CONCLUSION

From the results obtained in the current study, the relative proportion of these flavonoids was reduced by maceration conventional technique, while microwave and ultrasonic techniques in combination with 70% ethanol solvent were the most efficient. It may suggest that microwave and ultrasonic methods using 70% ethanol are suitable for fast extraction of flavonoids in a simple way, also considering extraction yield and extraction time. These methods also permitted the acquisition of flavonoids from reduced raw plant material.

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Resumo: O presente estudo teve como objetivo verificar a melhor metodologia de extração para rápida e eficiente obtenção de flavonóides a partir de *Alpinia zerumbet*. Folhas secas foram extraídas com água destilada e etanol 70%, utilizando as metodologias de extração: maceração sob agitação, ultrassom, microondas e agitador. Para verificação dos flavonóides rutina e kaempferol-3-*O*-glicuronídeo foram utilizadas as técnicas de CCD e CLAE em fase reversa. O solvente etanol 70% foi mais eficiente como extrator. Para as metodologias ultrassom, microondas e agitador, não houve variação significativa para o rendimento utilizando etanol 70% (11 a 14%). A concentração relativa de rutina e kaempferol-3-*O*-glicuronídeo, respectivamente, foi maior pelos métodos de extração por ultrassom (1,5 e 5,62 mg g^{-1} folha seca) e microondas (1,0 e 6,64 mg g^{-1} folha seca), utilizando etanol 70%. Procedimentos rápidos e simplificados de extração otimizam o trabalho fitoquímico e a obtenção de metabólitos secundários.

Palavras-chave: cromatografia líquida de alta eficiência, maceração, microondas, ultrassom, Zingiberaceae

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SPOT-TEST IDENTIFICATION AND RAPID QUANTITATIVE SEQUENTIAL ANALYSIS OF DIPYRONE

M. Tubino[1], A. C. Biondo[1], M. M. D. C. Vila[2], L. Pezza[3] and H. R. Pezza[3]*
[1] State University of Campinas - UNICAMP, Institute of Chemistry, P.O. Box 6154, 13083-970 Campinas, SP, Brazil,
[2] Sorocaba University - UNISO, Sorocaba, SP, Brazil
[3] São Paulo State University- UNESP, Chemistry Institute of Araraquara, Araraquara, SP, Brazil
**tubino@iqm.unicamp.br*

Abstract: A qualitative spot-test and tandem quantitative analysis of dipyrone in the bulk drug and in pharmaceutical preparations is proposed. The formation of a reddish-violet color indicates a positive result. In sequence a quantitative procedure can be performed in the same flask. The quantitative results obtained were statistically compared with those obtained with the method indicated by the Brazilian Pharmacopoeia, using the Student's ***t*** and the ***F*** tests. Considering the concentration in a 100 µL aliquot, the qualitative visual limit of detection is about 5×10^{-6} g; instrumental LOD ≅ 1.4×10^{-4} mol L^{-1} ; LOQ ≅ 4.5×10^{-4} mol L^{-1}.

Keywords: dipyrone, spot-test, analysis, qualitative, quantitative

Introduction

Dipyrone (sodium salt of 1-phenyl-2,3-dimethyl-4-methylaminomethane-sulfonate-5-pyrazolone) (Fig. 1) is a water-soluble pyrazolone derivative widely used in therapeutics as a analgesic, antipyretic and antispasmodic drug [1]. Dipyrone was developed in Germany and was introduced into clinical practice in 1922. It is still in use in many countries for adults and children, where it is sold as an over-the counter (OTC) painkiller [2,3]. Due to its strong analgesic effect, available parenteral formulation, and low cost, dipyrone is widely used, generating a consumption of more than 10 thousand tons/year. Dipyrone is very popular in Brazil and is marketed in the sodium salt form or as the magnesium salt, as well as in association with other drugs [4]. However, the use of dipyrone was proscribed more than twenty years ago in the U.S.A. due to its putative role in depressing bone marrow, causing aplastic anemia and agranulocytosis. However, this has been criticized by many authors [2,4,5].

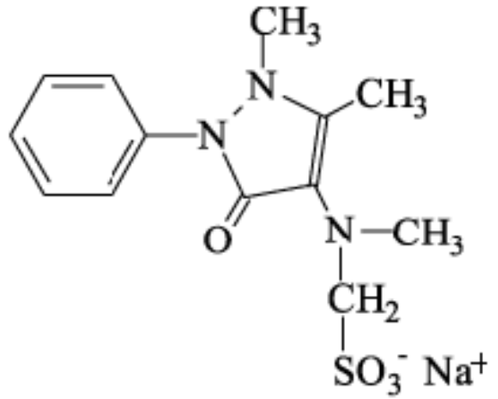

Figure1. Structural formula of dipyrone.

