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A Study on the Concentration of Citrus Essential Oils by Adsorption

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A STUDY ON THE CONCENTRATION OF CITRUS ESSENTIAL OILS BY ADSORPTION

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RESEARCH REPORT

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ABSTRACT

Deterpenation by concentration of the flavor bearing oxygenated compounds present in Citrus Essential Oils using the column chromatographic method and the parameters affecting the adsorption of these oxygenated compounds at maximum economy versus reasonable efficiency in separation from the non-oxygenated compounds have been studied. Particular attention was given to the maximum number of adsorption-desorption-regeneration cycles that a single column charge could be subjected to before the adsorbent should be replaced.

The results of this study suggested the following conditions are of importance with regard to the development of an efficient and economic operation:

1) deactivation of the silica gel column by passage of a raffinate;

2) chilling of the column and feed oil to 5^{o} C;

3) use of a minimum silica gel/oil ratio;

4) in-place regeneration of the silica gel.

The results of this study also demonstrates that no rearrangements of the non-oxygenated terpenes occurred.

INTRODUCTION

The purpose of this research was to determine the maximum economic operating parameters consistent with production of a high quality concentrated citrus essential oil produced by silica gel column chromatographic separation of the terpenes and the oxygenated compounds. The various aspects of the economics of column adsorption refining (i.e., deterpenation - a reduction in the concentration of non-polar terpenes) is markedly dependent upon the selectivity, adsorbent/adsorbate ratio, and the size and life of the adsorbent. The first three properties are important considerations in determining the size and investment required for a projected design, and the rate of decline in activity of the adsorbent is an important factor in its operating cost. In addition, the possibility of terpene isomerization during silica column chromatographic concentration of essential oils (a factor that could be detrimental to the quality of adsorbate) must be considered[1-6].

A batch adsorption process was discounted as an economical method for study for the following: (1) the process equipment would involve several pieces (i.e., a centrifuge, mixing tanks, etc.) that are not required in a column operation, (2) the attrition rate of the adsorbent during the mixing tank stirring-equilibrium process and the wear on the equipment due to the abrasive action would involve equipment and material replacement, (3) the adsorbent/adsorbate ratio would

be higher than that required in a column operation, (4) the regeneration of the adsorbent, and economical consideration, could not be done in place.

The only advantage that a batch operation has over a column operation is that no cooling is required. That is the larger volume of liquid in contact with the adsorbent dissipates the heat of adsorption and prevents the isomerization of sensitive terpenes[7].

Citrus Essential Oils

Citrus essential oils are a complex mixture of numerous compounds possessing widely differing chemical and physical characteristics[8-12]. Chemically speaking, the constituents of citrus essential oils can be divided into four general categories.

1) Non-polar $C_{10}H_{16}$ terpenes with atmospheric boiling points of 155-180°C. Some examples are d-limonene (monocyclic), myrcene (straight chain), and sabinene (dicyclic).

2) Polar compounds that have boiling points in the range between and overlapped by the terpenes and sesquiterpenes. This fact makes sharp separations by distillation difficult. Some examples are linalool, decanal, and methyl anthranilate.

3) Non-polar $C_{15}H_{24}$ sesquiterpenes with atmospheric boiling points of 240-300°C. Some examples are bergamotene, valencene, and bisabolene.

4) A high boiling residue (wax/resin) of undetermined composition. It is of non-polar (i.e., ethyl alcohol non-soluble) and polar (i.e., hexane non-soluble) high molecular weight composition.

The principal flavoring components of citrus essential oils are oxygenated compounds[11,13,14]. The main flavor bearing constituents, as an individual class of compounds are aldehydes[11] (i.e., decanal, citral, and octanal). These aldehydes may comprise as little as 1.0% and as much as 8.5% by weight of the cold pressed oil[12,13].

The major non-flavoring, non-oxygenated compounds present in cold pressed citrus essential oils are d-limonene (60-95%), alpha and beta pinenes, myrcene, alpha and sigma terpinenes and sabinene (2-15%) and bergamotene, caryophyllene, and valencene (0-5%)[11,15]. The presence of these terpenes diminishes the oils solubility in alcohol - a factor of considerable imporatnce in the soft drink and perfumery industries. In addition, these terpenes and sesquiterpenes tend to oxidize and resinify on exposure to air under normal conditions[16,17]. This deterioration of the non-polar compounds results in an unpleasant odor and a very pronounced off-flavor (i.e., terpentine like flavor) that completely mask the original flavor of the oil. These difficulties have led to attempts to separate or at least reduce the terpene content by concentrating the oxygenated compounds.

Methods For Concentrating Essential Oils

There are three general classifications on industrial methods for concentrating citrus essential oils.

1) Distillation[11,18,19]

Vacuum

Steam

Alcoholic

2) Extraction[20-23]

Alcoholic

DMSO

Hydrotropic

3) Adsorption and absorption[24]

Polar

Non-polar

Derivatising is not commonly employed, although a US patent has been granted for a proposed process[25].

Each of the above methods suffer to some extent when subjected to analysis as to economics of operation and quality of product produced. All of the methods except the adsorption process require sophisticated process equipment and monitoring instruments, while others (i.e., alcoholic distillation and extraction) require government licensing or produce a product that is only partially deterpenated (i.e., steam distillation, vacuum distillation and hydrotropic extraction).

When all factors are considered the adsorption process appears to offer distinct advantages with respect to the simplicity of the equipment required, the ease of operation, and the possibility of the complete separation of non-oxygenated and oxygenated terpenes.

