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ARTICLE

Selective Removal of Monoterpenes from Bergamot Oil by Inclusion in Deoxycholic Acid

Giancarlo Fantin,*,† Marco Fogagnolo,† Silvia Maietti,§ and Stefano Rossetti#

†Dipartimento di Chimica, Università di Ferrara, Via Borsari 46, 44100 Ferrara, Italy, §Dipartimento di Biologia ed Evoluzione, Università di Ferrara, C.so Ercole I d'Este 32, 44100 Ferrara, Italy, and #ISOF-CNR sez. Ferrara, c/o Dipartimento di Chimica, University of Ferrara, via L. Borsari 46, I-44121 Ferrara, Italy

A new approach for removing monoterpenes (MTs) from bergamot oil by selective inclusion in deoxycholic acid (DCA) is proposed. The inclusion process is very efficient, the included fraction being composed mainly of limonene (71.7%) and γ-terpinene (19.8%). On the other hand, the deterpenated bergamot oil fraction showed for the linalool and linalyl acetate derivatives significant increases from 16.6 and 21.4% to 18.3 and 42.2%, respectively. The major advantages of this methodology are its simplicity, the mild conditions employed, and the quantitative recovery of both host (DCA) and guest (monoterpenes) compounds. Differential scanning calorimetry (DSC), thermal gravimetry (TG), powder X-ray diffractometry (XRPD), infrared spectroscopy (IR), and proton magnetic resonance (^{1}H NMR) analysis were used to investigate and characterize the inclusion compounds.

KEYWORDS: Deoxycholic acid; host−guest; inclusion; deterpenation; bergamot oil

INTRODUCTION

The separation of multicomponent mixtures into their individual components may be carried out by exploiting differences in physical properties. Distillation, crystallization, and liquid−liquid extractions are commonly employed operations aimed to isolate constituents of a mixture, based on differences in volatility or solubility. In the case of components having similar physical properties, such as molecular isomers, traditional separation techniques can be inefficient or unusable; therefore, less conventional approaches such as selective inclusion (*1*−*3*) may be an attractive alternative. The inclusion methodology is based on the host−guest supramolecular chemistry whereby a solid host compound spatially incorporates a guest molecule within its confines. If selectivity is somehow displayed by the host toward a specific guest, this derivative is included and it can be separated from a solution mixture by simple filtration of the solid inclusion compound. The guest can then be recovered under mild conditions, and the host material is recycled. It follows that the precise control of host cavities (*4*) for guest recognition is a basic requirement to obtain selective and efficient accommodation processes. Molecules with well-defined geometries and limited conformational freedom are ideal candidates for designing, building, and controlling host cavities, and steroids (*5*), in particular bile acids, are suitable for the scope. This family of derivatives, in fact, has shown a particular ability in the inclusion of different organic guest molecules such as aliphatic and aromatic hydrocarbons, alcohols, ketones, esters, nitriles, epoxides, and amides (*6*).

*Corresponding author (telephone +39-0532-455946; fax +39-0532-240709; e-mail fnn@unife.it).

We have recently studied the inclusion ability of some bile acid derivatives for the resolution of organic racemates (*7*) including the precise definition of the structures involving the host−guest assemblies (*8*−*10*), and we have also successfully employed 3α,12α-dihydroxy-5β-cholan-24-oic acid, commonly called deoxycholic acid (DCA), as host in the separation and isolation of lycopene from crude tomato extract (*11*).

The purpose of the present work is to evaluate the possibility of carrying out the deterpenation of bergamot oil by means of the host−guest inclusion methodology using DCA, one of the cheapest and easily available naturally occurring bile acids, as host.

