Journal of Molecular Structure 1021 (2012) 112–117

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Enrofloxacinium citrate monohydrate: Preparation, crystal structure, thermal stability and IR-characterization

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HIGHLIGHTS

- Novel pharmaceutical salt $EnrH_2^+ \cdot H_3HCit^- \cdot H_2O$ has been synthesized.
- X-ray single crystal investigation reveals a layered structure.
- The importance of inter- and intramolecular interactions in crystal formation has been shown.

ARTICLE INFO

Article history:
Received 6 February 2012
Received in revised form 18 April 2012
Accepted 19 April 2012
Available online 25 April 2012

Keywords:
Enrofloxacin
Citric acid
Crystal structure
IR spectra
Thermal analysis

ABSTRACT

Enrofloxacinium citrate monohydrate (**I**), $C_{19}H_{23}FN_3O_3^+ \cdot C_6H_7O_7^- \cdot H_2O$, [$C_{19}H_{22}FN_3O_3$ – enrofloxacin, EnrH] has been crystallized from the mutual solution of citric acid and enrofloxacin in ambient conditions. The colorless crystals have been investigated using X-ray single crystal and powder techniques, and characterized by differential scanning calorimetry, thermogravimetry and infrared spectroscopy. The obtained compound can be considered as a salt with enrofloxacinium in the role of a cation and citrate as an anion. The ions ratio equals to 1:1. The compound crystallizes in the triclinic lattice with $a = 9.0489(8)$ Å, $b = 9.6531(8)$ Å, $c = 14.913(1)$ Å, $\alpha = 98.813(1)°$, $\beta = 92.029(1)°$, $\gamma = 91.013(1)°$, $Z = 2$, $V = 1286.1(2)$ Å^3, S.G. $P\bar{1}$. The crystal structure determination reveals the importance of inter- and intramolecular interactions in the crystal formation. The $EnrH_2^+$ and H_3Cit^- molecular ions are packed in alternating layers with water molecules inserted into the citrate layers. A citrate ion in the layer is linked via H-bondings with two adjacent ones and three water molecules. Enrofloxacinium cations are packaged by means of a benched mode and every cation is linked by three intermolecular thymus type H-bondings with nitrogens of adjacent cations and by two links with the oxygen of the citrate ions. The infrared spectra gave the evidence of H-bonding formation in the obtained salt. The π-stacking interactions are observed between the aromatic cycles of the adjacent cations which are located in an antiparallel style in a layer.

1. Introduction

The synthesis and design of multicomponent crystals from active pharmaceutical ingredients (APIs) has attracted considerable attention in recent years [1]. As an alternative to the extensively used common inorganic salts the preparation of organic salts has recently been suggested. APIs in the form of organic crystals are generally more preferable because of higher solubility that has been shown to improve therapeutic utility while reducing side effects [2–4].

Fluoroquinolone antibiotics display a wide spectrum of antibacterial activity. Enrofloxacin, $C_{19}H_{22}FN_3O_3$ [1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate, EnrH] (Fig. 1) is a member of the fluoroquinolone series. It widely used as a veterinary drug and for the treatment of uncomplicated and complicated urinary tract infections, pyelonephritis, sexually transmitted diseases, prostatitis, skin and tissue infections, and urethral and cervical gonococcal infections [5]. It has been proposed that fluoroquinolones bioavailability can be limited by both solubility and permeability [6]. Low solubility and bitter taste are the unfavorable properties associated with most of fluoroquinolones which limit their formulation [7]. So, it has been realized as a challenging task to develop API products improving their solubility without compromising performance. Indeed, a widely accepted

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http://dx.doi.org/10.1016/j.molstruc.2012.04.059

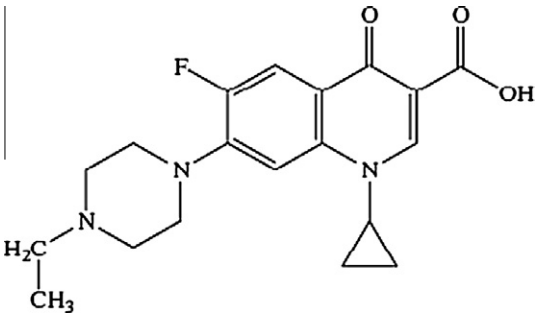

Fig. 1. Molecular structure of enrofloxacin.

