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## Fluorocarbons as solvents for thin-layer chromatographic analysis*

In a previous publication[1] we reported that fluorocarbons exhibit unusual properties when used as chromatographic solvents. For example, both a perfluoroalkane mixture and a mixture described as perfluorokerosene separated the sesquiterpene hydrocarbons (C15) from the monoterpene hydrocarbons (C10) on thin layers of Aluminum Oxide G. Under the conditions of the analysis the monoterpenes did not leave the origin. On the other hand, hydrocarbon solvents moved both the C10 and C15 terpenes but did not separate them. Consequently, the fluorocarbons appear more non-polar in their chromatographic behavior than the hydrocarbons.

To determine if other fluorocarbons exhibit this same behavior, samples of four additional aliphatic fluorocarbons and chlorofluorocarbons, and three aromatic

TABLE I

$R_F$ VALUES OF REPRESENTATIVE TERPENES ON SILICA GEL G LAYERS USING AROMATIC SOLVENTS

| *Compound* | *Class of compound* | $R_F$ | | | |
|---|---|---|---|---|---|
| | | *Benzene* | *Fluoro-benzene* | *Penta-fluoro-benzene* | *Hexa-fluoro-benzene* |
| *p*-Isopropenyltoluene | Aromatic hydrocarbon | 0.98 | 0.98 | 0.92 | 0.94 |
| Valencene | Sesquiterpene hydrocarbon | 0.98 | 0.95 | 0.93 | 0.92 |
| Thymyl methyl ether | Aromatic ether | 0.92 | 0.93 | 0.86 | 0.83 |
| Citronellal | Aldehyde | 0.65 | 0.64 | 0.43 | 0.33 |
| Linalyl acetate | Ester | 0.56 | 0.53 | 0.37 | 0.30 |
| Citral | Aldehyde | 0.34 | 0.35 | 0.28 | 0.22 |
| Linalool | Alcohol | 0.26 | 0.23 | 0.14 | 0.12 |
| α-Terpineol | Alcohol | 0.15 | 0.13 | 0.10 | 0.07 |

* Cooperative research by the Florida Citrus Commission and the Florida Citrus Experiment Station.

TABLE II

$R_F$ VALUES OF REPRESENTATIVE TERPENE HYDROCARBONS ON ALUMINUM OXIDE G LAYERS USING FLUOROCARBON SOLVENTS

| *Terpene* | *Class of terpene* | $R_F$ | | |
|---|---|---|---|---|
| | | *Perfluoro-methyl cyclohexane* | *Perfluoro-n-hexane* | *Hexane** |
| Ylangene | Sesquiterpene | 0.86 | 0.84 | 0.96 |
| Cedrene | Sesquiterpene | 0.74 | 0.63 | 0.96 |
| β-Caryophyllene | Sesquiterpene | 0.56 | 0.48 | 0.94 |
| γ-Bisabolene | Sesquiterpene | 0.44 | 0.26 | 0.93 |
| α-Humulene | Sesquiterpene | 0.24 | 0.16 | 0.90 |
| *d*-Limonene | Monoterpene | 0.00 | 0.00 | 0.93 |
| Terpinolene | Monoterpene | 0.00 | 0.00 | 0.92 |
| γ-Terpinene | Monoterpene | 0.00 | 0.00 | 0.93 |
| Sabinene | Monoterpene | 0.00 | 0.00 | 0.93 |

* Data reported in a previous publication.

fluorocarbons were studied. These were perfluoromethylcyclohexane, perfluoro-*n*-hexane, 2,3-dichlorooctafluorobutane, 1,2-dichlorohexafluorocyclo-1-pentene, hexafluorobenzene, pentafluorobenzene, and fluorobenzene.

## *Experimental*

Chromatoplates were 8 × 8 or 2 × 8 in. with layers of Silica Gel G or Aluminum Oxide G. Silica Gel was preferred for all solvents except perfluoromethylcyclohexane and perfluoro-*n*-hexane which gave best results with Aluminum Oxide. The detection spray was vanillin–$H_2SO_4$ as described earlier[2].

Perfluoromethylcyclohexane, hexafluorobenzene, and pentafluorobenzene were obtained from Imperial Smelting Corporation Ltd., Bristol, England, while perfluoro-*n*-hexane, 2,3-dichlorooctafluorobutane, 1,2-dichlorohexafluorocyclo-1-pentene, and fluorobenzene were obtained from Peninsular ChemResearch, Inc., Gainesville, Florida.

## *Results and discussion*

Fluorination of benzene produced compounds which were only slightly more chromatographically non-polar than benzene itself as shown in Table I. Although the $R_F$ values using hexafluorobenzene were significantly different for oxygenated terpenes compared to those obtained using benzene alone, the chromatographic difference was slight when compared to that between hexane and perfluorohexane (Table II). In the latter case the completely fluorinated alkane separated the monoterpenes from the sesquiterpenes on Aluminum Oxide, whereas the hydrocarbon made no separation even on Silica Gel. Further study showed that substitution of even a small percentage of the fluorines by chlorines destroyed this property. Dichlorooctafluorobutane and dichlorohexafluorocyclopentene showed chromatographic properties more like those of the hydrocarbons than the perfluorocarbons (Table III).

In summary, complete fluorination of an aliphatic hydrocarbon produces a solvent whose chromatographic properties are greatly different from the non-fluorinated parent compound. However, substitution of chlorine for fluorine almost comple-

TABLE III

$R_F$ VALUES OF REPRESENTATIVE TERPENES ON SILICA GEL G LAYERS USING CHLOROFLUOROCARBON SOLVENTS

| Compound | Class of compound | $R_F$ | |
|---|---|---|---|
| | | *2,3-Dichloro-octafluoro-butane* | *1,2-Dichloro-hexafluoro-cyclo-1-pentene* |
| *p*-Isopropenyltoluene | Aromatic hydrocarbon | 0.65 | 0.85 |
| Valencene | Sesquiterpene Hydrocarbon | 0.78 | 0.90 |
| Thymyl methyl ether | Aromatic ether | 0.33 | 0.62 |
| Citronellal | Aldehyde | 0.04 | 0.15 |
| Linalyl acetate | Ester | 0.03 | 0.09 |
| Citral | Aldehyde | 0.00 | 0.05 |
| Linalool | Alcohol | 0.00 | 0.03 |
| Cedrene | Sesquiterpene hydrocarbon | 0.98 | — |
| β-Caryophyllene | Sesquiterpene hydrocarbon | 0.70 | — |
| γ-Bisabolene | Sesquiterpene hydrocarbon | 0.65 | — |
| α-Humulene | Sesquiterpene hydrocarbon | 0.60 | — |
| *d*-Limonene | Monoterpene hydrocarbon | 0.77 | — |
| Terpinolene | Monoterpene hydrocarbon | 0.81 | — |
| γ-Terpinene | Monoterpene hydrocarbon | 0.81 | — |
| Sabinene | Monoterpene hydrocarbon | 0.81 | — |

tely restores the original hydrocarbon properties. Complete fluorination of an aromatic hydrocarbon produces a solvent with chromatographic properties fairly similar to those of the parent compound.

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*Florida Citrus Commission, Lake Alfred, Fla. (U.S.A.)*

JOHN A. ATTAWAY

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