxymethyl)ethyl hexadecanoate and 2,3-dihydroxypropyl octadecanoate as in the previous case. The insoluble fraction showed the presence of α-D-glucopyranose and β-D-galactopyranose. All these data on cedar wood fit with our previous reported results on water extractives.[9] In both the experimental sets the main products were esters of fatty acids. In the case of ethanol-toluene extractives the main products are found in the presence of relevant amounts of some other compounds (those reported in Table 2)

Alder wood extraction in the presence of silica supported MoO_3 gave almost the same quantity of extractives (3.5%) in comparison with those obtained without the presence of the oxidant (3.2%, Table 1). However, the chloroform soluble fraction of the extractives increased until 37.6%. The main components of this fraction are shown in Table 3.

Table 3. Composition of the chloroform soluble fraction of alder wood extracted in the presence of silica supported MoO_3.

Compound	r.t. [min]	KI	Lit. KI
4-(4-Hydroxyphenyl)-2-butanone	9.55	1571	1555
β-Curcumene	10.27	1692	1733
4-[(1*E*)-3-Hydroxy-1-propenyl]-2-methoxyphenol	10.69	1701	
Decyl isobutyl phthalate	11.34	1889	
cis-9-Hexadecenoic acid	11.66	1901	1898
Hexadecanoic acid	11.75	1965	1950
3,5-Dimethoxy-4-hydroxycinnamaldehyde	12.01	2016	
cis-10-Heptadecenoic acid	12.20	2048	2073
Methyl (*E*)-9-octadecanoate	12.58	2112	2087
(*Z*,*Z*)-9,12-Octadecadienoic acid	12.85	2152	2158
Octadecanal	15.40	2459	2452
(*E*)-5-Eicosene	16.25	2612	
Bis(2-ethylhexyl) decanedioate	22.91	3014	

The insoluble fraction of the extractives obtained from alder in the presence of silica supported MoO_3 contains mainly β-D-ribopyranose, α-D-glucopyranose, myo-inositol, and sucrose.

The extraction of alder wood in the presence of polyoxometalated catalyst gave a neat increase of the amount of extractives (15.5%). Only 6.1% of this amount is soluble in chloroform. The composition of the soluble fraction is shown in the Table 4.

Table 4. Composition of the chloroform soluble fraction of alder wood extracted in the presence of $H_3PMo_{12}O_{40}$.

Compound	r.t. [min]	KI	Lit. KI
1-Methyl-2-(phenylmethyl)benzene	9.48	1560	
2,2′-dimethylbiphenyl	9.52	1560	
Tetradecanoic acid	10.68	1758	1761
4-Hydroxy-3,5-dimethoxybenzoic acid	11.05	1834	1823
Decyl isobutyl phthalate	11.35	1889	
Stigmastan-3,5-diene	11.44	1908	
Methyl hexadecanoate	11.56	1927	1927
Hexadecanoic acid	11.74	1965	1950
Ethyl hexadecanoate	11.91	1998	1993
Methyl (*Z*,*Z*)-9,12-Octadecadienoate	12.84	2151	2093
Ethyl linoleate	12.84	2151	2159
Ethyl oleate	13.05	2167	2171
Ethyl octadecanoate	13.17	2200	2229
Ethyl eicosaonate	14.96	2400	
1,19-Eicosadiene	15.39	2458	
1-Nonadecene	16.25	2612	
(*Z*)-9-Octadecen-1-ol	16.77	2707	
Bis(2-ethylhexyl) decanedioate	22.88	3014	
β-Sitosterol	30.07	3408	3408
γ-Sitosterol	30.14	3410	

The insoluble fraction of extractives obtained from alder wood in the presence of $H_3PMo_{12}O_{40}$ showed the presence of methyl α-D-ribopyranoside, methyl α-D-mannopyranoside, ethyl α- and β-D-glucopyranoside, α- and β-D-glucopyranose, and myo-inositol.

It is evident that the presence of oxidant catalysts changes the composition of the extractives in both the wood species we used. In the case of cedar, the main components found were hexadecanoic and octadecanoic acid derivatives, clearly deriving from the oxidative fission of cellular membranes of the wood. In few cases some compounds can be originated from the waxes. Only in the case of alder, the extraction in the presence of oxidants gave compounds whose origin could be the lignin.

Conclusions

The effect of the oxidants seems to induce mainly the oxidative fission of cellular membranes. The above described procedure could be used on residues of wood industries to obtain in good yields fatty acids derivatives (to be used for biodiesel production, i.e.) in the case of cedar and carbohydrates in the case of alder.

