

NATURAL OR SYNTHETIC SWEETENERS, SOURCE OF WINE ADULTERATION II. STUDIES ON MEDIUM-SWEET WINE ADULTERATION BY ADDING SYNTHETIC SWEETENERS TO MARKETABLE WINES

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ABSTRACT - Medium-sweet wine counterfeiting, based on dry and medium-dry wines, represents a possible practice in winemaking industry. The primary objective of the study conducted was to improve the TLC method-Thin Layer Chromatography, by replacing the cellulose layer, recommended by STAS 6182 (17-8), with silica gel, fluorescein included. This type of layer which coats an aluminium foil removes the spraying action of fluorescein in order to detect spots of synthetic sweeteners. Another objective of this paper was the detection of synthetic sweeteners by using TLC-60254 plates, in the case study conducted on a lot of 16 wine samples which were purchased. Among the analyzed medium-sweet wine samples we identified two adulterated wines, namely sample 8, which was obtained from medium-dry wine with addition of saccharin in order to be included in the category of medium-sweet wines, and wine sample 9, for which a dry wine was used, to which an unidentified sweetener was added with 0,29 Rf.

Key words: Wine; Sweeteners; Saccharin; Sodium cyclamate.

REZUMAT – **Îndulcitorii naturali sau sintetici, sursă de falsificare a vinurilor II. Cercetări privind depistarea falsificării vinurilor demidulci prin adaos de îndulcitori sintetici în vinurile comercializate.** Imitarea vinurilor demidulci, pornind de la vinuri seci și demiseci, este o practică posibilă în industria vinului. Studiul întreprins a avut un prim scop îmbunătățirea metodei TLC-Thin Layer Chromatography, prin înlocuirea suportului de celuloză, recomandată în STAS-ul 6182 (17-8), cu silicagel, având fluoresceina inclusă. Acest tip de suport etalat pe folie de aluminiu elimină operațiunea de pulverizare a fluoresceinei pentru identificarea spoturilor de îndulcitori sintetici. Un alt scop al prezentei lucrări l-a constituit depistarea îndulcitorilor sintetici prin utilizarea plăcilor de TLC-60254, în studiul de caz, efectuat pe un lot de 16 probe de vin, procurate din comerț. În probele de vinuri demidulci analizate au fost identificate două vinuri falsificate, și anume proba 8, care s-a obținut dintr-un vin demisec, la care s-a efectuat o corecție cu zaharină, pentru încadrarea în categoria vinurilor demidulci, și proba de vin 9, în

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cazul căreia s-a utilizat un vin sec, la care s-a adăugat un îndulcitor neidentificat, cu Rf-ul de 0,29.

Cuvinte cheie : vin; edulcoranți; zaharină; ciclamat de sodiu.

INTRODUCTION

Law no. 244/2002 on vine and winemaking prohibits the use of sweetening agents for grapevine and wine products, but nevertheless, these substances are fraudulently used for counterfeiting sweet wines (Mihalca *et al.*, 2002). A wide range of synthetic sweeteners are sold nowadays, among which saccharin is most widely used by counterfeiters in winemaking industry (Nămoșanu *et al.*, 2005). In most cases, when there is a rather high concentration of sweeteners in wine, these ones may be detected by organoleptic testing, being persistent in the oral cavity, with no secondary sensation (Pomohaci *et al.*, 2000). In the case of natural sugars, sweet taste is pure and lasts only for a few minutes, leaving a secondary sour flavour due to the enzymes' action from the oral cavity (Cotea, 1985).

One of the modern methods approved for sweetener detection in wine extracts, performed with organic solvents, is the TLC method -Thin Layer Chromatography. This method allows the accurate identification of the type of sweetener, the Rf of the extract being equal to the Rf obtained by the migration of the control solution with a given concentration of the studied synthetic sweetener (Ranca *et al.*, 2010; Țârdea, 2007; Țârdea *et al.*, 2010).

For sweetener detection we used the same lot of wine samples as in the study on the detection of natural sugars (Savin *et al.*, 2011).