Bergamot oil is a valuable citrus oil widely used in the food, cosmetic, and pharmaceutical industries (*12*). This essential oil is obtained by pressing the peel of the bergamot fruit (*Citrus aurantium Bergamia* Risso). As compared with other citrus oils, bergamot oil is characterized by a lower amount of limonene (25.6−53.0%) and higher amounts of linalool (1.7−20%) and linalyl acetate (15.6−40.4%) (*13*). Generally, these volatile compounds represent approximately 90% of the bergamot oil. The most important contribution to the flavor of the oil comes from oxygenated compounds (OCs), such as linalool and linalyl acetate, whereas monoterpenes (MTs), such as limonene and pinene, tend to decompose, producing off-flavor compounds upon heating or contact with air. Thus, it is necessary to remove MTs to obtain a product of higher stability and more soluble in water while maintaining its characteristic flavor and fragrance. Several methods are employed for the deterpenation of citrus oils. Classical methods include vacuum and steam distillations, which are carried out at high temperatures. As already pointed out, heating may cause degradation of certain components and loss of

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Table 1. Composition of the Starting, Included, and Deterpenated Bergamot Oil (Data Obtained Using GD-FID Analysis)

			RA[b]			
no.	RI[a]	identified compound	starting bergamot oil	included guests	deterpenated bergamot oil after one inclusion cycle	deterpenated bergamot oil after two inclusion cycles
1	939	1*R*-α-pinene[c]	1.60 ± 0.03		0.70 ± 0.04	0.77 ± 0.04
2	975	sabinene[c]	1.38 ± 0.04		0.57 ± 0.04	0.77 ± 0.03
3	979	*β*-pinene[c]	6.30 ± 0.04		4.09 ± 0.03	4.16 ± 0.03
4	991	myrcene[c]	1.48 ± 0.02	1.54 ± 0.03	0.71 ± 0.02	0.15 ± 0.01
5	1025	*p*-cymene[c]	0.23 ± 0.01		0.26 ± 0.02	0.28 ± 0.02
6	1029	D-limonene[d]	38.85 ± 0.01	71.71 ± 0.02	24.63 ± 0.02	10.91 ± 0.02
7	1037	*cis*-ocimene[c]	0.37 ± 0.03		0.28 ± 0.01	0.31 ± 0.02
8	1060	*γ*-terpinene[d]	9.13 ± 0.03	19.79 ± 0.03	5.75 ± 0.04	2.19 ± 0.02
9	1089	terpinolene[c]	0.59 ± 0.04	3.06 ± 0.03		
10	1097	linalool[d]	16.66 ± 0.02	1.59 ± 0.01	18.29 ± 0.01	21.66 ± 0.01
11	1257	linalyl acetate[d]	21.41 ± 0.02	2.26 ± 0.01	42.22 ± 0.02	55.75 ± 0.01
12	1349	α-terpinyl acetate[c]	0.18 ± 0.03		0.25 ± 0.04	0.31 ± 0.03
13	1362	neryl acetate[c]	0.48 ± 0.02		0.57 ± 0.02	0.60 ± 0.04
14	1381	geranyl acetate[c]	0.32 ± 0.02		0.32 ± 0.01	0.41 ± 0.03
15	1419	caryophyllene[c]	0.54 ± 0.02		0.70 ± 0.04	0.97 ± 0.04
16	1435	*trans*-bergamotene[c]	0.41 ± 0.03		0.58 ± 0.03	0.72 ± 0.04

[a] Retention index. [b] Relative area percentage (peak area relative to total peak area percent) calculated on a GC-FID with an SE52 column. [c] Tentatively identified on the basis of comparison with MS database spectra and retention indices. [d] Identified by comparison of mass spectra and retention times with those of pure standards.

the more volatile fractions. To avoid these disadvantages, the use of supercritical CO_2 has proven to be a valid alternative for the fractionation and/or deterpenation of bergamot oil (*14*, *15*). Removal of specific fractions with organic solvent or ionic liquids has been reported as well (*16*).

In the present work we report an innovative methodology for the removal of undesired light monoterpenes from bergamot oil, exploiting the sequestrating ability of host−guest interactions.

The proposed process is endowed with several convenient features: first of all, it occurs with high efficiency in mild conditions, avoiding side-degradation reactions or volatilization of desired components, ensuring a better quality of the resulting raw bergamot oil. Besides this advantage, it provides operational simplicity and is low cost, and it allows recovery and reusability of the host, as well as quantitative recovery of both the residual deterpenated oil and the included monoterpenes. In addition, the influence of the relative ratio between MTs and OCs on the efficiency of the inclusion process has been investigated, using a synthetic binary mixture (limonene/linalool) as probe.