Essential Oils Concentrated By Adsorption

In 1952 Kirchner and Miller[26] reported a lab scale process for

the concentration of citrus essential oils by adsorption for which they were subsequently granted a US patent[27]. Several other authors[28-35] have also reported their observations regarding concentration of citrus oils by adsorption.

Other workers[1-6] have reported that terpene hydrocarbons isomerize when passed through a silica gel column at room and at elevated temperatures. To avoid these undesired rearrangements, methods and materials used to deactivate the silica have been reported[6,35,36]. However, these techniques are complicated, use materials not approved for food use, contaminate the adsorbate product, and/or are cost prohibitive.

Adsorption Defined

A working definition of adsorption is:

> A process which involves placing into contact a liquid substance with a rigid particulate sorbent which has the property of selectively taking up and storing one or more solute components originally contained in the liquid substance[43].

The "ideal" adsorbent should hold relatively large quantities of the materials to be adsorbed, the adsorbent must not decompose the adsorbed substance, the adsorbed substance should be eluted completely from the adsorbent, the adsorbent must have a certificate of compliance as a food additive, and the cost of the adsorbent should not prohibit its commerical use.

EXPERIMENTAL

Proposed Process To Be Studied

The following diagrammed operation shows the concentration of the major polar flavor-bearing components that are present in low concentration in citrus essential oils through their differences in physical properties from those terpene non-polar hydrocarbons present in a citrus essential oils in high concentrations. This operation is, for all practical intentions, a physical separation much the same as boiling points are during a distillation process.

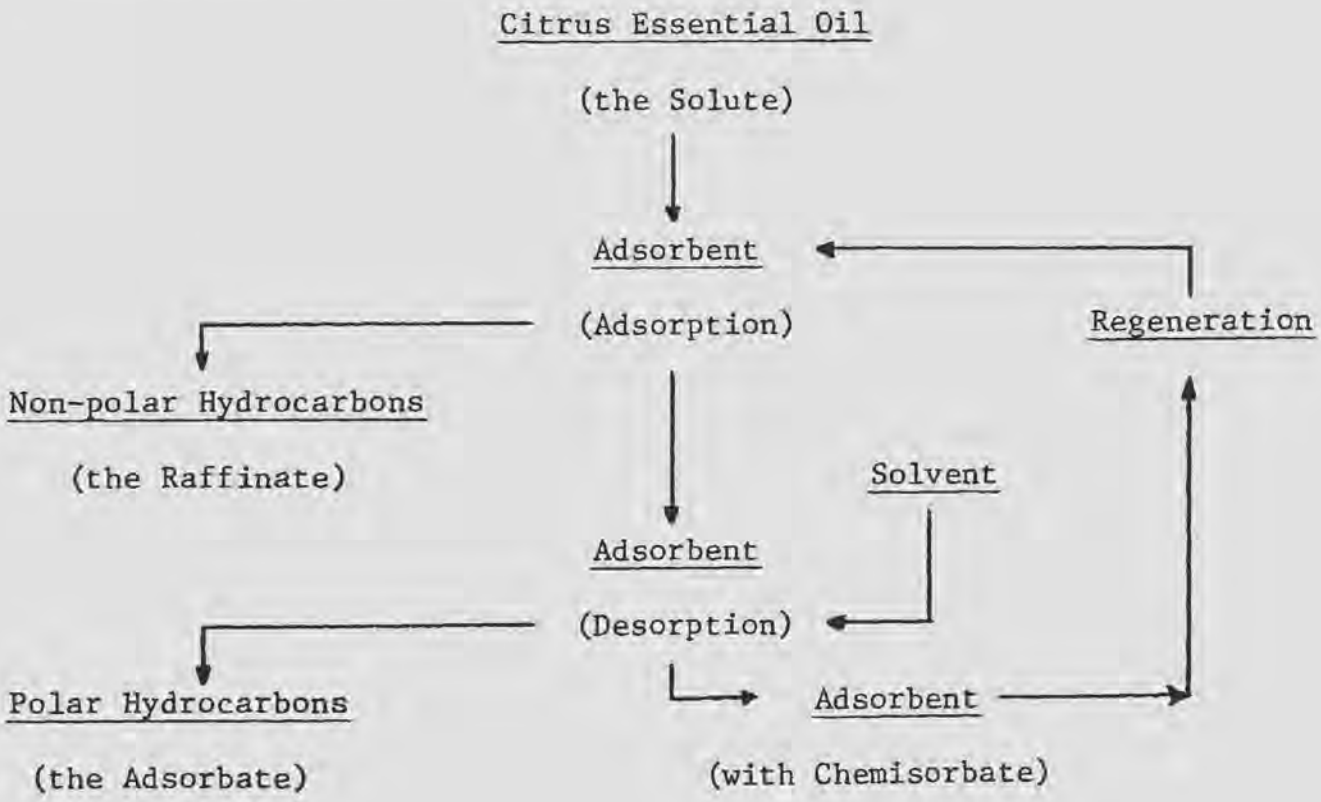


Figure 1. The Adsorption process.

The steps involved in the general adsorption process shown in Figure 1 are as follows:

ADSORPTION involves placing a citrus essential oil (the SOLUTE) into contact with a rigid particulate sorbent (the ADSORBENT) which has the property of selectively taking up and storing one or more SOLUTE components originally contained in the SOLUTE. The SOLUTE components deposited on the surface of the ADSORBENT is called the ADSORBATE and after equilibrium is attained (saturation of the adsorbent with adsorbate) the initial SOLUTE is then referred to as the RAFFINATE.

