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Separation and Determination of the Volatile Oil of the Parts of the Ginseng Growing on the Ground

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Introduction

In this paper, we described that the parts of ginseng growing above the earth's surface (stem, leave and flower bud) were extracted by ether, a yellow volatile oil (GVO) 0.2 wt% has been obtained, 56 compounds were determined by the analytical method of GC/MS, 19 of them are sesquiterpenes, 22 of them have been checked by the method of GC/FTIR. The volatile oil can send forth delicate fragrance of ginseng and the sesquiterpenes make up the characteristic constituents of the oil and sesquiterpene compounds were classified into the same group. This result has a practical value; this volatile oil, the by-product on ginseng trade, can be used to prepare the perfume and the medicine.

Experiment

1. GC/MS: A gas chromatograph with a Hp-5 capillary column (i.d. 0.2 mm × 25 m) was used.

The mass analyzer: ITD (Ion Trap Detector) and NBS (The National Bureau of standards, U.S.A.) libray of 42222 spectra were used.

2. GC/FTIR: A gas chromatograph with a OV-101 capillary column (i.d. 0.53 mm × 12 M) was used.

FTIR: The FTIR spectrometer has the EPA Environmental Protection Agency U.S.A.) Vapor Phase IR Spectral Library with 3300 Standard spectra.

3. The silica gel GF_{254} TLC was used, and the n-hexane-ethylacetate (10.8:1) as flowing phase. The sesquiterpenes were obtained from this oil. The sesquiterpenes were isolated in the first group ($R_f = 0.91$).

Result and Discussion

1. GC/MS analysis; The repeated ions chromatogram of the volatile oil (Fig. 1) shows 128 peaks, which are explained.

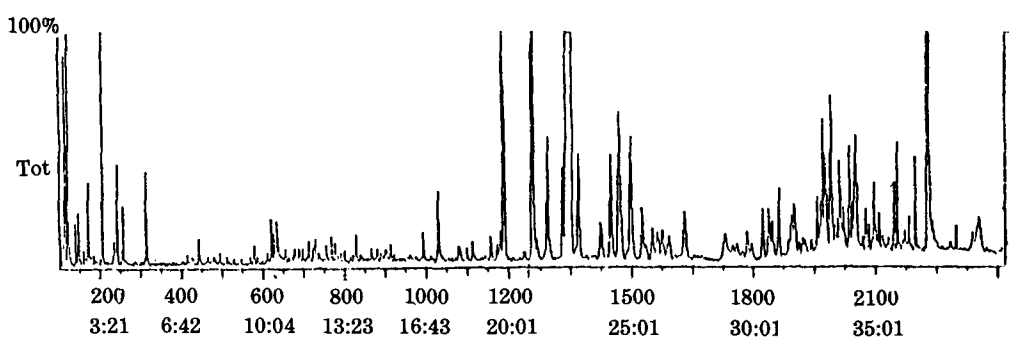


Fig. 1. The chromatogram of the volatile oil of Jilin ginseng GVO by GC/MS

Table 1. Analytic results of the volatile consituents of Jiiln ginseng's GVO by GC/MS

