



Volatile acid content of some maquis species

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Abstract

In recent years, the increased demands for raw materials in wood industry have led researchers to investigate alternative raw material sources. Therefore, this study examined the volatile acid contents, which are considered as an important parameter in the different fields of wood utilization, from maquis species which are *Laurus nobilis*, *Tamarix parviflora*, *Vitex agnus-castus*, *Styrax officinalis*, *Fontanesia philliraeoides*, *Myrtus communis*, *Paliurus spina-christi* and *Pistacia terebinthus*. The formyl and acetyl contents were determined between 2.21-3.58 mmol/100 g and 84.16-89.42 mmol/100 g for maquis species, respectively. Total volatile acid contents calculated from formyl and acetyl groups were ranged from 3.69 to 3.94%. Results of the study indicated that mentioned maquis species are comparable to hardwood species.

Keywords: Maquis species, Formic acid, Acetic acid, HPLC.

Bazı maki türlerindeki uçucu asitlerin miktarı

Öz

Hammaddeye olan talebin son yıllardaki artışı orman endüstrisini alternatif kaynakları araştırmaya yöneltmiştir. Bu nedenle çalışmada maki bitkileri olan *Laurus nobilis*, *Tamarix parviflora*, *Vitex agnus castus*, *Styrax officinalis*, *Fontanesia philliraeoides*, *Myrtus communis*, *Paliurus spina-christi* ve *Pistacia terebinthus* ele alınmış ve söz konusu türlerde uçucu asitlerin miktarları belirlenmiştir. Bitkilere ait örneklerde formil ve asetil miktarları sırasıyla 2.21-3.58 mmol/100 g ve 84.16-89.42 mmol/100 g aralığında tespit edilmiştir. Formil ve asetil gruplarının toplam değerleri materyallerde %3.69 ile 3.94 aralığında sıralanmıştır. Maki bitkilerinden elde edilen sonuçların yapraklı ağaç türleri ile karşılaştırılabilir düzeyde olduğu görülmüştür.

Anahtar Kelimeler: Maki türleri, Formik asit, Asetik asit, HPLC

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1. Introduction

Wood has generally a lightly acidic pH-reaction with water (Stamm, 1961; Roffael, 2008). Moreover, wood releases different amounts of volatile acids namely formic and acetic acids under different chemical conditions (Packman, 1960; Sandermann et al., 1970). Acetic acid arises mainly from acetyl groups in hemicelluloses which are methylglucuronoxylan of hardwoods and galactoglucomannan of softwoods (Fengel and Wegener, 1984). Formic acid appears from formyl groups in the wood and can also occur as decomposition product of wood polysaccharides under acid or alkaline conditions (Runkel, 1951; Timell, 1957; Choon and Roffael, 1990).

The volatile acids have important effects in different industrial processes of wood utilization. Wood-composite production steps such as drying (particleboard), steaming and thermohydrolysis (fiberboard) promote the formation of volatile acids from wood. Furthermore, volatile acids can be generated during manufacture of particleboard and fiberboard through interaction between wood and binder. Wood-based panels liberate different amounts of volatile acids according to binder type. Using alkaline curing phenol-formaldehyde resins, bonded particleboards release greater amounts of acetic and lower amounts of formic acid compared to those particleboards bonded with acid curing urea-formaldehyde resins. Amount of liberated volatile acids depend also on pulping techniques used. Fibers produced using chemo-thermo-mechanical process by sodium hydroxide and sodium sulphite as pulping agents release more acetic and lower formic acid than those produced with thermo-mechanical pulping process (Klauditz, 1957; Meyers, 1978; Poblete and Roffael, 1985a,b; Roffael et al., 1990; Zanuttini and Marzocchi, 1997; Roffael, 2008).