approach to overcome API poor solubility is its preparation in the salt form. Citric acid can be considered as a complementary component for the salt formation. It is widely used in pharmaceutical preparations thus providing enhanced aqueous dissolution and bioavailability. It can improve the physical properties of active APIs such as solubility, hygroscopicity, stability, fluidity, filterability, density, and taste.

To the best of our knowledge there are only four compounds contain enrofloxacin as a moiety investigated by X-ray crystal structure analysis: all compounds OH—CH_2—$CH_2NH_3^+Enr^-$ [8], [Cu(1,10-Phenanthroline) EnrCl]. $4H_2O$, [Cu(2,2′-Bipy)(H_2O) $EnrCl^-$]·0.5Bipy·$6H_2O$ [9], Bipy – bipyridine, $[Zn(Py)_2(Enr)_2]CH_3OH·6H_2O$ [10], contain enrofloxacin as an anion Enr^-. There are no data describing structures where enrofloxacin is in the role of $EnrH_2^+$ cation.

2. Experimental section

2.1. Chemical and reagents

Enrofloxacin $C_{19}H_{22}FN_3O_3$, with ⩾98.0% of purity was purchased from Fluka, Citric acid $C_6H_8O_7$ was analytical grade from Acros. All the chemicals were used as received without any further purification.

2.2. Synthesis

The enrofloxacinium citrate monohydrate was prepared by mixing 2 mL of an aqueous solution containing 106 mg (0.56 mmol) of citric acid and 200 mg (0.56 mmol) of enrofloxacin. Colorless crystals precipitated after 5 days of solution ageing in ambient conditions. The crystals were separated from the solution by filtering and washed by a small amount of water. The product output was about 65% The chemical analysis was carried out with the C,H,N-analyser: EURO EA Elemental Analyser. The elemental analysis for $C_{25}H_{32}FN_3O_{11}$: Calc.: C, 52.72%; H, 5.66% N, 7.38%; Found: C, 52.24%; H, 5.85%; N, 7.28%.

2.3. Physical measurements

X-ray powder diffraction data were obtained using the diffractoctometer X'Pert PRO (PANalytical) equipped by a PIXcel detector with a graphite monochromator, Cu Kα radiation was applied. The sample was grinded in an agate mortar and prepared in a standard cuvette by the direct loading. The scanning conditions were following the range from 3° to 90° on 2θ, with a step of 0.013°, Δt −50 s/point. The interpretation of X-ray power patterns was sxmade using ICDD-PDF2 data base [11] and indexing softwear described in [12,13].

For single crystal investigation a crystal of 0.21 × 0.43 × 0.48 mm dimensions was chosen. The intensities were collected using SMART APEX II X-ray single crystal diffractometer (Bruker AXS) with a CCD-detector, graphite monochromated and Mo Kα-radiation. The absorption corrections were applied using the SADABS program [14] via the multi-scan method. The structure was solved using the direct methods SHELXS and refined in anisotropic approach for non-hydrogen atoms using the SHELXTL program [15]. The hydrogen atoms were located by the difference electron density maps. All the hydrogen atoms connected with the carbon atoms were refined in a constrained mode, all the other were refined as independent ones. The experimental data and the refinement conditions are listed in Table 1. The supramolecular π–π interactions in the structure were analyzed using PLATON program [16]. The crystallographic data are deposited in Cambridge Crystallographic Data Centre (CCDC #824500) [17].

Table 1
The crystal data of $C_{19}H_{23}FN_3O_3^+ \cdot C_6H_7O_7^- \cdot H_2O$.