DESORPTION of the components that make up the ADSORBATE results from continuous competition of the displacing polar SOLVENT for the limited number of adsorption sites on the ADSORBENT by mass action as the ADSORBATE is forced from the sites. The polar SOLVENT used is removed from the ADSORBATE by distillation and by a series of cold water washes.

The CHEMISORBATE is that material which will not be displaced by the displacing agent.

REGENERATION is the term applied to reactivation of the ADSORBENT by the application of heat. Heating removes the polar SOLVENT from the active sites and some of the CHEMISORBATE material as well. Upon cooling, the ADSORBENT is ready to repeat the cycle of ADSORPTION - DESORPTION - REGENERATION.

It becomes readily apparent that the most important properties of the adsorbent in this proposed process are:

1) Capacity

A "wetting capacity" which is that amount of combined solute, adsorbate, and raffinate required to saturate the adsorbent at the adsorbate saturation point. Such information is required for determination of the solute/adsorbate ratio based on the operating aldehyde load capacity for the adsorbent, and from a structural point of view, for consideration of plant design for a column.

A "holdup capacity" which is that amount of raffinate and adsorbate that remains on the adsorbent at the operating aldehyde load capacity. Such information is useful when it is desired to partially deterpenate the citrus essential oil. That is, without the adsorbent being subjected to a washing agent for maximum removal of raffinate and maximum deterpenation.

An "operating aldehyde load" capacity which is that amount of aldehyde that the adsorbent will adsorb at maximum economics and quality of adsorbate. This differs from the aldehyde saturation point which is the condition where aldehyde overload has taken place and is apparent by aldehyde leakage into the raffinate.

2) Elution Sequence Of Oxygenated Compounds

Since it is desirable to maintain the ratio integrity of the oxygenated compounds present in the adsorbate to equal that present in the initial citrus essential oil and, because of speed of analysis, to use the aldehyde analysis as a control tool the elution sequence of oxygenated compounds at adsorbent overload is of importance.

3) Catalytic Behavior

Before a process can be adapted on a commerical scale, any reported rearrangements that might adversely affect the quality of the final product must be avoided.

4) Adsorbent Regeneration

Regeneration is important from the standpoint of adsorbent economy and time required for a number of adsorption - desorption - regeneration cycles to take place.

Silica Gel

Before an adsorbent is selected for study, it must have a certificate of compliance as a food additive from the FDA. The reasons are two-fold:

1) All citrus essential oils are classified as natural food additive ingredients by the FDA[37]. In order to maintain this desired classification, only approved materials by the FDA can come into contact with the oils.

2) If an unlisted adsorbent (e.g., Florisil) was used in this study and found to be acceptable, implementation of a proposed process could take several years because of the present status of testing required for a petitioned food additive.

Only one adsorbent, silica gel, carries a certificate of compliance as a food additive under the FDA rules and regulations[38]. Coincidentally, silica gel is the most universally suitable adsorbent for the separation of complex mixtures consisting of oxygenated compounds present in essential oils.

Solvents

As in the selection of a food grade adsorbent, the selection of any proposed wash and desorbing solvents is based upon FDA approval. This FDA approval is reflected in the tolerance for solvent residues as set by the FDA.

Since there are no solvent residue tolerance levels specifically set by the FDA for citrus flavor concentrates, the FDA tolerance for solvent residues in oleoresins[39] was used to select the solvents.

The solvents chosen were:

Hexane, as the wash solvent (tolerance level 25 ppm).

Acetone, as the desorbing solvent (tolerance level 30 ppm).

Each of the above solvents used in the proposed process were reagent grade as supplied by the Ashland Chemical Company.

Apparatus

The apparatus used in this adsorption study is shown in Figure 2. An all glass column (Kontes Glass Company) 100 cm long, 5 cm internal diameter, equipped with a jacket suitable for cold/hot passage of a glycol-water solution, with a 2-liter glass wool insulated reservoir connected by a clamp to its top and with a teflon stopcock adapter connected by a clamp to its bottom was used as the chromatographic column. A 2-liter filter flask was used as the collector. Interposed between the teflon stopcock adapter and jacketed column was placed a 200-mesh stainless steel screen to act as a support for the adsorbent. A type J thermocouple attached to a series 400 Omega pyrometer was inserted through the side tube of the collector. This

thermocouple was used to monitor the temperature of the eluting raffinate.

The column was dry packed with 988.6 grams of silica gel grade 12 (W.R. Grace & Company), giving an effective working column length of 70 cm. To act as a distributor plate, a 200-mesh stainless steel screen was placed on top of the packing. To the top of the reservoir was attached a 0.25 inch internal diameter copper tube to which, when required, could be attached a silica gel packed drying tube or a nitrogen line. When required, a flow meter was attached to the collector side tube to measure the nitrogen flow rates.

The silica gel grade 12 has the following properties[40]:

Particle size	28-200 mesh
Apparent bulk density	46 lb/ft^3
Surface area	720-760 m^2/g
Pore volume	0.43 cc/g
Pore diameter (average)	22 Å
Specific heat	0.22 BTU/lb/°F
Thermal conductivity	1 BTU/ft /hr/°F/in

The silica gel grade 12 was used as supplied by the manufacture. No attempt was made to modify its activity.