Wood acidity is effective on fixation of wood preservatives (Sandermann et al., 1970), hardening of synthetic resins used in board production (Johns and Niazi, 1981), corrosion of metals by wood (Krilov and Lasender, 1988; Sandermann and Rothkamm, 1959; Packman, 1960), wood-cement compatibility (Hachmi and Moslemi, 1990), discoloration of wood, pulping and plastification of wood (Fengel and Wegener, 1984). The acidity difference between wood species are related to free and bound organic acids of extractives, phenolic constituents (Krilov and Lasender, 1988; Matteoli et al., 1992) and noncellulosic polysaccharides (Sandermann et al., 1970). The quantity and kind of these components differ between wood species (Fengel and Wegener, 1984).

Acetic and formic acids are main volatile acids and contribute to wood acidity like other acidic compounds in wood (Timell, 1957; Sandermann et al., 1970). Balaban and Ucar (2001) determined higher values of acidity for heartwood of *Quercus petraea* and *Castanea sativa*. Although these heartwoods were highly acidic, they contained lower content of volatile acids. However, there was no correlation between wood acidity and content of volatile acids in wood (Balaban and Ucar, 2003).

The emission of volatile organic compounds from wood and wood products is effective on the indoor environment (Risholm-Sundman et al., 1998). Building components, including furniture, are mainly the major sources of volatile organic compounds in the indoor environment (Gustavsson, 1992). For this reason, information about content of volatile organic compounds in the wood or wood products is required (Roffael, 1989; Sundin et al., 1992; Wolkooff, 1995; Risholm-Sundman et al., 1998; Balaban and Ucar, 2003).

Maquies plants have a wide distribution in the Mediterranean flora region of Turkey (Kaya and Aladağ, 2009) (Figure 1). Although maquies plants offer high amount of biomass, there is no information available about usage of the wood of these plants in industrial area or in other areas.

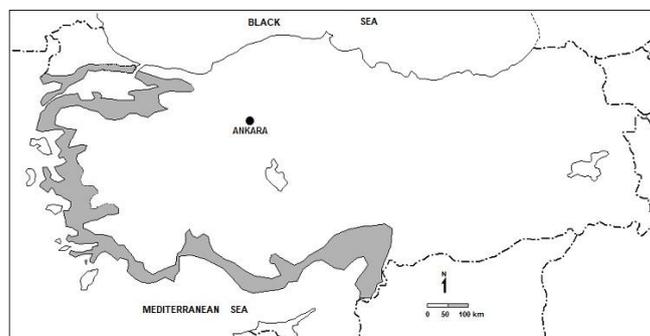


Figure 1. Distribution of maquies plants in Turkey (Kaya and Aladağ, 2009).

The increased demands for raw materials in wood industry have led researchers to investigate other natural biomasses as alternative raw material (Cooper ve Balatinecz, 1999). However, some maquis species attracted interest as alternative raw materials for wood industry (Yaşar et al., 2016a,b; Yaşar et al., 2017), information was required about volatile acids of these plants. Therefore, formic and acetic acid contents from *Laurus*

nobilis, *Tamarix parviflora*, *Vitex agnus-castus*, *Styrax officinalis*, *Fontanesia philliraeoides*, *Myrtus communis*, *Paliurus spina-christi* and *Pistacia terebinthus* were investigated in this study.

2. Material and method

2.1. Material

Stem and branch samples from *Laurus nobilis*, *Tamarix parviflora*, *Styrax officinalis*, *Vitex agnus-castus*, *Fontanesia philliraeoides*, *Myrtus communis*, *Paliurus spina-christi* and *Pistacia terebinthus* were obtained from Asagi Gokdere-Isparta of Turkey in September of 2010. Stem and branch samples were between 2 and 10 cm in diameter. After debarking, stem and branch samples were chipped, air-dried and mixed. The mixed material was milled to 1 mm using Retsch SK 1 mill and submitted to volatile acids analysis. All analysis were completed in 2 months after samples were collected.

