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TECHNICAL NOTE

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Identification of Ascorbic Acid and Its Degradation Products in Black Powder Substitutes

ABSTRACT: Low explosives such as smokeless powder, black powder, and black powder substitutes have been used in illicit pipe bombings throughout the United States. Some of the newer black powder substitutes are formulated with ascorbic acid, which gradually decomposes as the powder ages, making it difficult if not impossible for the forensic chemist to identify it by traditional bulk techniques. A sensitive method for the identification of residual levels of ascorbic acid in black powder substitutes is presented. Powder samples are extracted with a mixture of acetonitrile and *bis*(trimethylsilyl)acetamide (BSA), which converts carboxylic acid and alcohol functional groups to trimethylsilyl esters and ethers, respectively. Samples are then analyzed by gas chromatography-mass spectrometry (GC-MS). Results have shown that trace amounts of ascorbic acid can be identified at detection limits that are well below those for traditional bulk techniques. Degradation products for ascorbic acid (hydroxylated carboxylic acids, furanones, and lactones) can also be detected.

KEYWORDS: forensic science, explosives, black powder substitutes, ascorbic acid, gas chromatography-mass spectrometry, derivatization, BSA

While black powder has been in use as a propellant for over 400 years, it is only recently that formulations have been designed to improve upon its burning characteristics and chemical properties. State and federal regulations regarding the transportation and storage of black powder have also given impetus to the development of substitutes that could be handled more safely (1). In particular, ascorbic acid (AA) has been used as a replacement for elemental sulfur in various black powder substitutes. This organic acid serves as a fuel for potassium nitrate (KNO_3) and potassium perchlorate ($KClO_4$) oxidizers, and eliminates the formation of corrosive reaction products from sulfur that can lead to barrel fouling. In addition, such powders have been classified by the Department of Transportation as flammable solids (2), making them easier to transport and store than black powder.

A number of commercial products containing ascorbic acid have been developed, although the market has remained somewhat unsteady. The original patent for Golden Powder (containing KNO_3 and AA) was granted in 1985. The Golden Powder formulation was later modified and produced as Black Mag Powder (containing KNO_3, $KClO_4$, and AA) by the Arco Powder Company from early 1996 through January 1997 (personal communication: Lee Hearn, Arco Powder, 1/9/03). This product has been most recently re-released as "Black Mag '3." Legend Products manufactured Black Canyon Powder (containing KNO_3 and AA) in 1996 and 1997 (personal communication: Brett Epstein, Legend Products, 12/4/96). Subsequently, the same personnel established Clean Shot Technologies and introduced Clean Shot Powder (using a similar recipe to Black Mag that contains KNO_3, $KClO_4$, and AA) in 1999. Most recently, GOEX briefly produced Clear Shot Powder (containing KNO_3 and cooked sugars, rather than AA) in 2001 (personal communication: Mick Fahringer, GOEX, Incorporated, 1/9/03).

Traditional methods of analysis for intact black powder substitutes rely upon examining their morphology, ignition susceptibility, and identification of oxidizers and fuels using bulk chemical methods such as X-ray powder diffraction (XRPD) (3). However, the identification of ascorbic acid in such products is often complicated by the chemical degradation of this fuel and the resulting inability to confirm its presence in older samples.

Due to interest in the long-term viability of Vitamin C in various food products, the degradation pathway for AA has been well studied. It has been found that ascorbic acid reacts readily with oxygen, particularly when in the presence of moisture, light or heavy metal ions (4). In all cases, degradation initially proceeds by reversible conversion of AA to dehydroascorbic acid, which then irreversibly degrades to 2,3-diketogulonic acid (5). At this point, further degradation will yield dozens of compounds whose relative amounts may differ depending upon degradation conditions. Figure 1 depicts an example of one such degradation pathway (personal communication: Sam Margolis, NIST, 12/17/02). Many other degradation products are also possible. These include 2,3-diketo-4,5,5,6-tetrahydroxyhexanoic acid; 2,4-diene-2,3,5,6-tetrahydroxyhexanoic acid, 1,4-lactone; glyco- and glyceraldehydes, and other related compounds (6,7).

