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# Adducts Formation at Fullerenes $C_{60}$ and $C_{70}$ Dissolution in Essential Oils

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**Abstract—**It was established by the method HPLC-MS with electrospray ionization that in solutions of fullerenes $C_{60}$ and $C_{70}$ in some essential oils a chemical reaction occurred leading to adducts of fullerenes with unsaturated terpenes. In the course of time the quantity of the adduct in solution increased and a component originating from addition of two molecules of terpene to a molecule of fullerene is formed. This can be the reason of abnormally high solubility of light fullerenes in mixtures of terpene hydrocarbons.

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Solubility of fullerenes in organic solvents attracts attention both due to its theoretical interest (determination of thermodynamic characteristics and prediction of retention data in the chromatographic analysis [1, 2]) and practical opportunities of applying these solutions. A number of studies was carried out up till now investigating various theoretical aspects of solubility of light fullerenes and their mixtures in pure or mixed solvents [1–5]. Among the practical applications of fullerenes cosmetology, pharmacology, and medicine should be mentioned. For this reason the selection of solvents for fullerenes introduction in cosmetic, pharmaceutical, and medical complex mixtures should be regarded as a challenge.

It is well known that aromatic hydrocarbons and their derivatives (toluene, *o*-xylene, and chlorobenzenes) [3, 6] are efficient solvents of light fullerenes $C_{60}$ and $C_{70}$. Solubility of fullerenes and their mixtures in oils had been studied [4, 5]. The application of these solutions is of certain potential in cosmetology [7, 8] and pharmacology [9]. These processes require monitoring, hence building devices for calibration of measuring instruments for such monitoring [10]. For the safety reasons the most desirable solvents of fullerenes for medical and pharmaceutical purposes are those of natural oils i.e., of animal and plant origin.

In the studies on the solubility of light fullerenes in certain plant and essential oils (olive, sunflower, juniper, clove, etc.) [5] it is presumed in explicit or implicit form that the solutions of fullerenes are true ones. In many cases of application of traditional solvents such statement is correct, though in some instances the solvent acts not entirely as a solution medium. Due to relatively high reactivity of fullerenes [6] it is impossible to rule out the likelihood of chemical processes between fullerenes and thea solvent or its components. This is particularly true in the case of applying complex mixtures like fats, essential oils etc. Just this phenomenon we detected in the course of development of standard samples of fullerenes solutions in oils.

We prepared solutions of fullerenes in some essential oils (tangerine, lemon, orange, clove, rosemary, lavender, eucalyptus) and subjected them to HPLC and HPLC-MS procedures to determine their qualitative composition. Mass chromatograms of fullerene $C_{60}$ solutions in essential oils are presented in Fig. 1.

The mass chromatograms of fullerene $C_{60}$ solutions in essential oils besides the peak characteristic of genuine fullerene $C_{60}$ (*m*/*z* 720), contain also the peaks *m*/*z* (720 + 136) and *m*/*z* (720 + 136 + 136). Similar data are registered also for the solutions of fullerene $C_{70}$: $C_{70}$ (*m*/*z* 840), and satellite components *m*/*z* (840 + 136), (840 + 136 + 136).

Based on the fact that the majority of terpenes are components of the essential oils under study (pinenes,