To the best of our knowledge this is the first example of a deterpenation process realized via selective inclusion methodology. The above-described characteristics, the use of naturally occurring nontoxic materials, and the lack of waste make it of interest for low environmental impact exploitations.

MATERIALS AND METHODS

Materials. Bergamot oil was supplied by FLORS s.r.l. (Pisa, Italy). Limonene (4-isopropenyl-1-methyl-1-cyclohexene, 97% by GC), linalool (3,7-dimethyl-3-octanol, 98% by GC), linalyl acetate (3,7-dimethyl-1,6-octadien-3-yl acetate, 97% by GC), and *γ*-terpinene (1-isopropyl-4-methyl-1,4-cyclohexadiene, 98.5% by GC) were obtained from Sigma-Aldrich. Deoxycholic acid (3α,12α-dihydroxy-5*β*-cholan-24-oic acid; DCA) have been supplied by ICE industry (Reggio Emilia, Italy).

Amorphous Deoxycholic Acid. Ten grams of crystalline DCA was slowly dissolved in 250 mL of 5% aqueous NaOH. This solution was slowly added, under good stirring, to 250 mL of 5% aqueous HCl. The white precipitate, collected by filtration and abundantly washed with water, was finally dried at 60 °C in a ventilated oven.

Gas Chromatographic (GC) Analysis. Bergamot oil constituents were analyzed and the relative peak areas for individual constituents averaged. The relative percentages were determined using a ThermoQuest GC-Trace gas chromatograph equipped with a FID detector and a Mega SE52 (Mega, Legnano, Italy) poly-5% diphenyl-95%-dimethyl-siloxane bonded phase column (i.d., 0.32 mm; length, 30 m; film thickness, 0.15 μm). Operating conditions were as follows: injector temperature, 280 °C; FID temperature, 280 °C; carrier gas (helium) flow rate, 2 mL/min; and split ratio, 1:40. The oven temperature was initially 55 °C, raised to 100 °C at a rate of 1 °C/min, then raised to 250 °C at a rate of 5 °C/min, and finally held at that temperature for 10 min. The inclusion compounds (20 mg) were disgregated with aqueous $NaHCO_3$ and extracted with 1 mL of ethyl acetate. One microliter of each extract was analyzed. The percentage composition of the oils was computed by the normalization method from the GC-FID peak areas, without using correction factors.

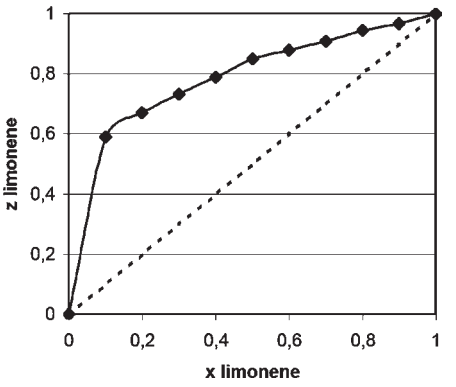

Figure 1. Competition experiment result for limonene versus linalool. *X* is the mole fraction of limonene in the liquid mixture, and *Z* is the mole fraction of limonene in the crystalline compound.

Gas Chromatography−Mass Spectrometry Analysis. Essential oil constituents were then analyzed by a Varian GC-3800 gas chromatograph equipped with a Varian MS-4000 mass spectrometer using electron impact and connected to the NIST library. The main components, limonene, linalool, linalyl acetate, and *γ*-terpinene, were identified by comparing their GC retention times, linear retention indices (LRI), and MS fragmentation pattern with those of other essential oils of known composition, with pure compounds, and by matching the MS fragmentation patterns and retention indices with the above-mentioned mass spectral libraries and with those in the literature (*17*). The GC conditions were the same reported as for GC analysis, and the same column was used. The MS conditions were as follows: ionization voltage, 70 eV; emission current, 10 μA; scan rate, 1 scan/s; mass range, m/z 40−500; trap temperature, 150 °C, transfer line temperature, 300 °C. A mixture of aliphatic hydrocarbons (C_8−C_{24}) in hexane (Sigma-Aldrich, St. Louis, MO) was injected under the above temperature program to calculate the retention indices using the generalized equation by Van den Dool and Kratz (*18*).

