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Determination of some organic acids in cotton leaves of Çukurova region

by

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Determination of some organic acids in cotton leaves of Çukurova region

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ABSTRACT

Some organic acids were detected and determinated after capsule ripening stage of cotton plant of Çukurova region. It is found that the leaves have rather high content of citric and malic acids and may be considered as a good source of citric acid. Organic acids were extracterd by ethanol-water mixture and esters of the acids were prepared by methylation with diazomethane. Determinations were carried out by gas-chromatography using Silicone GE SE 30 column.

INTRODUCTION

It was found that cotton leaves have a very high content of some carboxylic acids such as citric, malic, tartaric, lactic and oxalic acids. A.S. Dadykov, D.A. Shkurgina, and D.M. Guseva (1) determinated some carboxylic acids at four different stages of the development of cotton plants of Russia. They have reported that the content of citric acid rose gradually from 2.9 % of the dry weight at the flowering period to 8.5 % at capsule ripening period.

The aim of this work was the recovery of citric acid from cotton leaves left on the fields after harvest and mostly burnt for weed control.

In this work carboxylic acids have been extracted by ethanol – water mixture from dried cotton (Gossipium L) leaves. Carboxylic acids were isolated from extract via their potassium salts. The mixture of carboxylic acids methylated with diazomethane. Qualitative and quantitive analysis of methyl esters were carried out in a Perkin Elmer Model F 11 gas-chromatography apparatus using GE SE 30 column.

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EXPERIMENTAL

MATERİAL:

Cotton (Gossipium L) leaves were obtained from Çukurova region in the season of 1976.

Chemicals were obtained from Fluka.

Extraction of the cotton leaves:

The fresh green leaves were first dried in air. The air dried leaves were kept at 105 °C for 3 hours and cooled in a dessicator. 35–45 g dry leaves were used for each extraction. The dry leaves were extracted with 500 ml ethanol – water (1:1) in an ordinary Soxhelet apparatus for 8 hours. The main part of the solvent was removed by vacuum distillation at 30 °C/25 mm Hg.

The concentrated solution (50 ml approxymately) was added to 100 ml of concentrated potassium hydroxide solution. This basic mixture extracted several timeş with ether to remove non-acid organic impurities. Busic aquous layer was acidified to about pH = 1 to recover free carboxylic acids. Most of the water was removed by distillation under diminished pressure (30 °C/25 mm Hg). The residue was extracted by ether several times and ether was removed by distillation. The residue was diluted to 100 ml with methanol.

Methylation of the carboxylic acids:

Nitroso methyl urea was prepared according to the Arnth – Avan method[2] from ammonia, dimethyl sulfate, sodium nitrite and urea. Diazomethane pre pared as etheral solution from nitrosomethyl urea and potassium hydroxide and used for methylation of carboxylic acids mixture. Diazomethane solution was cooled and added gradually to the methanol solution of the carboxylic acids (cooled to below 0 °C,) until the colour of the acidic methanol solution became yellow and no nitrogene evaluation appears.

Excess of the diazomethane and ether removed by evaporation. The residue was diluted to 100 ml with methanol and used for determination in gas chromatography.

Standarts:

Trimethyl citrate, dimethyl oxalate, dimethyl tartarate, di-

methyl malate, methyl lactate, methyl acetate, and methyl formate were prepared from pure carboxylic acids by methylation with diazomethane. The purity of carboxylic acids examined by determination of physical constants.

Qualitative analysis:

GE SE 30 column was found the most suitable among other materials have been tested. Although 0V 1 column gave satisfactory peaks for many esters it was not satisfactory for the esters of malic and citric acids.

The most suitable conditions were found as below:

Solvent	methanol
Temp. programming	64–200 °C
Injection temp.	250 °C
Initial period	1 min
Rate of heating	8°/min
H_2 (lb. f/in	10
Air (lb. f/in)	10
N_2 (ml/min)	50
Chart speed (mm/min)	10
Range	$20x10^2$

Gas chromatography showed that the extract contains 8 different compounds. The main components were identified as methyl lactate, dimethyl oxalate, dimethyl malate and trimethyl citrate. The minor components have not been identified.

Quantitative analysis:

Quantitative analysis was applied only to dimethyl malate and trimethyl citrate because of their industrial importance. A calibration curve was prepared using a standard methanol solution contatining 0.2 g of sample in 5 ml. Different amount of standard solution were injected and the peak areas calculated for each experiment. The calibration curve obtained by plot of the peak areas versus the amount of standard substance. The peak areas were estimated according to the Gaussian method[3]

The average of these determinations were:

Malic acid .... 4.5 % of the dry weight

Citric acid .... 5.17 % of the dry weight

RESULTS

Citric acid content has been estimated as 5.17 % of the dry weight of leaves picked from Çukurova plantations before harvesting. Since citric acid is a water soluble compound it may beasily extracted from green leaves. It seems hopeful to recover citric acid – and other carboxylic acids such as malic, lactic and oxalic acidus – from cotton leaves in Turkey.

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ÖZET

Bu çalışmaya başlarken kimya endüstrisinin önemli maddelerinden biri olan sitrik asidin pamuk yaprağından üretilmesi olanaklarının saptanması amaçlanmıştı. Bu maksatla kuru pamuk yaprakları su-etanol karışımı ile özütlenmiş ve karboksilli asitler bu özütten potasyum tuzları üzerinden izole edilmiştir. Karboksilli asitler diazometanla metillendirilerek metil esterlerine çevrilmiş ve gaz kromatografi yöntemile tanınmaları yapılmıştır. Asitlerden sitrik ve malik asitlerin miktarları saptanmış ve sırasile kuru yaprak ağırlığının %5.17 ve 4.35 ini oluşturdukları bulunmuştur. Sonuç olarak her yıl tarlalarda terkedilen ve çoğu kez yabani ot mücadelesi için yakılan yapraklardan bu amaçla yararlanılabileceği görülmüştür.

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