

New Spectrophotometric Method for The Determination of Cardanol

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Abstract:

Cardanol, a phenolic compound is found in cashew nut shell liquid (CNSL) a by-product of cashew industry. It holds considerable promise because of its large availability in tropical areas, low cost, biodegradability and structural characteristics. The method is based on the reaction of cardanol with folin ciocalteu (FC), an electrophilic coupling agent in presence of iron (III) in mild hydrochloric acid medium. The bluish – green complex shows maximum absorbance at 660 nm. The colour complex can be extracted into chloroform. The methods obey Beer's law. As many as 10 anions and cations do not interfere. The methods have good reproducibility and can be satisfactorily applied to the determination of cardanol in various turmeric samples.

Keywords: agriculture by-product; Cardanol; Cashew nut, spectrophotometry, folin ciocalteu.

Introduction

Cardanol is a phenolic lipid obtained from anacardic acid, the main component of cashew nutshell liquid (CNSL), a byproduct of cashew nut processing. Cardanol finds use in the chemical industry in resins, coatings, frictional materials, and surfactants used as pigment dispersants for water-based inks. It is used to make phenalkamines, which are used as curing agents for the durable epoxy coatings used on concrete floors[1]. The name of the substance is derived by contraction from the genus *Anacardium*, which includes the cashew tree, *Anacardium occidentale*. The name of the genus itself is based on the Greek word for heart [2].

Despite all these uses, only a fraction of the cardanol obtained from cashew nut processing is used in the industrial field. Therefore, there is still interest in

developing new applications, such as new polymers [3].

The name cardanol is used for the decarboxylated derivatives obtained by thermal decomposition of any of the naturally occurring anacardic acids. This includes more than one compound because the composition of the side chain varies in its degree of unsaturation. Tri-unsaturated cardanol is the major component (41%) and the remaining cardanol is 34% mono-unsaturated, 22% bi-unsaturated, and 2% saturated [4].

Recently, it has been demonstrated that cardanol can be used for formation of eco-design of biobased polymeric microcapsules for pesticidal applications with potential to further extended for drugs, self-healing agents, catalysts [5].

Cardanol (3-pentadecenyl phenol) is a phenolic compound with C₁₅ aliphatic chains in the meta position. It is a mixture of saturated and unsaturated (mono-, di- and tri-) compounds [6] commonly found in cashew nut shell liquid (CNSL), an alkyl phenolic oil which constitutes 25% of the total weight of cashew nut (*Anacardium occidentale*) a well-known species of the Anacardiaceae family [7]. CNSL is obtained as a by-product of cashew industry, and is an important source of unsaturated hydrocarbon phenol [8].

Cardanol holds considerable promise because of its structural characteristics, [9], large availability in tropical areas, low cost and biodegradability [10]. The non-linear structure, unsaturation in the alkyl chain and substitution to phenolic group opens up new vistas in the innumerable applications in dyestuff, food, flavour, ion exchange resins, paints, plasticizers and polymers [11]. Significant studies have also been made in the technological application of cardanol and its derivative as pesticides [12] and surface-active agents [12] besides, in ceramics [9] and composites [10].

The phenomenal growth in the commercial applications of cardanol has encouraged the authors to develop sensitive, rapid and reliable methods for its determination. Survey of the literature revealed that no analytical method has been reported so far for its determination.

The work described in this paper forms part of a systematic investigation to develop new spectrophotometric methods for agri products - a field of paramount importance due to easy biodegradability and use of agricultural waste and by-products, in place of toxic chemicals - an area of current interest in environmental management.

The work described here is a novel and highly sensitive method for the determination of cardanol which is based on the reaction involving the use of iron (III) salts in the presence of electrophilic coupling reagent folin ciocalteu (FC) in mild hydrochloric acid medium. The proposed method offers the advantage of simplicity with respect to reagents, high sensitivity and stability without extraction, heating or distillation and reliability due to reproducibility.

Experimental

Material and methods

Apparatus: UV-VIS spectrophotometer UVIDEC-610 type with 1.0-cm matched cell (Jasco, Tokyo, Japan) was employed for measuring the absorbance values.

Reagents

Cardanol (Sami lab, India) folin ciocalteu (FC) (Sigma, USA) and iron (III) chloride (BDH, India) were used. All other chemicals and solvents were of analytical grade. Double distilled water was used throughout. Cardanol (100 mg) was dissolved in 100-ml of isopropyl alcohol. The stock solution was diluted with isopropyl alcohol to obtain solutions of required concentrations. Aqueous solutions of folin ciocalteu (0.1% w/v), iron (III) chloride (0.5% w/v) containing few drops of 2N (v/v) hydrochloric acid was prepared. Solution of folin ciocalteu was stored in amber bottle to protect from sunlight and ethyl alcohol was distilled before use. Chloroform (Ranbaxy, India) was used as received. Solutions of anions and cations were prepared by dissolving their corresponding salts.