To date, forensic laboratory methods for the identification of ascorbic acid have included the analysis of intact AA in water extracts of Clean Shot Powder (without derivatization) using electrospray ionization mass spectrometry (8). The use of trimethylsilyl (TMS) derivatizing agents has also been quite successful in the separation and analysis of AA, sugars, and their degradation products by GC-MS (6,7). This approach has been applied successfully to the analysis of simple sugars in intact and post-blast chlorate/sugar explosives (9). The present study demonstrates the feasibility of identifying ascorbic acid and /or its degradation products in aged

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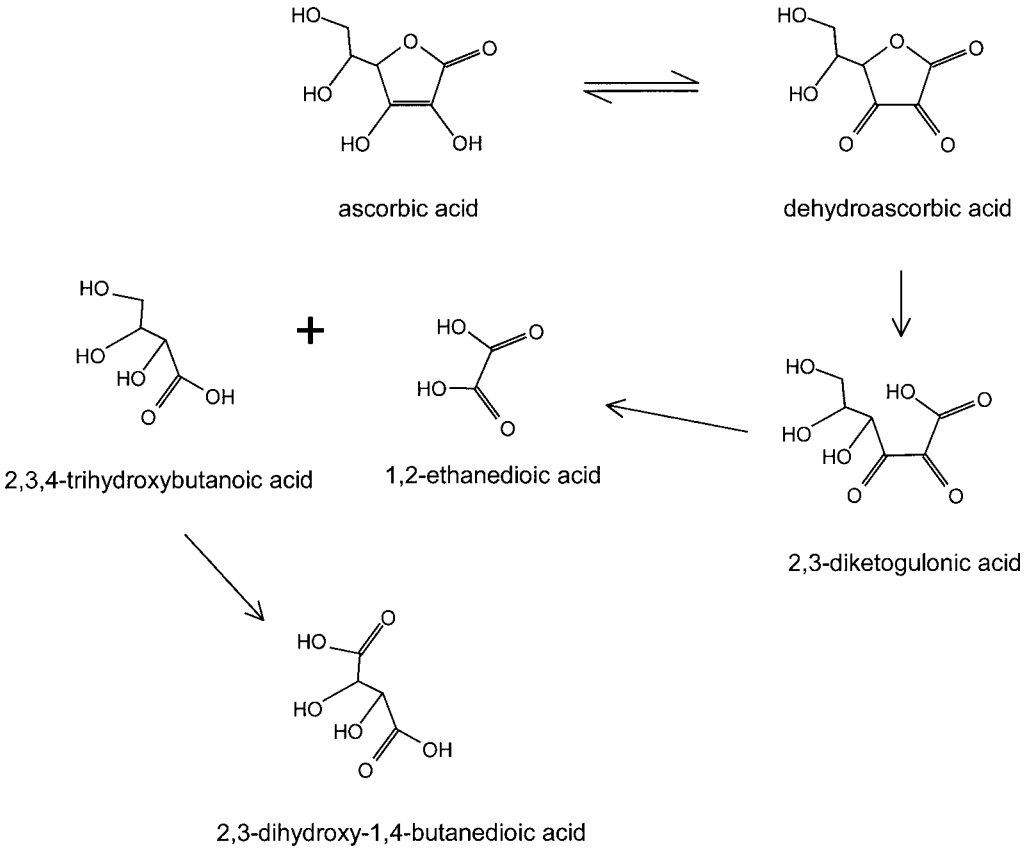

FIG. 1—*One oxidative degradation pathway for ascorbic acid. All hydrogen atoms shown are labile and can be replaced with trimethylsilyl functionalities using BSA.*

black powder substitutes by solvent extraction, TMS derivatization, and analysis by GC-MS.

Materials and Methods

High-purity acetonitrile (Burdick and Jackson, Muskegon, MI), N,O-*bis*(trimethylsilyl)acetamide (BSA) (Pierce Chemicals, Rockford, IL), D-fructose (Sigma-Aldrich, St. Louis, MO), dehydroascorbic acid (Sigma-Aldrich, St. Louis, MO), 1,4-butanedioic acid (Sigma-Aldrich, St. Louis, MO), and L-ascorbic acid (Fisher Scientific, Pittsburgh, PA) were obtained from chemical supply houses. Black Canyon Powder (lots from 1994 and 1996 obtained from Legend Products, Las Vegas, NV), Black Mag '3 Powder (Arco Powder, Hollywood, FL), Clean Shot Powder (Clean Shot Technologies, Whitewater, CO), Clear Shot Powder (GOEX, Incorporated, Doyline, LA), and Golden Powder (Oro-Tech Industries, Las Vegas, NV) were acquired from commercial sources.