Formula moiety	$C_{25}H_{32}FN_3O_{11}$
Molecular weight	569.54
Temperature (κ)	298
Space group	$P\bar{1}$
Z	2
a, b, c (Å)	9.0489(8), 9.6531(8), 14.913(1)
α, β, γ (°)	98.813(1), 92.029(1), 91.013(1)
V (Å^3)	1286.1(2)
ρ_{calc} (g/cm^3)	1.471
μ (mm^{-1})	0.12
F_{000}	600
Reflections measured	10,336
Reflections independent	5027
Reflections with $F > 4\sigma_F$	3216
$2\theta_{max}$ (°)	52
h, k, l – limits	$-11 \leqslant h \leqslant 11$; $-11 \leqslant k \leqslant 11$; $-18 \leqslant l \leqslant 18$
Refinement results	
The weighted refinement of F^2	$w = [\sigma^2 + (0.0558P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
Number of refinement parameters	386
$R1$ $[F_o > 4\sigma(F_o)]$	0.0461
$wR2$	0.1229
GooF	1.019
$(\Delta\rho)_{max}$ (e/Å^3)	0.23
$(\Delta\rho)_{min}$ (e/Å^3)	−0.19
$(\Delta/\sigma)_{max}$	0.000

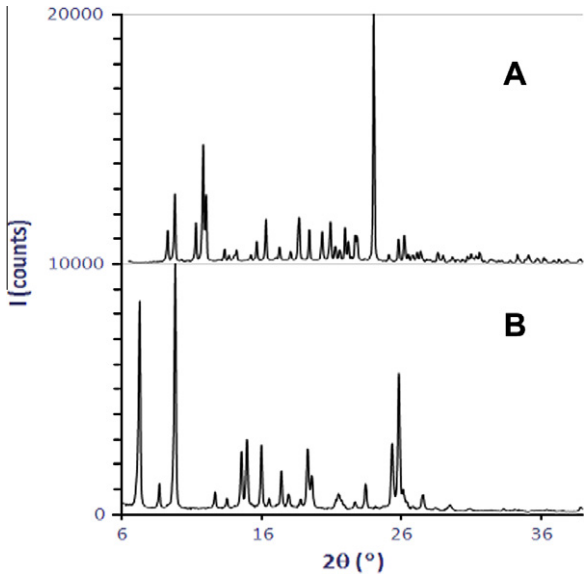

Fig. 2. X-ray powder patterns: (A) for the salt $EnrH_2^+H_3Cit^-$, (B) enrofloxacin.

The infrared spectra were recorded on a Bruker Vector-22 Fourier spectrometer in the range of 400–4000 cm^{-1}. The samples were prepared in the form of tablets 3 mm of thickness. Dry KBr was used as the filling material. It was shown by X-ray diffraction analysis that there was no chemical reaction of the compounds with KBr.

Thermal analysis was carried out using STA-449 Jupiter (Netzsch) in the temperature range 40–650 °C, in argon atmosphere with the gas flow of 30 mL/min. The substance was loaded into a platinum crucible in the amount of 5 mg. The heating rate was 10 °C/min.

3. Results and discussion

If an acidic and basic species are put together in a solution the expected crystallized form from such a solution would be a salt, a co-crystal formation, or a mixture of compounds crystallized separately. In this work it is shown that in the case of enrofloxacin $C_{19}H_{22}FN_3O_3$ (EnrH) and citric acid $C_6H_8O_7$ (H_4Cit) a new salt $EnrH_2^+H_3Cit^-$ (**I**) can be obtained. Fig. 2 presents X-ray powder patterns of the bulk samples of the starting compound enrofloxacin and the obtained salt. It confirms that the product is an individual compound without any impurities including enrofloxacin and citric acid in the amounts detectable by this technique. The enrofloxacin unit cell parameters determined from X-ray powder data were: a = 18.340 Å, b = 7.032 Å, c = 14.217 Å, β = 100.47°, Z = 4, V = 1802 Å^3, S.G. $P2_1/n$. The salt (**I**) was found to crystallize in the triclinic lattice with the unit cell parameters: a = 9.041 Å, b = 9.643 Å, c = 14.905 Å, α = 98.79°, β = 87.98°, γ = 88.89°, Z = 2, V = 1283 Å^3, S.G. $P\bar{1}$. These data were further confirmed by X-ray single crystal investigation (Table 1).

