ABOUT THE SAFETY OF SOME CONSUMER PRODUCTS IN HO CHI MINH CITY

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ABSTRACT: The analysis of some consumer products at the Center of Analysis and Experimentation, HCM City (CASE) revealed that they were either of bad quality or falsified. That was the case of the so-called nourishing candies that a businessman wanted to import and which did not contain any healthy element, rather the sex stimulating tadalafil for man, that of pretended agarwood which was, in reality, artificial or that of red edible bird's nest which was indeed the white one deliberately contaminated by sodium nitrite giving this red color by enzymatic reaction, or that of unallowed food additive dithionite acting like sulfite but cheaper than the latter for treating shredded or sliced vegetables, fruit jams, wines. In view of these unsafe products, it looks difficult to ensure totally and efficiently the safety of commercial products. Apparently, some dishonest traders are backed up by quite experienced scientific peoples. To contribute to the safety of consumer goods, we wish to propose a solution in this communication.

KEYWORDS: *consumer products, agarwood, nourishing candies, red and white edible bird's nest, dithionite, dishonest traders backed up by scientists.*

1. INTRODUCTION

While one of the aims of Ho Chi Minh City (HCM City) is to get rid of falsified or deceitful commercial products in the market, they are still sold stealthily in traditional markets. One of the big concerns is their safety while the City is making efforts to provide to its peoples good living, good health and longer life. Furthermore, they might pose a threat to the City International Economic Integration. In a recent communication submitted for publication in the Vietnam Journal of Analytical Sciences, we reported the case of "Bắc Thảo Duck Eggs or Century Eggs" deliberately contaminated by toxic chemicals used to shorten the time of incubation in order to get more illegal profit [1]. In fact, food safety in the market associated with public health risk, constitutes a worldwide human preoccupation in production, distribution, consumption and waste disposal. This certainly contributes to the establishment on April 7 1948 of WHO, a specialized agency of the United Nations, involved with international public health, actually headquartered in Geneva, Switzerland.

Our laboratory, well known by its excellent analytical services, the Center for Chemical Analysis and Experimentation of Ho Chi Minh City (CASE), by chromatographic and spectrometric analysis, identified three falsified products (the sex stimulating candies, the artificial agarwood and the fake red bird's nest) and one unallowed food additive which is dithionite, sold in the City. These cases show that HCM City must make more efforts to ensure the quality of its consumer products.

2. MATERIALS AND METHODS

2.1. Reagents, Reference and standards

-Tadalafil 98% (Merck).

-Agarwood containing the true incense as reference from a CASE client for the analysis of incense in other agarwood samples.

-Sodium Nitrite 99.99% (Sigma Aldrich).

-Sodium Dithionite for analysis EMSURE ≥ 85% (Merck).

-Sodium Hydroxymethanesulfinate (Rongalite) 98% (Sigma Aldrich).

-Sodium Hydroxymethanesulfonate (HMS) 95 % (Merck).

2.2. Instruments

-FTIR iS50 Infrared spectrometer, Thermo Fisher Scientific with resolution set at 4 cm^{-1}, spectral width from 400 to 4000 cm^{-1}, ATR with a built-in diamond crystal (32 scans), used for the identification of dithionite and nitrite in red bird's nest;

-GC-MS equipment: GC trace ultra 1310, ISQ 7000 Thermo Fisher Scientific operating with 70 eV electrons, used for the analysis of agarwood incense by Headspace-SPME-GC-MS:

+Injector temperature: 270°C;

+Column: DB-5MS, 30 m x 0.25 mm x 0.25 µm;

+Temperature program: 80 °C (hold 5 min), rising to 280°C at the rate of 20°C min^{-1} (hold 10 min), then to 300 °C at the rate of 20 °C min^{-1}(hold 5 min);

+Transfer line: 280 °C;

+Ion source set at 250 °C; mass range: 29-650u.

-Ion chromatography spectrometer DIONEX ICS-6000 Thermo Fisher Scientific, used for the analysis of sodium hydroxymethanesulfinate (rongalite), a derivative of dithionite;

+Injection volume: 20 µL;

+Dionex IonPac AS 11 HC Column: 250 mm x 2 mm x 4 µm;

+Mobile phase: KOH 30mM; Flow: 0.3 ml/min;

+Conductivity detector; Ion suppressor: ADRS 2mm, current 15mA.

-Hitachi UH5300 UV/Vis spectrometer, set at 538 nm for measuring nitrite.

-$LCMS^n$ linear ion trap LTQ XL Thermo Fisher Scientific used for the identification of tadalafil by further fragmentation of the molecular ion;

+Heater temperature: 300 °C, Sheath gas: 30 (arb), Aux gas: 10 (arb), ISpray voltage: 4000V,

+ Capillary temperature: 250 °C, Tube lens: 50 V, Ionization mode: positive;

+Mass range: 105 – 1000u for the identification of the molecular ion;

+MS^2: Argon gas was used as collision gas. Collision Energy was 35eV for further fragmentation of the molecular ion;

+The extract was directly injected into the ion source without a column separation.

