Electrochemical oxidation of abietanes

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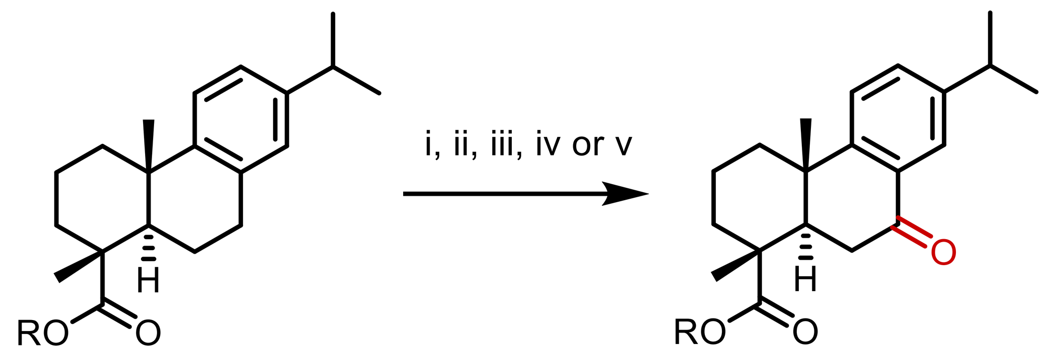
Introduction

From pine trees, we can attain gum, a non-wood product, and through the distillation of gum, two other products can be acquired, turpentine, an essential oil, and colophony, the main product acquired and a complex mixture of the neutral part and acidic diterpenes (divided in abietane or pimaric-type). These two products have a wide range of industrial applications, such as in the cosmetics, adhesive, and glue industries. Abietanes are tricyclic diterpenoids to which dehydroabietic acid belongs to and are known to possess a wide range of biological activities such as antimicrobial, antiviral, anti-inflammatory, and antimutagenic.

The benzylic oxidation of dehydroabietic acid (DHA) and its methyl ester derivative (MDHA) has been reported using oxidative protocols [1−4], as seen below. Herein we adapted and optimized reported protocols for the oxidation of the benzylic position using modern electrochemical methods [5−7], developing an alternative greener protocol for the formation of the benzylic ketone in DHA and MDHA.

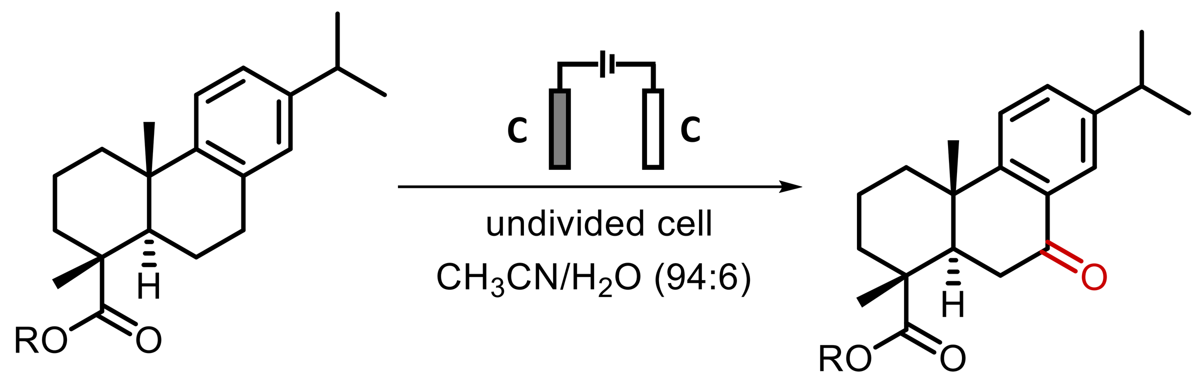


DHA (R = H) or MDHA (R = Me)

i) Stoichiometric CrO_3 (67% yield) (***Cavaleiro*, *2001***)
ii) Jones reagent (11% yield) (***Alvarez-Manzaneda*, *2007***)
iii) Swern oxidation (52% yield) (***Hergenrother*, *2014***)
iv) Catalytic CrO_3 and TBHP (71% yield) (***Zhou*, *2019***)
v) Electrosynthesis (***This work***)

Results and discussion

Table 1. Reaction conditions and results of the oxidation reactions of DHA and MDHA[a]



DHA (R = H) or MDHA (R = Me)

Entry	MDHA/DHA	Supporting electrolyte	Current (mA)	Potential (V)	Time (h)	Yield (%)
1	MDHA (0.03 M)	$LiClO_4$ (0.094 M)	5.0	-------	17.3	18
2	MDHA (0.06 M)	**$LiClO_4$ (0.15 M)**	5.0	-------	18.75	80
3	**MDHA (0.03 M)**	**$LiClO_4$ (0.15 M)**	10.0	-------	2	66
4	**MDHA (0.03 M)**	**$LiClO_4$ (0.15 M)**	**20.0**	-------	**1**	**85**
5	MDHA (0.06 M)	TBATFB (0.15 M)	20.0	-------	8.5	16
6	DHA (0.02 M)	$LiClO_4$ (0.15 M)	5.0	-------	16	traces
7	DHA (0.02 M)	$LiClO_4$ (0.15 M)	2.5	-------	16.2	traces
8	DHA (0.06 M)	$LiClO_4$ (0.15 M)	-------	2.4	8	65

[a]Reactions performed at room temperature without care to remove air or moisture.

Oxidation of MDHA:

- Higher constant currents results in faster reaction with lower formation of impurities;
- Concentration and type of supporting electrolyte can greatly affect the yield of the reactions.

Oxidation of DHA:

- Constant potential offers more selective reactions and higher yields of the desired product.

Conclusion

In this work we achieved the direct electrochemical benzylic oxidation of both DHA and MDHA under simpler and more environmentally friendly conditions, with the use of fewer and less toxic reagents compared to reported protocols. Moreover, the oxidations were generally faster, accompanied by full conversion of the starting materials resulting in greater yields.

References

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Acknowledgments

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