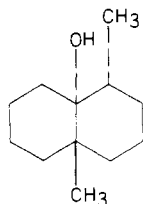


Determination of Geosmin in Beet Juice by Gas Chromatography

A method was developed for the determination of geosmin (*trans*-1,10-dimethyl-*trans*-(9)-decalol) in beet juice. Geosmin was extracted with Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane), concentrated, and purified by adsorption on Florisil. Geosmin was quantified using gas chromatography. The geosmin concentration was calculated by comparing the peak height of geosmin to that of an internal standard (1-undecanol). The accuracy and precision of the analysis were examined by adding known concentrations of geosmin to a model solution (10% w/w ethanol in water) and to freshly expressed beet juice. Recovery of geosmin averaged 109% with a standard deviation of 11.7% over the range of 0.31–10.00 ng/g.

Geosmin (*trans*-1,10-dimethyl-*trans*-(9)-decalol) has been identified as an odor contaminant in water, catfish, rainbow trout, and dry beans (Rosen et al., 1970; Lovell, 1972; Yurkowski and Tabachek, 1974; Buttery et al., 1976).



Geosmin has also been isolated from red table beets, not as an odor contaminant, but as part of the characteristic beet aroma (Acree et al., 1976; Murray et al., 1975). In high concentrations geosmin may be detrimental to the flavor quality of table beets. A quantitative method for determination of geosmin in beet juice is necessary to ascertain at what level geosmin becomes a flavor problem. This paper describes a method for quantifying geosmin in beet juice. Yurkowski and Tabachek (1974) previously reported a method for the quantitative estimation of geosmin in fish. This method is not suitable for geosmin determination in beet juice because of its relative complexity, small sample capacity, and insufficient sensitivity.

EXPERIMENTAL SECTION

Beet Juice. Red table beets (*Beta vulgaris* L., cv. Ruby Queen) grown at the New York State Agricultural Experiment Station during the 1977 season were harvested and washed. Beets (approximately 7 kg) were ground in a U.S. Berkel meat grinder. Two kilograms of the resultant beet pulp were weighed into a stainless steel beaker for each batch, and 200 g of 95% ethanol was added. The mixture was allowed to stand for 2 h. Separate 1-L juice samples were obtained with a small hydraulic press. One sample of each pair of beet juice samples was enriched with geosmin using a known standard.

Model Solutions. Six model solutions were prepared by adding 90.9 g of 95% ethanol to 909 g of distilled water to make a total weight of 1 kg. Different levels of geosmin standard were then added to each solution.

Geosmin Synthesis. Geosmin, (\pm)-*trans*-1,10-dimethyl-*trans*-(9)-decalol, was synthesized according to the procedure of Marshall and Hochstetler (1968). The resulting mixture of *cis* and *trans* decalols (450 mg of a nearly colorless oil) was separated on a 40-mL Florisil column by successively washing the column with three column volumes of petroleum ether, 4% ether-petroleum ether, and pure ether. The 4% ether-petroleum ether fraction contained all of the geosmin as demonstrated by a single peak (emerging from the gas chromatograph-mass spectrometer system) with a mass spectrum virtually identical with that of authentic geosmin (Kikuchi et al., 1972). The GC-MS system consisted of a Varian 1440 gas chroma-

tograph coupled to a time of flight mass spectrometer (Bendix Model 12 modified with a CVC Mark IV) through a methylsilicone helium separator (Black et al., 1969). Ionization took place at 30 °C and 70 eV. The gas chromatograph was operated isothermally for the first 3 min at 60 °C and then programmed at 4 °C/min for 35 min. The column used was the same as the one described below in the gas chromatography section.

Reagents. Precision Cleaning Agent (E. I. DuPont), Freon 113, (1,1,2-trichloro-1,2,2-trifluoroethane) was purchased from Buffalo Solvent and Chemical Corp., Buffalo, N.Y. It required no redistillation.

A 1 ppm solution of 1-undecanol (98%, Alltech Association, Ann Arbor, Mich.) in Freon 113 was used as the gas chromatographic internal standard.

The standard solution of geosmin was prepared by adding pure synthetic geosmin at 1 ppm to absolute ethanol.

Florisil, 60–100 mesh (Fisher Scientific, Fairlawn, N.J.), was heated to 870 °C for 2 h and 10% water was added to the adsorbent before use.

Concentration. All sample extracts were concentrated with a Büchi Rotovapor (Rinco Instrument Co., Greenville, Ill.) in a 20 °C water bath using Concentratubes (Laboratory Research Co., Los Angeles, Calif.).