2.2. Method

Volatile acids were isolated by following procedure from Balaban and Ucar (2003). Three g of milled material (on oven dry basis) were placed in a 250 mL erlenmeyer flask with ground neck and 100 mL of 0.1 M NaOH were added. Content of flask was stirred for 10 min at room temperature. Then flask was coupled with a condenser and incubated in a water bath at 70 (± 0.5) °C for 60 min. After cooling at room temperature, content of flask was acidified using 20 mL of 0.5 M H₂SO₄. The flask was capped and shaken at intervals for 5 min. Afterwards, content of flask was filtered under vacuum. Then 100 mL of acidified solution were pipetted in a 500 mL erlenmeyer flask with ground neck and 225 mL water were added to flask. The flask contained totally 325 mL liquid was placed on a heated stirrer plate and coupled with a distillation apparatus. Firstly, 250 mL solution were obtained by distillation under stirring. Then distillation was followed after addition of 100 mL water to the flask. When 100 mL solution obtained, 100 mL water added to the flask each time. Totally, 650 mL solution were collected after distillation. Using this solution, volatile acids were analyzed with HPLC.

HPLC analysis was carried out using SHIMADZU system (SCL-10 AVP System controller, LC10VP Pump, DGU 14A Degasser, SIL-10 ADVP Auto injector, CTO-10 AVP Column oven and SPDM10 VP Diode array detector). Separation of volatile acids was performed with C18 Luna 4.6x250 mm column. Twenty five mM KH₂PO₄ solution adjusted to pH 2.5 was used as mobile phase. The flow rate was 1 mL/min. Column temperature was 40 °C. The detector operated at 210 nm. Formic acid (HPLC grade) and acetic acid (HPLC grade) were used as external standards for preparation of calibration curves to determine amounts of formic and acetic acid in the samples. All determinations were done in duplicate.

3. Results and Discussion

Formic and acetic acid were determined as volatile acids in the samples of *Laurus nobilis*, *Tamarix parviflora*, *Styrax officinalis*, *Vitex agnus-castus*, *Fontanesia philliraeoides*, *Myrtus communis*, *Paliurus spina-christi* and *Pistacia terebinthus*. Chromatogram in Figure 2 shows volatile acid peaks of *Tamarix parviflora* sample analyzed using HPLC.

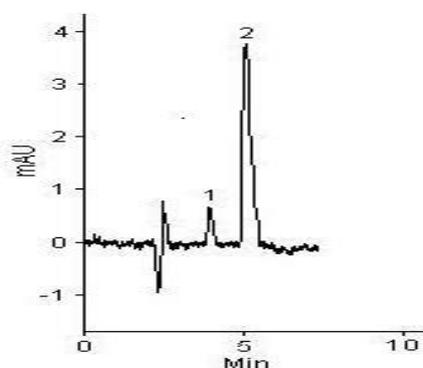


Figure 2. HPLC chromatogram of *Tamarix parviflora* sample, 1: Formic acid, 2: Acetic acid

Determined formic acid contents offered formyl contents in samples are shown in Figure 3. *Fontanesia philliraeoides* and *Tamarix parviflora* samples presented higher formyl contents with amounts of 3.58 and 3.21 mmol/100 g. Lower formyl contents were observed in *Styrax officinalis* and *Laurus nobilis* samples with values of 2.28 and 2.21 mmol/100 g. Formyl contents of other samples were ranged between 2.35 and 3.01 mmol/100 g.

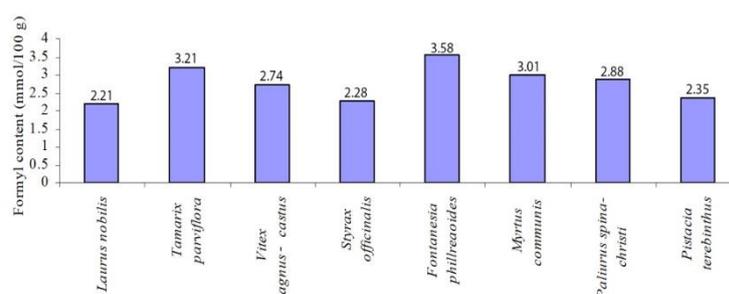


Figure 3. Formyl contents of maquis species samples.