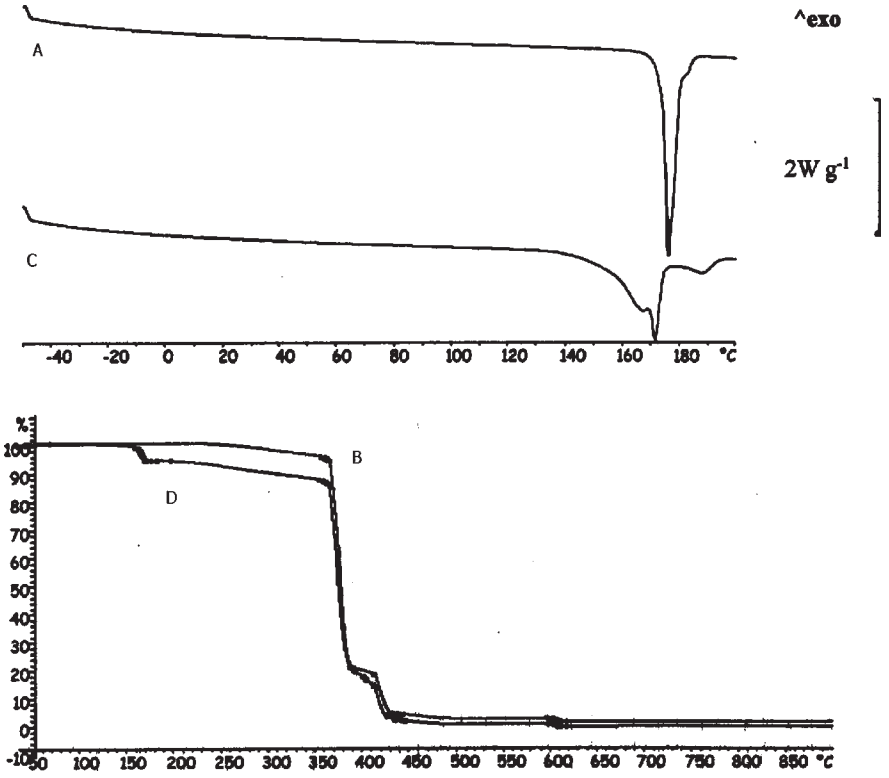

Figure 2. Compared thermal analyses: traces A and B, DSC and TG of DCA; traces C and D, DSC and TG of DCA·MTs.

Thermal Analysis. *Thermogravimetry* (*TG*). TG was carried out using a TGA/SDTA Mettler Toledo model 851. Samples were heated in a temperature range between 35 and 900 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere.

Differential Scanning Calorimetry (*DSC*). DSC measurements were performed with a Mettler Toledo model 820 calibrated with a standard grade indium sample. The samples, usually 8−9 mg, were heated in an aluminum pan from −50 to 200 °C at a heating rate of 20 °C min^{-1} under a continuous nitrogen purge.

X-ray Powder Diffraction Analyses (*XRDP*). Diffraction data (Cu $K\alpha_1, \lambda = 1.5406$ Å) were collected on a Bruker D8 advance diffractometer. The generator was operated at 40 kV and 40 mA. Receiving slit was 0.2 mm. A long scan was performed within $3 < 2\theta < 50°$, 0.020°/2 s.

Nuclear Magnetic Resonance (*NMR*). All NMR spectra were recorded on a Varian Gemini 300 VT spectrometer operating at 300.1 MHz and were carried out using 5−10 mg samples dissolved in 0.5 mL of CD_3OD in 5 mm tubes at 25 °C. The chemical shifts, δ, are given in parts per million (ppm), and the solvent signal was used for spectral calibration (^1H 3.31 ppm). ^1H NMR spectra were run using a standard pulse sequence "s2pul", with a 45.0° pulse, 3.00 s acquisition time, 8 repetitions, 4000 Hz spectral width, and 0.33 Hz FID resolution.