Methods Of Analysis

The aldehyde of the citrus essential oil, raffinate, and adsorbate was determined by the use of an alcoholic hydroxylamine hydrochloride reagent[41]. The formation of the oxime causes the liberation of hydrochloric acid, which is titrated with alcoholic sodium hydroxide

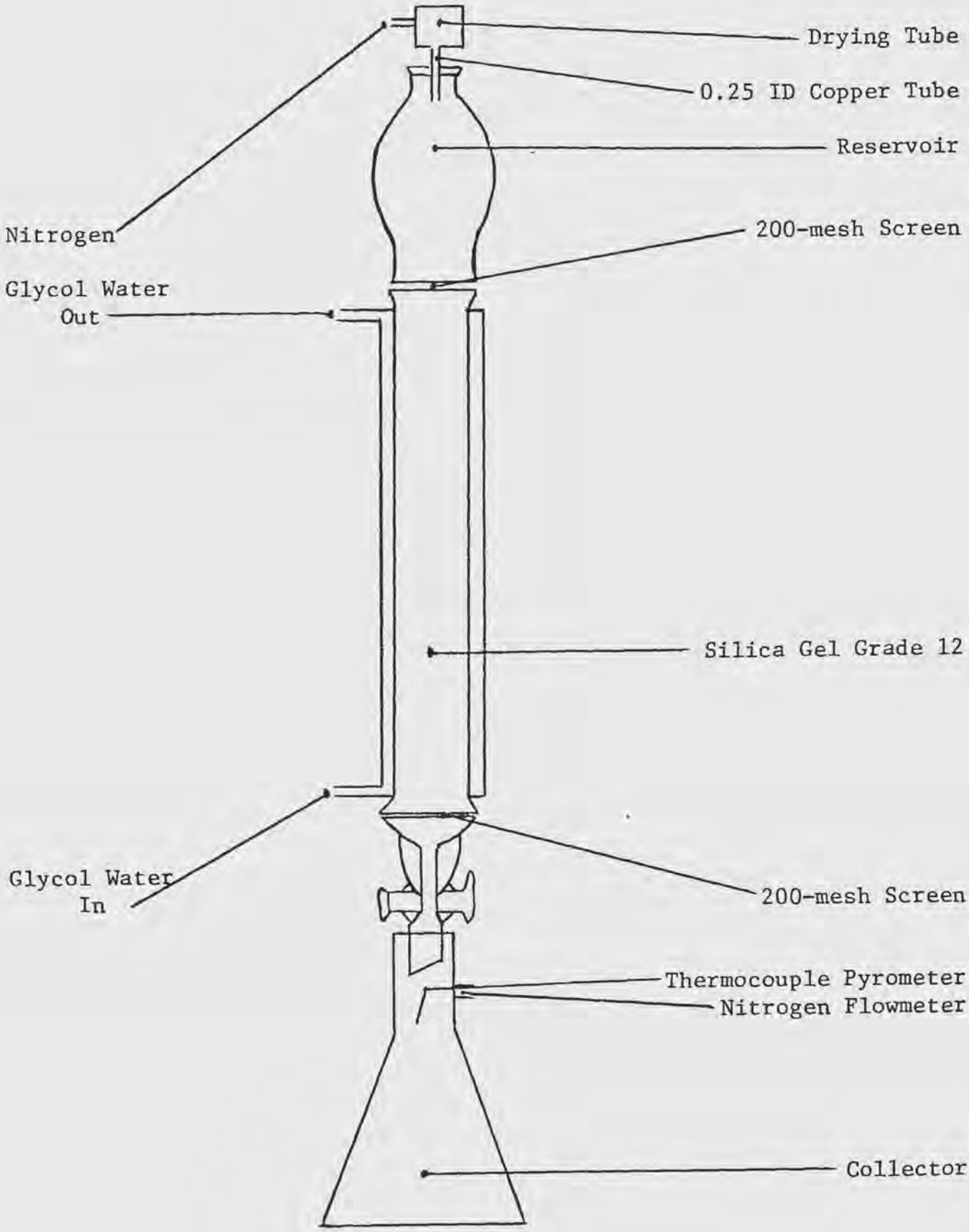


Figure 2. Chromatographic apparatus

solution. The amount of acid titrated is a measure of the aldehyde strength of the oil. The reaction times and size of sample used are given in Table I. The aldehyde strength determination was expressed as percent weight per weight of the sample titrated.

Table I

Aldehyde Determination

Sample	Weight	Reaction Time
Starting Oil	5.0 g	30 minutes
Raffinate	20.0 g	15 minutes
Adsorbate	0.2 g	30 minutes

The components of the starting oils, adsorbates, and raffinates were separated and analyzed using the equipment and conditions given in Table II. In order to have a basis of comparison whereby the determination of the ratio of the oxygenated compounds present in the adsorbate is equal or not to that present in the starting citrus essential oil, peak numbers were assigned to selected esters, alcohols, and aldehydes of the starting oil as separated by gas chromatography. The ratios of the selected oxygenated compounds were determined by using the peak areas generated by the integrator and are shown in Table III.

Table II

Conditions For Standard Of Comparison

Gas Chromatograph	Perkins-Elmer Model 900
Detector	Flame Ionization
Column	Glass Capillary
Liquid Phase	20M Carbox
Temperature	Column 80-200°C (2°/min)
	Det. 250°C Inj. 225°C
Carrier Gas	Nitrogen 10 cc/min
Flow Rate	Hydrogen 15 cc/min
Sample Size	2.0 microL Raffinate
	0.5 microL Adsorbate
Integrator	P&E Model PEP-1 data system

Table III

Peak Area Ratios

	Oil A	Oil B	Oil C
Esters	2:1:5	1.5:1:2	1.5:1:2
Alcohols	18:1:2	11:1:14	9:1
Aldehydes	1.5:1:2.6	0.5:1:1.2	0.2:1:3

In order to determin if any rearrangement of reported non-polar terpene hydrocarbons had taken place the raffinate was monitored. The reported non-polar terpenes that undergo rearrangement are d-limonene[2] and sabinene[42]. Since each of these are present in all citrus essential oils, their monitoring proved to be of no difficulty. As a basis of comparison hexane was added to the initial oil and the peak areas generated by the integrator for hexane, d-limonene and sabinene were recorded, again as ratios. The data is shown in Table IV.