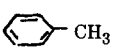
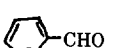
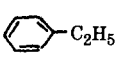
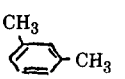
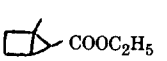
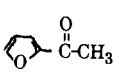
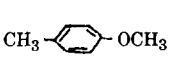
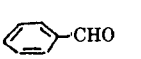
No. Scannumber	Compounds	Formula M+	Structure	CAS Fit	GC/MS tR (min)	Composition area%
1 108	Ethanol	C_2H_6O 46	CH_3CH_2OH	64-17-5 987	1.8	0.88
2 112	Ethyl formate	$C_4H_8O_2$ 88	$HCOOC_3H_7$	110-74-7	1.86	0.94
3 119	Ethyl acetate	$C_4H_8O_2$ 88	$CH_3COOC_2H_5$	141-78-6 953	1.98	2.00
4 146	Acetic acid	$C_2H_4O_2$ 60	CH_3COOH	64-19-7 874	2.43	0.24
5 169	1-ethoxy-butane	$C_6H_{14}O$ 102	$C_4H_9OC_2H_5$	628-81-9 960	2.82	0.31
6 204	1,1-diethoxy-ethane	$C_6H_{14}O_2$ 118	EtO EtO CH-CH_3	105-57-7 893	3.40	1.62
7 241	1-ethoxy-pentane	C_7H_6O 116	$EtOC_5H_{11}$	17952-11-3 875	4.02	0.55
8 258	Toluene	C_7H_8 92		108-88-3 962	4.30	0.33
9 306	2,3,3-trimethyl-1,4-pentadiene	C_8H_{14} 110	$CH_2=C-C(CH_3)_2-CH=CH_2$	756-02-5 966	5.10	0.01
10 312	Hexanal	$C_6H_{12}O$ 100	$C_5H_{11}CHO$	66-25-1 862	5.20	0.59
11 377	Furaldehyde	$C_5H_4O_2$ 96		98-01-1 845	6.28	0.01
12 428	Ethylbenzene	C_8H_{10} 106		100-4-4 969	7.13	0.03
13 441	1,3-dimethylbenzene	C_8H_{10} 106		108-38-3 893	7.35	0.17
14 464	Bicyclo (2,1,0) pentane-5-carboxylic acid, 1-methyl ethyl ester	$C_9H_{14}O_2$ 154		74810-55-2 912	7.73	0.02
15 510	2-ethanoyl furan	$C_6H_6O_2$ 110		1192-62-7 943	8.50	0.04
16 546	methoxy-4-methy-benzene	$C_8H_{10}O$ 122		100-84-5 885	9.10	0.03
17 568	(+)-camphene	$C_{10}H_{16}$ 136		79-92-5 930	9.47	0.03
18 585	benzaldehyde	C_7H_6O 106		100-52-7 963	9.7	0.03
19 619	6-methyl-6-hepten-2-one	$C_8H_{14}O$ 126	$H_3C-C(=O)-(CH_2)_3-C(CH_3)=CH_2$		10.32	0.32

Table 1. Continued

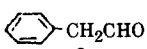
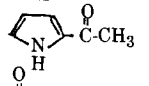
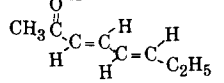
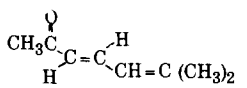
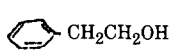
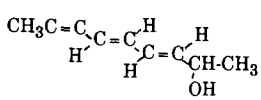
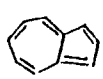
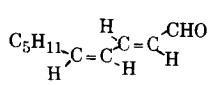
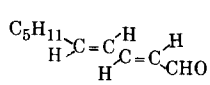
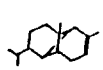
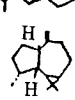
No. Scannumber	Compounds	Formula M^+	Structure	CAS Fit	GC/MS tR (min)	Composition area%
20 697	Phenylacetaldehyde	C_8H_8O 120		122-78-1 955	11.62	0.12
21 721	2-acetylpyrrole	C_6H_7ON 109		1072-83-9 975	12.0	0.07
22 754	(3E,5E)-2-keto-octadiene	$C_8H_{12}O$ 124		30086-02-3 954	12.57	0.08
23 769	(E)-6-methyl-2-keto-3, 5-heptadiene	$C_8H_{12}O$ 124		16647-04-4 929	12.82	0.17
24 783	Phenylethanol	$C_8H_{10}O$ 122		60-12-8 916	13.05	0.05
25 789	(3E,5E)-7-alkyne-2-hydroxy-nonediene	$C_9H_{12}O$ 136		43142-43-4 942	13.15	0.05
26 864	Azulene	$C_{10}H_8$ 128		275-51-4 986	14.40	0.07
27 992	(2E,4Z)-decadienal	$C_{10}H_{16}O$ 152		25152-83-4	16.53	0.23
28 1029	(2E,4E)-decadienal	$C_{10}H_{16}O$ 152		25152-84-5 901	17.15	0.66
29 1098	α-cubebene	$C_{15}H_{24}$ 204		17699-14-8 975	18.30	0.10
30 1156	α-copaene	$C_{15}H_{24}$ 204		3856-25-5 980	19.27	0.23
31 1171	(+)-aromadendrene	$C_{15}H_{24}$ 204		489-39-4	19.52	0.16
32 1180	β-bourbonene	$C_{15}H_{24}$ 204		5208-59-3 936	19.67	0.39
33 1190	β-elemene	$C_{15}H_{24}$ 204		515-13-9 930	19.83	3.93
34 1237	(3Z,6E)-β-farnesene	$C_{15}H_{24}$ 204		26560-14-5 861	20.62	0.12
35 1257	α-santalene	$C_{15}H_{24}$ 204		512-61-8 980	20.95	5.93

