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Note

Use of capillary gas chromatography for the identification of brominated vegetable oils

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Brominated vegetable oils (BVOs) are food additives used in citrus-based beverages to disperse the flavoring oils. Although a number of methods have been investigated for their determination, only packed column gas chromatography (GC) after transesterification[1] or treatment with sodium methoxide[2,3] has been able to identify individual BVOs. In this work we report on the use of capillary GC to separate and detect the constituent brominated fatty acid methyl esters after treatment of the BVOs with sulfuric acid–methanol solution. Seven different BVOs were characterized and the results compared with those of previous work done with packed column GC. In addition, the technique was applied to the determination of BVOs in an orange flavored soft drink.

EXPERIMENTAL

Reagents

The brominated vegetable oils, olive, sesame and cottonseed, were purchased from Abbott Labs. (North Chicago, IL, U.S.A.). Brominated corn, soybean, and partially hydrogenated soybean oil were prepared in the laboratory by a procedure described earlier[4]. A commercially prepared brominated soybean oil, Akwilox 133, was obtained from Swift Specialty Chemicals (Chicago, IL, U.S.A.).

Standards of the methyl esters of 9,10-dibromostearate (DBS), 9,10,12,13-tetrabromostearate (TBS) and 9,10,12,13,15,16-hexabromostearate (HBS) were prepared in the laboratory by a procedure described earlier[2]. Methyl heptadecanoate (MHD) (Sigma, St. Louis, MO, U.S.A.) was used as an internal standard. All solvents were distilled-in-glass grade materials.

Gas chromatography

A Hewlett-Packard 5720 A gas chromatograph equipped with a flame ionisation detector, a Durabond fused-silica column (30 m × 0.25 mm I.D.) and an on-column injector were employed for the separations. The conditions were as follows: hydrogen carrier gas, 2 ml/min; detector temperature, 260°C; nitrogen was used as the make-up gas. Samples were injected at 80°C then the temperature was rapidly raised to 180°C followed by temperature programming at 8°C/min to 300°C.

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BVO preparation

Hexane solutions of the BVO samples were treated with sulfuric acid–methanol to convert the fatty acid glycerides to their methyl esters[1]. The final products were dissolved in hexane for GC analysis.

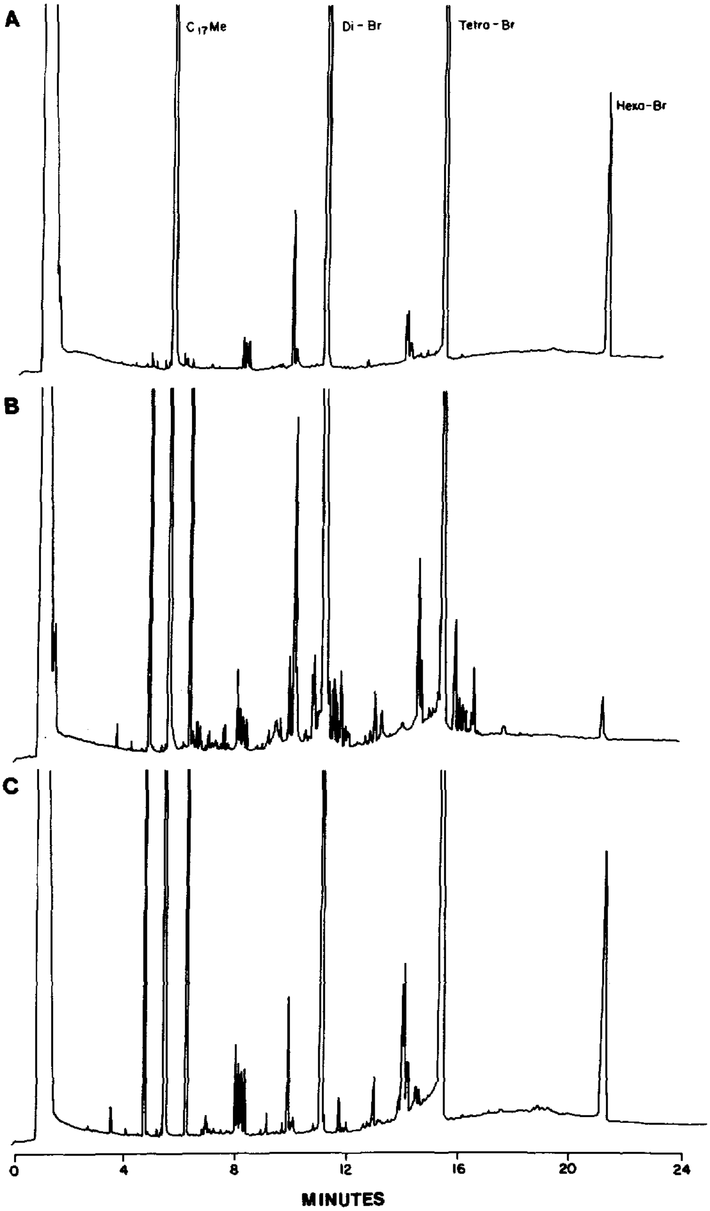

Fig. 1. Chromatograms of (A) standard mixture of the methyl esters of dibromo, tetrabromo and hexabromostearate; (B) brominated corn oil; (C) brominated soybean oil. Conditions as described in the text. $C_{17}Me$ is the internal standard.