Procedures

(i) Direct spectrophotometry (Method A)

Aliquots of standard solutions of cardanol were transferred into 10-ml calibrated flasks. 1.0 ml of folin ciocalteu (0.1% w/v) and 2.0 ml of iron (III) chloride (0.5% w/v) was added and after 10 min the solutions were made up to mark using alcohol. The absorbance was measured at 660 nm against the corresponding reagent blank and calibration graphs was constructed.

(ii) Extractive spectrophotometry (Method B)

Appropriate volume of standard cardanol solution, 1.0 ml of folin ciocalteu (0.1% w/v) and 2.0 ml of iron (III) chloride (0.5% w/v) and 2.0 ml of ethyl alcohol were added to a 125-ml separating funnel. To this 6.0 ml of chloroform was added and the contents were extracted. The organic layer was collected and passed over about 1.0 g of sodium sulphate and made up to mark using chloroform in

10-ml calibrated flask. The absorbance was measured at 660 nm against the corresponding reagent blank and calibration graphs was

constructed. The optical characteristics determined are presented in Table 1.

Table 1: Spectral data for the determination of cardanol using Folin ciocalteu

Parameters	DS (Method A)	ES (Method B)
Colour	Bluish green	Bluish green
λ_{\max} (nm)	660	660
Stability (h)	8	8
Beer's law (ng ml ⁻¹)	0.4-9.0	0.2-7.0
Recommended drug concentration ($\mu\text{g ml}^{-1}$)	3.0	2.0
Molar absorptivity (L mol ⁻¹ cm ⁻¹)	4.90×10^4	5.76×10^4
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0067	0.0053
Regression equation*		
Slope (a)	0.0765	0.1213
Intercept (b)	0.0773	0.0442
Correlation coefficient	0.9785	0.9854

* $y=ax+b$ where x is the concentration of cardanol in $\mu\text{g ml}^{-1}$

Results and Discussion

Folin-ciocalteu (FC) is an electrophilic coupling reagent and is a mixture of phosphomolybdate and phosphotungstate used for the colorimetric determination in vitro assay of phenolic and polyphenolic antioxidants.[13]. This reagent does not measure only phenols, but will react with any reducing substance. It therefore measures the total reducing capacity of a sample, not just phenolic compounds. This reagent is part of the Lowry protein assay, and will also react with some nitrogen-containing compounds such as hydroxylamine and guanidine[14]. The reagent has also been shown to be reactive towards thiols, many vitamins, the nucleotide base guanine, the trioses glyceraldehyde and dihydroxyacetone, and some inorganic ions.

Reaction mechanism

The chemical reaction in the procedure described for the spectrophotometric determination of cardanol involves the reduction of iron (III) chloride by folin ciocalteu which subsequently couples with cardanol to form a bluish-green product having a maximum absorption at 660 nm. The colour intensity remains constant for 8 h. Addition of a few drops of 2N HCl (v/v) is necessary to prevent precipitation of iron (III) as hydrated ferric oxide. The factors affecting the colour development, reproducibility, sensitivity and adherence to Beer's law were investigated.

Spectral characteristics

A bluish-green coloured product with maximum absorbance at 660 nm was formed when cardanol was allowed to react with iron (III) chloride in the

presence of folin ciocalteu in mild hydrochloric acid medium.

Optimization of analytical variables

For a fixed concentration of cardanol and folin ciocalteu the colour intensity remains constant with 1.5-4.0 ml of (0.5% w/v) of iron (III) chloride. Hence, 2.0 ml of iron (III) chloride was sufficient for routine analysis. Similar procedures were adopted to know the amount of folin ciocalteu required for constant colour intensity. It was found that 0.5-4.0 ml of folin ciocalteu (0.1% w/v) was required to provide maximum colour intensity and stability. Hence, 1.0 ml of 0.1% (w/v) of folin ciocalteu was found to be optimum to get reproducible results.

Order of addition

The sequence of addition of cardanol, folin ciocalteu and iron (III) chloride was studied via the formation of the bluish-green complex. The study indicated that the sequence of addition of reactants had profound influence on the intensity and the stability of the colour, for example, (1) folin ciocalteu + iron (III)chloride +ccardanol and (2) iron (III) chloride + cardanol + folin ciocalteu gave less intense and unstable colour. While, the order: (3) cardanol + folin ciocalteu + iron (III) chloride gave more intense stable bluish-green colour.

Temperature and stability

Development of bluish-green colour was carried out at room temperature and this intensity decreases rapidly when diluted with water or when the temperature is increased. Ethyl alcohol stabilizes the colour for more than 8 h. Isopropyl alcohol was

the preferred solvent for preparing stock solution of cardanol as ethyl alcohol and methyl alcohol interfered only, if added before the development of the colour. Subsequently, both the solvents do not interfere in the reaction. Conversely, isopropyl alcohol is discouraged, as it is costlier to ethyl alcohol and methyl alcohol. Ethyl alcohol was preferred to methyl alcohol as it is nontoxic.