Table 1. Continued

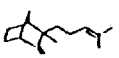
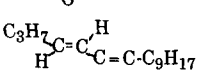
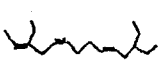
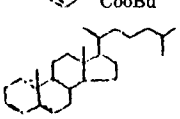
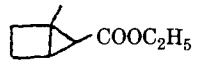
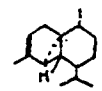
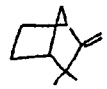
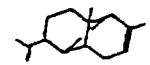
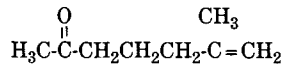
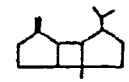
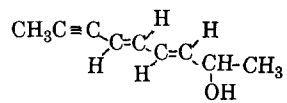
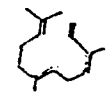
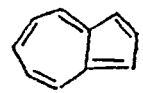
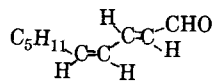
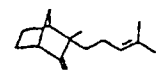
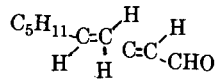
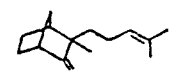
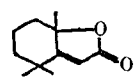
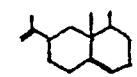
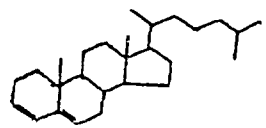
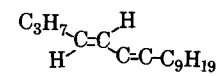
No. Scannumber	Compounds	Formula M+	Structure	CAS Fit	GC/MS tR (min)	Composition area%
36 1266	β-caryophllene	$_{15}H_{24}$ 204		87-44-5 969	21.10	0.25
37 1293	α-bergamotene	$C_{15}H_{24}$ 204		17699-05-7 964	21.55	1.72
38 1330	(+)-epi-β-santalene	$C_{15}H_{24}$ 204		25532-78-9 960	22.17	1.15
39 1350	(Z)-β-farnesene	$_{15}H_{24}$ 204		28973-97-9 964	22.50	20.78
40 1369	(±)- -santalene	$C_{15}H_{24}$ 204		511-59-1	22.82	1.26
41 1422	β-maaliene	$C_{15}H_{24}$ 204		489-29-2 952	23.70	0.59
42 1447	β-cubebene	$C_{15}H_{24}$ 204		13744-15-5 950	24.12	1.51
43 1467	Alloaromadendrene	$C_{15}H_{24}$ 204		25246-27-9 920	24.45	2.77
44 1495	α-selinene	$C_{15}H_{24}$ 204		473-13-2 960	24.92	1.90
45 1522	(+)-β-bisabolene	$C_{15}H_{24}$ 204		29837-09-0 962	25.37	0.73
46 1556	(10),11-eremphilene	$C_{15}H_{24}$ 204		10219-75-7 937	26.00	0.48
47 1586	-cadinene	$C_{15}H_{24}$ 204		3909-41-9 968	26.43	0.40
48 1626	Dihydroactinidiolide	$C_{11}H_{16}O_2$ 180		15356-74-8 978	27.10	0.95
49 1752	Nerolidol	$C_{15}H_{26}O$ 222		142-50-7 937	29.20	0.15
50 1790	Dendrolasin	$C_{15}H_{22}O$ 218		23262-34-2 950	29.83	0.23
51 1830	(4E)-6-alkyne-hexadecene	$C_{16}H_{28}$ 220		74744-51-7 959	30.50	0.62
52 1855	3,12-diethyl-2,5,9- tetradecatrene	$C_{18}H_{32}$ 248		74685-87-3 884	30.92	0.82
53 1893	Methyl-6,9-dialkyne- octadeatate	$C_{19}H_{32}O_2$ 290	$C_5H_{11}C \equiv CCH_2C \equiv C(CH_2)_7COOCH_3$	56847-03-1 906	31.55	0.78
54 2185	Hexadecandicacid	$C_{16}H_{32}O_2$ 256	$CH_3(CH_2)_{14}COOH$	57-10-3 871	36.42	0.53
55 2218	Dibutyl-1,2-phenyl- formate	$C_{16}H_{22}O_4$ 278	 CooBu CooBu	84-74-2 941	36.97	18.53
56 2239	Cholesta-3,5-diene	$C_{27}H_{44}$ 368		747-90-0	37.32	0.63

