ABSTRACT: In this work, the use of plant-derived raw materials, such as terpenes, gives great strength from a sustainability perspective and enables dealing with the biocarbonate concept. Biocarbonates are produced only from CO$_2$ and residues or bio-derived compounds, describing cycloaddition reactions that couple CO$_2$ and a terpene, the latter after epoxidation, avoiding environmental charges from petroleum-derived epoxides. In this work, a comprehensive database (derived from 30 terpenes) accounting bioepoxides and corresponding biocarbonates was developed, by means of molecular simulation. Optimized structures realized by the DFT method allow using a priori tools to scan the possible applications of this new class of sustainable solvents. Using a COnductor-like Screening Model for Realistic Solvents, different biocarbonates were evaluated for their physical properties and capacity to remove value-added or contaminant solutes from aqueous mixtures, namely, furfural, phenolic compounds, and volatile fatty acids. It was found that biocarbonates derived from terpenes generally present a higher affinity for solutes in comparison with neat terpenes. Indeed, biocarbonates allowed achieving the recovery of 99% of phenol, 98% of furfural, and 87% of acetic acid, also pointing to an advantageous scenario of higher boiling points and densities and comparable solvent losses in the aqueous phase to terpenes.

KEYWORDS: biocarbonate, terpene, COSMO-RS, CO$_2$ conversion, liquid−liquid extraction
furfural or volatile fatty acids (VFAs). Terpenes are natural solvents of plant origin with outstanding technical and chemical properties. Therefore, terpenes can be considered a renewable, ecological, and economical raw material. Therefore, terpenes could be successful substitutes for petroleum solvents, such as dichloromethane, toluene, or hexane, for the extraction of several solutes, even emerging applications in the extraction of natural products. These green natural products can be transformed into novel and valuable compounds used to produce fragrances, perfumes, or pharmaceuticals, as well as into useful synthetic intermediates. More recently, terpenes have been presented as a sustainable alternative to fix CO$_2$ and produce cyclic carbonates, enabling the biocarbonate concept. It requires a prior intermediate step where terpene in the presence of an oxidizing agent generates a terpene oxide (epoxide). This epoxide is capable, in the presence of a suitable catalyst, to react with CO$_2$ in a cycloaddition reaction to produce biocarbonates in a similar way to other petroleum-derived epoxides.

Biosolvents are emerging compounds of different nature that aim at addressing green and sustainable principles in the solvent formulation. There are different options in the literature such as biomass-derived compounds (i.e., furfural, lactic acid, and their derivatives, glycerol, and its derivatives), carbohydrates, terpenes, ionic liquids, and natural eutectic solvents, among others. Hydrophobic biosolvents stand as relevant to water treatments, replacing VOCs, methyl isobutyl ketone, or ethyl acetate. The role of this new class of hydrophobic biosolvents emerges interestingly and synergistically by contributing to the CO$_2$ circular economy.

The objective of this work is to enable the development of biocarbonates through a CONductor-like Screening Model (COSMO) and guide the terpene selection from both physical properties and extractive property points of view. First, the design of a database of bioepoxides (30) and biocarbonates (30) derived from terpenes and CO$_2$ is done by DFT molecular simulations. This is found to be essential in the literature due to the lack of synthesized and characterized species, namely, limonene carbonate, pine carbonate, myrcene carbonate, terpinen-4-ol carbonate, or carvone carbonate. Second, the physical properties of the biocarbonates and the corresponding terpenes were cross-evaluated by using predictions of a COSMO for Realistic Solvents (COSMO-RS), as well as by determining how they are influenced by adding one or more CO$_2$ groups in the chemical structure, in looking for solvents that provide a more efficient CO$_2$ consumption. Third, these biocarbonates have been tested in applications in which terpenes have been proven to be effective extractors of common solutes from water to phenolic compounds, furfural, 

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**Scheme 1. Possible Biocarbonates That Can Be Formed from Limonene and Geraniol**

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[Diagram of biocarbonates from limonene and geraniol]
and VFAs, which is accomplished by means of activity coefficients at infinite dilution and liquid–liquid extraction calculations driven also by the COSMO-RS. The COSMO-RS is a trustable and valid method to predict the use of potential biocarbonates because it was massively validated for the same terpene–solute systems, providing an adequate qualitative and quantitative image that helps select the most appropriate terpene for each application. Because the carbonate group is equivalent to other functional groups that massively covered screening terpenes, it is reasonable to find acceptable COSMO-RS predictions for these new biosolvents.

