HPLC and capillary electrophoresis for determination of acids, terpenes and aldehydes in natural rosins

Louise Mckeon, Fiona Regan, Barry Burns* and Ray Leonard*
School of Chemical Sciences, Dublin City University, Ireland.
***Henkel Ireland Ltd. (Manufacturing & Research), Tallaght , Dublin 24**
louise.mckeon2@mail.dcu.ie

Background

Rosins are natural compounds derived from pine tree resin. They have many uses in industry, including paints, adhesives and soldering fluxes. In this work HPLC and CE was used to characterise rosin samples which are composed of 90% acidic compounds and 10% neutral compounds including aldehydes and terpenes. Cyclodextrin-modified CE methods were developed for the separation of acids, terpenes and aldehyde groups. The presence and concentration of acids in several rosin samples was investigated.

HPLC Method

Rosin samples were analysed by an Agilent Technologies 1100 series HPLC using a reverse-phase amide column. Mobile phase: 0.1% acetic acid 97:3 ACN:water. Flow rate: 1 mL min^{-1} with 20 µL injections. UV detection at 254 nm (Figure 1). The terpenes eluted as a group, and the acids were also found to coelute.

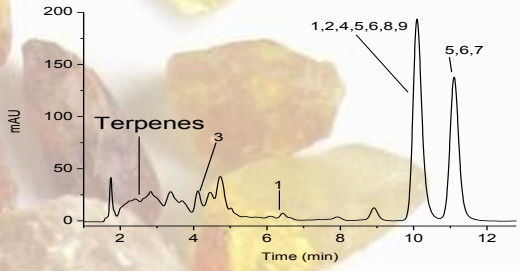
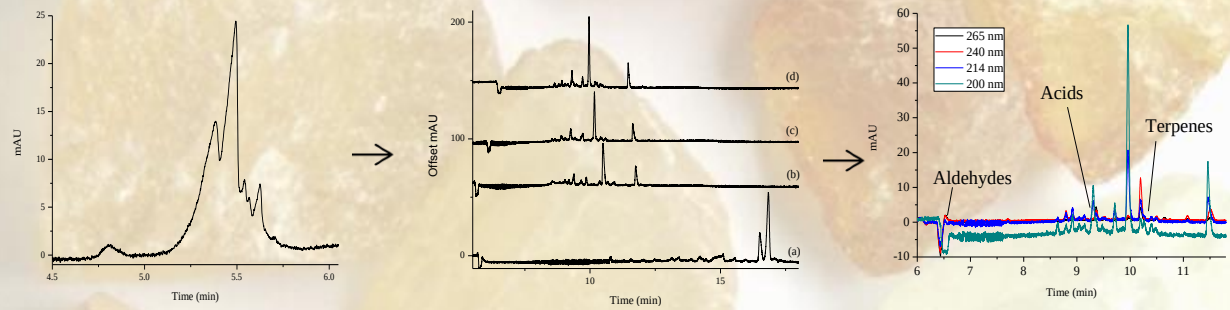


Figure 1. Chromatogram of 0.1% w/v rosin in MeOH samples analysed using 0.1% acetic acid 97:3 ACN:water mobile phase, 20 µL injection at 1 mL min^{-1}, UV detection at 254 nm. Numbers indicate acids as follows, dehydroabietic acid (1), abietic acid (2),7-oxodehydroaietic acid (3), palustric acid (4), isopimaric acid (5), pimaric acid (6), neoabietic acid (7),levopimaric acid (8) and sandaracopimaric acid (9).

Capillary Electrophoresis Method

The use of an Agilent G1601A CE system in the quantification of acids in rosins is novel. Various buffers and cyclodextrins (CD) were optimised and the 3 chemical groups present in rosin samples, acids, aldehydes and terpenes, were separated (Figure 2). A combination of a charged (sulfobutylether -β-cyclodextrin) and a neutral (methyl- β-cyclodextrin) cyclodextrin resulted in the best separation of the groups.



