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Isolation of Volatiles from *Panax ginseng* Root by Vacuum-Distillation with Freeze-Drying

Hoon Park, Hyun Joo Sohn and Byung Goo Cho
Korea Ginseng and Tobcco Research Institute, Science Town, Daejeon 305-345, Korea
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Abstract□ The isolation of volatile compounds by vacuum-distillation with freeze-drying was tested with fresh ginseng roots. The roots were frozen at −80 °C; they were dried at −40 °C under vacuum(40 torr) for 24 hours; and the ice condensed at the surface of condenser in the freeze-dryer was thawed at room temperature. The ether extract of the resulting aqueous solution was analyzed by gas chromatography (GC) equipped with a flame ionization detector (FID) or a nitrogen-phosphorus detector(NPD) and by gas chromatography/mass spectrometry(GC/MS). More than forty peaks were observed in the GC(FID) profile, and more than ten peaks were observed in the GC(NPD) profile. Among them, thirteen components including one aldehyde, four hydrocarbons, two esters, four alcohols, and two pyrazines were identified; six components the molecular ions of which were *m/z* 204 were estimated to be a series of azulene compounds; and the other components unidentified were estimated to have molecular weights of lower than 254. Therefore, the freeze–drying technique is thought to be useful for the isolation of volatile compounds of such low molecular weights from vegetables, fruits, and biological fluids as well as fresh ginseng roots under the tested conditions.

Keywords□ *Panax ginseng* C.A. Meyer, volatile oils, vacuum-distillation with freeze-drying.

Introduction

Essential oils are defined as volatile materials derived by physical processes from the odorous material of a single botanical form and/or species with which it agrees in name and odor[1]. The methods used for the isolation of the volatiles are generally categorized into distillation techniques and extraction techniques: the former include simple distillation, steam distillation, vacuum dustukkatuibm and carbon dioxide distillation; and the latter include solvent extraction, simultaneous distillation-extraction, carbon dioxide extraction, and supercritical fluid extraction[2]. Among them the most popular technique is the steam distillation under reduced pressure, which usually produces larger amounts of from a given quantity of starting material. However, the technique is not adequate for the isolation of heat-labile constituents because they may readily undergo rearrangment. The loss of some of the terpene alcohol esters during distillation amounted to 30 to 90%, and a variety of new products was formed[3]. Distillation caused the almost total disappearance of alpha-thujene, neral, and geranial which occurred in lime itself, with coincident production of alpha-phellandrene, and alpha-and beta-terpineols, and it was pointed out that the low temperature expression was more adequate for the isolation of such volatiles than the distillation[4]. Freeze-drying technique, whcih is well-known method used for the removal of water from moisture-rich materials such as fruits, vegetables, and biological fluids, is thought to be also used for the isolation of volatiles as long as they are volatile enough to be distilled under a given condition.

In this study, we observed the occurrence of more than forty components in the vacuum-dis-

tillates derived from fresh ginseng roots during freeze-drying, and some of them were identified by use of gas chromatography(GC) and gas chromatography/ mass spectrometry(GC/MS).

Materials and Methods

Materials

Vacuum distillates derived from fresh ginseng roots (6 year-old) during freeze-drying were used as samples. Here, the ginseng roots were harvested at Agronomy Research Center, Korea ginseng and tobacco Research Institute in September, 1989. All solvents used were GR grade; and the instruments used were freeze-dryer(Dura-Dry, FTS System Inc.), GC(Hewlett-Packard 5880A and 5890A), and GC/MS(Varian MAT 212; 70eV, EI Mode).

Methods

Fresh ginseng roots were frozen at -80 °C, and they were dried at -40 °C under vacuum (40torr) for 24 hours by use of freeze-dryer.

