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Experimental (FT-IR, FT-Raman, ¹H, ¹³C NMR) and theoretical study of alkali metal syringates

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Influence of alkali metals on the electronic system of the syringic was studied.
- Methods were applied: FT-IR, FT-Raman, and NMR quantummechanical calculations.
- Good correlation between experimental and calculated IR and NMR spectra was noted.
- Aromaticity indices, atomic charges, dipole moments and energies were calculated.

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Introduction

In previous works [1–3] it was observed that the biological activity of benzoic acid derivatives depends on their molecular and electronic structure. Therefore, it may be possible to find compounds with no specific biological activity not by a process of trial and error, but based on strictly described dependencies between the structure and biological activity of compounds.

In the last years growing interest of benzoic acid derivatives as components of the diet is noticed, because these compounds have antioxidant properties, together with polyphenols and ascorbic

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ABSTRACT

In this work the influence of lithium, sodium, potassium, rubidium and cesium on the electronic system of the syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid) was studied. This paper presents spectroscopic vibrations (FT-IR, FT-Raman) and NMR (¹H and ¹³C) study of the series of alkali metal syringates from lithium to cesium syringates. Characteristic shifts of band wavenumbers and changes in band intensities along the metal series were observed. Optimized geometrical structures of the studied compounds were calculated by the B3LYP method using the 6-311++G^{**} basis set. Aromaticity indices, atomic charges, dipole moments and energies were also calculated. The theoretical wavenumbers and intensities of IR and NMR spectra were obtained. The calculated parameters were compared to experimental characteristics of studied compounds.

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acid they protect the body against oxidative stress. Syringic acid is a hydroxylic acid vastly present in edible plants and fruits. In medicine it is used as a sedative and local anesthetic. 4-Hydroxy-3,5-dimethoxybenzoic acid has been demonstrated to exert antioxidant, antiproliferative, anitumor and antiendotoxic properties [4,5]. Phenolic compounds, a group of secondary plant metabolites, are important in the growth and the development of vascular plants. They give color to fruits and flowers, and are responsible for their sour and bitter taste. Syringic acid is one of the compounds included in the plants such as: cinnamon, basil, rosemary, clove, thyme, commonly used as a spice. [6]. An abundant source of syringic and other phenolic acids are cereal seeds, where these compounds locate mainly in the outer plies of grains.

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Iwan et al. investigated properties of lanthanide(III) complexes with 4-hydroxy-3,5-dimethoxybenzoic acid. These compounds were characterized by elemental analysis, IR spectroscopy, X-ray diffraction patterns, solubility, and thermal studies [7]. Belkov et al. measured FT-IR spectra of benzoic, vanillic and syringic acids in CCl₄ solutions and in microcrystals [8]. Features of the formation of intra-and intermolecular hydrogen bonds were analyzed. Mechanisms of the intermolecular interactions are shown to be defined by the character of the substituents attached to the benzene ring in the para- and meta-positions relative to the carboxylic group [8]. Phelps and Young [9] investigated microbial metabolism of the plant phenolic compounds, viz. ferulic and syringic acids under anaerobic conditions. The results of this study indicated that these compounds can be easily decomposed by methanogenic, denitrifying and sulfonic bacterial strains. The effect of some metals on the electronic system of benzoic acid derivatives was investigated and also reported in our earlier papers [10–15].

The influence of alkali metals (lithium, sodium, potassium, rubidium and cesium) on the electronic system of the syringic acid was investigated. In the present work many different analytical methods, which complement one another, were used: FT-IR, FT-Raman, ¹H and ¹³C NMR spectra and quantum mechanical calculations (geometry of the structure, atomic charges, theoretical spectra of IR and NMR). Optimized geometrical structures of studied compounds were calculated by B3LYP method using 6-311++G^{**} basis set. Atomic charges, aromaticity indices, energies and dipole moments were calculated. The calculated parameters were compared to the experimental characteristics of the studied compounds.