The metabolism of dipyrone has been recently reviewed. It was demonstrated that it inhibits cyclooxygenase (COX). However, in contrast

to classical COX-inhibitors, such as aspirin-like drugs, dipyrone has no anti-inflammatory effect and a low gastrointestinal toxicity, indicating a different mode of action. The authors suggested that the pharmacologically active metabolites of dipyrone inhibit COX activity by sequestering radicals that initiate the catalytic activity of this enzyme or through the reduction of the oxidized states of the COX protein [6]. After oral intake, it is spontaneously hydrolyzed in the gastric fluid to its main metabolite, 4-methylaminoantipyrine (4-MAA), which is rapidly and nearly completely absorbed. 4-MAA is then converted to variety of metabolites by various enzymatic reactions. The effect of dipyrone occurs approximately fifteen minutes after oral administration. The biotransformation takes place at the hepatic level, the duration of this effect is approximately 4-6 hours, and its elimination occurs at the renal level [7].

Recently, additional beneficial effects of dipyrone, such as vascular smooth muscle relaxation, and as antiapoptotics and anticolvulsants, have been reported and have increased the interest in dipyrone [3].

A great problem related with pharmaceutical products around the world is falsification. These incidents probably occur more frequently in developing and poor countries but certainly Europe and United States are not completely free of them. In Brazil the problem was denounced some years ago [8,9] and involved antibiotics, contraceptives, cancer medicines and also common analgesics and antipyretics like dipyrone and aspirin. There is suspicion that such anomalies still remain. From these considerations, it is clearly apparent that it is very important to develop quick, simple, reliable and low cost analytical procedures that could be used routinely for screening examinations to detect possible falsifications.

Some methods have been developed for dipyrone determination, such as titrimetry [1], HPLC [10], spectrophotometry [11-15], potentiometry [16], amperometry [17,18], turbidimetry [19], voltammetry [20], and reflectometry [21]. The iodometric titration of dipyrone is recommended by the Pharmacopoeia [1] but this procedure is very slow and laborious, thus less applicable to large-scale analysis.

The aim of the present work is to develop a simple and reliable spectrophotometric method for the qualitative spot-test [22] associated with a rapid quantitative sequential analysis of dipyrone in pharmaceutical preparations. A similar qualitative procedure has been reported [23] but in the present work the sequential quantitative analysis using iron III as catalyst was developed. The method is based on the selective oxidation of dipyrone, a characteristic reaction of a pyrazolone, in the presence of concentrated sulfuric acid, splitting off formaldehyde which reacts with chromotropic acid producing a reddish-violet compound [11]. The sulfuric acid addition promotes the oxidation of dipyrone and guarantees the temperature necessary for the reaction, to occur, as it interacts with the small quantity of water intentionally added in order to take advantage of the highly exothermic process of the hydration of this acid. The formation of the reddish-violet compound identifies the dipyrone. In case of positive qualitative result the quantitative analysis can be sequentialy performed.

Experimental

Reagents

All chemicals were of analytical grade and were used without further purification. Concentrated sulfuric acid (96%) was obtained from Synth®. Chromotropic acid (disodium salt, dihydrate, $C_{10}H_6O_8S_2Na_2.2H_2O$) and dipyrone ($C_{13}H_{16}N_3NaO_4S$) were obtained from Sigma-Aldrich®. Distilled water was obtained from a glass distillation device.

Pharmaceutical dosage forms of dipyrone were purchased from reliable drugstores. The commercial tablets comprising dipyrone tested were: - Novalgina® (500 mg); Conmell® (320 mg); Anador® (500 mg); Lisador® (500 mg); Buscopan® (250 mg) and Generic Medley® (500 mg).

Solutions

Chromotropic acid solution: prepared daily by dissolving 0.2002 g of chromotropic acid in 5 mL of distilled water, in order to obtain a 0.1 mol L^1 concentration.

Iron (III) chloride 0.1 mol L^{-1} solution: to prepare 25 mL of a 0.1 mol L^{-1} solution about 0.67 g of analytical grade (Vetec®) $FeCl_3.6H_2O$ were dissolved in a volumetric flask.