XRPD analyses were performed on a Philips XRG 3100 Powder Diffractometer with a long fine focus copper anode X-ray tube set at 45 kV and 35 mA. A scintillation detector was scanned from 10° to 80° (2θ) at 0.02° steps with a 1-s integration time. Solid samples were ground in a mortar and pestle and loaded into glass depression slides for analysis.

Sample derivatives were prepared by placing a small amount (60–250 mg) of the ground sample into a 4 mL glass vial, then adding 1.5 mL acetonitrile and 0.5 mL BSA. Samples were then thoroughly mixed, allowed to stand at room temperature for approximately 10 min, filtered through a 0.45 μm PTFE membrane into 2 mL GC vials, and immediately analyzed by GC-MS. GC-MS analyses were performed on an Agilent 6890/5973 GC-MS system

TABLE 1—*Major components of black powder substitutes containing ascorbic acid based on information from manufacturers.*

Black Canyon Powder	Black Mag Powder	Clean Shot Powder	Clear Shot Powder	Golden Powder
KNO_3 ascorbic acid	KNO_3 $KClO_4$ ascorbic acid	KNO_3 $KClO_4$ ascorbic acid	KNO_3 sugars	KNO_3 ascorbic acid

TABLE 2—*Crystalline phases identified by XRPD in black powder substitutes containing ascorbic acid.*

Black Canyon Powder	Black Mag Powder	Clean Shot Powder	Clear Shot Powder	Golden Powder
KNO_3	KNO_3 $KClO_4$ ascorbic acid	KNO_3 $KClO_4$ ascorbic acid	KNO_3	KNO_3 ascorbic acid

TABLE 3—*Results of GC-MS analysis of black powder substitutes containing ascorbic acid.*

	Black Canyon Powder		Black Mag Powder	Clean Shot Powder	Clear Shot Powder	Golden Powder
	1994	1996				
Sample Size (mg)	247.3	111.2	75.8	175.3	200.3	58.4
AA Detected?	trace	yes	yes	yes	no	yes

using a 1 μL injection volume into a split/splitless injector held at 250°C, with a 50:1 split ratio. Samples with lower organic content (i.e., Black Canyon (1994 lot) and Clear Shot) were analyzed with a 2 μL injection volume and a 20:1 split ratio. Separation was accomplished on a 30 m × 0.25 mm × 0.1 μm SPB-1 column (Supelco, Incorporated, Bellefonte, PA) with helium carrier gas. The oven temperature program had an initial hold at 60°C for 3 min, followed by a 20°C/min ramp to 300°C. After a 3 min solvent delay, the mass spectrometer monitored m/z 35 to m/z 500 at 1.5 scans/s.

Compound identification was performed by comparing background-subtracted sample spectra against the NIST/EPA/NIH library, Version 1.7a, build 7/18/2000, containing 107,886 spectra. Only library spectra with a match score of 800 out of 1000 or higher were considered as possible identifications and all computer-aided identifications were confirmed by visual examination of the sample and library spectra. However, because standards for all AA degradation products were not available, identifications of these compounds should be regarded as tentative.

Results and Discussion

Various extraction and derivatization procedures were evaluated during the course of method development. Extracting samples with a mixture of acetonitrile and BSA at room temperature (without heating or ultrasonication) allowed for the most sensitivity without further degrading any ascorbic acid present. In addition, while solutions of derivitized ascorbic acid were found to be stable for periods of at least 24 h, derivitized extracts of propellant samples did show continued degradation after standing for similar periods. Therefore, GC-MS analysis was always performed immediately after sample extraction and derivatization.

The efficiency of the derivatization procedure as well as the chromatographic behavior of derivatized ascorbic acid is illustrated in Fig. 2A. In this experiment, 1.5 mL of a 1.5 mg/mL solution of ascorbic acid in acetonitrile was reacted with 0.5 mL neat BSA. Under the reaction conditions used, there is no evidence of residual AA or derivatization side products. Furthermore, the excellent peak shape indicates that non-ideal solute-stationary phase interactions have been minimized. As little as 200 μg of ascorbic acid is readily detectable under the conditions used.