Infrared Spectroscopy (*IR*). IR spectra were recorded on a Perkin-Elmer 1310 grating infrared spectrometer using the nujol suspension technique.

Inclusion-Based Deterpenation. Solid DCA (4 g) was added to 2 g of bergamot oil. The heterogeneous mixture was mixed for 5 min with a spatula and then was left to stand at room temperature, in the dark, for 10 days. Diethyl ether (30 mL) was added, and the crystals were filtered off. The solid inclusion compound and the filtrate (deterpenated bergamot oil) were analyzed by GC-FID to determine the relative ratio of the different components.

The inclusion compound, further analyzed by GC-MS, ^1H NMR, TG, DSC, IR, and XRPD, was finally heated under vacuum (70 °C; 12 mmHg) to recover the included monoterpenes and restore the host, which may be used for further cycles.

Competition Experiments. These experiments were carried out in a solid−liquid biphasic system as follows: a series of 11 vials was prepared with a mixture of two guests, limonene and linalool, dissolved in diethyl ether, such that the mole fraction of a given guest varied from 0 to 1. The insoluble DCA host (50 mg, 0.125 mmol) was added to each mixture, keeping the total guest/host ratio at 15:1. The vials were sealed after 2 days and left at room temperature in the dark for 10 days. The inclusion compounds were filtered off, washed with diethyl ether, dissolved in an aqueous solution of sodium bicarbonate (5 mL), and extracted with 5 mL of ethyl acetate. The organic solutions were analyzed by GC as described above.

RESULTS AND DISCUSSION

Composition of Bergamot Oil. The composition of bergamot oil (FLORS s.r.l.) was determined using GC analysis. Totally, 16 compounds were identified in the essential oil, and the results are listed in **Table 1**. The key constituents, limonene (38.8%), γ-terpinene (9.1%), linalool (16.6%), and linalyl acetate (21.4%), were confirmed by comparison of mass spectra and retention times with those of pure standards. In the present work, limonene was used to represent MTs, whereas linalool and linalyl acetate stood for OCs.

Inclusion-Based Deterpenation. Two grams of bergamot oil was mixed with twice the amount of solid DCA. The bile acid selectively enclathrated on its lattice the MT fraction, leaving the OC constituents in liquid phase. The incorporation ratio was followed for 15 days by GC-FID and appeared to reach an equilibrium after 10 days. Diethyl ether (30 mL) was added, and the crystals were filtered off. The solid inclusion compound (DCA·MTs) and the filtrate (solution of partially deterpenated bergamot oil) were analyzed by GC-FID to determine the relative ratio of the different components (**Table 1**). The inclusion process was very efficient for removing MTs. In fact, the components included in DCA were mainly limonene (71.7%) and γ-terpinene (19.8%), and the deterpenated bergamot oil showed linalool and linalyl acetate increased from 16.6 and 21.4% to 18.3 and 42.2%, respectively. The inclusion compound was heated under vacuum (70 °C; 12 mmHg) to recover the included monoterpenes (0.25 g) and the host, which was unmodified and may be used for further