Experimental and computational methods

All reagents used were of analytical grade from Sigma–Aldrich. Lithium, sodium, potassium, rubidium and cesium syringates were prepared by dissolving the powder of syringic acid in water solution of the appropriate metal hydroxide in a stoichiometric ratio of 1:1. The mixed solution was left at the 70 °C until the sample crystallized in the solid-state. Then, the remaining solvent was removed by drying in convection dryer at 105 °C for 24 h. Obtained complexes were anhydrous in the IR spectra of solid state samples the lack of bands characterized for crystallizing water was observed. Spectrum was registered after drying.

The FT-IR spectra of 4-hydroxy-3,5-dimethoxybenzoic acid and its salts were recorded with an Equinox 55, BRUKER FT-IR spectrometer. Samples in the solid state were measured in KBr matrix pellets which were obtained with hydraulic press under 739 MPa pressure. Raman spectra of solid samples in capillary tubes were recorded in the range 4000–400 cm⁻¹ with a FT-Raman accessory of the Perkin Elmer System 2000. The resolution of the spectrometer was 1 cm⁻¹. The NMR spectra of DMSO saturated solution were recorded with a NMR AC 200 F, Bruker unit at room temperature. TMS was used as an internal reference.

To calculate the optimized geometrical structures of studied compounds a Density Functional Theory (DFT) in B3LYP/6-311++G(d,p) level was used. Theoretical calculations were performed using the GAUSSIAN 09 [16] package of programs running on a PC computer. The theoretical IR and NMR (¹H and ¹³C) spectra were obtained.

Results and discussion

Vibrational spectra

The wavenumbers, intensities and assignments of the bands occurring in the FT-IR and FT-Raman spectra of syringic acid and synthesized alkali metal syringates are presented in Tables 1 and 2, respectively. Complete assignments of all bands require application of both IR and Raman methods supported by theoretical calculations [16] and literature data [8,9,17]. Bands are numbered along with the notation used by Varsányi [18]. The calculated wavenumbers were obtained by B3LYP method and 6-311++G** basis set. Experimental FT-IR and FT-Raman spectra of syringic acid were recorded and presented in Fig. 2.

Characteristic vibration bands of the carboxylic group are present in the spectra of 4-hydroxy-3,5-dimethoxybenzoic acid. There are very intense, broad stretching bands: v(C=O): 1699 cm⁻¹ (IR), 1698 cm⁻¹ (R), 1771 cm⁻¹ (theoret.), v(C=OH): 1265 cm⁻¹

Table 1

Wavenumbers (cm⁻¹), intensities and assignments of bands occurring in the experimental FT-IR, FT-Raman and theoretical FT-IR spectra of syringic acid. The theoretical wavenumbers were calculated in B3LYP/6-311++C** level.