The mass spectrum of the derivative is shown in Fig. 2B. While the relative abundance of the molecular ion at m/z 464 is small, there is a strong peak at m/z 332 that likely arises due to a cyclic rearrangement. In addition, numerous other fragment ions appear, such as two alpha cleavage fragments at m/z 205 and 259. Combined with fragments at m/z 45 (CH_5Si^+), 73 ($C_3H_9Si^+$), and 449 ($[M - CH_3]^+$), confident identification based on the EI spectrum is possible.

Of the black powder substitutes examined, Golden Powder showed clear indications of KNO_3 and ascorbic acid via XRPD as well as no substantial degradation products via GC-MS (Fig. 3). In contrast to these results, however, were those for two samples of Black Canyon powder. Neither had detectable levels of ascorbic acid via XRPD. The GC-MS results (Figs. 4A and 4B) reveal near

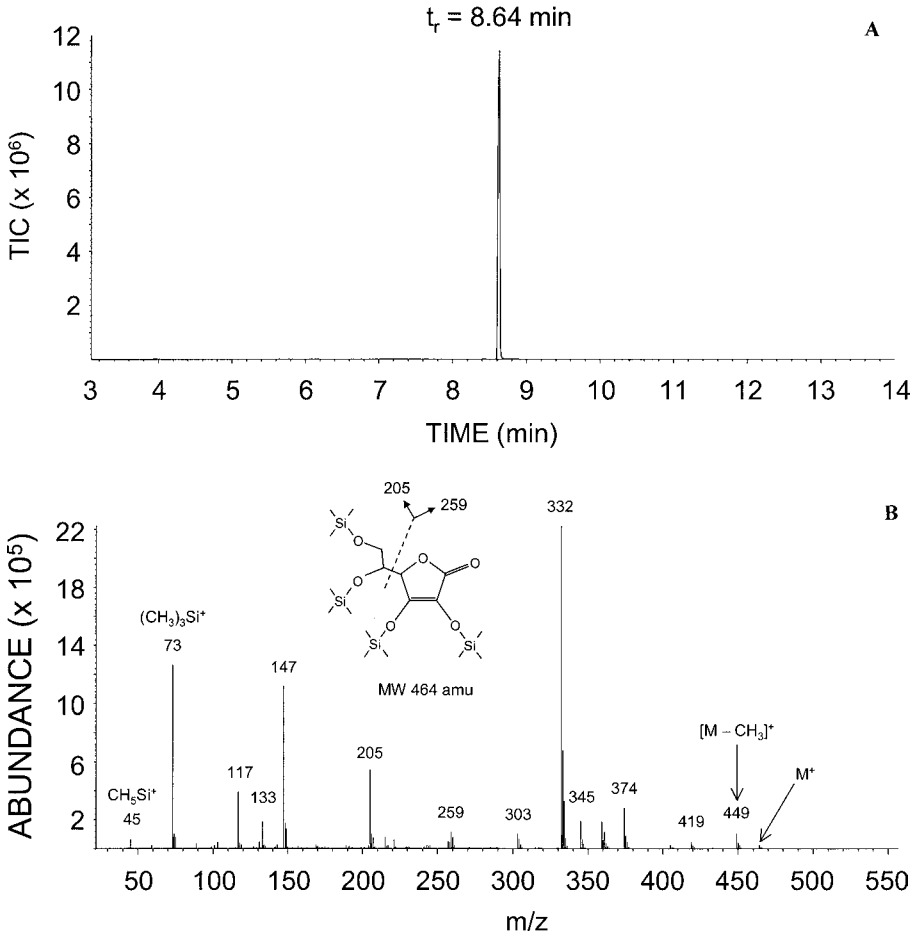

FIG. 2—(A) *Gas chromatogram, and* (B) *mass spectrum of a standard solution of ascorbic acid in acetonitrile, following TMS derivatization with BSA.*