The objective of this study was to promote TLC method -Thin Layer Chromatography, as it is sensitive, reproducible and easy to use in a large number of specialized laboratories, representing a means of discouraging the practice of sweet wine counterfeiting by using synthetic sweeteners.

MATERIALS AND METHOD

The detection of synthetic sweeteners, saccharine and sodium cyclamate was performed on TLC 60254 silica gel plates with fluorescein included in the silica gel, according to the OIV method, presented in the Compendium of International Methods of Analysis of Wine and Musts, 2010. Saccharine was extracted with benzene, and cyclamate with ethyl acetate. The solvent mix used in the migration tank had the following composition: 60 mL acetone, 30 mL ethyl acetate and 10 mL ammonia. The chromatographic plates were examined under the light of a UV lamp of 254 nm. The spots of saccharin and cyclamate have blue-violet colour on a greenish background.

RESULTS AND DISCUSSION

The extracts with organic solvents for separating saccharin and sodium cyclamate from medium sweet wine samples were obtained according to the work schemes shown in *Fig. 1* and *Fig. 2*.

SYNTHETIC SWEETENERS, SOURCE OF WINE ADULTERATION

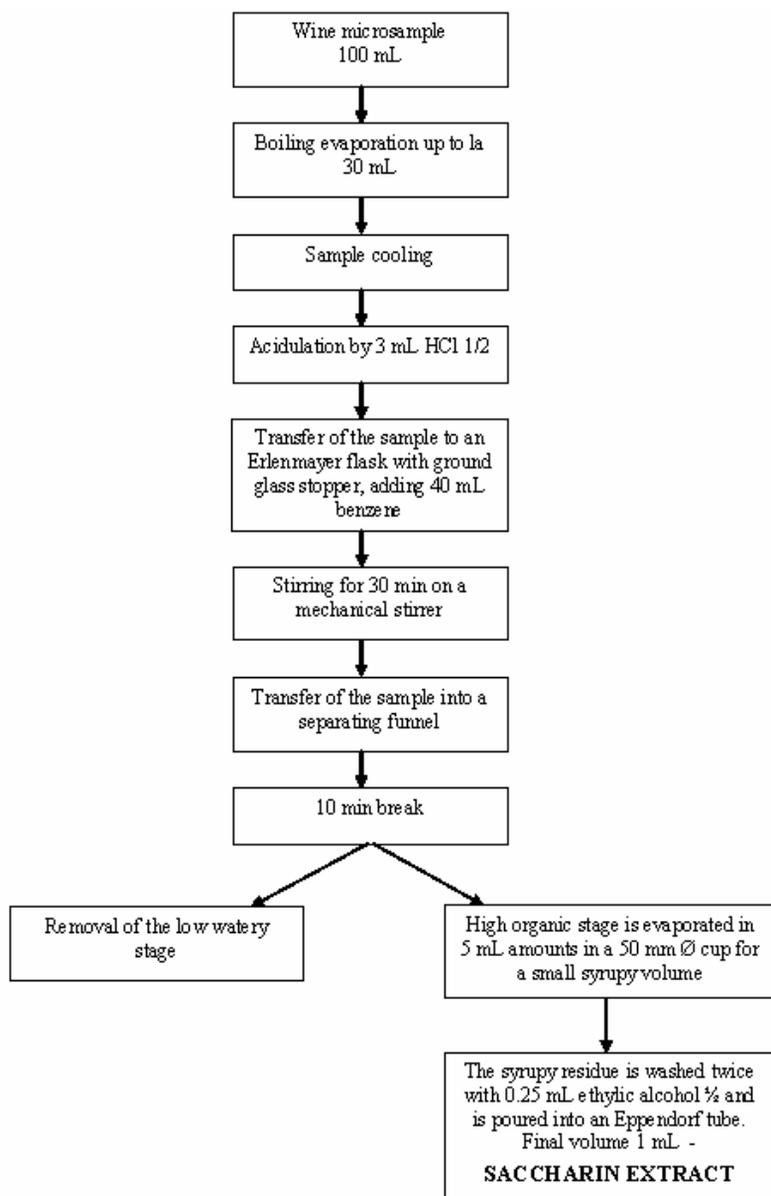


Figure 1 - Scheme of saccharin extraction from wine sample

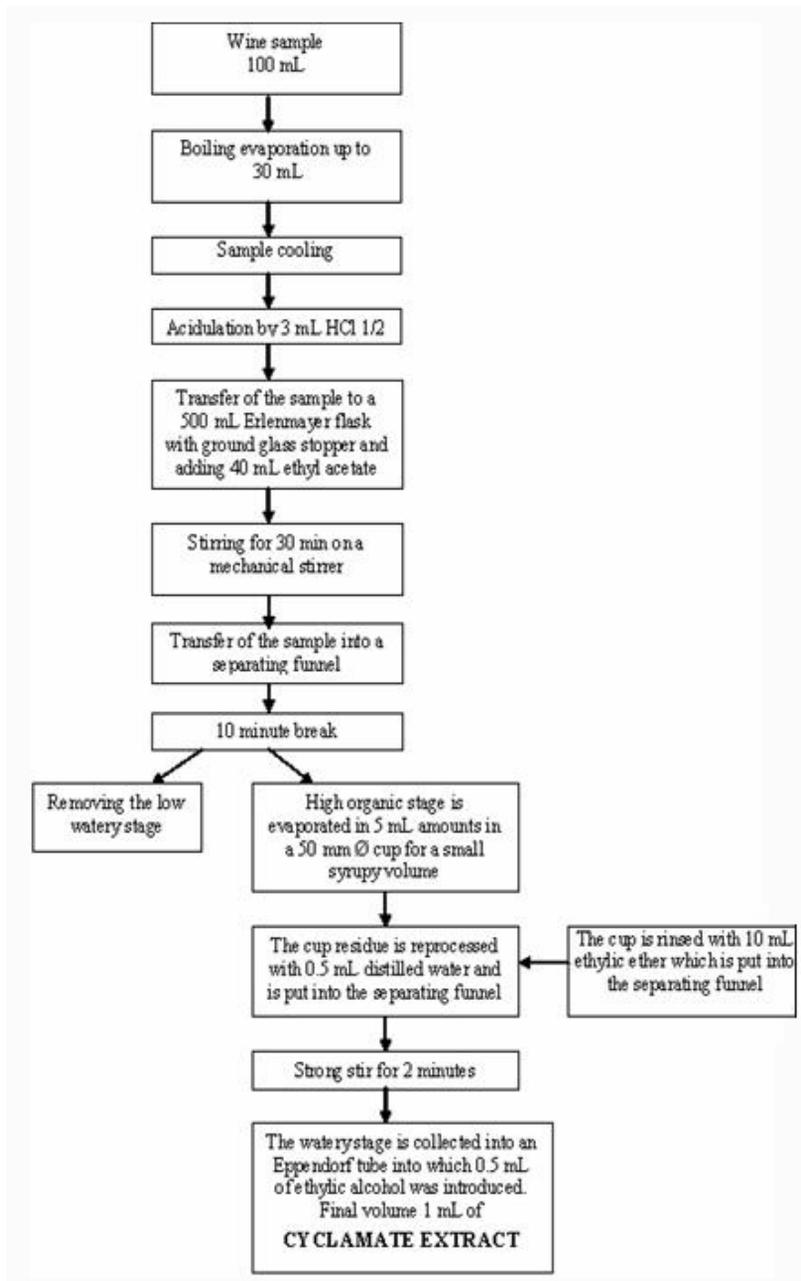


Figure 2 - Scheme of sodium cyclamate extraction from wine samples

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The results of the thin layer chromatography on benzenic extracts with saccharin from medium sweet

wine samples 1-7 and 10-16 are shown in the chromatograms from *Fig. 3 and Fig. 4*.