Table IV

Hexane:d-Limonene:Sabinene Ratios

Oil A	Oil B	Oil C
0.05:1:0.02	0.05:1:0.04	0.05:1:0.01

Calculation Of Wetting, Holdup and Aldehyde Capacity

The apparatus used has been described above. With a stream of nitrogen flowing through the column at an exit rate from the column of 15 ml per minute, cooling glycol water at 5°C was passed through the column jacket. The column was nitrogen flushed and cooled for one hour.

At the end of one hour, the nitrogen flow was turned off and to the reservoir was added Oil A, chilled to 5°C, that had been spiked with hexane as reported in Table IV. The initial aldehyde concentration of the oil charge was determined. The oil was allowed to percolate down through the column by gravity. To the reservoir

cap was attached a silica gel drying tube to reduce the absorption of water vapor by the oil charge.

Raffinate eluted from the column seventy minutes into the run. The temperature at the time of raffinate elution was 105 C. Samples of raffinate were collected in 100 ml sample flasks and analyzed for aldehydes and by gas chromatography for oxygenated compounds and signs of rearrangement of the monitored terpenes.

Fraction #23 (135 minutes into the run) showed an aldehyde value of 0.10% and the presence by gas chromatography of an ester. The column was shut down, any remaining Oil A in the reservoir was removed and weighed. The raffinate was also weighed and the wetting capacity of the column calculated.

The column was allowed to run dry and 50 ml fractions collected. These fractions were analyzed by gas chromatography to determine the elution sequence of the oxygenated compounds.

The column was then blown dry for 30 minutes with a nitrogen stream and the holdup capacity of the column was calculated. From the information collected, the aldehyde load capacity at an ester saturation was also calculated.

In a like manner, using a fresh charge of silica gel grade 12 each time, Oils B and C were chromatographed.

The results obtained are shown in Table V and Table VI.

Table V

Raffinate Analysis

Oil	1*	2**	3***	Sabinene Peak
A	23	105-108	0.10	Reduced
B	9	107-108	0.03	Reduced
C	7	103-106	0.12	Reduced

* Fraction number at which ester saturation was detected.

** Temperature range of raffinate, in 0^{o}C.

*** Aldehyde % at ester saturation.

Table VI

Silica Gal Capacity (g/g)

Oil	1*	2**	3***
A	0.63	0.42	0.08
B	0.61	0.43	0.03
C	0.64	0.41	0.06

* Wetting capacity.

** Holdup capacity.

*** Aldehyde load capacity at ester saturation.

The column raffinate of each of the oils studied remained free of oxygenated compounds, with a reduction in the concentration of sabinene as compared with no reduction in either the d-limonene or added hexane, until there was a gradual rise in the concentration of the esters, followed by the aldehydes then the alcohols, where upon the concentration of sabinene returned to its initial level. These compounds did not each elute as a single component, but rather as the ester peak increased in peak height, the other components peak heights also increased in the order given. This trend continued until the original peak heights of the initial oil eluted in the last raffinate. This elution sequence agrees with those reported in the literature[6,43].

With respect to the aldehyde concentration of the raffinate for Oil A and C, there was an initial sharp decrease in aldehyde content of the raffinate (with a corresponding color loss) followed by a sharp rise in aldehyde content of the raffinate to an aldehyde level even higher in concentration than in the initial oil followed by a gradual return to the original aldehyde concentration and color level of the initial oil charge.

Gas chromatographic analysis of the oil raffinate showed an initial sharp decrease in sabinene concentration. The rearrangement of sabinene, catalyzed by acids and silica gel, has been studied[42]. The results can be represented by Figure 3. No decrease in the concentration of d-limonene in the raffinate for any of the oils run was found.

When a comparison of sabinene concentration in the raffinate is

made with raffinate eluting temperature it was noted that as one goes up, the other goes down. If rearrangement of sabinene is dependent upon temperature and not some property of the silica gel, then the cooling ability of the column apparatus as described is inadequate. This may be a direct consequence for sabinene rearrangement due to temperature and not just the silica gel properties, since in several batch run adsorption experiments, no decrease in the sabinene concentration of the raffinate was noted. Naturally, one conclusion is that the large volume of oil in contact with a small particle of silica during a batch adsorption process dissipates the generated heat of adsorption.