-Acquity UPLC Waters for the quantitative determination of tadalafil; +Acquity UPLC BEH C18 column: 150 mm x 2.1 mm x 1.7 µm;

+Flow: 0.2 ml/min; Mobile phase: acetonitrile : H_2O (0.1% HCOOH) = 80 : 20;

+PAD detector Waters was set at 293.7 nm.

2.3. Sample preparation

2.3.1. Extraction of tadalafil from the "nourishing" candy

A piece of candy (4.5 g) was finely ground. Take 0.1 g of the powder and dissolve in 10 ml of methanol. The solution was centrifugated, filtered and identified by LC-MS linear ion trap-ESI (+) and quantified by UPLC-PDA detector.

2.3.2. Agarwood

Agarwood incenses were analyzed by Headspace-SPME-GC-MS from 2 g of well ground and homogenized agarwood samples incubated at 80 °C. The incubation time was 20 minutes without agitation. The adsorption was performed with a SPME 65 µm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) fused silica fiber. The desorption time was 2 minutes at 250 °C in the injector.

2.3.3. Edible bird's nest

For unprocessed white bird's nest with fibers not yet agglutinated by polysaccharides, deliberate contamination by sodium nitrite gives by some enzymatic reactions the red color of red bird's nest,. Thus, this produces the falsified red bird's nest, sold at a much higher price for illegal profit.

-Identification of nitrite: 10 g of this fake red bird nest were ultrasonically extracted with 50 ml of water at 80 °C. The extract was centrifugated, filtered, evaporated almost to dryness at 105 °C, then vacuum evaporated. The dried residue was identified by FTIR spectrum which showed the presence of nitrite salt.

-Quantitation of nitrite: The contaminant nitrite in both of the red and white bird's nest. either raw or finished products with fibers agglutinated by polysaccharides in the latter, was quantitatively determined by colorimetry. To 10 g of the sample were added 5 ml of saturated borax solution and 100 ml of hot water (70 °C); heat the solution of the sample in a hot water bath (70 °C) for 15 minutes. Then, allow the content to cool to room temperature and add 2 ml of the solution of 0.2 % of sulfanilamide and 2 ml of the solution of 0.1 % of N-1-naphthylethylenediamine dihydrochloride, let the solution stand for 30 minutes for precipitation of protein; filter the supernatant. In the presence of nitrite, a red coloured complex was formed and photometrically measured at 538 nm [2]

2.3.4. Dithionite [3]

The commercial powder sample was used for food preservation according to the vendor, even without knowing the nature of the product. The sample was identified by FTIR. For quantitation of the residue of dithionite in food products, the sample was dissolved and derivatized ultrasonically with 2 % basic formaldehyde solution in 15 minutes to give rongalite (sodium hydroxymethanesulfinate $HOCH_2SO_2Na$) and HMS (sodium hydroxymethanesulfonate $HOCH_2SO_3Na$).

$$Na_2S_2O_4 + 2\ CH_2O + H_2O \rightarrow HO\text{-}CH_2\text{-}SO_2Na + HO\text{-}CH_2\text{-}SO_3Na$$

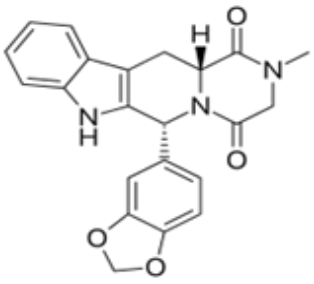
Sodium dithionite Rongalite HMS

The solution after ultrafiltration was injected into the IC system for rongalite analysis.

3. RESULTS AND DISCUSSIONS

3.1 Case of "nourishing" candies

These candies, which supposedly contained American ginseng, Cordyceps were sent to CASE by a trader for verification before importing them to Vietnam. In fact, no such precited compounds were present. Instead, tadalafil (Fig.1), a compound for the treatment of erectile dysfunction [4], preventing man premature ejaculation, was found. LC-MS/MS analysis gave peaks at m/z = 390 ($M + H^+$) and m/z = 268 (from MS/MS fragmentation of m/z = 390, giving by a concerted four-center mass fragmentation the ion m/z = 268 and the compound 4,5-phenylene-1,3-dioxolane of molecular weight 122).



Methanol extraction of tadalafil from one piece of candy and quantitative analysis by UPLC gave the average result 12426 mg/kg or 55.9 mg/4.5g piece of candy. By this analysis, CASE prevented just on time the importation of those dangerous candies.

Fig. 1.

