

cis-trans isomerization would be consistent from sample to sample and would be minimized due to the rapid sample preparation procedure.

Uses. This method is ideally suited for routine analyses of the major nonpolar carotenoids in orange juice. It is rapid and accurate and can be applied with a minimum amount of equipment. This method can be used to rapidly obtain nonpolar carotenoid data bases for orange juice nutrition, taxonomy, and regulatory or quality control studies.

Registry No. β -Cryptoxanthin, 472-70-8; α -carotene, 432-70-2; β -carotene, 7235-40-7.

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Production of Oxalic Acid from Dry Powder of *Parthenium hysterophorus* L.

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The process of preparing oxalic acid from dry powder of *Parthenium hysterophorus* L. is described. Favorable conditions for the production of oxalic acid in moderately high yield include conducting the oxidation of the plant material with a mixture of concentrated nitric and sulfuric acids (50:50) at a solid to liquid ratio of 1:10 (w/v), addition of ammonium vanadate catalyst at 0.005% of the oxidizing mixture, careful temperature control at 75 °C, and reaction period of 4 h. The purity of recovered oxalic acid was around 98%.

INTRODUCTION

Oxalic acid has a widespread industrial applications. It is extensively used as a souring agent to neutralize the residual alkalinity of washed fabrics. It is included in cleaning solutions intended for the removal of ink markings, stains, and discolorations caused by bleeding of dyes. The textile industry makes use of it for dye stripping of wool, degumming of silk, printing of cotton, cleaning and dyeing of fabrics, and bleaching plant fibers. A large-scale use for oxalic acid is in acidic formulations for removal of rust and scale. Other applications include whitening of leather, formulation of metal polishes, refining of tall oil, manufacture of dyes and numerous other chemical products as an intermediate, and many more.

Oxalic acid can be manufactured by four general methods that are based on the nature of raw material selected (Kirk and Othmer, 1967). These methods are (i) alkali fusion of cellulose, (ii) fermentation process for carbohydrates, (iii) synthetic process from formates, and

Table I. Effect of Reaction Conditions on Yield of Oxalic Acid from *P. hysterophorus* L. as Raw Material

variable	yield, ^a g	
nitric to sulfuric acid ratio, ^b mL	80:20	4.85 ± 0.08
	70:30	5.60 ± 0.12
	60:40	5.92 ± 0.10
	50:50	6.18 ± 0.17
reactn time, ^c h	2	5.20 ± 0.13
	4	5.80 ± 0.11
	6	5.47 ± 0.08
	8	5.32 ± 0.10
reactn temp, ^d °C	55	5.10 ± 0.12
	65	5.30 ± 0.15
	75	5.84 ± 0.11
	85	4.40 ± 0.15

^a Average of four experiments using 10 g of plant material.
^b Reaction conditions: vanadate catalyst, 75 °C, 4 h. ^c Reaction conditions: vanadate catalyst, acid ratio 60:40, 75 °C. ^d Reaction conditions: vanadate catalyst, acid ratio 60:40, 4 h.

(iv) oxidation by nitric acid. Among these methods, the latter two have been considered important for the commercial route to oxalic acid. However, the most widely acceptable commercial method for the manufacture of

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Table II. Production of Oxalic Acid from Different Plant Materials

plant matl	reactn conditions	% yield	reference
corn cob	plant to HNO ₃ (1:5)	85	Webber (1934)
sawdust	plant to HNO ₃ (1:6) fuming HNO ₃ 70–75 °C, 2 h, 0.003% ammonium vanadate	85	Bailey (1954)
pineapple waste	fuming HNO ₃ , 70 °C, V ₂ O ₅	75–80	Chaudhari and Rao (1963)
woodflour	commercial HNO ₃	38–40	
rice straw	commercial HNO ₃	40	
tuvar/arhar (pulses)	HNO ₃ /H ₂ SO ₄ , 75 °C, 0.013% V ₂ O ₅ , plant to HNO ₃ (1:5, w/v)	44.2	Kothalkar et al. (1975)
eucalyptus hybrid bark	HNO ₃ , 75–80 °C	40–45	Prabhu and Theagarajan (1977)
hardwood sawdust	HNO ₃ /H ₂ SO ₄ /V ₂ O ₅ , 75 °C, 2 h, 0.003% V ₂ O ₅ , H ₂ SO ₄ 50 wt %, sawdust to HNO ₃ (1:8), O ₂ flow 21.1 mL/min per g of sawdust	80.2	Sullivan et al. (1983)

oxalic acid is the oxidation of carbohydrates by nitric acid.