**COMPUTATIONAL DETAILS**

**Molecular Geometry Optimization.** Turbomole 7.4 software with the COSMO continuous solvation method was used to optimize the structure of all the compounds (terpenes: 30, bioepoxides: 32, and biocarbonates: 41) to its minimum energy state with BP86/TZVP computational levels using the solvent effect. The structures of all the bioepoxides and biocarbonates employed are shown in Tables S1 and S2, based on the terpene structure. As shown in Scheme 1, the oxidation of the terpene takes place at the double bond of the molecule in the corresponding terpene, where an oxygen atom is attached to each of the carbons. In the presence of a catalyst, this bond is opened for the cycloaddition of CO₂ and forms a cyclic carbonate. Although the most typical structures of the terpenes in Scheme 1 resulting from the epoxidation process are limonene oxide (LimoneneEO) and geraniol oxide (GeraniolEO), the fact that they have two different double bonds makes the formation of different carbonates and opens up the option to study how the site of cycloaddition or the presence of two cyclic carbonate groups in the same molecule would influence their properties. Only double-bonded terpenes were chosen for this study.

**Properties of Biocarbonates Derived from Terpenes.** The *.cosmo file obtained from Turbomole software was used to predict the different thermodynamic properties of the pure compounds in COSMOtherm v. 19 software. This software employs COSMO-RS for thermodynamic calculations. The properties computed were the octanol–water partition coefficients in wet octanol, normal boiling point, density, and molecular weight of the terpenes and their respective biocarbonates.

**Activity Coefficient Calculation with COSMO-RS.** Using COSMOtherm v. 19 software, the activity coefficients at infinite dilution at 298 K of solutes, phenols (phenol, 2-chlorophenol, 2-nitrophenol), bisphenol A, furfural, and VFAs (acetic acid, propionic acid, butyric acid, and valeric acid), in the different terpenes and their respective biocarbonates were calculated to compare the efficiency between the different compounds as solvents. It has been previously shown that the predictions of COSMO-RS for the calculations of activity coefficients with terpenes reasonably agreed with the experimental data. The *.cosmo files for the solutes not found in the COSMOtherm database were created following the same methodology as the biocarbonates.

**Liquid–Liquid Extraction Calculation with COSMO-RS.** A “liquid extraction” calculation for phenol, furfural, and acetic acid was performed using COSMOtherm software. The first phase (S) containing pure solvent (terpene or derived carbonate) was specified, while the second phase (F; 1 kg) consisted of the desired solute in water at a concentration based on the literature (0.5 mg/mL for phenol, 10 mg/mL for furfural, and 2 mg/mL for acetic acid). Two S/F (0.5 and 2) mass ratios were studied by changing the total mass of the S phase. The extraction yield (Yld) of the solutes was calculated as described in eq 1.

\[
Yld(\%) = \frac{C_{\text{i,F}} - C_{\text{i,S}}}{C_{\text{i,S}}} \cdot 100
\]

where \(C_{\text{i,S}}\) is the initial concentration of solute i in the aqueous phase and \(C_{\text{i,F}}\) is the concentration of solute i in the aqueous phase after the extraction.