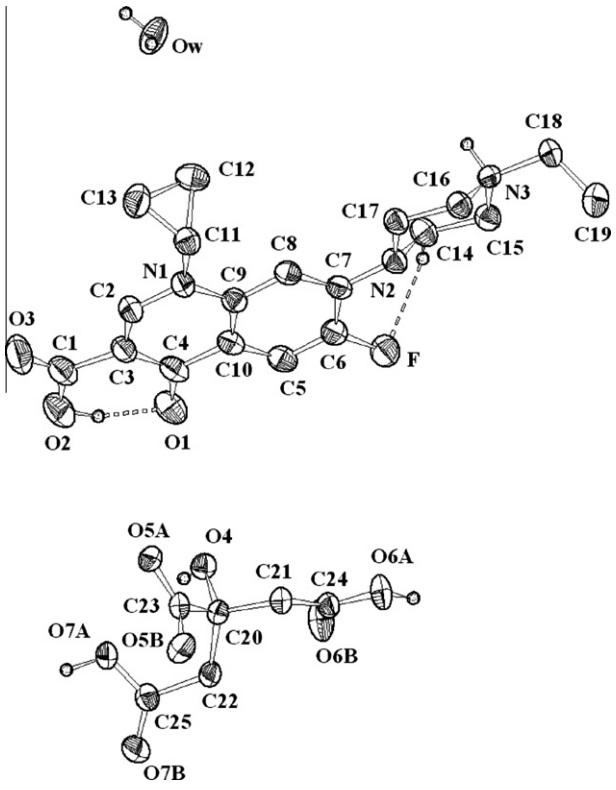

Fig. 3. ORTEP view of the (**I**) crystal structure. Ellipsoids are drawn at the 50% probability level, except for hydrogen atoms which are represented by circles of arbitrary radius.

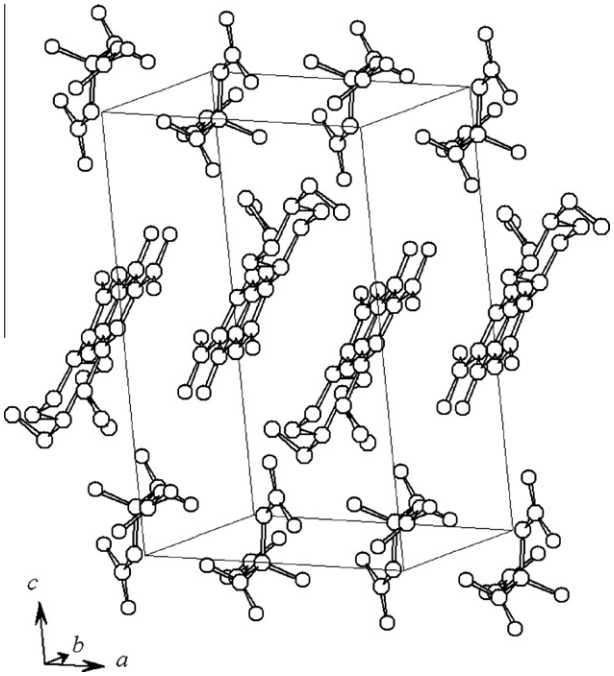

Fig. 4. A packing diagram for salt (**I**). H atoms and O atom of water have been omitted for clarity.