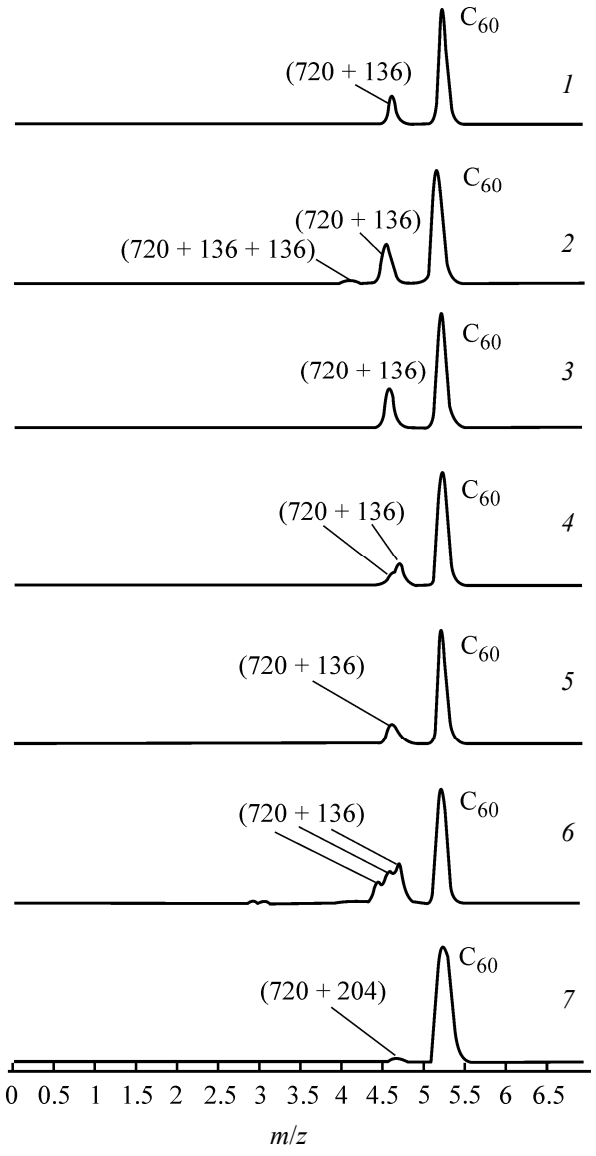



**Fig. 1.** ESI-Mass chromatograms of fullerenes $C_{60}$ solutions in (*1*) tangerine, (*2*) lemon, (*3*) orange, (*4*) rosemary, (*5*) lavender, (*6*) eucalyptus, and (*7*) clove oils. Chromatographic conditions are presented in Experimantal.

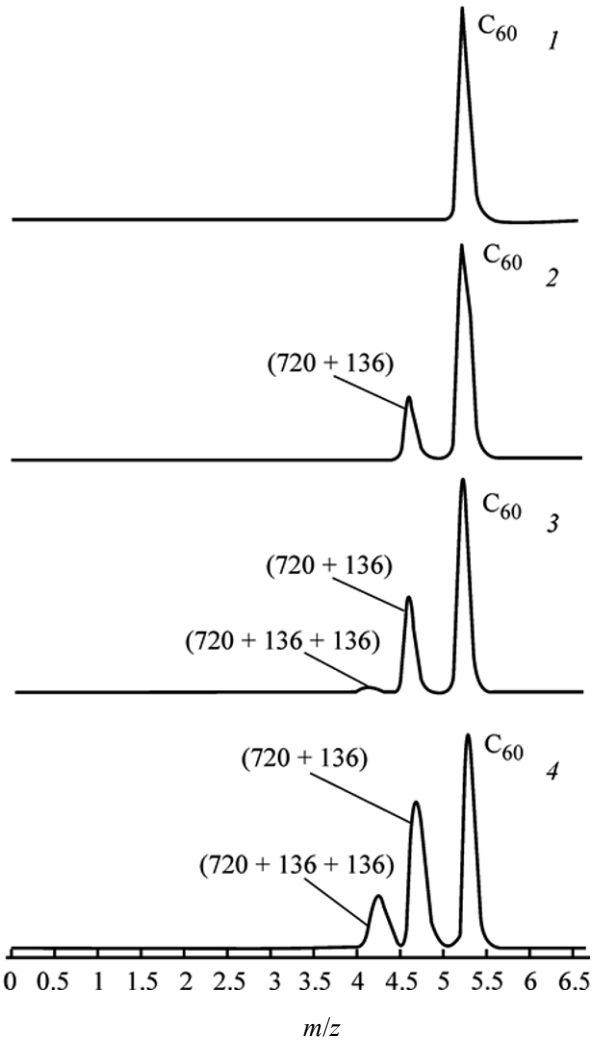


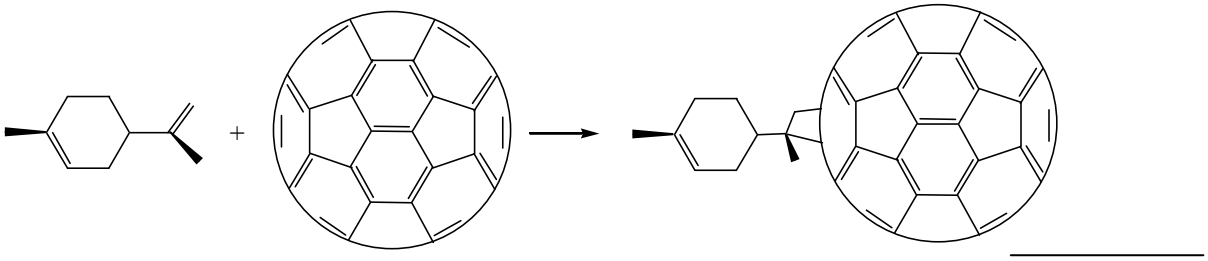

**Fig. 2.** ESI-Mass chromatograms of fullerenes $C_{60}$ solutions in (*1*) α-pinene, (*2*) β-pinene, (*3*) limonene, and (*4*) limonene after 1 week. Chromatographic conditions are presented in Experimantal.

limonene, myrcene, phellandrene, carene etc.) characterized by molecular mass 136, it is possible to suggest that in the course of dissolving fullerene in essential oil fullerenes molecules react with hydrocarbons of terpene series. The chromatogram of the solution of fullerene $C_{60}$ in clove oil exhibited a peak *m*/*z* (720 + 204) that corresponded to the adduct with caryophyllene $C_{15}H_{24}$ (*M* 204) which is a component of the clove oil.