20 mM Tris buffer at pH 8 with no cyclodextrins

20 mM Tris buffer at pH 8 with 10 mM SBCD and (a) 1, (b) 3, (c) 6 and (d) 10 mM MECD

20 mM Tris buffer at pH 8 with 10 mM SBCD and 10 mM MECD

Figure 2. 0.1% w/v rosin in methanol samples were analysed on an Agilent CE using buffers with varying CD concentrations

Acid determination in rosin

By varying the neutral CD a greater effect on the resolution of the peaks (varying the charged CD primarily affected the migration times) was observed. Neutral CD was investigated for the separation of the acids present in rosin samples. (2-hydroxypropyl)- γ-cyclodextrin (HPγCD) has a bigger cavity than MECD which resulted in the separation of a standard mixture of nine resin acids; abietic- (A), neoabietic- (B),dehydroabietic- (C), 7-oxo-dehydroabietic- (D), palustric- (E), levopimaric- (F), pimaric- (G), isopimaric- (H) and sandaracopimaric acid (I) (figure 4).

Using spiked samples and simultaneous UV detection wavelengths, the acid peaks present in the rosin electropherograms were identified (figure 5), and calibration curves used to quantify them.

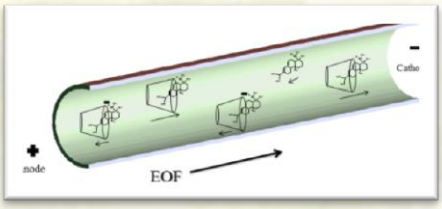


Figure 3. Schematic of a capillary during electrophoresis with the cyclodextrins interacting with the analytes.

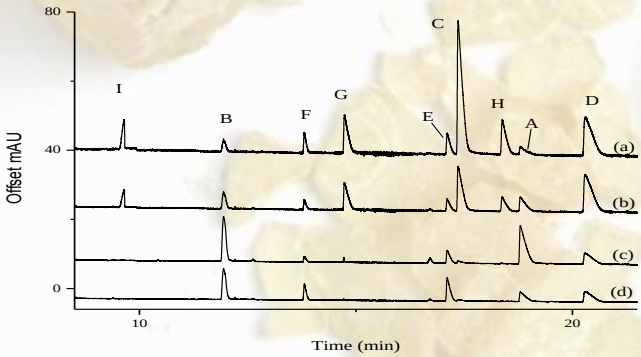


Figure 4. Electropherograms of 0.01% acid standards mix analysed in positive polarity, 20 kV, capillary 58 cm (50 cm to detector), 50 µm i.d., 25° C, 50 mbar 4 s injection time. Buffer:5 mM HPγCD 10 mM SBCD in 20 mM tris buffer pH 8. Letters indicate acids as assigned above. Wavelengths are (a) 200 nm, (b) 214 nm, (c) 240 nm and (d) 265 nm.

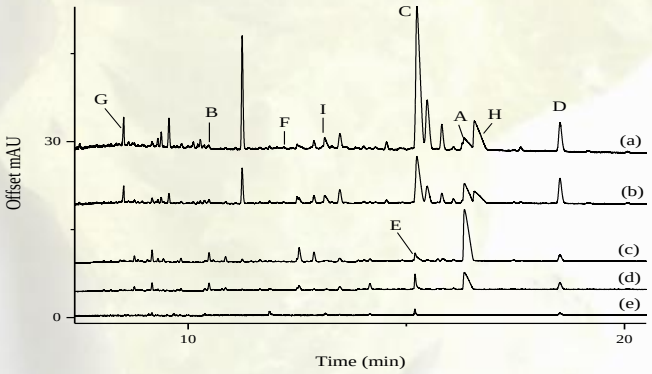


Figure 5. 0.1% w/v gum rosin sample analysed in positive polarity, 20 kV, capillary 58 cm (50 cm to detector), 50 µm i.d., 25° C, 50 mbar 4 s injection time. Buffer: 5 mM HPγCD 10 mM SBCD in 20 mM tris buffer at pH 8. Letters indicate acids as assigned above. Wavelengths are (a) 200 nm, (b) 214, (c) 240 nm, (d) 265 nm and (e) 310 nm.

Conclusions

A method was developed using capillary electrophoresis for the separation of the acid, terpene and aldehyde groups present in rosin samples where analysis using HPLC was not sufficient. The aldehydes coelute straight after the EOF followed by acids and terpenes. A further method was optimised for and the separation and identification of the resin acids found in rosins.

Acknowledgements

I would like to acknowledge the IRCSET Enterprise Partnership Scheme and Henkel for funding this project, and The Chromatographic Society for granting the author a Student Bursary award.