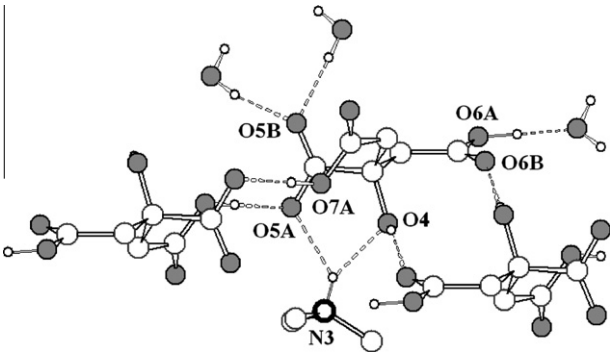

Fig. 5. The H-bonds of H_3Cit^- ion with neighbouring ions and with water molecules. Oxygen atoms are dark. Only N3 atom of$EnrH_2^+$ ion is presented with its environment.

The crystal structure of (**I**) determined by X-ray single crystal diffraction technique is presented in Fig. 3. The molecular unit consists of $EnrH_2^+$ and H_3Cit^- ions and one water molecule. The molecular cycles of C5—C6—C7—C8—C9—C10 (cycle 1) and N1—C2—C3—C4—C10—C9 (cycle 2) of the $EnrH_2^+$ ion possess a planar conformation, while the N2—C14—C15—N3—C16—C17 cycle adopts a chair conformation. The $EnrH_2^+$ and H_3Cit^- ions are packed in alternate specified layers parallel to the ***ab*** crystal plane (Fig. 4), and water molecules are located into the H_3Cit^- layers. As a result every H_3Cit^- ion in the layer is connected with two neighboring ones via four H-bonds of O—H···O type and with three water molecules via three H-bonds of the same type. The intermolecular H-bonding of H_3Cit^- ions (Fig. 5) presents two supramolecular homosynthons $R_2^2(8)$ and $R_2^2(12)$. Every $EnrH_2^+$ ion has only one intermolecular H-bond of thymus type between the N3 atom and two oxygen atoms of the H_3Cit^- ion (Fig. 5, Table 2), forming a 5-membered supramolecular heterosynthon, *viz.* $R_1^2(5)$. It was found that the N3 atom of the piperazine ring in enrofloxacin was protonated. It is consistent with the results obtained earlier in [11]. The intramolecular hydrogen bond O2—H2···O1 with

Table 2
Hydrogen-bond geometry (Å, °).

D—H	d(D—H)	d(H···A)	∠ DHA	d(D···A)	A	Transformation for A atom
N3—H3	0.91	2.09	144	2.881(2)	O4	$1-x, 1-y, 1-z$
N3—H3	0.91	2.12	134	2.834(2)	O5A	$1-x, 1-y, 1-z$
O2—H2	0.94(3)	1.65(3)	157(2)	2.540(3)	O1	
O6A—HO6A	1.03(3)	1.55(3)	176(3)	2.579(3)	OW	$1-x, 1-y, 1-z$
O4—HO4	0.79(3)	2.02(3)	156(3)	2.761(3)	O6B	$1-x, 1-y, 2-z$
O7A—HO7A	0.98(3)	1.65(3)	168(3)	2.611(3)	O5A	$1-x, -y, 2-z$
OW—HW1	0.82(3)	1.92(3)	174(3)	2.741(3)	O5B	$1+x, y, z-1$
OW—HW2	0.86(3)	1.92(3)	168(3)	2.768(3)	O5B	$1-x, -y, 1-z$
C14—H14B	0.97	2.25	124	2.908(3)	F	