Table 2. Twenty compounds identified newly in ginseng volatile oil

Bicyclo (2,1,0) pentane-5-carboxylic acid, 1-methyl ethyl ester	$C_9H_{14}O_2$ 154		α-cubebene	$C_{15}H_{24}$ 204	
(+)-camphene	$C_{10}H_{16}$ 136		α-copaene	$C_{15}H_{24}$ 204	
6-methyl-2-keto-6-heptene	$C_8H_{14}O$ 126		β-bourbonene	$C_{15}H_{24}$ 204	
(3E,5E)-7-alkyne-2-hydroxy-nonediene	$C_9H_{12}O$ 136		(3Z,6E)-α-farnesene	$C_{15}H_{24}$ 204	
Azulene	$C_{10}H_8$ 128		α-bergamotene	$C_{15}H_{24}$ 204	
(2E,4Z)-decadienal	$C_{10}H_{16}O$ 152		(±)-epi-β-santalene	$C_{15}H_{24}$ 204	
(2E,4E)-decadienal	$C_{10}H_{16}O$ 152		(±)-β-santalene	$C_{15}H_{24}$ 204	
Dihydroactinidiolide	$C_{11}H_{16}O_2$ 180		1 (10),11-eremophilene	$C_{15}H_{24}$ 204	
Cholesta-3,5-diene	$C_{27}H_{44}$ 368		Dendrolasin	$C_{15}H_{22}O$ 218	
Methyl-6,9-dialkyne-octadeatate	$C_{19}H_{30}O_2$ 290		(4E)-6-alkyne-hexadecene	$C_{16}H_{28}$ 220	