The probability of the reaction of fullerenes with components of essential oils was confirmed by dissolving fullerene $C_{60}$ in individual pure terpenes limonene, α- and β-pinenes (Fig. 2). Upon dissolving $C_{60}$ in α-pinene the reaction is not observed whereas the chromatograms of its solutions in limonene and β-pinene are similar to those registered for the solutions of $C_{60}$ in essential oils. Moreover, the chromatograms of solutions of $C_{60}$ in limonene registered after a week

of storage exhibited higher content of mono and bis adducts of limonene. Mass spectra of the products of reaction of fullerene $C_{60}$ with limonene are presented in Fig. 3.

Taking in consideration the essential oils composition [11, 12] it is possible to state the fact of the reaction of fullerenes with unsaturated terpenes that contain the terminal double bond. This assumption is justified by the behavior of fullerene $C_{60}$ in isomeric pinenes. The chromatogram of α-pinene solution showed only the peak of fullerene and in β-pinene the adduct peak was also registered. This reaction could proceed by the mechanism of photocatalytic [2+2] radical cycloaddition.



Adducts formation was observed only for the essential oils containing unsaturated terpenes either limonene and β-pinenes [*M* + 136] or caryophyllene [*M* + 204]. Hence, dissolution of fullerenes in some essential oils was accompanied by the cycloaddition and the solutions formed strictly speaking were not pure solutions of fullerene. This effect should be taken in consideration in the studies of biological activity of compositions containing fullerenes as well as in the estimation of conditions and time of storage followed by application of such mixtures.

## EXPERIMENTAL

In this study fullerenes used were of State Standard Specimens grade: $C_{60}$ ($C_{60}$-VNIIM-99.9 with fullerene content $C_{60}$ 99.8%) and $C_{70}$ ($C_{70}$-VNIIM-99.9 with fullerene content $C_{70}$ 99.6%). Solutions of $C_{60}$ and $C_{70}$ in essential oils were prepared without heating, treatment with ultrasound in other specific conditions.

The solutions were analyzed by HPLC-MS with electrospray ionization, spectrometer Agilent Triple Quard LC/MS 6460. Separation was performed on a column YMC-Pack Pro C18, 120A, 4.6×150 mm under isocratic conditions, eluent toluene-methanol (55 : 45), flow rate 0.8 $cm^3$/min. The peaks were registered as negatively charged ions upon scanning the full range spectrum, width 500-1500 Da. The fragmentor voltage was 380 V, spraying gas ($N_2$) temperature 350°C, drying gas ($N_2$) temperature 350°C, spraying gas flow rate 10 $dm^3$/min, drying gas flow rate 12 $dm^3$/min.

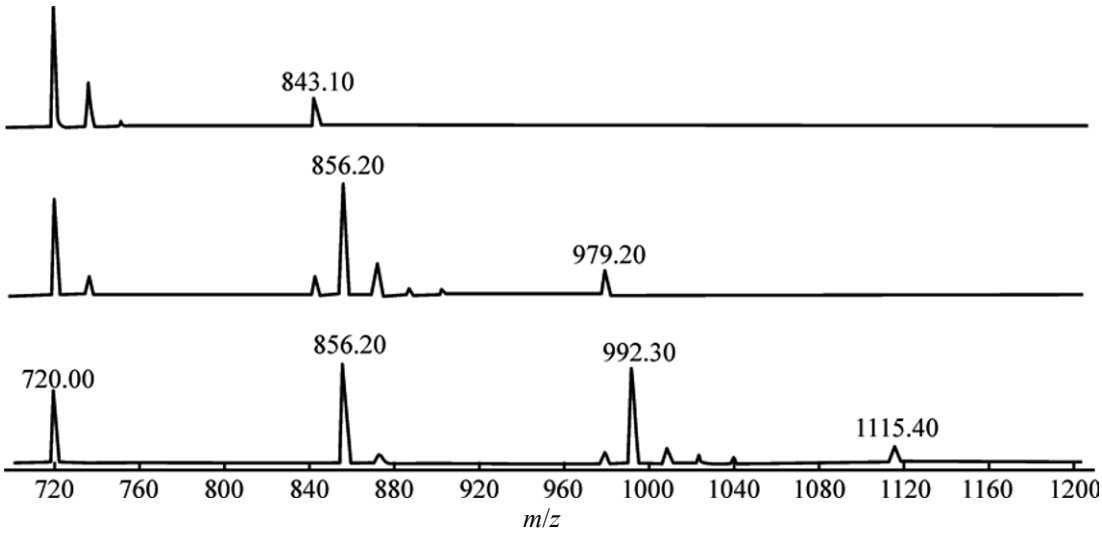



**Fig. 3**. Mass spectra (ESI) of components of solutions of fullerene $C_{60}$ in limonene. (*1*) Fullerene $C_{60}$; (*2*) fullerene $C_{60}$ adduct and limonene; (*3*) fullerene $C_{60}$ adduct and 2 molecules of limonene.

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