**RESULTS AND DISCUSSION**

**Database of Carbonates and Epoxides and Their Physical Properties.** After modeling the optimized structure of several conventional terpenes (selecting 10 representatives of the whole behavior as a reference shown in Table 1, while the remaining 20 are shown in Table S1), the structures of bioepoxides and biocarbonates derived from these terpenes were modeled (listed in Tables 1 and S1, S2). As explained above, for the terpenes with various double bonds, there are numerous biocarbonate/bioepoxide possible structures; thus, geraniol and limonene are selected as a reference to observe

| Table 1. Structure of the Main Terpenes and Their Corresponding Biocarbonate |
|-----------------|-----------------|
| Terpene         | Biocarbonate    |
| 3-Carene        |                 |
| Citronellal     |                 |
| Eugenol         |                 |
| Geraniol        |                 |
| Limonene        |                 |
| Linalool        |                 |
| Phellandrene    |                 |
| Alpha-pinene    |                 |
| Beta-pinene     |                 |
| Thymol          |                 |
how the position and number of the carbonate substituents influence on the properties of the compounds. Once these structures have been optimized, octanol–water coefficient ($K_{ow}$), boiling point, and density of terpenes and corresponding biocarbonates are predicted by means of COSMO-RS calculations.

As seen in Figure 1, terpenes exhibit a higher $K_{ow}$ value than biocarbonates ($500–18,000$ for terpenes against $8–100$ for carbonates). This indicates that, even though both types of compounds present a hydrophobic behavior, biocarbonates present higher polarity than terpenes, implying lower hydrophobicity despite the increase in the molecular size. Moving to boiling points (Figure 1), the addition of carbonate groups to terpenes implies remarkably lower volatility because boiling points of terpenes range between $160$ and $290$ °C while those of biocarbonates range between $380$ and $540$ °C. Finally, biocarbonates show higher densities and molecular weights than terpenes, as seen in Figure 2. In general, carbonate’s density is higher than water and approximately $25–35\%$ higher than that of terpenes.

The implications of these changes in the properties of carbonates with respect to terpenes are clear when employed in a liquid–liquid extraction to remove solutes from aqueous solution: (i) the higher affinity for water of the biocarbonates implies greater solvent losses in the water-rich phase than using terpenes; (ii) the increase in the boiling point helps biocarbonates to enhance the regeneration step in comparison with terpenes, allowing to design more sustainable systems; and (iii) the higher density of biocarbonates than water’s suggests that in a LLE the biocarbonate-rich phase would settle as the bottom layer, while when using terpenes, the solvent-rich phase would be the upper layer. To this respect, biocarbonates are the most beneficial in these operations as they are enhanced by working with more dense solvents due to mixing, mass transfer, and phase splitting processes.

Regarding the influence of adding more carbonate groups and their positioning, Figure S4 shows the $K_{ow}$, boiling point, densities, and molecular weights for limonene, geraniol, and their possible derivatives. As seen in Figure S1A, the hydrophobicity decreases with the addition of functional groups: using limonene as a reference, the terpene is the most hydrophobic compound (limonene), followed by the carbonates (carbonateC1 and limoneneC2), then the ones with one carbonate group (limoneneC1 and limoneneC2E1), and finally the one with two carbonate groups (limoneneC1C2). As seen in Figure S1B,C, the boiling points, molecular weights, and densities follow the opposite trend: adding more carbonate (or epoxide) groups increases the value of the three variables ($K_{ow}$ > limoneneC1E2 > limoneneC2E1 > limoneneC1C2 > limoneneC2 > limonene). This behavior is the same in the four studied properties for geraniol as for limonene.