3.2. Case of the agarwood

Headspace SPME GC-MS chromatogram of the reference agarwood incense sample and that of a commercial agarwood incense sample showed in fact significant differences in composition (Fig. 2): the intensities of the peaks of the commercial agarwood incense were much weaker by comparison with that of reference agarwood incense (retention times from 16 to 20.5 minutes). On the contrary, intense peaks below 16 minutes and above 21 minutes appeared in the commercial sample and were identified as dimethyl 3-hydroxy-3-methylpentane-1,5-dioate or dimethyl 3-hydroxy-3-methylglutarate (RT: 11.97 min), methyl nonanoate (RT: 12.06 min), benzylacetone (RT: 12.47 min), hydrocinnamic acid methyl ester or methyl 3-phenylpropionate (RT: 13.19 min), palmitic acid methyl ester or methyl palmitate (RT: 20.65 min), 9-octadecenoic acid methyl ester or methyl oleate (RT: 21.56 min). One way to produce the artificial agarwood was to dip pieces of *Aquilaria* wood not containing yet agarwood in a solution of the natural incense, this solution contained fatty acid methyl esters for incense retention. The incense solution penetrated into Aquilaria wood and artificial agarwood was therefore obtained and sold at quite high price.

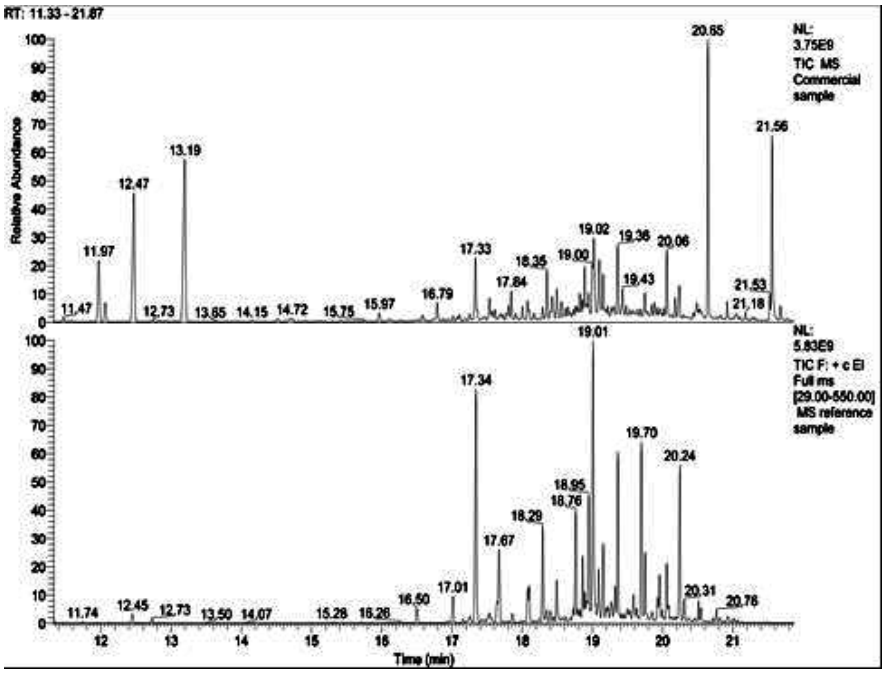


Fig. 2. Total Ion Chromatogram of commercial agarwood incense and reference agarwood incense samples

3.3. Edible bird's nest

Actually, there are two kinds of commercial bird's nests: the white and the red ones. Due to its higher nutritional value, better for human health, the red bird's nest is much more expensive than the white one. The higher value and the growing demand of the red ones attract counterfeiters to defraud buyers. One of the contaminants frequently found in the fake red bird's nests is sodium nitrite which, by some enzymatic reactions inside the solidified bird's saliva, gives this red color. Nitrite sodium was easily detected in CASE's laboratory by FTIR in the native bird's nest, not yet processed for commercial purpose, after ultrasonic extraction with water, decantation, filtration and vacuum evaporation. By colorimetric quantification, nitrite was found by us in the range 2181-5166 mg/kg. In the processed bird's nest, nitrite in excess was partially washed off, colorimetric analysis still gave the values 7 - 123 mg/kg. The maximum limit of nitrite allowed by China for importation and in Vietnam as well is 30 ppm [5,6].

3.4. Case of Dithionite

Commercial dithionite powder could be identified by FTIR. The FTIR spectrum showed strong bands at 632, 657, 997, 1112, 1147, 1229, 1640, 3300 cm^{-1} corresponding to sodium dithionite hydrate. It was also confirmed by ion chromatography method.