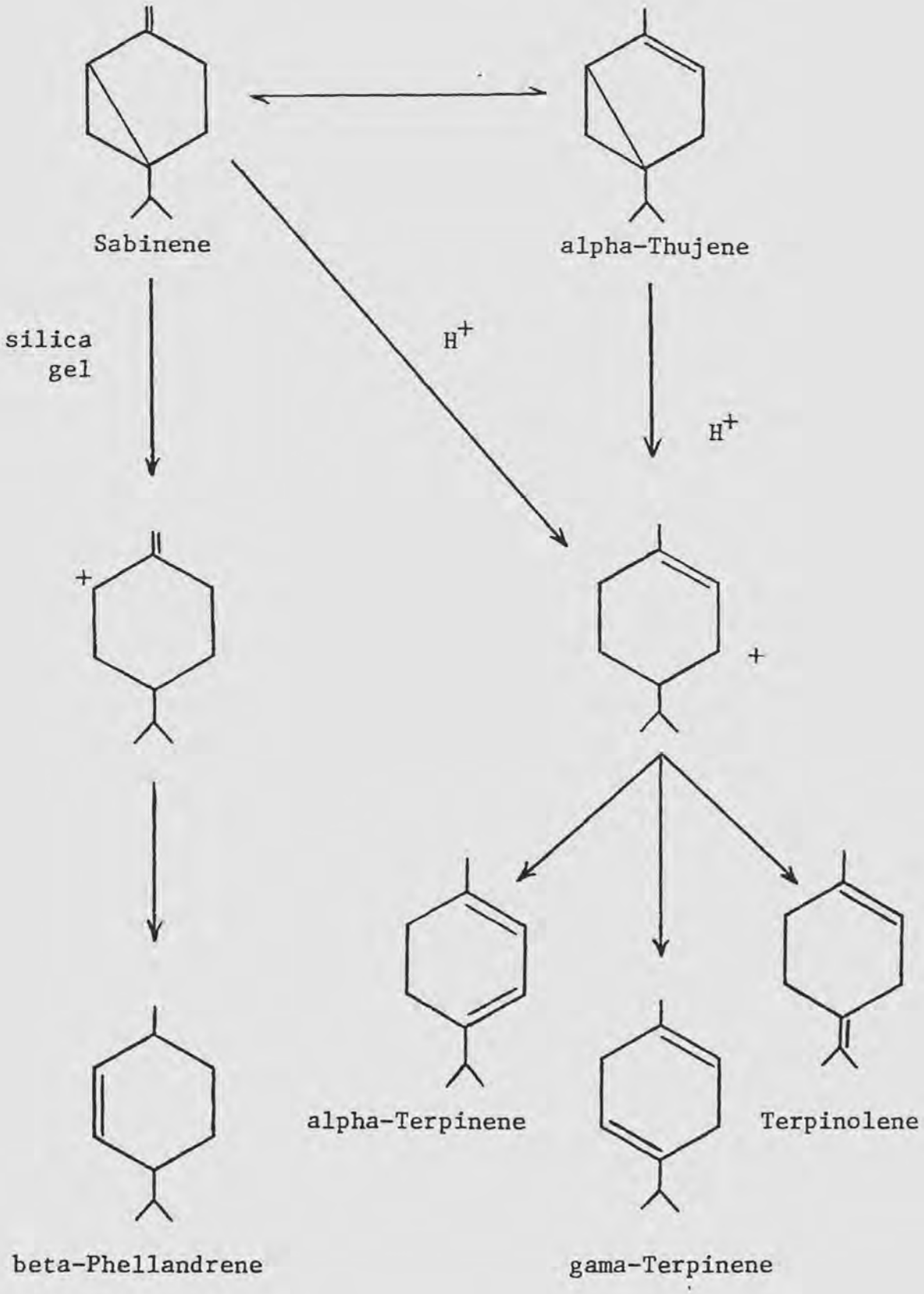


Figure 3. Sabinene isomerization.

Operating Procedure

Since the aldehyde load capacity at an ester saturation and the wetting capacity at an ester saturation for the column have been determined, the amount of Oil A, B, or C at some initial aldehyde A_x, required to give a mamimum operating aldehyde load capacity for the column can be calculated:

$$\frac{\text{(Aldehyde load capacity) X (Silica gel column charge)}}{A_x}$$

(minus)

(Wetting capacity) X (Silica gel column charge)

and gives the maximum oil charge to the column.

The apparatus used has been described above. A new column charge of 988.5 grams silica gel grade 12 was used.

Pre-column Conditioning

The column was nitrogen flushed for one hour, flowing at an exit rate from the column of 15 ml per minute and cooled with a glycol water solution at 5°C.

At the end of one hour, the nitrogen flow was turned off and to the reservoir was added 650.0 grams of 5°C chilled raffinate of Oil A collected from a previous run. The aldehyde concentration of this raffinate was 0.01%. The raffinate was allowed to percolate down through the column under the influence of gravity. To the reservoir cap was attached a silica gel charged drying tube. The raffinate was not allowed to elute from the column, but kept within the column to

allow cooling of the column packing for one hour.

Adsorption

At the end of one hour, to the reservoir was added the calculated maximum oil charge for Oil A (1849.0 grams). The drying tube was replaced and the oil allowed to percolate down through the column packing under the influence of gravity. At this time, the previously charged raffinate was eluted from the column and collected.

Solvent Wash

One hundred and thirty-five minutes into the run, when the oil charge is just below the top of the column packing, 1480.0 grams of 5°C chilled hexane (1.5 times the column charge) was added to the reservoir and allowed to percolate down through the column under the influence of gravity. At a point where the hexane starts to elute from the column (determined by scent) the collector was changed and the hexane raffinate collected.

The total time required to change the collector to begin collecting the hexane raffinate was 185 minutes into the run. The total raffinate collected at this point was 2108.5 grams. A sample was taken for gas chromatographic and aldehyde analysis.

Gas chromatographic analysis showed the presence of some hexane (less than 0.5%), but no aldehyde or esters. The aldehyde determination was 0.06%.

The column was then allowed to run dry. The total time to this point was 244 minutes. The hexane raffinate collected weight was 1509.0 grams. Gas chromatographic and aldehyde analysis showed no

trace of esters and 0.04% aldehyde.

In order to determine that a sufficient amount of hexane wash had been used, nitrogen was applied to the column to drive off any residual hexane. Nitrogen was applied for 30 minutes. The hexane raffinate was then collected, weighed, and evaporated to a small volume.

Gas chromatographic analysis showed the presence of raffinate, but when calculated on a percent basis of eluted hexane raffinate, it amounted to less than 1.0%. It was therefore felt that a sufficient amount of hexane had been used to wash the raffinate from the column.