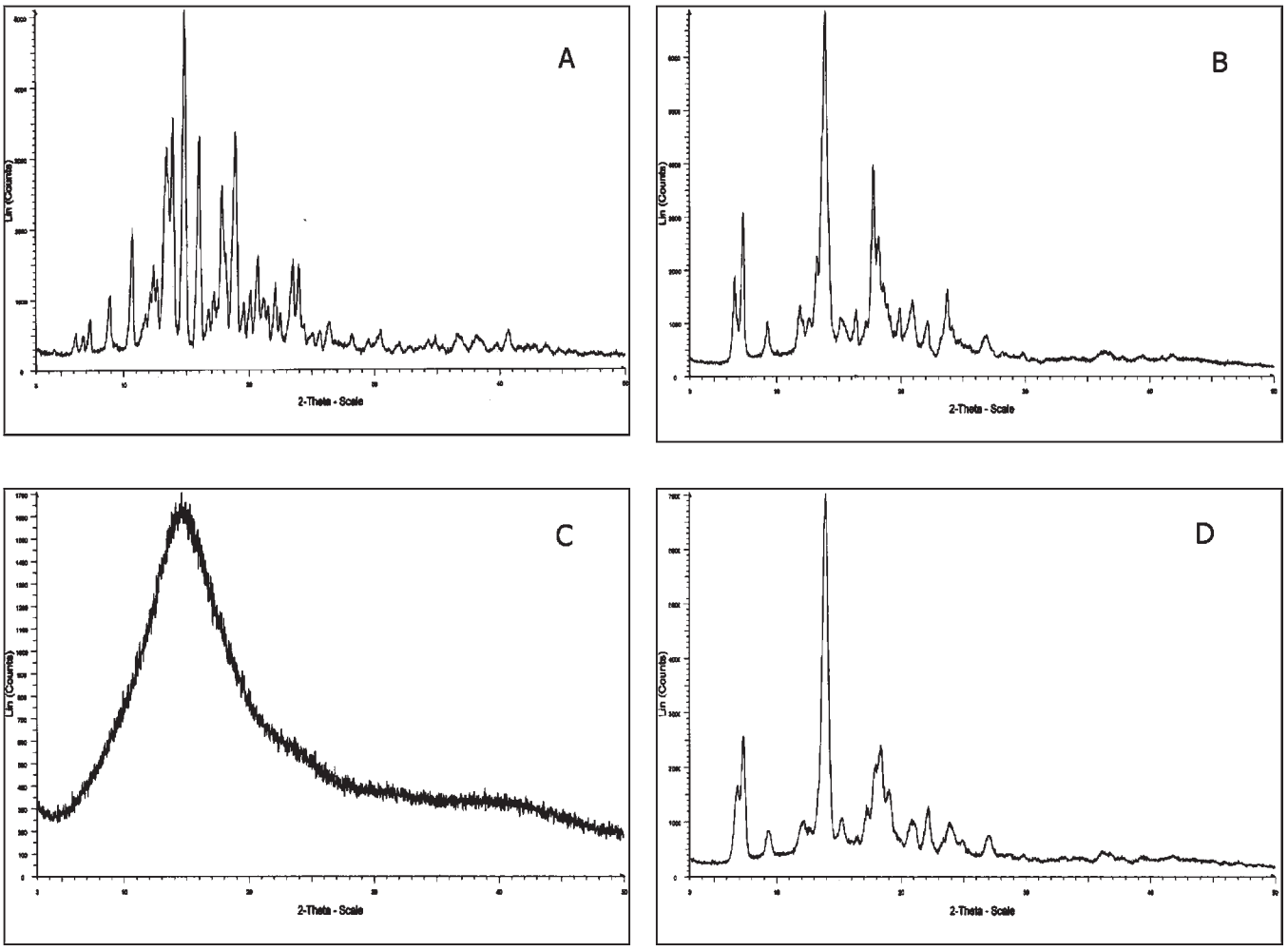

Figure 3. X-ray powder diffraction (XRPD) pattern of DCA as crystalline form (**A**) and relative inclusion compound (**B**), DCA amorphous form (**C**), and relative inclusion compound (**D**).