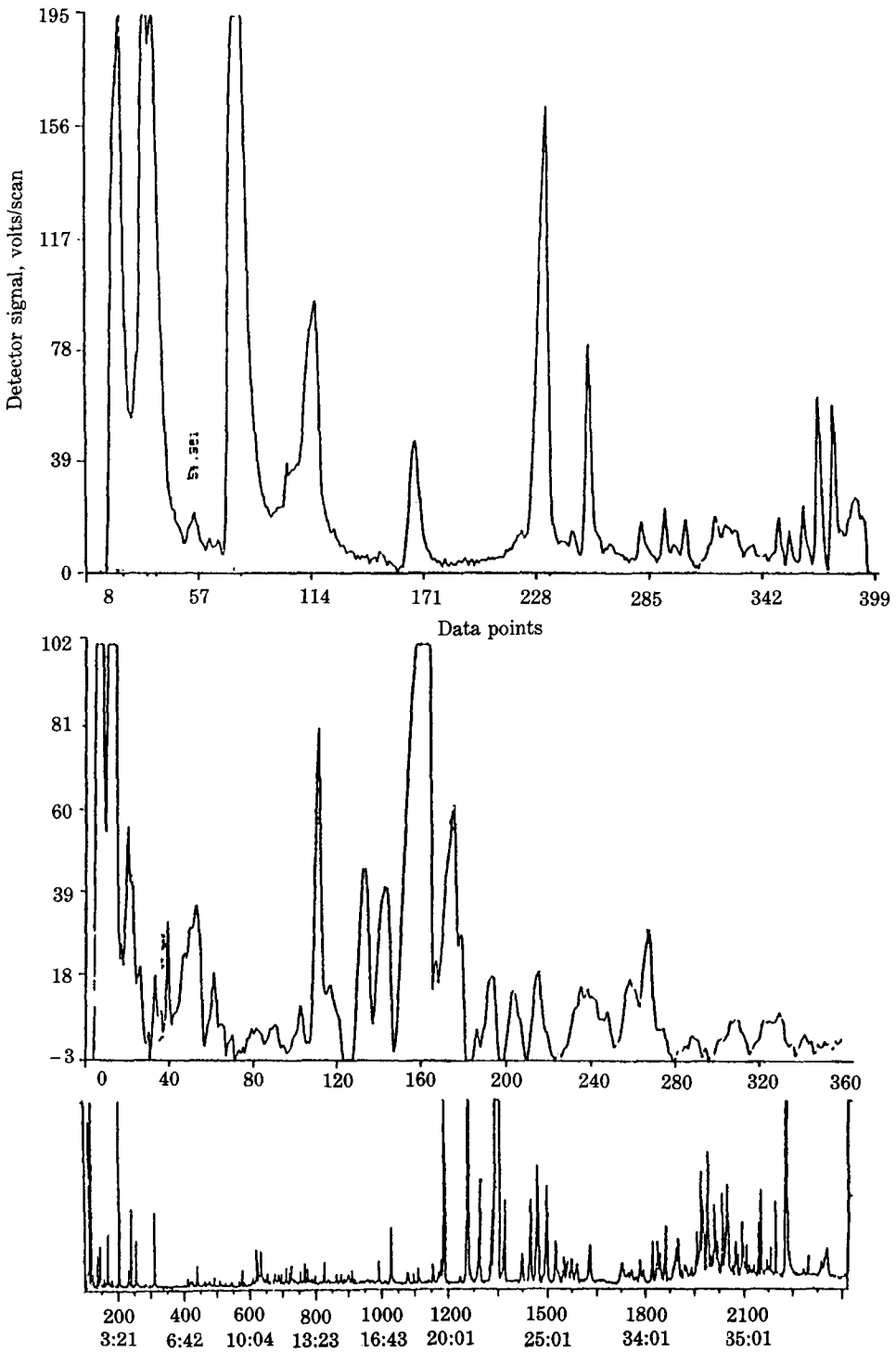
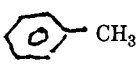
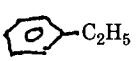
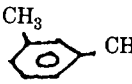
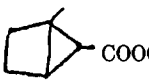
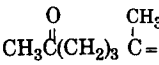
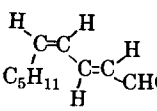
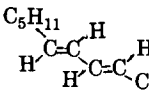
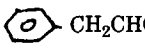
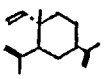
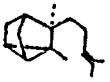
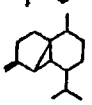
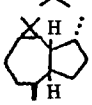


Fig. 2. The chromatogram of the GVO as low temperature (40-100°C) by GC/FTIR.
The chromatogram of the GVO as high temperature (100-200°C) by GC/FTIR.
The chromatogram of GVO by GC/MS.