Analytical Procedure. Each liter of beet juice or model solution was extracted with 400 mL of Freon 113. Two hundred milliliters of the extract was drawn off after an hour of settling and dried over anhydrous MgSO₄. The extract was then concentrated to a volume of about 1 mL on the rotary evaporator. The concentrated extract was washed onto a 3-mL Florisil column with five column volumes of pentane. Geosmin was selectively washed through the column with five column volumes of 8% diethyl ether in pentane. One milliliter of the 1 ppm 1-undecanol internal standard was then added directly to the wash containing geosmin. This fraction containing geosmin and undecanol was then concentrated to a volume of about 2 μ L and injected into the gas chromatograph.

Gas Chromatography. A 4 m \times 3 mm stainless steel column packed with 5% SP-1000 on Chromosorb W (a Carbowax modified with a terephthalic acid, Supelco Inc., State College, Pa.) was used in a Varian Model 1200 gas chromatograph equipped with a flame ionization detector. The column was operated isothermally at 190 °C with a carrier gas (He) flow rate of 25 mL/min. The amount of geosmin in each sample was calculated by measuring its peak height relative to the peak height of the 1-undecanol internal standard. The flame response of geosmin relative to 1-undecanol was 1.1. This was determined by injecting 1 μ g of geosmin and 1 μ g of 1-undecanol dissolved in 2 μ L of Freon 113 into the gas chromatograph at the conditions stated above. The amount of geosmin in each sample calculated from relative peak height measurement was divided by the relative flame response for geosmin in order

Table I. Recovery of Geosmin from Model Solutions and Beet Juices

Sample	Added, ng/g	Found, ng/g	Recd., ng/g	Recd., %
Model 1 ^a	0.00	0.00	0.00	
Model 2	0.31	0.34	0.34	110
Model 3	0.63	0.62	0.62	100
Model 4	1.25	1.38	1.38	110
Model 5	2.50	2.40	2.40	100
Model 6	5.00	5.96	5.96	120
Beet juice A	0.00	16.25	0.00	
Enriched A	5.00	22.83	6.58	130
Beet juice B	0.00	7.18	0.00	
Enriched B	7.50	15.22	8.04	110
Beet juice C	0.00	6.78	0.00	
Enriched C	10.00	15.59	8.81	90
			Av	109 ± 11.7

^a Model samples contain varying concentrations of geosmin in 10% ethanol in water.

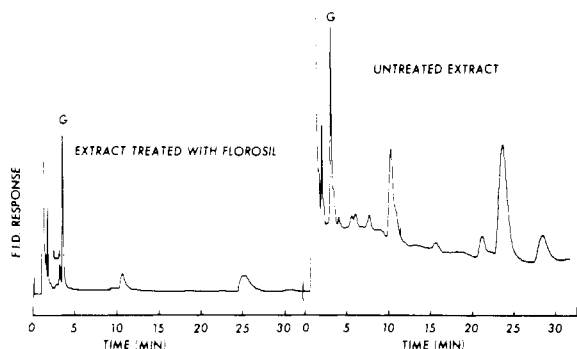


Figure 1. Two adjacent gas chromatograms showing the effect of Florisil adsorption treatment on beet juice extract. G is the symbol for geosmin and U is the symbol for undecanol in the chromatograms.

to obtain the values found in Table I.

RESULTS AND DISCUSSION

The digestion with ethanol was employed in the preparation of the beet juice samples to increase the yield of juice and minimize the formation of an emulsion. The application of adsorption chromatography in this procedure is illustrated in Figure 1. The chromatogram shows that high molecular weight components in the untreated extract interfere with the accurate measurement of the geosmin peak.

Geosmin was determined in model solutions (10% ethanol in water), beet juice, and beet juice enriched with geosmin. Samples were analyzed with added geosmin ranging from 0.31 to 10.00 ng/g. A plot of the geosmin recovered vs. the geosmin added was linear and approximated the line representing 100% yield. The correlation coefficient for the regression line was 0.995. This indicates

that the method is precise and accurate. Table I shows the geosmin content of model solutions, beet juice enriched with geosmin, and beet juice controls processed at the same time. The overall average recovery for the juices and model solutions was 109% with a standard deviation of 11.7%. The results indicate that Freon 113 extracts virtually all of the geosmin from the aqueous phase and that the Florisil adsorption column does not retain measurable geosmin.

The lowest concentration of geosmin detected in this study was 0.31 ng/g. This is between six and fifteen times the reported odor threshold concentration in water (Murray et al., 1975; Buttery et al., 1976). This method has a sample capacity of 1 L while the method of Yurkowski and Tabachek (1974) uses a sample of 12 g because of the size limitations of the distillation apparatus. The high-vacuum low-temperature distillation procedure used by Yurkowski and Tabachek (1974) is relatively complex compared to the solvent extraction procedure of our method. Geosmin was quantified below the level at which it occurred in the beet juices analyzed. This method is simple and potentially applicable to monitoring the contamination of foods, beverages, and water supplies with geosmin. It is presently being used to study the flavor chemistry of beets and other root crops.

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