Syringic ac	ıd				
IR	Calc.		Raman	Assignment	No. ^a
Exp.	Theoret.	Int. _{IR}	Exp.		
3374 vs ^b	3776	100.79		$v^{c}(OH)$	
3248 s	3762	146.30		v(OH) _{ar}	
3084 m	3238	1.73	3084 w	v(CH)	20a
3030 m	3223	2.86	3034 w	v(CH)	20b
2988 w	3193	2.06		v(CH)	
2972 m	3140; 3137	18.02; 20.15	2973 vw	$v_{as}(CH_3)$	
2941 m	3081; 3065	27.68; 35.34	2945 w	$v_{as}(CH_3)$	
2845 m	3018; 3006	44.60; 52.82	2833 vw	$v_s(CH_3)$	
1699 vs	1771	419.15	1698 vs	v(C=0)	
1618 s	1645	161.29		v(CC)	8a
1595 sh	1624	35.13	1594 s	v(CC)	8b
1522 s	1543	116.29	1521 w	v(CC)	19a
1460 vs	1505; 1504	35.77; 42.22	1468 w	$\delta_{as}(CH_3)$	
	1492; 1491	9.94; 10.06	1444 w	$\delta_{as}(CH_3)$	
1420 s	1454	133.28	1424 w	v(CC)	19b
1373 vs	1417	63.87	1371 m	v(CC)	14
1321 s	1489; 1483	63.01; 0.90	1322 m	$\delta_s(CH_3)$	
1265 m	1379	403.56	1261 w	$\nu C - (OH)$	
1246 s			1239 w	v(CH)	2
1206 vs	1329	14.70	1198 s	β(OH)	
	1303	90.50		$\beta(OH)_{ar}$	
	1272	33.46		v(CO)	
	1239	283.62		β(CH)	3
	1211; 1206	4.51; 5.23		$\rho(CH_3)$	
	1171	375.52		β(CH)	9a
	1169; 1168	0.37; 0.89		$\rho(CH_3)$	
	1144	402.02	1154 w	ν Ο –(CH ₃)	
	1116	88.06		β(CH)	18b
1177 vs	1064	4.31		ν Ο –(CH ₃)	
1113 vs	943	5.26	1116 vw	v(CH)	13
1040 m			1033 m	$\delta_{as}(CH_3)$	
908 m	918	26.91	909 w	v(CH)	7b
864 m	877	17.33	882 vw	γ(CH)	11
841 w	865	4.93		γ (CH)	_
804 m	808	23.51	804 m	v(CH)	7a
770 s	810	26.09		$\alpha(CCC)$	12
	763	8.08	50.4	$\gamma(CH)$	5
/3/ W	665	/4.01	/34 vw	$\beta(C=0)$	
689 s	593	6.56	689 W	$\varphi(\mathcal{U})$	4
6/1 m	//6	51.35	676 W	$\gamma(C=0)$	
581 m	580	37.28	581 W	γ(UH)	104
530 W	FF 1	1.00	546 W	$\varphi(\mathbf{CC})$	16D Ch
488 W	551	1.90	490 W	$\alpha(CC)$	6D 160
400 VW	520	42.22		$\psi(\mathbf{C}\mathbf{C})$	104
	407	108.32		γ(OH) _{ar}	

^a Ref. [17,18].

^b s – strong; m – medium; w – weak; v – very.

^c The symbol "v" denotes stretching vibrations. " β " denotes in-plane bending modes. " γ " designates out-of-plane bending modes; " φ (CCC)" denotes the aromatic ring out-of-plane bending modes. and " α (CCC)" designates the aromatic ring in-plane bending modes.

Table 2

Wavenumbers (cm⁻¹), intensities and assignments of bands occurring in the IR and Raman spectra of lithium, sodium, potassium, rubidium and cesium syringates. The theoretical wavenumbers were calculated in B3LYP/6-311++G^{**} level.