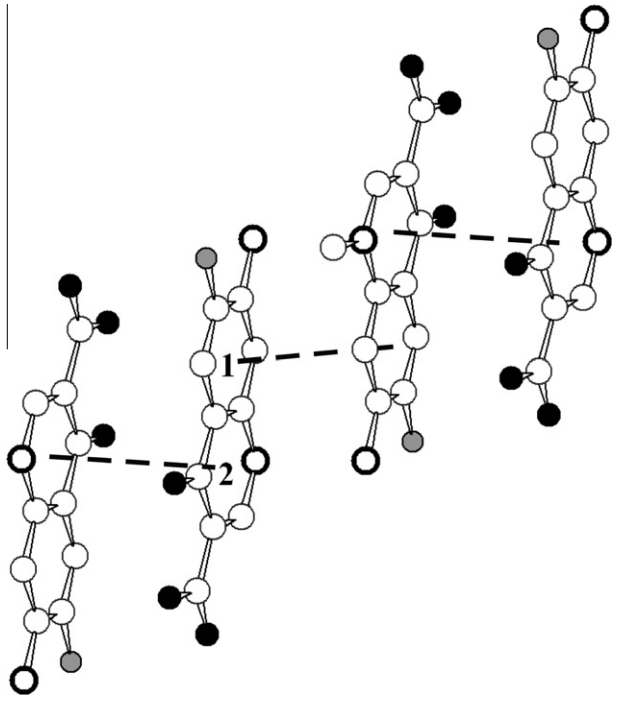

Fig. 6. The antiparallel stacking of $EnrH_2^+$ ions with π–π interaction between cycles. Only 1 and 2 cycles with nearest environment are shown, dotted lines connect interacting cycles. Black circles are oxygen, darken circles are fluorine, thick circuits are nitrogen atoms.

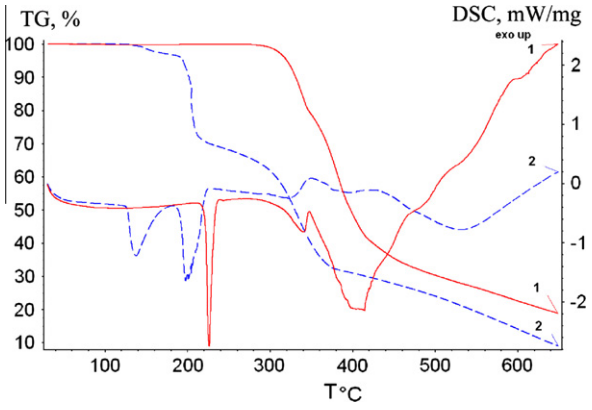

Fig. 7. TG and DSC curve for enrofloxacin (1) and enrofloxacinium citrate monohydrate (2).

O2···O1 distance 2.540(3) and intermolecular hydrogen bond O6A—H···OW with O6A···OW distance 2.579(3) can be classified as almost strong [18]. This intramolecular H-bond close up a 6-membered supramolecular synthon, S(6). Other hydrogen bonds can be classified as medium to weak interactions. There is C14—H···F, an intramolecular hydrogen bond, also forming a 6-membered supramolecular synthon, S(6).

All $EnrH_2^+$ ions in a layer are located antiparallel one to another with a supramolecular π–π interaction between cycles number 1 and the same interactions between cycles number 2 of the neighbouring ions (Fig. 6). As a result the $EnrH_2^+$ ions are packaged by means of a benched mode. Some parameters of the π–π interaction of the $EnrH_2^+$ are presented in the Table 3.

Salts and co-crystals are multicomponent crystals that can be distinguished by the location of the proton. The proton transfer spectrum is observable for a salt. On contrary, co-crystals do not present a proton transfer. The formation of a salt is usually provided if a pK_a difference between an acid and conjugate base is more than 3.0. Recently it has been found for enrofloxacin $pK_{a1} = 5.94 \pm 0.09$ [19] and for H_4Cit $pK_{a1} = 3.13$ [20]. It is well established that for any fluoroquinolone pK_{a1} corresponds to the carboxylic acid group [5]. However, pK_a values describe equilibrium phenomena in a solution and are not meant to be applied to the solid state. Both the acid and base strengths and the crystalline environment determine the extent of the proton transfer.

The distances O3—C1 and O2—C1 in the carboxylic group of $EnrH_2^+$ are equal to 1.203(3) Å and 1.335(3) Å, correspondently. It indicates that the first one is a double and the second is a single C—O bond. The similar distances O5A—C23 and O5B—C23 in H_3Cit equaled to 1.252(2) Å and 1.255(2) Å corresponding to the deprotonated carboxylic group. In the crystal structure, citric acid transfers one H^+ ion to enrofloxacin. The site of H^+ location is the carboxylic oxygen O2. Other bond distances and angles for compound (**I**) are in agreement with the corresponding values from

Table 3
Some parameters of π–π interaction between $EnrH_2^+$ molecular ions in a crystal of (**I**). The interacting molecules united with the inversion centre.