Supporting Information Summary

Supporting Information contains the description of all the procedures used in this article. The wood characterization procedures, the synthesis of the catalysts, the description of the extraction procedures, and of the methods used for characterize the extractives have been reported.

Acknowledgements

Chemistry Doctorate is gratefully acknowledged for the financial contribution to Marisabel Mecca.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cedar wood · Extracts · GC-MS analysis · molybdenum catalysts · polyoxometalated compounds

[1] R. M. Rowell, R. Pettersen, J. S. Han, J. S. Rowell, M. A. Tshabalala, in *Handbook of wood chemistry and wood composites*, (Ed. R. M. Rowell), CRC Press, Boca Raton, Florida, **2012**, pp.33-72.

[2] a) C. Li, X. Zhao, A. Wang, G. W. Huber, T. Zhang, *Chem. Rev.* **2015**, *115*, 11559–11624; b) R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx, B. M. Weckhuysen, *Angew. Chem. Int. Ed* . **2016**, *55*, 8164–8215.

[3] a) C. Bonini, M. D'Auria, L. D'Alessio, G. Mauriello, D. Tofani, D. Viggiano, F. Zimbardi, *J. Photochem. Photobiol. A: Chem.* **1998**, *113*, 119–124 b) C. Bonini, M. D'Auria, G. Mauriello, D. Viggiano, F. Zimbardi, *J. Photochem. Photobiol. A: Chem.* **1998**, *118*, 107–110;c) G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona, *J. Photochem. Photobiol. A: Chem.* **1999**, *128*, 139–143;d) G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona, G. Mauriello, *Chemosphere* **1999**, *39*, 2409–2417; e) G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona, G. Mauriello, *J. Photochem. Photobiol. A: Chem.* **2000**, *135*, 203–206;f) C. Bonini, A. Carbone, M. D'Auria, *Photochem. Photobiol. Sci.* **2002**, *1*, 407–411; g) C. Bonini, M. D'Auria, R. Ferri, Photochem. Photobiol. Sci. 2002, 1, 570–573; h) M. D'Auria, C. Bonini, L. Emanuele, R. Ferri, *J. Photochem. Photobiol. A: Chem*. **2002**, *147*, 153–156;k) M. D'Auria, R. Ferri, *J. Photochem. Photobiol. A: Chem*. **2003**, *157*, 1–4;i) G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona, *Biomass Bioener.* **2003**, *24*, 233–238;j) C. Bonini, M. D'Auria, *Ind. Crops Prod.* **2004**, *20*, 243–259;l) C. Bonini, M. D'Auria, P. Di Maggio, R. Ferri, *Ind. Crops Prod.* **2008**, *27*, 182–188.

[4] M. D'Auria, C. Colella, N. Masini, *Francesco Mauro - un chimico lucano* (Francesco Mauro - a lucan chemist). Edizioni Scientifiche Italiane, Napoli, 2014.

[5] A. Podgoršek, M. Zupan, J. Iskra, *Angew. Chem. Int. Ed.* **2009**, *48*, 8424–8450.

[6] a) J. A. Nault, *Wood Sci. Technol.* **1987**, *21*, 311–316; b) C. I. Johansson, R. .P Beatson, J. N. Saddler, *Wood Sci. Technol.* **2000**, *34*, 389–401; c) P. I. Morris, R. Stirling, *Wood Sci. Technol.* **2012**, *46*, 991–1002; d) R. Stirling, P. I. Morris, *Wood Sci. Technol.* **2016**, *50*, 399–412.

[7] a) O. Bikovens, L. Roze, A. Pranovich, M. Reunanen, G. Telysheva, *Bioresources* **2013**, *8*, 350–357; b) L. Roze, O. Bikovens, G. Telysheva, *Proceedings of 8th International Scientific and Practical Conference* **2011**, *Vol. 1*, pp 329–332; c) S. Janceva, T. Dizhbite, L. Vevere, A. Arshanitsa, G. Telysheva, M. Dzenis, *Mat. Sci. Eng.* **2016**, *111*, 012013; doi: 10.1088/1757/1757-899X/111/012013.

[8] M. Kuroyanagi, M. Shimomae, Y. Nagashima, N. Muto, T. Okuda, N. Kawahara, T. Nakane, T. Sano, *Chem. Pharm. Bull.* **2005**, *53*,1519-1523.

[9] M. D'Auria, M. Mecca, L. Todaro, *J. Wood Chem. Technol.* **2017**, in press, doi: 10.1080/02773813.2016.1253102.

Submitted: January 17, 2017
Revised: February 28, 2017
Accepted: March 1, 2017