The ice condensed at the surface of condenser in the freeze-dryer was thawed at room temperature, and the resulting aqueous solution was extracted with diethyl ether directly. The ether extract was analyzed by GC and GC/MS after dehydrating it with anhydrous sodium sulfate. Here, GC column used was a SPB-1 fused silica Capillary(0.25mm id × 30m; Supelco) or a SP-2340 fused silica Capillary(0.25mm id × 30m; Supelco); and the detector used was a flame ionization detector (FID) or a nitrogen-phosphorus detector (NPD). Thirteen of the volatile components in the ether extract were identified by co-chromatographying with authentic compounds (Tokyo Kasei Co.); Six of them were estimated from their mass fragment ions; and the molecular weights of the other components unidentified were estimated by comparing them with those of authentic n-hydrocarbon compounds (Tokyo Kasei Co.).

Results and Discussion

A GC(FID) profile of ether extract from vacuum-distillates is shown in Fig. 1, where more than forty peaks appear. Eleven of them(peak # 1-11) were identified by co-chromatographying with authentic compounds, and six of them(peak # 12-17) were estimated from their mass fragment ions.

The components identified were 2-methyl-1-pro-

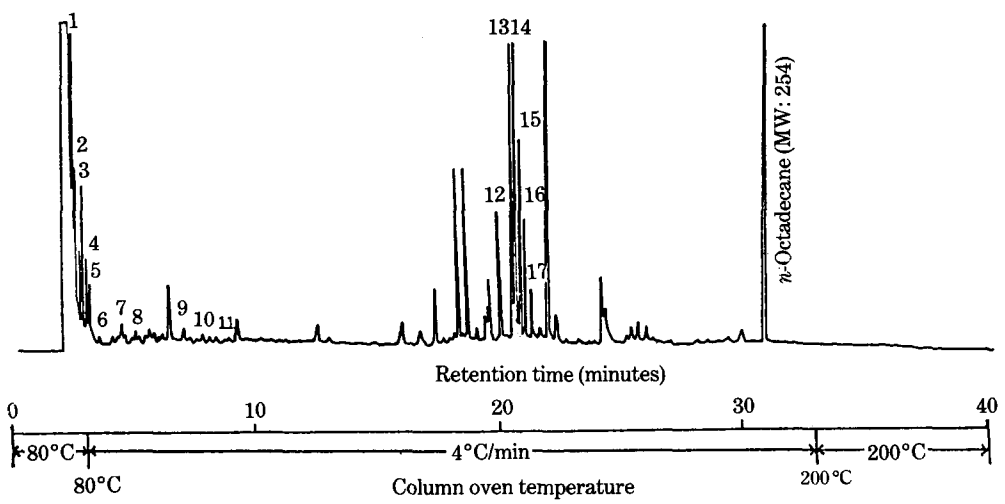

Fig. 1. GC (FID) profile of ether extract of vacuum distillates derived from fresh ginseng roots during freeze-drying. The column used was a SPB-1 fused silica capillary (0.25 mm id×30 m; Supelco), and the detector used was a flame ionization detector (FID). 1, 2-methyl-1-propanol; 2, 2-pentanol; 3, ethyl butanoate; 4, butyl etanoate; 5, ethyl benenze; 6, *o*-dimethyl benzene; 7, alpha-pinene; 8, benzaldehyde, 9, 1-heptanol; 10, *p*-cymene; 11, linalool; 12 – 17, m/z 204.

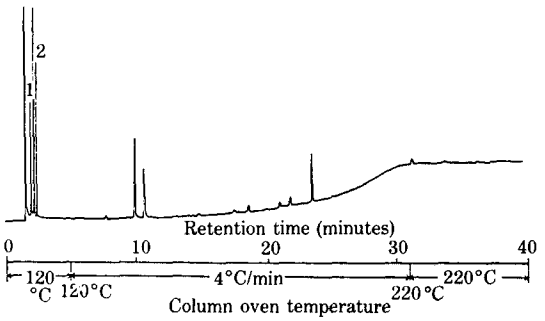

Fig. 2. GC (FID) profile of ether extract of vacuum-distillates derived from fresh ginseng roots during freeze-drying. The column used was a SP-2340 fused silica capillary (0.25 mm id×30 m; Supelco), and the detector used was a nitrogen-phosphorus detector (NPD). 1, 2,6-dimethyl pyrazine; 2, 2,3,5,6-tetramethyl pyrazine.