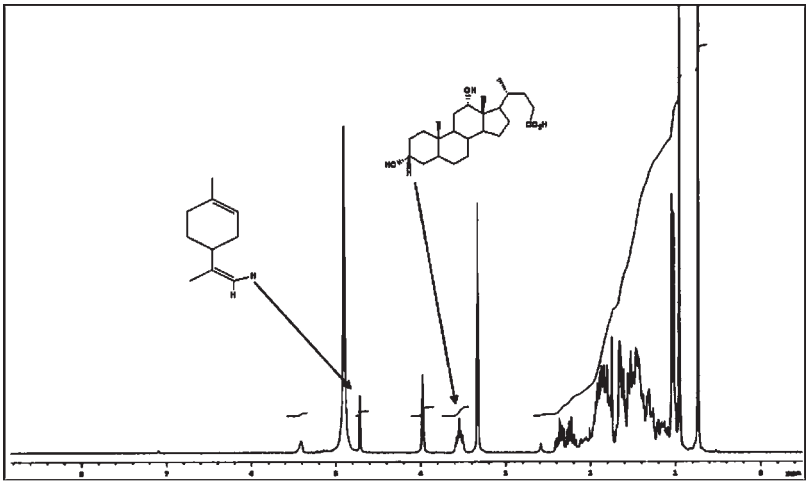

Figure 4. ^{1}H NMR of inclusion compound DCA·MTs.

cycles. Finally, the solution enriched in OCs was evaporated under vacuum, without heating, giving 1.7 g of partially deterpenated bergamot oil (**Table 1**).

If the selectivity of DCA toward limonene is maintained over the whole concentration range, the inclusion methodology enables, in principle, the removal of MTs from bergamot oil only after a few consecutive inclusion cycles.

This consideration has led us to investigate the selectivity of DCA host in competition experiments between the two main components of citrus oil, limonene and linalool.

These experiments were carried out using mixtures of the two guests by varying their mole fraction from 0 to 1 and keeping the total guest/host ratio at 15:1. The results are shown in **Figure 1**, where X represents the mole fraction of the limonene guest in the

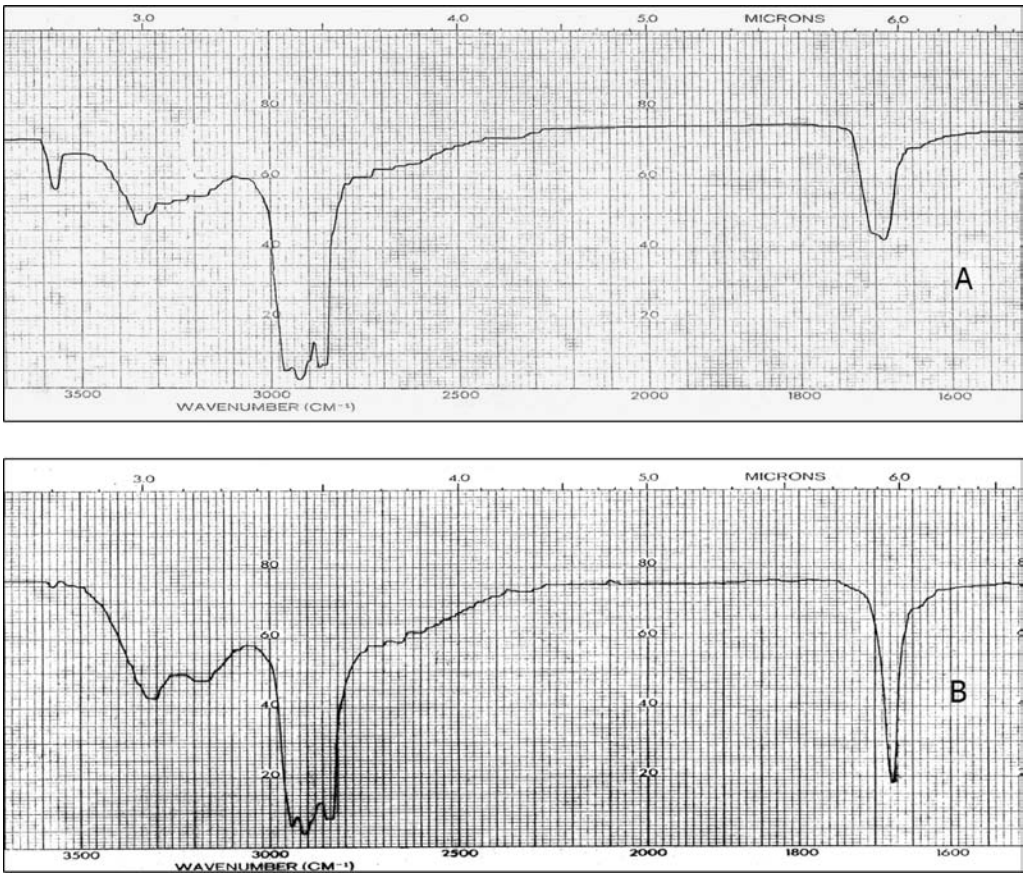

Figure 5. IR spectra of the DCA (**A**) and of the DCA·MTs (**B**).