Regarding melting points, they cannot be easily estimated by COSMO-RS but the addition of polar groups, from the terpene structure to the biocarbonate one, can be quickly linked to an increase in the melting and boiling points, the latter predicted and discussed above. Available biocarbonates

![Figure 1. Octanol–water partition coefficient at infinite dilution of selected terpenes (striped bars) and their corresponding biocarbonate (solid bars) calculated by COSMO-RS at 298 K and boiling point (bp) of selected terpenes (striped line) and their corresponding biocarbonate (solid line) calculated by COSMO-RS at 1 atm.](image)

![Figure 2. Density against molar weight of the main terpenes (blue) and their corresponding biocarbonate (orange) calculated by COSMO-RS at 298 K.](image)
are liquids, namely, limonene carbonate and pinene carbonate, but carbonates derived from terpenes with higher melting points could be solids at room temperature, depending on the self-interaction promotion or not by adding new polar groups. The uncertainty in this issue; however, opens three different routes to use biocarbonates in water treatment: (i) liquid−liquid extraction from room temperature to optimal temperatures considering conditioning of regenerated solvent (above room temperature due to the solvent boiling point); (ii) liquid−liquid extraction from the melting point of the terpene to optimal temperature considering conditioning of the regenerated solvent (greater because the solvent boiling point will be above the melting point); and (iii) enabling lower temperatures in the extraction step by creating biocarbonate-based eutectic solvents to increase the liquid range of use.

Activity Coefficient Screening. After having evaluated the properties of terpene-derived carbonates, their suitability as solvents for the extraction of compounds of interest from water is analyzed using the activity coefficient at infinite dilution of the solute in these solvents, a reference thermodynamic parameter. Figure 3 reports the activity coefficient for phenol, 2-nitrophenol, 2-chlorophenol, and bisphenol A in the 10 selected terpenes and their corresponding biocarbonates. As seen, terpenes exhibit diverse values for the activity coefficient for all solutes, ranging from low (ln\(\gamma\) ≈ −5) to great values (ln\(\gamma\) ≈ +7). However, the derived carbonates always present a favorable interaction with these solutes, that is, the logarithm of the activity coefficient is negative in all cases, which suggests high extraction yields. Moreover, for both carbonates and terpenes, the solvent−solute interaction is not strongly influenced by the different phenolic compounds: when the interaction is favorable, it is generally favorable for the four solutes and vice versa. It can be observed that there are certain terpenes for which the solute−solute interaction is unfavorable, such as alpha-pinene, 3-carene, or beta-pinene, while their corresponding carbonates present a favorable interaction, which consequently establishes these carbonates as good candidates for the substitution of these terpenes. On the other hand, there are terpenes, such as geraniol or linalool, for which both the terpene and corresponding carbonate show a favorable interaction with the solutes, so that although carbonates appear more favorable than terpenes, it is not a significant improvement. Therefore, it is concluded that there are certain terpenes whose performance in the extraction of these solutes could be greatly improved by the addition of carbonate groups, but the extent of this improvement depends on the terpene, as can be seen in Figure S2 in Supporting Information for a more extended terpene database. In addition, generally, bisphenol A and 2-nitrophenol show greater improvements of the activity coefficients in biocarbonates with respect to terpenes, while 2-chlorophenol’s activity coefficients in terpenes or biocarbonates are the most similar.

Next, the activity coefficients of furfural in the selected terpenes and their derived biocarbonates are shown in Figure 4. It is observed that except for eugenol and thymol, the remaining terpenes show an unfavorable interaction with furfural (positive values of ln\(\gamma\)). In the case of biocarbonates, generally, they present remarkably more favorable solute−solute interaction than terpenes, except for eugenol and thymol. It follows that, except in cases where the interaction of terpene with furfural is favorable (ln\(\gamma\) < 0), biocarbonates are expected to perform better as extracting solvents than the corresponding terpenes. However, it is worth noting that biocarbonates show less affinity for furfural (ln \(\gamma\) ≈ −0.3 to...
respectively. As seen, in the case of limonene, the addition of carbonate or epoxide functional groups, are studied and derivatives, depending on the quantity or positioning of acetic acid in limonene, geraniol, and their possible carbonate derivates. As a result of the addition of an epoxide group and a carbonate group is the most favorable option (limoneneC2E1 or limoneneC1E2), due to the increased hydrogen bond acceptor (HBA) character of the molecules, as can be seen in the \( \gamma \)-profiles collected in Figure S8B of Supporting Information. In the case of geraniol, for phenol and acetic acid, the picture is the same: the higher HBA character of geraniolC1 (Figure S8C in Supporting Information) improves the affinity for the solutes with respect to the terpene, while the other alternative biocarbonates present lower affinity with the solutes. In the case of furfural, compared to terpene, all possible carbonates improve the affinity, with geraniolC1C2 showing the most affinity to furfural, due to its both acceptor and donor characters.