Standard dipyrone solution: prepared by dissolving an adequate mass of dipyrone in 50.0 mL of distilled water, in order to obtain a 0.1 mol L^1 concentration. From this solution, by appropriate dilutions, the other solutions of the dipyrone were prepared.

Sample preparation: Twenty tablets were powdered in a mortar after weighing. An accurately weighed portion of one tablet, equivalent to about 15 mg of anhydrous dipyrone, was dissolved in 10.0 mL of water, in a volumetric flask, to obtain a solution with a concentration of approximately 4.5×10^{-3} mol L^{-1}.

Procedure

Add, with a micro spatula, to the tube (straight walled volumetric flask of 5.0 mL) about 2 to 3 mg of solid chromotropic acid. Transfer carefully 100 µL of dipyrone solution into this tube. Gently dissolve the chromotropic acid. Add a drop of the 0.1 mol L^{-1} iron (III) chloride solution and homogenize. Then add 500 µL of good quality concentrated sulfuric acid. The acid should be rapidly added, all at once. Shake the tube carefully in order to homogenize. If a reddish-violet color appears the test is positive for dipyrone. To sequentially perform the quantitative analysis the volume is completed to 5.0 mL with water. The absorbance is measured at 576 nm using the volumetric flask as the spectrophotometric cell. Alternatively spectrophotometric cuvettes can be used.

Apparatus

A Femto 600 single beam spectrophotometer was used for all absorbance measurements. The absorbance measurements were performed using a straight walled volumetric flask also used for the reaction. Spectrophotometric glass cuvettes 1.00 cm optical path were also used.

The 5.00 mL straight walled volumetric flask used is essentially an adequately calibrated tube with 11 cm total height, 1.0 cm ID, 1.4 cm OD and fitted with a stopper to allow shaking without losing solution. It is similar to the usual 1.0 and 2.0 volumetric flasks. This format was used in order to promote the most intimate contact of the analyte and of the reagents due to the format and to the dimensions of the bottom of the flask.

As the volumetric tubes were not of optical quality their transmittance (filled with water) at 576 nm was compared. No significant difference was observed and, therefore, they were used without necessity of any correction in the measured absorbances.

Volume measurements of the aliquots and of the sulfuric acid were done using Eppendorf® micropipettes.

Reference method

To analyze the samples by the classic iodometric method, the preparation procedure recommended by the Brazilian Pharmacopoeia [1] was used.

Statistical analysis

The statistical ***t***-Student test and the **F** tests [24] were applied to compare the recovery results obtained by the two analytical methods, the proposed and the titrimetric ones [1].

Results and Discussion

The reaction used in the method developed in this work is based on the reaction of dipyrone analogue, 1-phenyl-2,3-dimethyl-4-dimethylamino-5-pyrazolone [22], which makes use of a very selective oxidation of that compound in the presence of concentrated sulfuric acid, splitting out formaldehyde. The reducing action of pyramidone is related to its tendency to tautomerise [25];

the oxidation probably begins with the isomeric methoxy form of the pyrazolone [22]. The formaldehyde formed is identified by reacting it with warm chromotropic acid, yielding a red-violet color [22]. The nature of this chromogen has never been unambiguously determined but some experimental evidence suggests the hypothesis that it has a mono-cationic dibenzoxanthylium structure [26]. In this work, we use the highly exothermic hydration process of the sulfuric acid and its very low heat capacity to provoke the necessary temperature increase for the reaction to occur [23]. In order to accelerate the reaction iron III was used as catalyst. A drop of a 0.1 mol L^{-1} iron (III) chloride solution was added directly in the solution containing the dipyrone with the chromotropic acid. When the sulfuric acid is added, the increase of the reaction rate can be visually observed when compared to the reaction without the addition of iron III.

The absorption spectrum of the reaction product was obtained using the final solution in the volumetric flask. With the defined working conditions the maximum absorption wavelength was observed at 576 nm.

The stability of the product formed was studied over time. Measurements performed 15 days later showed that the reddish-violet compound formed is completely stable in this time interval when stored at ambient temperature (*ca.* 25 °C).

The molar ratio of the analyte to the analytical reagent and the volume ratio of the concentrated sulfuric acid were investigated. The best conditions were: 1:10 ratio of dipyrone to chromotropic acid using 500 µL of concentrated sulfuric acid.

The absorbance was measured at 576 nm using the volumetric flask as spectrophotometric cell. These results were compared with those obtained with spectrophotometric cuvettes.