Simpson (1936) described the oxidation process for oxalic acid starting with a 60% glucose solution. In this process, 1 ton of glucose produced about 1.5 tons of oxalic acid, which corresponds to 2.1 M yield. It is known that sucrose, cane molasses, Gur, and cane juice can also be used as raw materials (Deshpande and Vyas, 1979; Bose et al., 1971; Raha et al., 1976; Gupta et al., 1980) to yield 2.2, 1.8, 2.0, and 1.83 mol of oxalic acid/mol of hexose available, respectively. The manufacture of oxalic acid from plant materials is described by Dube et al. (1982).

It has been observed that utilization of plant waste or weeds for production of oxalic acid is not fully explored. In India, irradiation of *Parthenium hysterophorus* L. has taken on increased importance. Characterized as a vigorously growing widespread weed, it is found in cultivated and uncultivated areas. The present paper describes the conversion of this weed into oxalic acid by nitric acid oxidation.

MATERIALS AND METHODS

The quantity of oxalic acid was calculated by the following formula:

$$\text{oxalic acid (g/10 g dry powder)} = \frac{0.1 \times V \times R \times DF \times 45}{S \times 1000}$$

where V = volume of the filtrate (mL), R = titration reading (mL), DF = dilution factor (16), and S = volume of filtrate diluted (16 times) for oxalate precipitation (10 mL). Oxalic acid was recovered from the filtrate by crystallization induced by cooling.

RESULTS AND DISCUSSION

When the chemical reaction is carried out, advantage is taken of the fact that concentrated nitric acid is capable of oxidizing carbohydrates in the presence of vanadium compounds as catalytic agents. However, preliminary results indicated that a substantial quantity of the plant material remained unreacted. This problem was eliminated by addition of concentrated sulfuric acid, which is essential for hydrolysis of polysaccharides. Evolution of NO₂ gas was vigorous, and the reaction was exothermic during the addition of sulfuric acid. Since oxalic acid decomposes above 90 °C, the addition of liquid reactants was carried out at temperature of about 5–6 °C. Moreover, charring of the plant material due to sulfuric acid was avoided. In our opinion, oxidation of plant material to oxalic acid by HNO₃/H₂SO₄ is superior to that by HNO₃ alone.

Table I shows results on experiments carried out for the maximum yield of oxalic acid with varying acid ratio, reaction time, and temperatures. Ammonium vanadate was used as catalyst as it afforded better results than vanadium pentoxide. The yield of oxalic acid improved with an increase in the proportion of concentrated sulfuric acid in

the acid ratio from 80:20 to 50:50 with respect to concentrated nitric acid when the reaction was carried out at 75 °C for 4 h. The optimum reaction period seems to be 4 h. The oxidation was slow below 75 °C, and destruction of oxalic acid was evident at 85 °C, leading to low yield. The loss of oxalic acid can be minimized mainly by careful temperature control, by avoiding excess of nitric acid, and by maintaining an optimum sulfuric acid concentration. The chemical conversions of certain plant materials to oxalic acid are summarized in Table II. In comparison with these data, our yields under optimum conditions were moderately high around 60%. The yields of oxalic acid from different plant materials may be influenced by chemical composition and the nature of plants and reaction parameters. It is known that when carbohydrates or sugars are oxidized by nitric acid under suitable conditions, oxalic acid is produced in high yields. Stokes and Barch (1941) and Soltzberg (1945), however, noted that under different conditions organic acids other than oxalic acid may comprise substantial or major proportions of the products.

In conclusion, favorable conditions for converting the parthenium plant material into oxalic acid were as follows: plant material to oxidizing mixture ratio, 1:10 (w/v); nitric acid to sulfuric acid ratio, 50:50; ammonium vanadate catalyst at 0.005% of oxidizing mixture; temperature, 75 °C; reaction time, 4 h. The purity of recovered oxalic acid was around 98%. Nitric acid can be recovered by absorbing the fumes of NO₂ gas in water or in alkaline medium as nitrate.

Registry No. HNO₃, 7697-37-2; H₂SO₄, 7664-93-9; HO₂CCO₂H, 144-62-7; NH₄VO₃, 7803-55-6.

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