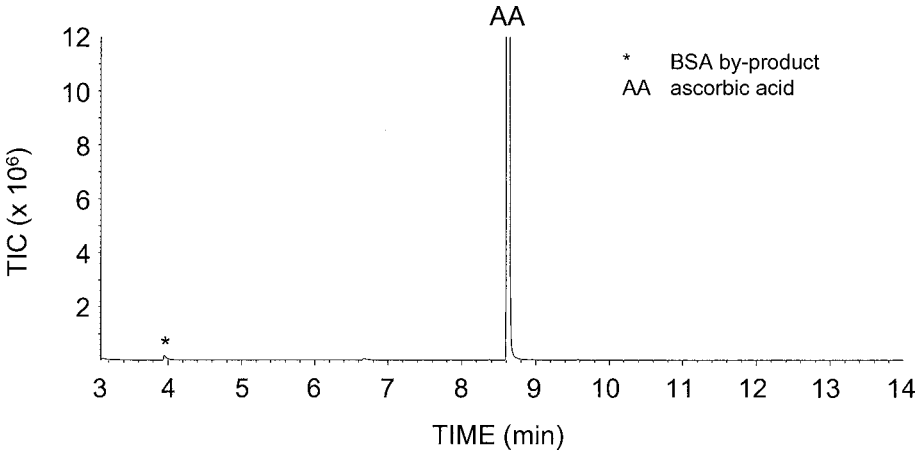

FIG. 3—*GC-MS analysis of Golden Powder, an example of a non-degraded black powder substitute containing ascorbic acid.*

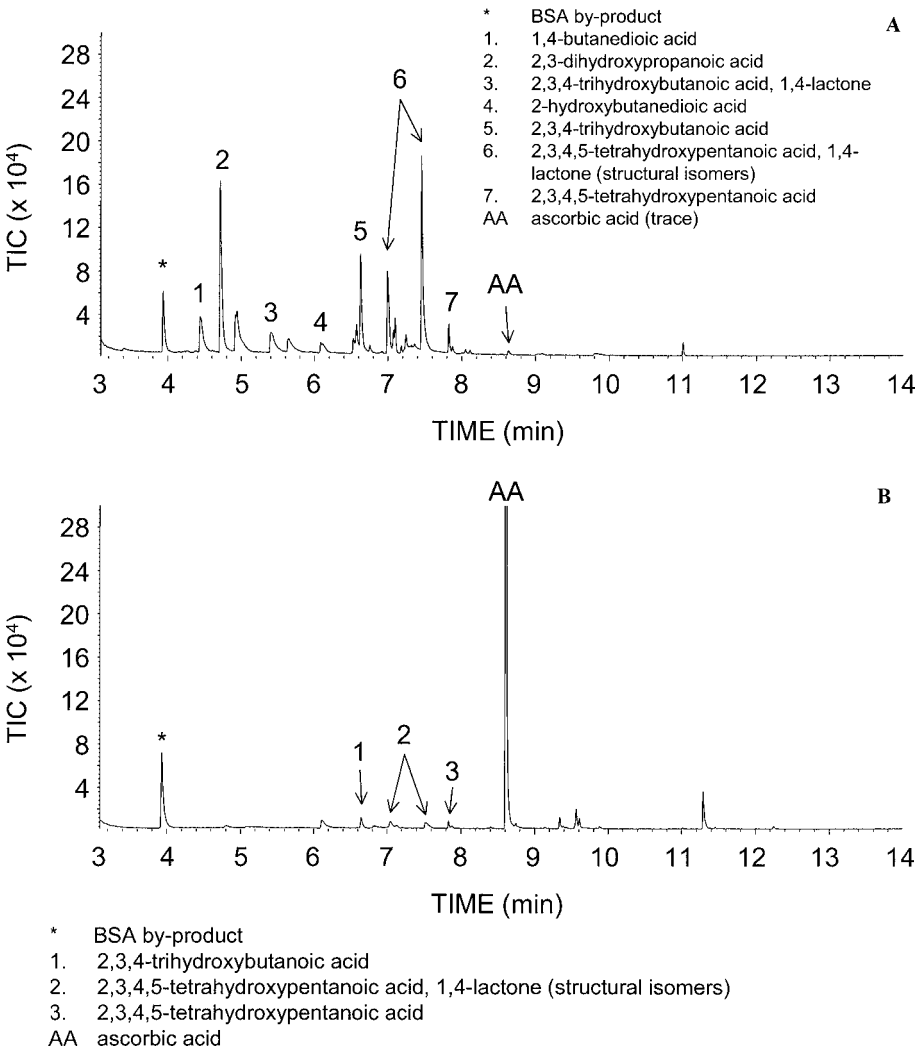

FIG. 4—*GC-MS analysis of* (A) *Black Canyon Powder (1994), and* (B) *Black Canyon Powder (1996) showing varying amounts of ascorbic acid degradation, which prevented its detection by XRPD.*