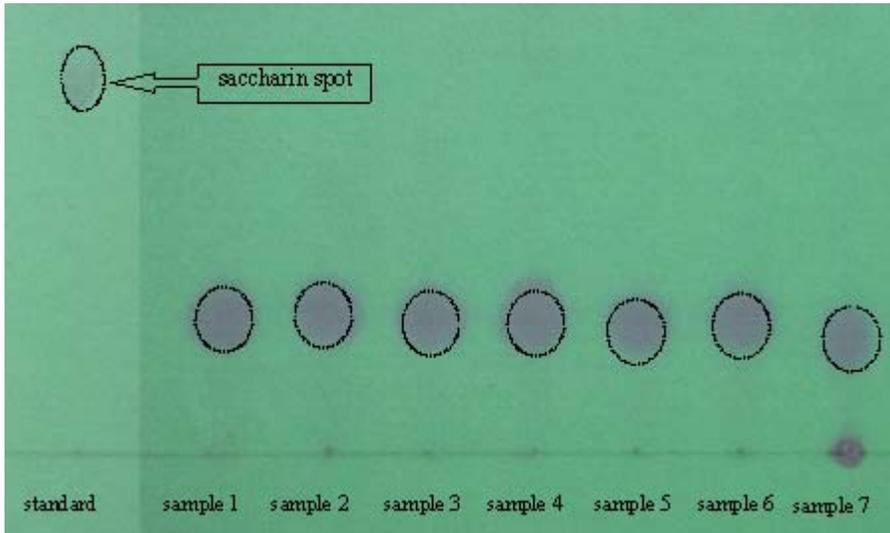


Figure 3 - Chromatogram of benzene extracts obtained from 1-7 wine samples, in comparison with the saccharine control specimen

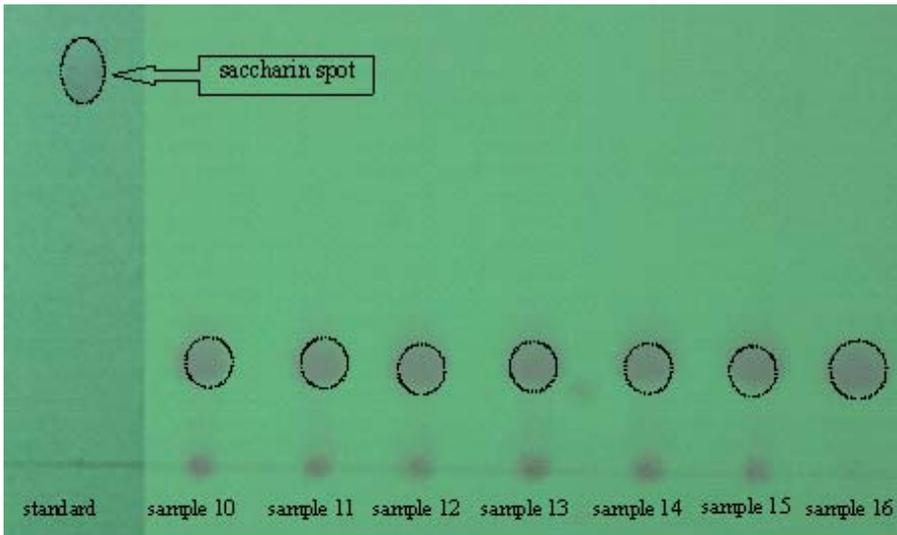


Figure 4 - Chromatogram of benzene extracts obtained from 10-16 wine samples, in comparison with the saccharine control specimen

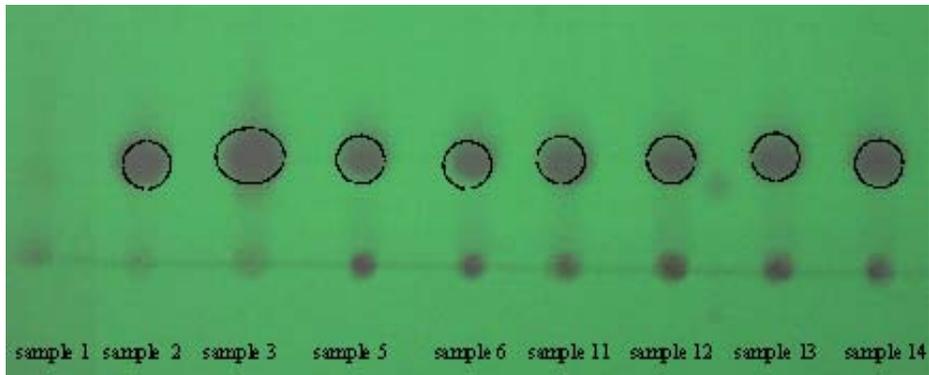


Figure 5 - Chromatogram of benzene extracts: dry wine sample (1st position on the right) samples from medium sweet DOC - CMD wine (positions 2 and 3), bulk wine samples (positions 5 and 6) and samples from wine in PET bottles (positions 11-14)