initial solution and Z that of the same guest entrapped in the crystals. The diagonal line represent zero selectivity. From this graph it can be seen that the DCA includes preferentially the limonene over the whole concentration range.

Thus, a second inclusion cycle carried out on the partially deterpenated bergamot oil from the first cycle confirmed the expected results, that is, a lowering of the limonene percentage from 24.6 to 10.9% . The composition of the genuine bergamot oil compared to the composition of the partially deterpenated oil after one and two cycles is listed in **Table 1**.

The dependence of the inclusion phenomenon with the structure of the host was proved by comparing the results obtained using crystalline DCA with those of a batch of DCA having an amorphous structure. The results were exactly the same in the two cases, proving the independence of the host−guest inclusion complexation from the solid state structure of DCA.

PHYSICOCHEMICAL CHARACTERIZATION OF THE INCLUSION COMPOUND

Thermal Analysis: TG and DSC Analyses. DSC and TG collected for the pure DCA and for the inclusion compound are shown in **Figure 2**. DCA showed a single endothermic peak due to melt at 176 °C (DSC trace A) without mass loss (TG trace B), whereas the same analyses run on the inclusion compound showed, in addition to the melting peak at 172 °C, a new endothermic transition at 167 °C (DSC trace C) with concomitant 6.5% mass loss (TG trace D) associated with the release of the guest. The lowering of the melting point upon inclusion is due to the guest, which represents a kind of impurity for pure DCA. The host/guest ratio, calculated from TG analysis, corresponded to 5:1 stoichiometry, in good agreement with the value obtained from ^{1}H NMR analysis (see below).

XRPD Analyses. In **Figure 3** are reported the XRDP traces of DCA with and without guests. In particular, pattern **A** refers to DCA crystalline form, pattern **C** to DCA amorphous form, and patterns **B** and **D** to those of their respective inclusion compounds. The **B** and **D** diffraction patterns are identical, having the same number of peaks at the same θ angle values; trace **D** is only less resolved. This implies that a unique crystalline assembly of the inclusion derivative was obtained even starting from two different forms of DCA.

Quantification of Host−Guest Stoichiometry by ^{1}H NMR. The inclusion derivative was dissolved in methanol-d_4 and examined by ^{1}H NMR (**Figure 4**). The host/guest ratio, calculated from proton integration of the signals at 3.78 ppm (H-3β of DCA) and 4.70 ppm ($H_2C=$ of limonene), corresponded to a 4.5:1 stoichiometry (DCA/limonene), in good agreement with the value obtained from TG analysis (see above).

IR. The IR spectra of "empty" DCA **1** shows, among others, four distinctive absorptions at 1680 and 1710 cm^{-1} in the region of carbonyl stretching and at 3330 and 3570 cm^{-1} in the region of hydroxyl stretching. Otherwise, the IR spectrum of the inclusion derivative presents, in these regions, only two absorption peaks, shifted at 1675 cm^{-1} and at 3330 cm^{-1} (**Figure 5**). The changes in the absorption wavenumber of the hydroxyl and carbonyl moieties mean that the guest induces remarkable alterations in the host hydrogen-bonding networks.

In conclusion, we have developed a new approach for removing monoterpene components from bergamot essential oil via selective inclusion in solid deoxycholic acid as host.

The formation of the inclusion compound has been confirmed by means of XPDR, DSC, TG, NMR, and IR. Operational simplicity, mild conditions, and reuse of the host are the key features of the presented methodology. Further investigation is

underway to extend the host−guest inclusion methodology to other essential oils to improve their quality as well as to isolate single components.

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