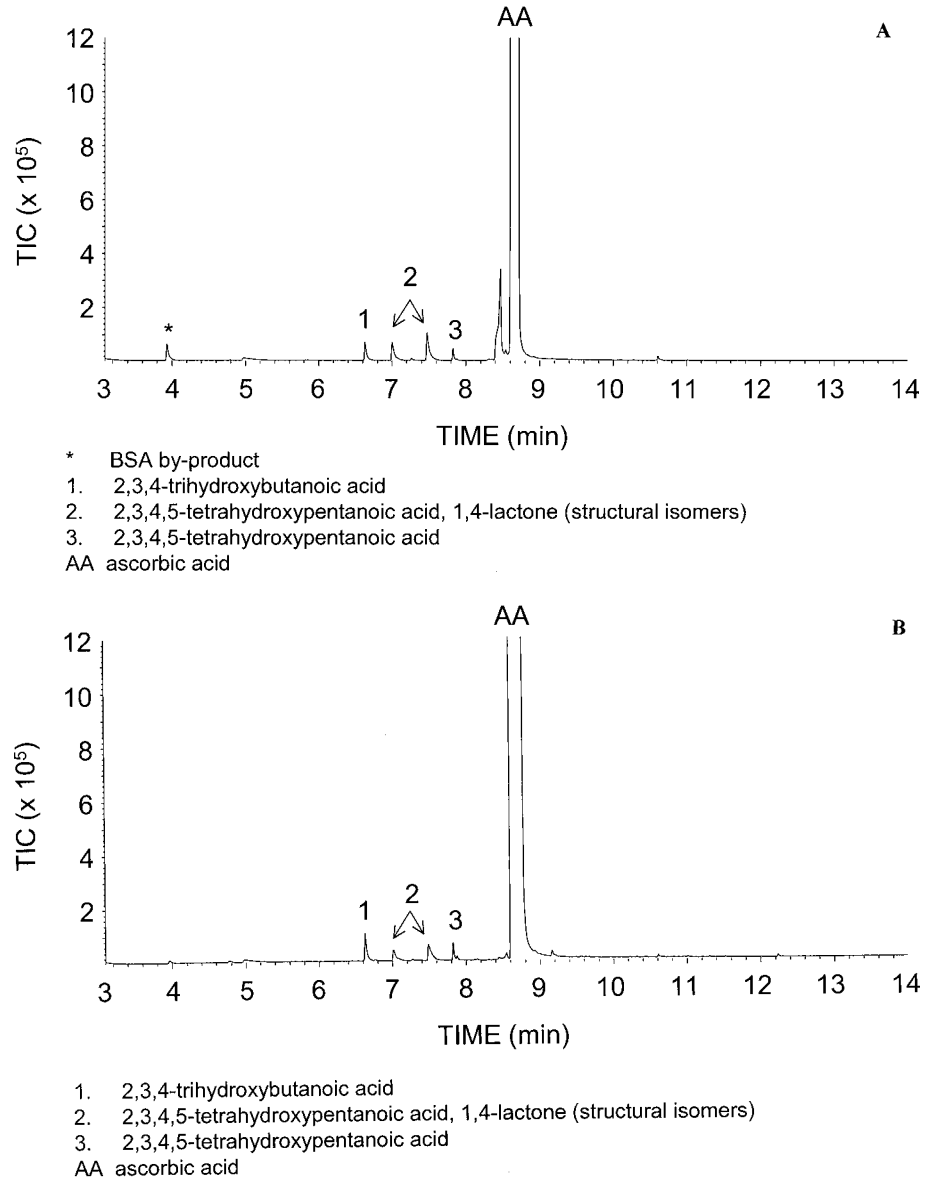

FIG. 5—*GC-MS analysis of* (A) *Black Mag Powder, and* (B) *Clean Shot Powder illustrating the minor degradation present in $KClO_4$-containing black powder substitutes.*

total degradation of the ascorbic acid in the 1994 sample and partial degradation in the 1996 sample. Although readily detectable by GC-MS, these residual levels of ascorbic acid were clearly below the detection limit of the XRPD instrument.