Acids like hydrochloric, sulphuric, nitric and perchloric; solvents like acetone, acetic acid, acetonitrile were not effective in stabilizing the colour; while bases such as sodium hydroxide and ammonia were found to give a red colour with cardanol. Conversely, methyl alcohol and ethyl alcohol have profound influence and enhances the stability of the colour and for routine analysis, ethyl alcohol is preferred as it is nontoxic and is cost effective.

Calibration and spectral data

The bluish-green colour obeyed Beer'law. The optical characteristics such as optimum range, as evaluated from a ringbom plot, molar absorptivity, sandell's sensitivity, slope, intercept, correlation coefficient is shown in Table 1.

Interference

The effect of various anions and cations on the determination of cardanol was studied as per the proposed procedure and the results are presented in Table 2 and Table 3. In general, 100 mg of the salt was added individually to aliquots containing 4.0 $\mu\text{g ml}^{-1}$ and 3.0 $\mu\text{g ml}^{-1}$ of cardanol with iron (III) and folin ciocalteu.

Table 2: Effect of anion on the determination of cardanol

Salt of the anion added	Salt added mg	% Recovery of cardanol* \pm RSD**	
		Method A	Method B
Ammonium tartarate	100	99.8 \pm 0.53	99.4 \pm 1.03
Calcium carbonate	100	98.2 \pm 1.02	98.2 \pm 0.52
Potassium bromate	100	100.6 \pm 1.09	99.6 \pm 0.76

Potassium chloride	100	99.6 ± 0.98	98.8 ± 0.82
Potassium iodate	100	97.8 ± 0.66	100.4 ± 0.96
Potassium sulphate	100	98.4 ± 0.68	98.8 ± 0.96
Sodium fluoride	100	98.6 ± 1.04	99.6 ± 0.80
Sodium nitrate	100	99.4 ± 0.74	100.4 ± 0.78
Sodium phosphate	100	99.4 ± 0.62	98.6 ± 0.86
Sodium sulphate	100	99.6 ± 0.84	99.6 ± 1.06

*3.0 µg ml⁻¹ and 2.0 µg ml⁻¹ of cardanol for method A and B, respectively

** relative standard deviation(n=5)

Table 3: Effect of cation on the determination of cardanol

Salt of the anion added	Salt added mg	% Recovery of cardanol* ± RSD**	
		Method A	Method B
Ammonium molybdate	100	99.8 ± 0.70	98.4 ± 0.54
Barium sulphate	100	96.8 ± 0.80	99.4 ± 0.65
Cadmium sulphate	100	99.4 ± 0.52	100.6 ± 0.98
Lead nitrate	100	98.6 ± 1.07	98.7 ± 0.86
Magnesium sulphate	100	97.5 ± 0.66	99.4 ± 0.79
Manganese sulphate	100	96.4 ± 0.54	98.2 ± 0.65
Potassium chromate	100	98.2 ± 0.65	99.5 ± 0.87
Strontium nitrate	100	98.7 ± 1.02	98.4 ± 0.67
Tin chloride	100	99.8 ± 0.98	99.6 ± 0.79
Zinc sulphate	100	99.3 ± 0.76	98.6 ± 0.86

*3.0 µg ml⁻¹ and 2.0 µg ml⁻¹ of cardanol for method A and B, respectively

** relative standard deviation(n=5)

Applications

Four crude samples of cardanol procured from different sources were analyzed by the conventional

standard addition method. Each sample was analyzed with four replicates and the result of RSD was within 2%, and this margin of error is acceptable in all spectrophotometric determinations (Table 4).

Table 4: Cardanol content determined in various crude samples

Sample	Amount of cardanol found by proposed method (g)	Cardanol added to the same sample (g)	Amount of cardanol found by difference (g)	Recovery**%
1	0.1020	0.100	0.0989	98.9
2	0.0994	0.100	0.0992	99.0
3	0.0976	0.100	0.0982	98.2
4	0.0980	0.100	0.1010	101.0

Conclusion

One of the recent frontiers of sustainable development has been the utilization of agricultural by-products. Effective utilization of any product is based on its quality, which, in turn, depends on the analytical data.

The procedure described in this paper is the spectrophotometric method which meets most of the demands of analytical chemists namely; selectivity, sensitivity, simplicity, rapidity, reliability and cost of analysis. In this method, it is necessary to use iron (III) as the oxidizing agent; the use of such simple reagents makes the procedure cost-effective. One of the important facts is that this study will open up a new area of research. Further value-addition to this method can be achieved, if the procedure is combined with on-line or at-line system and this is currently under investigation.

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