Acetyl contents of samples were obtained from determined acetic acid contents and are given in Figure 4. *Tamarix parviflora* sample had highest acetyl content with value of 89.42 mmol/100 g. *Styrax officinalis* and *Laurus nobilis* samples presented lower acetyl contents with amounts of 85.32 and 84.16 mmol/100 g. In the other samples, acetyl contents were determined between 86.53 and 88.53 mmol/100 g.

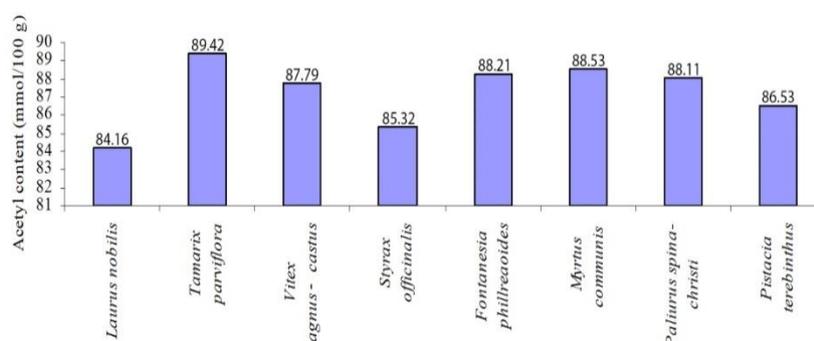


Figure 4. Acetyl contents of maquis species samples

Formyl amount was added to acetyl amount to obtain total volatile acid content for each sample. Total volatile acid contents of samples were expressed as a percentage of oven-dried material weight. *Tamarix parviflora* sample indicated highest total content with 3.94%. Lower total contents were obtained in *Styrax officinalis* and *Laurus nobilis* samples with 3.74 and 3.69%, respectively. Except for *Tamarix parviflora*, *Styrax officinalis* and *Laurus nobilis*, the samples presented the total volatile acid contents between 3.79 and 3.90% (Figure 5).

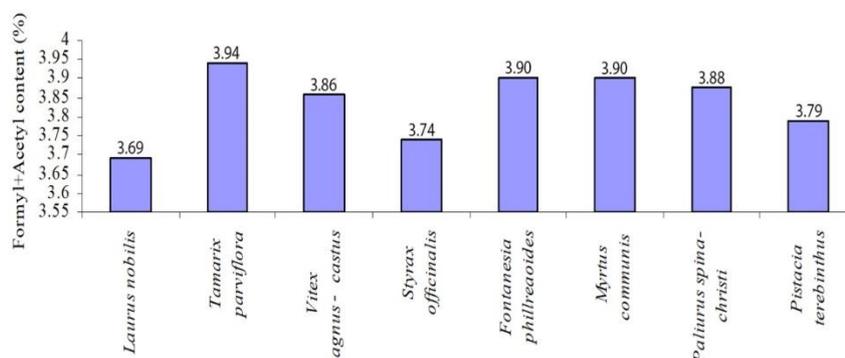


Figure 5. Total volatile acid contents of maquis species samples

Formyl and acetyl contents and also total volatile acid contents calculated from formyl and acetyl groups in the examined samples are summarized in Table 1.

Table 1. Formyl, acetyl and total volatile acid contents in the maquis species samples

| Species | Formyl (mmol/100 g) | Acetyl (mmol/100 g) | Total (%) |
|---------------------------------|---------------------|---------------------|-----------|
| <i>Laurus nobilis</i> | 2.21 | 84.16 | 3.69 |
| <i>Tamarix parviflora</i> | 3.21 | 89.42 | 3.94 |
| <i>Vitex agnus-castus</i> | 2.74 | 87.79 | 3.86 |
| <i>Styrax officinalis</i> | 2.28 | 85.32 | 3.74 |
| <i>Fontanesia phillireoides</i> | 3.58 | 88.21 | 3.90 |
| <i>Myrtus communis</i> | 3.01 | 88.53 | 3.90 |
| <i>Paliurus spina-christi</i> | 2.88 | 88.11 | 3.88 |
| <i>Pistacia terebinthus</i> | 2.35 | 86.53 | 3.79 |