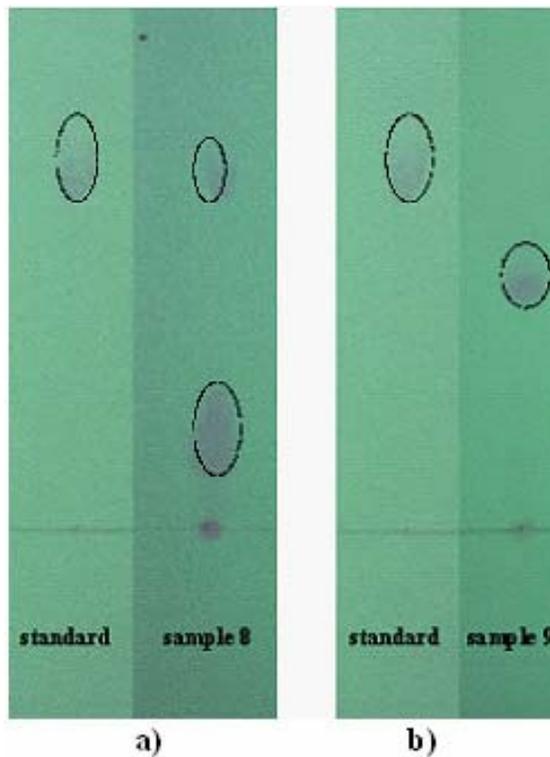


Figure 6 - Chromatogram of benzene extracts obtained from 8 (a) and 9 (b) wine samples, in comparison with the saccharine control specimen

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After having studied them we observed that all extracts determined the migration of a spot, at an equal distance from the start line, both in the case of DOC - CMD wines, and in the case of bulk table wines or in PET bottles. We believe that this behaviour is determined by natural sugars from medium sweet wines which, under the conditions of solution mix for synthetic sweetener migration, led to spots with Rf of 0.125. This statement is supported by the aspect of the chromatogram from *Fig. 5*, in which, the benzenic extract from dry wine sample occupies the 1st position, and the following positions were occupied by medium sweet wine extracts from samples 2-6 and 11-14.

In the benzene extract obtained by processing wine sample 8, the chromatogram 6 (a) pointed out two spots, one near the start line and the second at the level of the saccharin control specimen. In this case we noticed that the medium sweet wine sample 8 was adulterated, being obtained from natural medium dry wine with saccharin correction in order to be included in the category of medium sweet wine.

In the chromatogram from *Fig. 6 (b)*, we illustrate the benzene extract from wine sample 9. The aspect of the chromatogram is specific for dry wine in which an unidentified synthetic sweetener was added, with Rf of 0.29. This conclusion is also supported by the chromatogram from *Fig. 5*, in which the benzenic extract from dry wine sample was placed in the 1st position.

According to the analysis of chromatograms with extracts obtained with ethyl acetate for detecting cyclamate we observed that this synthetic sweetener was not added in the studied medium sweet wine samples.

CONCLUSIONS

In the lot of medium sweet wines bought from supermarkets, we detected two adulterated wines, namely wine sample 8, in which case we found saccharin, and sample 9, in which we detected a synthetic sweetener with a Rf of 0,29, different from the Rf of saccharin and cyclamate control specimens.

The results of chromatographic assays performed with TLC 60254 plates, fluorescein included in silica gel, recommend the replacement of TLC cellulose plates which do not allow the viewing of spots of synthetic sweetener control specimens as well as of extracts from the studied wine samples.

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