Beverage extraction

A 280-ml volume of orange flavored soft drink was saturated with sodium chloride and extracted three times with 75 ml of diethyl ether. The organic extracts were combined and washed successively with 2 × 30 ml of 2 *M* sodium hydroxide, 1 × 30 ml 2 *M* hydrochloric acid and 3 × 30 ml water. The ether phase was removed and dried over anhydrous sodium sulfate then treated with sulfuric acid–methanol as described above for the BVOs.

RESULTS AND DISCUSSION

Fig. 1 shows some typical chromatograms obtained with the capillary system employed. HBS is readily observed in brominated soybean oil as is a smaller amount in brominated corn oil. The DBS, TBS and HBS peaks are all easily detected and quantitated in the oils. By packed column GC, HBS was difficult to chromatograph reproducibly[1]; however, in the present work we have found very reproducible results for this compound. In fact, we were able to observe HBS in oils such as brominated corn and olive oil where we could not detect it by packed column GC.

The capillary GC response factors for DBS and TBS compared well with those obtained by packed column GC (DBS, 1.55 and 1.57, respectively; TBS, 2.40 and 2.55, respectively). The response factor for HBS by capillary GC was 4.75 while for the packed column it was about 7, indicating decomposition during chromatography with the latter.

Table I presents the brominated fatty acid weight content of the various oils studied. The TBS/DBS ratio can be a useful means of identifying these oils in unknown samples. However, with BVOs such as cottonseed, corn and soybean, the ratios are similar, thus unequivocal identification of these becomes difficult using the ratios alone. With capillary GC, the identification can be supported by the relative amounts of HBS found. As can be seen from the table, the three oils have very different HBS contents, and thus can be identified.

The two soybean samples and the commercially prepared Akwilox 133 show different TBS/DBS ratios and different HBS contents. This is likely a result of differing degrees of hydrogenation of the parent oils.

TABLE I

COMPOSITION OF BROMINATED OILS BY PERCENT WEIGHT

NA = not analysed; – = not detected.

Brominated oil	*DBS (%)*	*TBS (%)*	*HBS (%)*	*Ratio TBS/DBS*	*Ratio TBS/DBS (packed column)*
Olive	65	7	0.4	0.11	0.11
Sesame	33	34	–	1.03	1.10
Cottonseed	16	52	–	3.25	3.33
Corn	20	62	0.9	3.10	3.26
Soybean	20	58	10.2	2.90	2.88
Soybean (partially hydrogenated)	31	46	5.1	1.48	NA
Akwilox 133	40	31	1.4	0.78	0.85

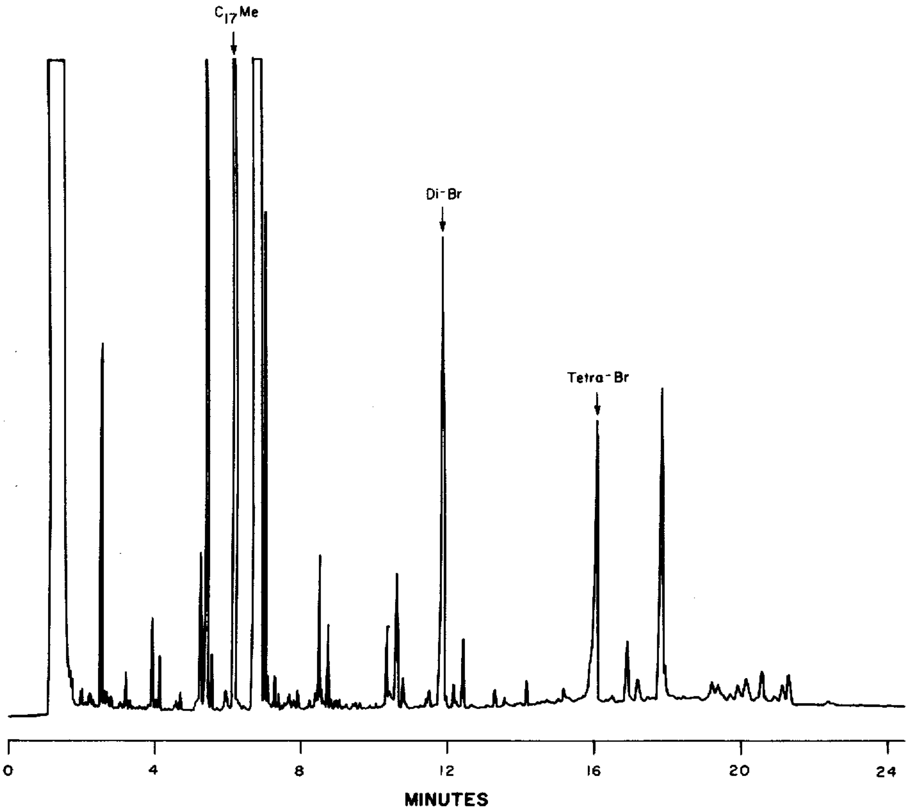

Fig. 2. Chromatogram of an extract of an orange flavored soft drink containing a BVO.

Fig. 2 shows a chromatogram of a soft drink analysis. Although many peaks are present, the internal standard, DBS and TBS could easily be detected. A small peak corresponding to HBS was also observed. The peak area ratio for TBS/DBS for this drink was 0.87 suggesting the presence of a commercial preparation of brominated partially hydrogenated soybean oil such as Akwilox 133. No peaks at retention times equivalent to DBS or TBS were observed in drinks that did not contain BVO.

The use of capillary GC for the identification of BVOs and their determination in beverages offers definite advantages over existing methods, in terms of resolution, stability and ease of determination of HBS.

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