By Balaban and Ucar (2003), formyl and acetyl content and also total volatile acid content found to be between 1.7-2.1 mmol/100 g (average 1.9 mmol/100 g), 25.7-34.6 mmol/100 g (average 29.5 mmol/100 g) and 1.2-1.5 % (average 1.3 %) in different softwood species which were *Pinus nigra*, *Pinus sylvestris*, *Abies nordmanniana*, *Picea orientalis*, *Cupressus sempervirens* and *Juniperus excelsa* and 1.5-3.8 mmol/100 g (average 2.8 mmol/100g), 45.5-119 mmol/100 g (average 81.3 mmol/100 g) and 2-5.2 % (average 3.6 %) in different hardwood species which were *Populus tremuloides*, *Quercus petraea*, *Castanea sativa*, *Alnus glutinosa*, *Acer campestre*, *Carpinus betulus*, *Tilia argentea*, *Fagus orientalis* and *Fraxinus excelsior*. Examined maquis species contained distinctly more formyl and acetyl contents and also total volatile acid contents than softwood species, whereas the findings from maquis species were comparable to hardwood species. Obtained values were also indicated that maquis species are rich in hemicelluloses. Consequently, mentioned species have the potential to be utilized with hardwoods.

4. Conclusion

Recently, maquis species attract attention as alternative raw materials for some wood industrial processes such as paper, fiberboard and particleboard production. Therefore, the volatile acids that play an important role in different fields of wood utilization were examined in *Laurus nobilis*, *Tamarix parviflora*, *Vitex agnus-castus*, *Styrax officinalis*, *Fontanesia philliraeoides*, *Myrtus communis*, *Paliurus spina-christi* and *Pistacia terebinthus* samples. The results indicated that formyl, acetyl contents and also total volatile acid contents calculated from formyl and acetyl groups of mentioned maquis species were higher than softwood, but comparable to hardwood species. Consequently, examined maquis species can be evaluated at same level with hardwood species for raw material in the wood industry according to their volatile acid contents.

References

1. **Balaban, M., Ucar, G (2001)**. The correlation of wood acidity to its solubility by hot water and alkali. Holz Roh-Werkstoff, 59: 67-70.
2. **Balaban, M., Ucar, G (2003)**. Estimation of volatile acids in wood and bark. Holz Roh Werkst, 61: 465-468.
3. **Choon, KK., Roffael, E (1990)**. The acidity of five hardwood species. Holzforschung, 44: 53-58.
4. **Cooper, P., Balantinecz, J (1999)**. Agricultural waste materials for composites: A Canadian reality. Centre for Management Technology Global Panel Based Conference, Nikko Hotel, Kuala Lumpur, 18-19 October.
5. **Fengel, D., Wegener, G (1984)**. Wood-Chemistry, Ultrastructure, Reaction. Walter de Gruyter, Berlin.
6. **Gustavsson, H (1992)**. Building materials identified as major sources for indoor air pollutants. BFR D10, 1992.
7. **Hachmi, H., Moslemi, AA (1990)**. Effect of wood pH and buffering capacity on wood-cement compability. Holz als Roh- und Werkstoff, 44: 425-430.
8. **Johns, WE., Niazi, KA (1981)**. Effect of pH and buffering capacity of wood on the gelation time of urea-formaldehyde resin. Wood and Fiber, 12(4): 255-263.
9. **Kaya, B., Aladağ, C (2009)**. Maki ve garig topluluklarının Türkiye'deki yayılış alanları ve ekolojik özelliklerinin incelenmesi. SÜ Sosyal Bilimler Enstitüsü Dergisi, 22: 67-80.
10. **Klauditz, W (1957)**. Zur biologisch-mechanischen Wirkung der Acetylgruppen im Festigkeitstgewebe der Laubhölzer. Holzforschung, 11: 47-55.
11. **Krilov, A., Lasender, WH (1988)**. The acidity of heartwood and sapwood in some Eucalyptus species. Holzforschung, 42(4): 253-258.
12. **Matteoli, U., Menchi, G., Staccioli, U., Tamburini, U (1992)**. Acids groups structure in wood as shown using selective reduction. Holz als Roh- und Werkstoff, 50: 438-440.
13. **Meyers, GC (1978)**. How adjusting fiber acidity improved strength of dry-formed hardboards. Forest Prod. J., 28: 48-50.
14. **Packman, DF (1960)**. The Acidity of Wood. Holzforschung, 14: 178-183.
15. **Poblete, H., Roffael, E (1985a)**. Über chemische Veränderungen in Holzspänen bei der Herstellung von Phenol-Formaldehydharz-gebundenen Spannplatten. Adhäsion, 29(3): 21-28.
16. **Poblete, H., Roffael, E (1985b)**. Über chemische Veränderungen in Holzspänen bei der Herstellung von Harnstoff-Formaldehydharzgebundenen Spannplatten. Holz Roh Werkst, 43: 57-62.
17. **Risholm-Sundman, M., Lundgren, M., Vestin, E., Herder P (1998)**. Emissions of acetic acid and other volatile organic compounds from different species of solid wood. Holz Roh Werkst, 56: 125-129.
18. **Roffael, E (1989)**. Abgabe von flüchtigen organischen Säuren aus Holzspänen und Holzspanplatten. Holz Roh Werkst, 47: 447-452.
19. **Roffael, E., Miertsch, H., Schröder, M (1990)**. Zum Mechanismus der Bildung von flüchtigen Säuren bei der Verleimung mit alkalisch härtenden Phenolformaldehydharzen. Holz-Zentralblatt, 116: 1684-1685.