Desorption

To the reservoir was added 1480.0 grams of 5°C chilled acetone (1.5 times the column charge), the drying tube replaced, and the acetone allowed to percolate down through the column under the influence of gravity. The column was allowed to run dry. The total time to this point was 330 minutes.

In order to determine that a sufficient amount of acetone had been used to displace the adsorbed oxygenated compounds from the column, nitrogen was applied to the column to drive off any residual acetone adsorbate. Nitrogen was applied for 30 minutes, the residual acetone adsorbate collected, weighed and the acetone evaporated.

Gas chromatographic analysis showed the presence of alcohols. Therefore, another 500 grams of acetone was added to the column. The column was again allowed to run dry, and nitrogen applied for 30 minutes. The eluted acetone was collected, weighed and the acetone

evaporated to a small volume. Gas chromatographic analysis showed no presence of oxygenated compounds. Total time to this point was 515 minutes.

Column Appearance

At this point the silica gel packing had a very light yellow color and the column packing length has decreased by 2.54 cm.

Column Regeneration

To the collector flask was added 1000 grams of water and to the vacuum port of the flask was attached a hose leading to a drain. Nitrogen was applied to the column top at a sufficient pressure to give a flow rate of 25 ml per minute at column exit. The glycol water solution running through the column jacket was heated to 80°C. The apparatus was allowed to run in this mode for 12 hours. At the end of 12 hours, the silica gel packing had a light tan appearance and the packing length had decreased a total of 3.0 cm.

Preparation For The Next Run

The column was conditioned as outlined in Pre-column Conditioning.

Solvent Removal From The Adsorbate

The acetone was distilled from the acetone adsorbate at 35°C with 25 mm Hg of vacuum using a Claisen distilling head-condenser combination. The condenser was chilled to 5°C. After distillation of the major portion of acetone, the adsorbate was then washed with 3 X 400 grams of 10°C water. This removed any gas chromatographic detectable traces of acetone in the product.

The hexane was distilled from the hexane raffinate using the same equipment and conditions as for the acetone distillation. The raffinate pot material still contained some gas chromatographic detectable hexane, but at an amount less than the level set by the FDA.

Column Reusability

Twenty-four more runs were performed on the same column charge using the same Oil A lot. The acetone and hexane were re-cycled. Any discrepancy in the weights of solvents required was made up with new solvent. The results are shown in Table VII.

Table VII

Oil A Adsorption Runs

Constant Conditions

1) Column charge: 988.6 g silica gel grade 12.

2) Pre-column conditioning: 650.0 g Oil A raffinate.

3) Oil A charge: 1849.0 g at 3.2% w/w aldehyde.

4) Solvents: hexane at 1480 g and acetone at 1980 g.

5) Column regeneration: 80 C, 25 ml per minute nitrogen.

Symbols used:

A Raffinate collected, g-wt.

B Hexane make-up, g-wt.

C Hexane raffinate collected, g-wt.

D Acetone make-up, g-wt.

E Product collected, g-wt.

F Aldehyde of product, w/w %.

G Aldehyde recovered based on oil charge, w/w %.

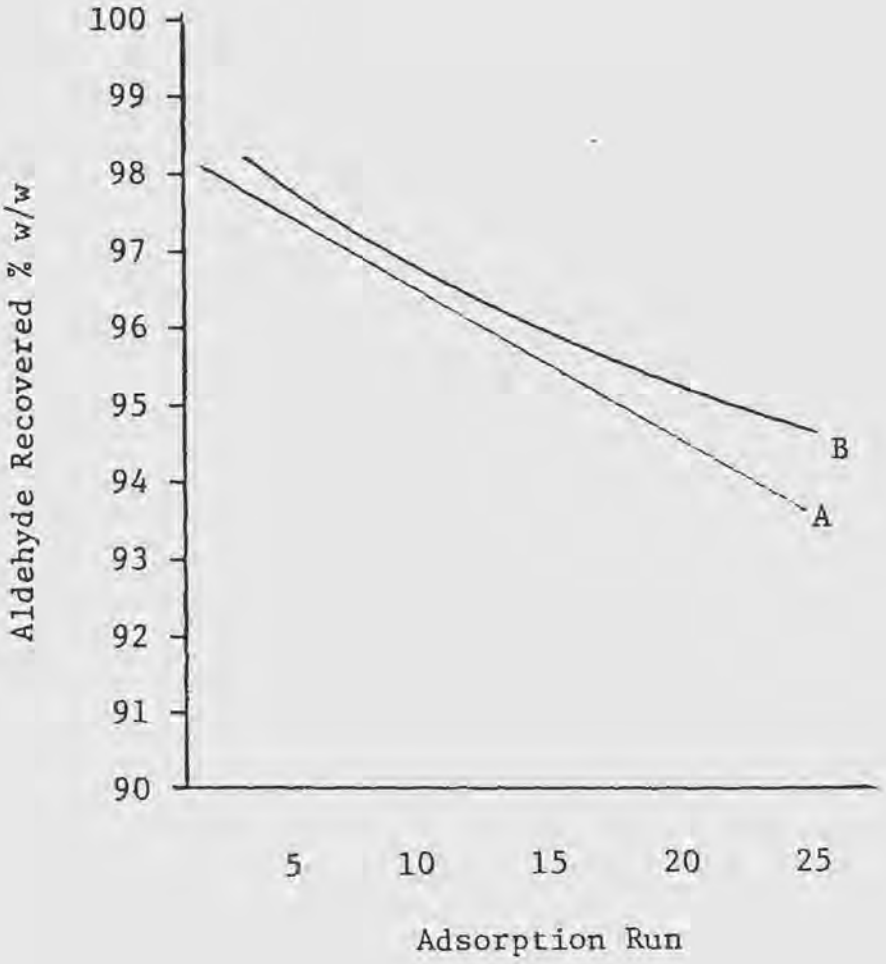
H Column regeneration time in hours.