Analytical results of GVO as low temperature (40°C-100°C) by GC/FTIR

No. Scan-number	Compounds	Formula	Structure	Wavenumber (cm^{-1})	Analytical method
1 29	Ethanol	C_2H_6O	C_2H_5OH	3674,2971,1454,1396,1251, 1063,898	a
2 33	Propylformate	$C_4H_8O_2$	$HCOOC_3H_7$	2990,2929,1758,1450,1386, 1180,1028,843	a
3 76	Ethylacetate	$C_4H_8O_2$	$CH_3COOC_2H_5$	2993,1770,1456,1376,1242, 1050,926	a
4 102	Acetic acid	$C_2H_4O_2$	CH_3COOH	3582,1800,1390,1272,1178, 993	a
5 116	1,1-diethoxy-ethane	$C_6H_{14}O_2$	$CH_3CH(OC_2H_5)_2$	2987,2941,2907,1382,1346, 1146,1106,954	a
6 166	1-ethoxy-pentane	$C_7H_{16}O$	$C_2H_5OC_5H_{11}$	2966,2920,2873,1472,1382, 1133	b,d
7 233	Toluene	C_7H_8		3076,3038,2936,2881,1609 1499,1385,727	a
8 254	Hexanal	$C_6H_{12}O$	$CH_3(CH_2)_4CHO$	2964,2941,2883,2810,2711 1745,1464,1387,1120	a
9 281	Propylacetate	$C_6H_{12}O_2$	$C_2H_5COOC_3H_7$	2970,2937,2882,1763,1375 1241,1056	a,d
10 292	Ethylbenzene	C_8H_{10}		3076,3037,2973,2930,1499, 1459,701	a
11 318	1,3-dimethyl benzene	C_8H_{10}		3029,2936,2880,1614,1515, 1385,1093,1050,767	a
12 323	Bicyclo (2,1,0) pentane-5-carboxylic acid, 1-methyl ethyl ester	$C_9H_{14}O_2$		2972,2930,2883,1776,1466, 1379,1268,1157,1095,755	b,d
13 350	6-methyl-2-keto-6-heptene	$C_8H_{14}O$		3093,2973,2932,1734,1598, 1445,1371,1156,992,898	b,d
14 371	(2E,4Z)-decadienal	$C_{10}H_{16}O$		3026,2975,2945,2888,2709 1709,1639,1593,1260,1153, 1103, 990,730	b,d,e
15 378	(2E,4E)-decadienal	$C_{10}H_{16}O$		3029,2980,2943,2897,2734, 1709,1650,1602,1164,1102,992	b,d,e
16 389	Decanoic acid	$C_{10}H_{20}O_2$	$CH_3(CH_2)_8COOH$	3578,2969,2942,1779,1462, 1383,1143,1100	a

Analytical results of GVO as high temperature (100°C-200°C) by GC/FTIR

No. Scan-number	Compounds	Formula	Structure	Wavenumber (cm^{-1})	Analytical method
1 37	Phenylacetaldehyde	C_8H_8O		3103,3027,2920,2818,2720, 1712,1622,1410,1105	b,d
2 131	β-elemene	$C_{15}H_{24}$		3088,3075,3009,2977,2938, 2870,1642,1451,1420,1379, 1004,910,893	b,d,e[59]
3 142	α-santalene	$C_{15}H_{24}$		3059,2980,2955,2933,2883, 1641,1460,1380,1084,849	b,d,e[55]
4 160	(Z)-β-farnesene	$C_{15}H_{24}$		3095,3087,3014,2974,2931, 2867,1666,1636,1596,1447, 1384,1108,989,896,823	b,d,e[60]
5 166	β-cubebene	$C_{15}H_{24}$		3077,2966,2937,2880,1644, 1457,1379,889,707	b,d,e[61]
6 174	Alloaromadendrene	$C_{15}H_{24}$		3084,2975,2938,2922,2876, 2854,1646,1457,1380,891	c[62] b,d,e[63]

2. 56 compounds in the total oil have been determined (Table 1) and the 20 compounds are new (Table 2). The percentage of the area of each peak has been calculated out as A% by using the integral programme.

3. Among the 56 compounds, 19 are sesquiterpenes with their molecular ions peaks as 204, and molecular formula as $C_{15}H_{24}$ and form a group of characteristic compounds.

4. GC/FTIR analysis: Because the sensitivity of FTIR is lower than that of MS, and only a few standard spectrograms have been stocked. In this case, the column with a wide diameter and an apparatus of no split stream sample were used in the experiment. Thus the sensitivity was raised to 2 orders of magnitude 22 organic compounds from the oil have been determined, five of them are sesquiterpenes. The contrast relationship between the peaks of GC/FTIR and the peaks of GC/MS can be found in Fig. 2. Thus the components obtained by GC/MS were checked by GC/FTIR, which can also be used to distinguish some isomers, but the MS can be not.

5. The parts of ginseng growing above the earth's surface are the by-product in a ginseng garden. The volatile oil extracted from it can be used as the additive for processing or making cigarette, sugar, tea, drink, medicine, cosmetics and as the reference for making up essence artificially. If the volatile oil is extracted firstly and then the ginsenoside from the parts of ginseng growing above the earth's surface not only the quality of ginsenoside can be raised, but also the economic benefit can be increased by the comprehensive utilization.

6. We found that the GVO can inhibit the cancer cells growth.