Cg_i—Cg_j	d(Cg—Cg) (Å)	α (°)	β (°)	γ (°)	Cg_i_p	Cg_j_p	Shift (Å)
Cg_1—Cg_1	3.911(1)	0	21.56	21.56	3.6378(8)	3.6378(7)	1.437
Cg_2—Cg_2	3.671(1)	0	13.85	13.85	−3.5641(8)	−3.5641(7)	0.879

Cg_1 is the C5, C6, C7, C8, C9, C10 ring; Cg_2 is the N1, C2, C3, C4, C10, C9 ring. d(Cg—Cg) – distance between ring centroids. α – dihedral angle between planes i and j. β – angle between Cg_i—Cg_j or Cg_i—Me vector and normal to plane i. γ – angle between Cg_i—Cg_j vector and normal to plane j.
Cg_i_p – perpendicular distance of Cg_i on ring j. Cg_j_p – perpendicular distance of Cg_j on ring i.
Shift – distance between Cg_i and perpendicular projection of Cg_j on ring i.

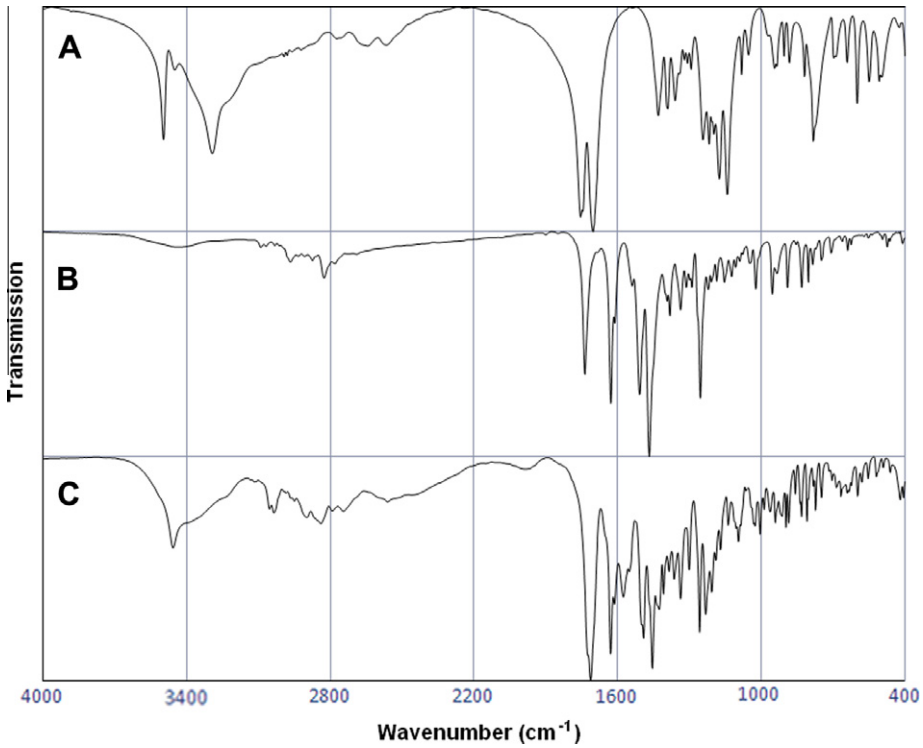

Fig. 8. IR- spectra of (**I**) (C) in comparison with enrofloxacin (B) and citric acid monohydrate (A).

the literature [17]. These data evidence that compound (**I**) is the salt $EnrH_2^+ \cdot H_3Cit^- \cdot H_2O$.