I Acetone level in the raffinate, v/v %.

Table VII (cont.)

Oil A Adsorption Runs

Run	A	B	C	D	E	F	G	H	I
1	2108.5	---	1509.0	---	123.1	47.2	98.2	--	----
2	1991.6	518	1564.0	594	123.9	46.8	98.0	12	0.40
3	2110.0	444	1496.0	634	123.0	47.0	97.7	12	0.46
4	2098.4	492	1519.6	636	123.0	45.9	95.4	12	0.47
5	2110.6	453	1500.3	612	122.8	46.7	96.9	12	0.43
6	2110.0	507	1515.7	626	122.5	46.9	97.1	52	0.17
7	2105.4	501	1511.2	600	122.6	46.7	96.8	12	0.50
8	2099.7	440	1518.7	591	122.8	46.9	97.3	12	0.41
9	2097.3	473	1520.1	619	122.0	46.5	95.9	12	0.43
10	2108.0	442	1505.9	589	122.4	46.0	95.2	12	0.46
11	1995.0	517	1625.2	620	123.1	46.4	96.5	52	0.21
12	2110.0	500	1500.0	597	122.6	46.7	96.8	12	0.48
13	2109.7	590	1517.8	595	122.4	46.1	95.4	12	0.43
14	2106.0	561	1505.1	610	121.3	46.7	96.0	12	0.50
15	2112.3	584	1592.5	600	122.1	45.9	94.7	12	0.45
16	2100.5	505	1517.0	602	123.0	46.3	96.2	52	0.15
17	2109.1	459	1504.8	611	122.5	45.7	94.6	12	0.44
18	2111.1	448	1500.6	693	121.8	46.9	96.5	12	0.49
19	2105.6	518	1519.1	660	122.2	45.8	94.6	12	0.46
20	2108.6	475	1509.8	592	121.7	45.6	93.8	12	0.48
21	2100.1	463	1514.7	634	122.7	46.3	96.0	52	0.20
22	2100.9	461	1506.9	616	122.0	46.4	95.7	12	0.41
23	2098.2	469	1510.9	642	122.1	45.8	94.5	12	0.46
24	2107.6	445	1509.1	600	119.7	46.8	94.7	12	0.43
25	2112.4	457	1501.1	596	121.3	46.4	95.2	12	0.42
Av	2097.0	476	1516.2	611	122.3	46.4	96.0		



Legend:

Line A for a least squares fit

Curve B for 52 hour regeneration

Figure 4. Aldehyde recovered % w/w versus adsorption run

RESULTS AND DISCUSSION

Inspection of Figure 4 indicates the following:

1) There is a gradual decrease in aldehyde recovery where column regeneration is only done for 12 hours (line A).

2) There is a gradual decrease in aldehyde recovery where column regeneration is done for 52 hours. This decrease (curve B) is of a more gentle decline in aldehyde recovery than line A.

Since the raffinate from runs 2 through 25 showed the presence of acetone (at an average high level of 0.45% for times where the column was regenerated for 12 hours, to an average low level of 0.18% for times where the column was regenerated for 52 hours) and since acetone in the raffinate is an indication of incomplete column regeneration, is it possible to bring the column back to its original level of adsorption capacity by changing the regeneration conditions?

Rejuvenation Of Silica Gel

In order to determine if the regeneration temperature of the column is too low and if the original aldehyde capacity of the silica gel could be restored, the silica gel was subjected to the following:

1) The silica gel was removed from the column after the 25th regeneration (performed after the 25th run) and placed for two hours in an air circulated oven set at 260°C where it was gently stirred from time to time. During this high temperature regeneration of the adsorbent, some of the chemisorbate material was volitized as evidenced by the

generation of a sweet aroma. After this regeneration, the hot silica gel was cooled in a desiccator to prevent any adsorption of water from the atmosphere. After this heating and cooling, the silica particles had a very light tan color.

2) The column was repacked and the 26th run performed as previously described. The results are shown in Table VIII.

Table VIII

26th Oil A Run

Silica gel charged column, g-wt	980.2
Oil A charge, g-wt	1833.3
Raffinate collected, g-wt	2073.5
Hexane charge, g-wt	1480.0
Hexane raffinate collected, g-wt	1487.2
Acetone charge, g-wt	1980.0
Product collected, g-wt	122.3
Aldehyde of product, w/w %	47.1
Aldehyde recovered based on oil charged, w/w %	98.1

This 26th run on the rejuvenated silica gel demonstrates that the regeneration column temperature is not high enough to insure rejuvenation of the silica gel in order to give consistant recoveries of aldehyde, and with proper regeneration temperature the silica gel can be used indefinitely.

CONCLUSIONS

1. The column regeneration conditions have been standardized whereby in over 100 runs using the same packing charge the % w/w aldehyde recovered is 98.1 $\pm$ 0.5%.

2. The flow rate of each citrus essential oil studied has been standardized and rates consistent with economic production have been established.

3. The economic consideration of solvents, column packing, and pounds of product produced per run have been resolved whereby solvents and column packing account for less than 10% of the ingredients cost and pounds product produced per run are consistent with established economic guidelines.

4. The reported rearrangements of terpenes on silica gel columns has been eliminated.

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