20. **Roffael, E (2008)**. On the release of volatile acids from wood-based panels – chemical aspects –. Holz Roh Werkst, 66: 373-378.
21. **Runkel, ROH (1951)**. Zur Kenntnis des thermoplastischen Verhaltens von Holz. Holz Roh Werkst, 9: 41-50.
22. **Sandermann, W., Rothkamm, M (1959)**. Über die Bestimmung der pH Werte von Handelshölzern und deren Bedeutung für die Praxis. Holz als Roh- und Werkstoff, 17: 433-440.
23. **Sandermann, W., Gerhardt, U., Weissmann, G (1970)**. Untersuchungen über flüchtige organische Säuren in einigen Holzarten. Holz Roh Werkst, 28: 59-67.
24. **Stamm, AJ (1961)**. A comparison of three methods for determining the pH of wood and paper. Forest Prod. J., 11: 310-317.
25. **Sundin, B., Risholm-Sundman, M., Edenhalm, K (1992)**. Emission of formaldehyde and other volatile organic compounds from sawdust and lumber, different wood-based panels and other building materials. Proc. 26th Int. Particleboard/Composite Materials Symposium, Pullman.
26. **Timell, TE (1957)**. The acyl groups in wood. Svenks Papperstidning, 60: 762-766.
27. **Wolkoff, P (1995)**. Volatile organic compounds - Sources, measurements, emissions and the impact on indoor air quality. Indoor Air, Supplement No 3/95.
28. **Yaşar, S., Demir, F., Karatepe, Y (2016a)**. Bazı maki türlerinin kimyasal içeriği ve fenolik ekstraktifleri üzerine araştırmalar. Turkish Journal of Forestry, 17(2): 187-193.
29. **Yaşar, S., Ceviz, AU., Karatepe, Y (2016b)**. *Laurus nobilis*, *Vitex agnus-castus* ve *Tamarix parviflora* türlerinin kimyasal içeriği ve fenolik ekstraktiflerinin incelenmesi. SDÜ Fen Bilimleri Enstitüsü Dergisi, 20(2): 182-187.
30. **Yaşar, S., Beram, A., Güler, G (2017)**. Kermes meşesi (*Quercus coccifera* L.) odunu fenolik ekstraktifleri. MAKÜ Fen Bilimleri Enstitüsü Dergisi, (Özel Sayı 1), 73-78.
31. **Zanuttini, M., Marzocchi, V (1997)**. Kinetics of alkaline deacetylation of poplar wood. Holzforschung, 51: 251-256.