The calibration curves were constructed in the range from 1.0×10^{-3} mol L^{-1} to 6.0×10^{3} mol L^{-1} considering the concentration in the aliquot. They can be described by the equations: a) **A** = 0.15 + 110 **C** (r=0.999) where **A** is the absorbance at 576 nm and **C** is the concentration in mol L^{-1} in the aliquot; when using the spectrophotometer with the straight walled volumetric flask and b) **A** = 0.16 + 114 **C** (r=0.998) with the cuvettes.

For both procedures, using the volumetric tubes for spectrophotometric measurements or using the cuvettes, the instrumental limits of detection, LOD, and of quantitation, LOQ, are: LOD ≅ 1.4×10^{-4} mol L^{-1} (LOD ≅ 3.3 SD / slope); limit of quantitation LOQ ≅ 4.5×10^{-4} mol L^{-1} (LOQ ≅ 10 SD / slope). The visual qualitative limit of detection is about 5×10^{-6} g of dipyrone in the aliquot.

Alternatively, in order to obtain results more rapidly, a simple proportional calculation can be done using as standard a solution prepared with the expected concentration of dipyrone in the sample. If the obtained result for the sample is within the established limits, the pharmaceutical preparation can be considered in conformity with the pharmacopoeia recommendations.

In order to test the proposed method six commercial pharmaceutical preparations, purchased in local pharmacies, were analyzed. The results were compared with those obtained with the titrimetric procedure recommended by the Brazilian Pharmacopoeia [1], using the paired Student's statistical ***t*** test and the **F** test [24]. As it can be observed in Table 1, for a confidence coefficient of 0.05, in four cases values of ***t***, slightly higher than the theoretical value, were obtained. However, the **F** test shows complete agreement in all cases. For the confidence coefficient of 0.01 complete agreement was achieved in the Student's ***t*** and in the **F** tests.

Table 1. Comparison, using the paired statistical ***t*** test of Student and the **F** test, between the results obtained with the titrimetric Brazilian Pharmacopoeia procedure and those obtained with the method proposed in this work.

Sample a	Label values /mg	Refer.b	Proposed I c	Proposed II d	tI e	tII f	FI g	FII h	FI-II i
A	5^{00}	$5^{00 \pm 3}$	$5^{07 \pm 10}$	$5^{04 \pm 3}$	$0^{.95}$	$1^{.33}$	$1^{1.1}$	$1^{.0}$	$1^{1.1}$
B	320	320 ± 2	312± 8	330± 6	1.37	3.16	16.0	9.0	1.8
C	500	494± 2	491 ± 1	498 ± 4	2.68	1.26	4.0	4.0	16.0
D	500	504±3	512 ± 1	495± 3	3.58	3.00	6.0	1.0	9.0
E	500	518 ±3	501± 6	498 ± 5	3.62	2.43	4.0	2.8	1.4
F	250	245 ±3	258± 3	246 ± 2	4.33	0.39	1.0	2.3	2.3

[a]Other components present in the pharmaceutical preparation besides dipyrone:

A- magnesium stearate; macrogol;
B - starch; lactose; talc; magnesium stearate;
C - hypromelose; polyvidone; silicon dioxide; sucrose; quinoline yelow; starch; talc; magnesium stearate;
D - prometazin hydrochloride, adiphenine hydrochloride, magnesium stearate; silicon dioxide; talc; starch; sucrose;
E - silicon dioxide; magnesium stearate; polyvidone, magnesium silicate;
F - hyoscine butylbromide, calcium phosphate dibasic; starch; silicon dioxide; tartaric acid; stearic acid; polyvidone; sucrose; talc; gum arabic; titanium dioxide; macrogol;carnauba wax; white wax.

[b] Reference titrimetric method [1].

[c] Proposed method I, using straight volumetric tubes.

[d] Proposed method II, using spectrophotometric cuvettes.

[e] Paired calculated Student's ***t*** values, comparing the proposed method I with the reference titrimetric method.

[f] Paired calculated Student's *t* values, comparing the proposed method II with the reference titrimetric method.

[g] **F** values comparing method I with reference titrimetric method.

[h] **F** values comparing method II with reference titrimetric method

[i] **F** values comparing method I with method II.

Theoretical: Students's ***t*** = 2.78 (confidence coefficient, α=0.05) and 4.60 (confidence coefficient, α=0.01) for the degree of freedom ν= 4 ($\nu = n_1 + n_2 - 2$); $n_1 = n_2 = 3$; **F** = 19.00 (α=0.05).