**Liquid—Liquid Extraction Analysis.** Once the solute—solvent interactions have been preliminary analyzed, a study of the solute extraction from water using terpenes and biocarbonates is carried out by COSMO-RS. Figure 6 collects phenol, furfural, and acetic acid extraction yields, in selected terpenes and their derived biocarbonates. As expected, a higher S/F mass ratio benefits the extraction of solutes in every case. Attending to terpene performance, alpha-pinene, 3-carene, beta-pinene, phellandrene, and limonene exhibit a low extraction yield for both S/F ratios and with the three solutes, while the corresponding biocarbonates, eugenol, citronellal, linalool, geraniol, and thymol, exhibit high extraction yields with both S/F. As observed, solute extraction with terpenes of this first group is always improved by the addition of carbonate groups. Thus, the addition of a carbonate group is highly recommended in the extraction of these solutes for this group of terpenes, while it is not too relevant for the rest.

In the case of phenol (Figure 6A), biocarbonates show a homogeneous behavior independently of the S/F ratio, ranging from 82 to 96% for a S/F = 0.5 and almost a complete recovery of phenol (>95%) for a S/F = 2 when using any carbonate. The differences in the extraction yield between different terpenes and different carbonates are anticipated in Figure 3, given that the terpenes and carbonates presenting the best extraction yields are those with the lowest activity coefficients and vice versa.

Moving to furfural (Figure 6B), the behavior is not as homogeneous as with phenol and the extraction yields are...
Table 2. Thymol, Geraniol, Thymol-Derived Biocarbonate, and Geraniol-Derived Biocarbonate Losses in the Water-Rich Phase for an S/F Mass Ratio of 2 with Different Solutes

<table>
<thead>
<tr>
<th>Solutes</th>
<th>Terpene Losses (%)</th>
<th>Biocarbonate Losses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

CONCLUSIONS

In this work, a database of terpene-derived biocarbonates with optimized molecular structures has been successfully created. It has been evidenced, by COSMO-RS computational analysis, that the addition of carbonate groups to terpenes causes an increase in polarity, density (obtaining higher values than water), and boiling temperature. These biocarbonates have also been tested in the separation of compounds of different natures from water: such as phenolic compounds, VFAs, or furfural, which are relevant in the removal of pollutants or recovery of value-added compounds’ current studies. Their performance in these separations has been compared with that of the original terpenes from which they are derived, by means of activity coefficients at infinite dilution and extraction yields. Biocarbonates have demonstrated great potential as solvents, being a competitive alternative to terpenes in the extraction of these solutes from water, reaching high extraction yields (87–99%). Therefore, the use of terpene-derived biocarbonates is a sustainable way of employing captured CO₂ with useful applications, even improving the performance of terpenes in some cases. It has been found that biocarbonate losses in water can be slightly higher than terpenes’ ones, related to lower K_{ow} values; however, environmental compatibility of terpenes and biocarbonates derived from terpenes smoothens this negative drawback, comparable or even better solvent performance, and an easier regeneration due to higher boiling points of biocarbonates in comparison with terpenes.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c02993.

Structure of terpenes, bioepoxides, and biocarbonates; terpene and biocarbonate losses in water in the extraction of phenol, acetic acid, and furfural; octanol–water partition coefficient, boiling point, density, and molecular weight of biocarbonates derived from limonene and geraniol; predicted activity coefficients of furfural, phenols, and VFAs in terpenes and biocarbonates; and sigma profiles of biocarbonates derived from limonene and geraniol (PDF).

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Notes

The authors declare no competing financial interest.

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