The TG and DSC curves of enrofloxacin and enrofloxacinium citrate monohydrate are presented in Fig. 7. The thermal behavior of the discussed substances gives additional evidence about its individual nature. The DSC of the enrofloxacin exhibits a strong endotherm at 230 °C, corresponding to its melting point (onset 222.3 °C), followed by exotherms at 340 °C and 400 °C ascribed to drug decomposition. The measured melting enthalpy is about 90.75(5) J/g. Its pyrolytic decomposition begins at 310 °C and well corresponds to the data presented in [21]. TG analysis shows that the dehydration process of the salt (**I**) goes in the temperature range from 120 °C to 185 °C. A strong endothermic peak in the DSC curve at 127.4 °C shows the maximum of dehydration process. The weight change (estimated −3.27% and calculated −3.35%) corresponds to the lost of one water molecule. The pyrolysis of compound (**I**) begins at 190 °C and goes further than 650 °C. At least three steps can be separated at TG curve besides dehydration. The sharp step in the range of 200–210 °C is responsible for the decomposition and outlet of citrate anions. It corresponds to the weight lost (~25%) and the previously reported citric acid decomposition data [22]. The second one covers the range 210–380 °C and well repeats the enrofloxacin active decomposition stage discussed in [22]. The last stage presents the low rate carbonization process which continues further than 650 °C.

The IR spectra of fluoroquinolones are quite complex due to the presence of numerous functional groups in the molecules. They are most indicative in the region of 1880–1250 cm^{-1}. In the IR spectrum of EnrH (Fig. 8B) the bands at 1736 cm^{-1} and 1628 cm^{-1} can be assigned to the valence vibration of the carboxylic stretch $\nu(C{=}O)_c$ as ν(COOH) and pyridone stretch $\nu(C{=}O)_p$, respectively [23]. These bands can be distinguished in the spectrum of (**I**) (Fig. 3C). The band at 1755 cm^{-1} in the IR spectrum of citric acid monohydrate (Fig. 8A) which is also attributed to the absorption of the ν(COOH), donates in the range and change the band intensity. The band of citric acid at 1700 cm^{-1} disappeared in the IR spectrum of (**I**) due to the loss of acidic hydrogen atom. This fact is in agreement with the complete proton transfer from H_4Cit to EnrH and the crystal data. The network of hydrogen bond is one of the important factors which influences the positions and intensities of the band ascribed to the vibration of the hydrogen-bonded $(C{-}O)_c$ group of fluoroquinolones [23]. Other strong bands at 1510, 1470 and 1250 cm^{-1} which are characteristics of both EnrH and compound (**I**) can be ascribed to valence vibrations of (C=O), (C—N) and (C—F) bonds correspondently. The broad band of the medium intensity at 3456 cm^{-1} in the IR spectrum of (**I**) is assigned to the OH stretching vibration ν(O—H) for the cell water molecule.

In conclusion, a novel pharmaceutical salt $EnrH_2^+ \cdot H_3HCit^- \cdot H_2O$ was prepared. X-ray single crystal and powder diffraction, differential scanning calorimetry, thermogravimetry analysis and infrared spectroscopy were used for the compound characterization. The results obtained from these techniques are consistent. The product obtained by crystallization from the aqueous solution was the single phase substance. The thermal and X-ray phase analysis showed that the reaction between the precursors was completed and the obtained crystalline salt (**I**) was of high purity. Under hitting condition in the air the salt lost one water molecule at 120 °C, the pyrolysis began at 190 °C and went in three stages. The structure of (**I**) was solved by X-ray single crystal techniques. The $EnrH_2^+$ and H_3Cit^- molecular ions are packed in alternate specified layers and water molecules are located into the H_3Cit^- layers. Every H_3Cit^- ion in the layer is connected with other anions and water molecules via a net of H-bonds. In the crystal structure, citric acid transfers one H^+ ion to the enrofloxacin. All $EnrH_2^+$ cations in a layer are located antiparallel to one another with a supramolecular π–π stacking interaction between the corresponding cycles. It makes a benched mode in $EnrH_2^+$– cation packing. Infrared spectroscopy also gave evidence of the salt formation.

Acknowledgements

The authors are grateful to the Ministry of Education and Science (Government Contracts # 02.740.11.0629) for the financial support of the investigation.

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