Conclusion

The analytical method described in this work, despite the complexity of the analyte, presents extreme chemical and instrumental simplicity, very low cost, quite good accuracy and precision, rapidity and reliability. The quantitative determination can be performed in less than five minutes. Therefore, considering these characteristics, it can be suggested for the determination of dipyrone in the bulk drug and in pharmaceutical preparations.

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Resumo: Um método "spot-test" qualitativo e seqüencialmente quantitativo é proposto para análise de dipirona em fármaco "puro" e em preparações farmacêuticas. A formação de coloração vermelho-violeta indica um resultado qualitativo positivo. Na seqüência, um procedimento quantitativo pode ser realizado no mesmo frasco. Os resultados quantitativos obtidos foram comparados estatisticamente com os resultados obtidos pelo método indicado pela Farmacopéia Brasileira, utilizando o teste ***t*** de Student e o teste ***F***. Considerando a concentração em uma alíquota de 100 µL, o limite qualitativo visual de detecção foi de cerca 5×10^{-6} g; instrumentalmente o limite de detecção foi de LOD $\cong$ 1.4×10^{-4} mol L^{-1} e o limite de quantificação de LOQ $\cong 4.5\times10^{-4}$ mol L^{-1}.

Palavras-chave: dipirona, spot-test, análise, qualitativa, quantitativa

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PRODUCTION OF BIODIESEL FROM BABASSU OIL USING METHANOL-ETHANOL BLENDS

F. C. Silva [A], K. S. B. Cavalcante [A,B], H. C. Louzeiro [A,B], K. R. M. Moura [A], A. P. Maciel [A], L. E. B. Soledade [B], A. G. Souza [B]*

[a] Departamento de Química, Universidade Federal do Maranhão, UFMA, Avenida dos Portugueses s/n, Campus Bacanga, CEP 65080-040, São Luís, MA, Brazil.
[b] Departamento de Química, Universidade Federal da Paraíba, UFPB, Campus I, Cidade Universitária, CEP 58059-900, João Pessoa, PB, Brazil.
** Corresponding author. Phone: +55-98-2109-8277*
E-mail address: fernasil@ufma.br

Abstract: Maranhão state in Brazil presents a big potential for the cultivation of several oleaginous species, such as babassu, soybean, castor oil plant, etc... These vegetable oils can be transformed into biodiesel by the transesterification reaction in an alkaline medium, using methanol or ethanol. The biodiesel production from a blend of these alcohols is a way of adding the technical and economical advantages of methanol to the environmental advantages of ethanol. The optimized alcohol blend was observed to be a methanol/ethanol volume ratio of 80 % MeOH: 20 % EtOH. The ester content was of 98.70 %, a value higher than the target of the ANP, 96.5 % (m/m), and the biodiesel mass yield was of 95.32 %. This biodiesel fulfills the specifications of moisture, specific gravity, kinematic viscosity and percentages of free alcohols (methanol plus ethanol) and free glycerin.

Keywords: Babassu oil, methanol, ethanol, methyl esters, ethyl esters.

I. Introduction

Babassu nut is the main product of the vegetal extractive activities in Maranhão state, Brazil, and one quarter of its territory is covered by such native palm tree (*Orbignya phalerata*). The activities related to the babassu nut generate about 300 thousand jobs, from the collect normally made by the "babassu breakers", up the oil refining [1,2].

Maranhão is the biggest producer of babassu nuts in Brazil. It is responsible for the production of almost 80% of the country output, corresponding to 120 thousand metric tons in the 2005 base year. [3]. The local industries produce about 60 thousand metric tons /year of babassu oil, being most of it transported to other Brazilian states [4].

Babassu oil displays a high percentage of saturated fatty acids, 91%, mainly composed of lauric acid (48%), myristic acid (16%), palmitic acid (10%), stearic acid (2%) and others (5%). It also presents 19% of unsaturated fatty acids, chiefly oleic (14%) and linoleic (5%) acids [5].

Maranhão is also the second biggest soybean producer in Northeastern Brazil, only behind Bahia state. In the 2006/2007 harvest, according to CONAB, the soybean production in Maranhão was of about 0.967 million metric tons, while the whole Brazilian output was of around 56.71 million metric tons [6].

Besides these two cultures, Maranhão displays a big potential for the cultivation of other oleaginous species (castor oil plant, cotton, tame nut, etc.), due to its weather conditions, geogra-