panol, 2-pentanol, ethyl butanoate, butyl etanoate, ethyl benzene, *o*-dimethyl benzene, alpha-pinene, benzaldehyde, 1-hetanol, *p*-cymene, and linalool, the molecular weights of which ranged from 73 to 153. The components estimated to be azulene compounds also occurred in the ether extract. Any of them was not identified exactly because their mass fragment ions were very similar each other, but seeing that the molecular ion peaks of m/z 204 appeared in all of their mass spectra at least one of them seemed to be alpha-gurjunene, beta-patchoulene, (−)-aromadendrene, beta-elemene, or delta-cadinene, which had been identified in n-hexane extract from distillation-concentrate of fresh ginseng roots[5]. Seeing that the retention time of the last peak component in the GC chromatogram (Fig. 1) was little shorther than that of *n*-octadecane, the molecular weights of the other components unidentified were estimated to be lower than 254.

Fig. 2 shows a GC(NPD) profile of ether extract from vacuum-distillates, where more than ten peaks appear. Two of them (peak # 1-2) were identified by co-chromatographying with authentic compounds.

The components identified were 2,6-dimethylpyrazine and 2,3,5,6-tetramethylpyrazine, the molecular weights of which were 108 and 136, respectively. The other components except the two compounds were thought to be nitrogen- or phosphorus-containing compounds since they were detected by NPD, a nitrogen- and phosphorus-selective detector. Five methoxypyrazine and eight alkylpyrazine derivatives had been identified as major flavor components in ginseng roots[6], but only one (2,3,5,6-tetramethyl-pyrazine) of which was identified in the ether extract of vacuum-distillates in this study.

As mentioned above, a variety of components occurred in ether extract of vacuum-distillates derived from fresh ginseng roots during freeze-drying, and all the components identified or unidentified were thought to have molecular weights of lower than 254. Conclusively, the freeze-drying technique may be useful for the isolation of volatile compounds the molecular weights of which are lower than 254 from vegetables, fruits, and biological fluids as well as fresh ginseng roots under the tested conditions. The number of volatile compounds may by increased, and they may be fractioned by varying the degree of vacuum.

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초 록

동결건조시 감압증류되는 휘발성 물질의 분리를 수삼을 시료로 하여 시도하였다. 영하 80도에서 동결시킨 수삼을 영하 40도, $\frac{1}{19}$ 기압에서 24시간 건

조시킨 후 동결건조기 내의 냉각관 표면에 응축되어 있는 얼음을 실온에서 녹이고 에테르로 추출하여 불꽃이온화검출기(FID) 또는 질소-인검출기(NPD)를 부착시킨 기체크로마토그래피(GC) 및 기체크로마토그레피/질량분석계(GC/MS)로 분석하였다. GC(FID) 크로마토그램 에서는 40여 개의 피이크가 관찰되었고 GC(NPD) 크로마토그램에서는 10여 개의 피이크가 관찰되었다. 이 중에서 13개의 피이크성분을 동정하였는데 이들은 알데히드 1종, 탄화수소류 4종, 에스테르류 2종, 알코올류 4종 및 피라진계 화합물 2종이었고, m/z 204인 6개의 피이크성분은 azulene계 화합물일 것으로 추정되었으며, 나머지 피이크성분은 n-탄화수소류와 대조한 결과 n-옥타데칸보다 적은 분자량을 갖는 화합물일 것으로 추정되었다. 따라서, 동결건조법은 수삼은 물론 채소, 과일, 생물체액 등 수분을 다량 함유하고 있는 시료로부터 저분자의 휘발성 물질은 분리하는 데에 활용될 수 있을 것으로 사료된다.