Sodium dithionite is used in textile and paper industry as a whitening agent. Although it is not allowed as a food additive, it is being used intentionally as preservative for jams, sliced vegetables, shredded banana florets (Fig. 3), fruit juices, wines for replacing sulfites because of its much lower price, while sulfites are allowed in food as preservatives with some restrictions linked to asthma however. On July 1986, FDA banned the use of sulfites in all fresh fruits and vegetables that are eaten raw. Therefore, dithionite and sulfites must be controlled in foods. Their analysis may be performed by ion chromatography [3] and LCMS/MS [7].(Figure 4)

Fig. 3. Shredded banana florets remaining white when treated with dithionite

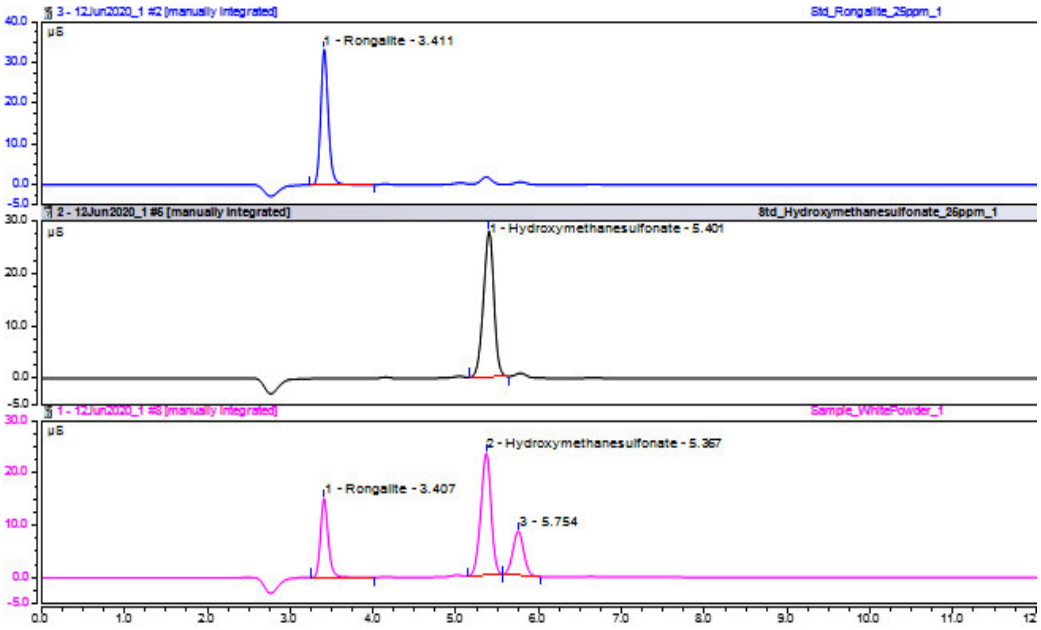


Fig. 4. IC chromatogram of rongalite, HMS standards and derivatives from reaction of commercial dithionite with HCHO showing the presence of rongalite and HMS (with unidentified impurity)

These few examples show that to ensure the quality of many consumer products is at the present time a pretty challenging task, while they constitute one of the essential elements for Vietnam economic development and International Economic Integration. Strong measures have to be therefore taken.

We wish to propose that HCM City authorities would every two or three years reserve some funds for purchasing recent high resolution and high sensitivity analytical equipment to be installed in some already known good analytical laboratories and especially for continuously training chemical analysts to be good interpreters of analytical results. Well-equipped mobile laboratories are actually available such as the Agilent mobile unit with sample preparation facilities, analytical capabilities, allowing on-site analysis in a number of cases and therefore helping in rapid decision making [8].

Besides, the HCM Patriotic Front in collaboration with HCM Department of Commerce and Industry and HCM Food Safety Committee, would organize several seminars, short-term courses and inspection operations on the quality and safety of commercial products to various district authorities and members of district Patriotic Fronts. In fact, many small sub-district market vendors may unconsciously violate the quality of their goods because of not knowing their origin. Others

dispose their consumer products on thin and old dirty covers or even directly on the ground, therefore subjected to possible microbial contamination. Sub-district authorities with the participation of their Patriotic front members would efficiently help keeping the product quality and safety because they are residents there and certainly have interest to do so. Also, we wish that close relations between the official organizations in charge of Commercial Product Quality and Food Safety Survey and the system of quality control laboratories would be established. This would help rapid and fruitful exchange, sample collection and analysis in needed cases.

4. CONCLUSION

In this communication, the Center of Analytical Services and Experimentation succeded in identifying and analyzing three falsified consumer products and one unallowed food additive with its quite precise, selective, sensitive spectrometric and chromatographic equipment and well-trained analysts, able to interpret their analytical results. These types of analytical laboratories may significantly contribute to improve the quality of consumer products for both export and local consumption, therefore helping ln promoting greater trade, faster reduction of dishonesty in fraudulent trading. This constitute one of the keys to speed up the national economic development and therefore possibly, the International Economic Integration.

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