The presence of degradation products can also be quite characteristic as they have been found to be reproducible among the various products tested, particularly 2,3,4-trihydroxybutanoic acid, 2,3,4,5-tetrahydroxypentanoic acid, 1,4-lactone, and 2,3,4,5-tetrahydroxypentanoic acid. Note that 2,3,4,5-tetrahydroxypentanoic acid, 1,4-lactone appears to arise as a mixture of two structural isomers, as a result of the numerous chiral centers present in the original ascorbic acid molecule. Also, in samples where the organic content is low, the total ion chromatogram will be of a lower intensity, and the presence of BSA by-products will be more noticeable (e.g., the peak at approximately 3.9 min). However, residual BSA and BSA by-products are sufficiently volatile that they do not create chromatographic interference with other components.

A second class of black powder substitutes contains both KNO_3 and $KClO_4$, such as Black Mag and Clean Shot. Both of these powder samples were well behaved in that ascorbic acid was readily detectable via XRPD. However, analysis by GC-MS allowed for an assessment of the extent of degradation in these samples (Figs. 5A and 5B). Because products such as Clean Shot retain most of their ascorbic acid content, sample sizes of 3 mg or less have been successfully analyzed.

Lastly, Clear Shot differs from the above products in that "cooked fruit sugars," rather than ascorbic acid, are used as the alternative fuel. The presence of KNO_3 can be easily established in this product via XRPD. GC-MS analysis (Fig. 6) clearly shows various simple sugars such as fructose, glucose, and galactopyranose. Interestingly, some of the same degradation products (e.g., 2,3,4,5-tetrahydroxypentanoic acid, 1,4-lactone) appear in this material as well as in the ascorbic acid-containing products. It is possible that these arise from ascorbic acid contained in the fruit or juice used to prepare the fruit sugars, or from the caramelization of the sugars

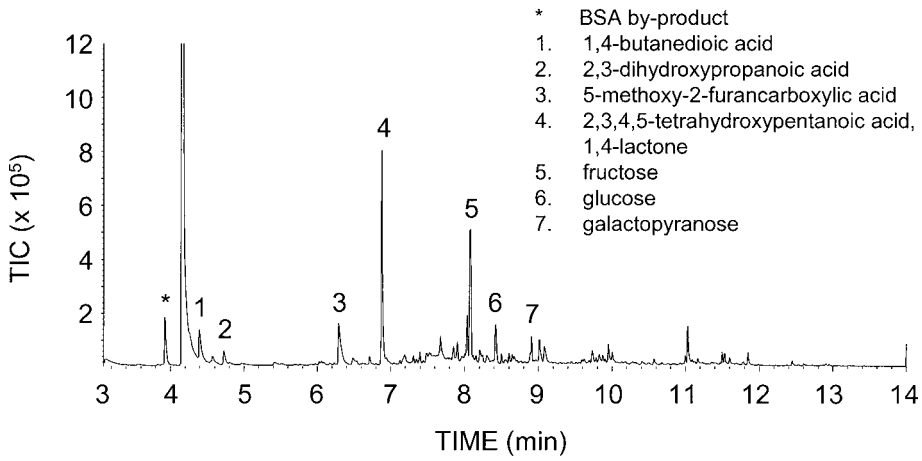

FIG. 6—*GC-MS analysis of Clear Shot Powder, indicating the presence of various simple sugars as alternative fuels.*

themselves. However, this product remains easily distinguishable from the other ascorbic acid-containing products due to the presence of intact sugars such as fructose.

Conclusion

GC-MS analysis combined with BSA derivatization can provide an identification of aged and degraded samples of black powder substitutes containing ascorbic acid, cooked sugars, or both. This method is particularly helpful in those cases where bulk methods such as XRPD fail.

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