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Assignment No.ª	Cs syringate		te	Rb syringate		K syringate				ate	Na syring			e	Li syringat	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		Raman	IR	Raman	IR		Raman		IR		Raman		IR		Raman		IR
3495 s 3769 ^b 130.65 3410 s 3772 124.09 3443 s 3772 124.98 3418 s 3418 s 3447 s 3074 w 3226 4.07 3079 w 3226 6.34 3090 w 3073 w 3226 5.44 3072 w 3073 w 3071 w 3013 vw 3224 1.55 3015 w 2997 w 3225 1.74 2999 w 3011 w 3225 2.53 3014 w 3010 vw 3017 vw 3011 w 3025 w 3001 w 3003 w 2976 w 2974 w 2974 w 2995 vw 3002 w 2998 w 2963 w 3135 21.76 2970 m 3132 24.25 2977 w 2955 w 3132 24.10 2977 w 2976 w 2979 vw 2974 w		Exp.	Exp.	Exp.	Exp.	Exp.	Int. _{IR}	Theoret.	Exp.	Exp.	Int. _{IR}	Theoret.	Exp.	Exp.	Int. _{IR}	Theoret.	Exp.
3074 w 3226 4.07 3079 w 3226 6.34 3090 w 3073 w 3226 5.44 3072 w 3073 w 3071 w 3013 vw 3224 1.55 3015 w 2997 w 3225 1.74 2999 w 3011 w 3225 2.53 3014 w 3010 vw 3017 vw 3011 w 3025 w 3001 w 3003 w 2976 w 2970 m 3132 24.25 2977 w 2955 w 3132 24.10 2977 w 2976 w 2979 vw 2974 w 2963 w 3135 21.76 2970 m 3132 24.25 2977 w 2955 w 3132 24.10 2977 w 2976 w 2979 vw 2974 w	v(OH) ^c _{ar}		3447 s		3418 s		124.98	3772	3443 s		124.09	3772	3410 s		130.65	3769 ^b	3495 s
3013 vw 3224 1.55 3015 w 2997 w 3225 1.74 2999 w 3011 w 3225 2.53 3014 w 3010 vw 3017 vw 3011 w 3025 w 3001 w 3003 w 2976 w 2976 w 2974 w 2995 vw 3002 w 2998 w 2963 w 3135 21.76 2970 m 3132 24.25 2977 w 2955 w 3132 24.10 2977 w 2976 w 2979 vw 2974 w	v(CH) 20a			3071 w	3073 w	3072 w	5.44	3226	3073 w	3090 w	6.34	3226		3079 w	4.07	3226	3074 w
3001 w 3003 w 2976 w 2974 w 2995 vw 3002 w 2998 w 2963 w 3135 21.76 2970 m 3132 24.25 2977 w 2955 w 3132 24.10 2977 w 2976 w 2979 vw 2974 w	v(CH) 20b	3025 w	3011 w	3017 vw	3010 vw	3014 w	2.53	3225	3011 w	2999 w	1.74	3225	2997 w	3015 w	1.55	3224	3013 vw
2963 w 3135 21.76 2970 m 3132 24.25 2977 w 2955 w 3132 24.10 2977 w 2976 w 2979 vw 2974 w	v(CH)	2998 w		3002 w	2995 vw				2974 w				2976 w	3003 w			3001 w
	v _{as} (CH ₃)		2974 w	2979 vw	2976 w	2977 w	24.10	3132	2955 w	2977 w	24.25	3132	2970 m		21.76	3135	2963 w
3132 24.43 3129 26.99 3129 26.88 2020 2020 2020 2020 2020 2020 2020 20			0055	00.40	20.44	00.40	26.88	3129	20.40	2020	26.99	3129	2020	2020	24.43	3132	2022
2938 m 30//6 31.39 2939 w 2938 w 30/3 33.28 2939 w 2940 w 30/3 33.22 2942 w 2941 w 2943 w 2955 w	$V_{as}(CH_3)$		2955 W	2943 w	2941 W	2942 w	33.22	3073	2940 w	2939 w	33.28	3073	2938 w	2939 w	31.39	3076	2938 m
3062 37.72 3059 39.88 3059 39.88 3059 39.80 2012 52.60 2047 m 2047 m 2045 m 2045 m 2046 m 2046 m 2046 m 2046 m		2040	2045	2045	20.42	2047	39.80	3059	2045	2044	39.88	3059	2020	2042	37.72	3062	2020
2839 III 3015 30.12 2842 W 2839 III 3013 33.04 2844 W 2845 W 3013 32.08 2847 W 2843 III 2845 W 2845 W 2840	V _s (CH ₃)	2840 W	2845 W	2845 W	2843 111	2847 W	52.68	3013	2845 W	2844 W	53.04	3013	2839 111	2842 W	50.12	3015	2839 111
	V(CC) 83		1645 sh		1647 m	1656 w	63.83	1651	1684 m		54 12	1651	1686 m		61.56	1650	1661 m
1604 m 1624 19.96 1603 vc 1616 m 1626 12.96 1600 vc 1613 m 1625 13.86 1502 vc 1603 sh 1592 vc 1614 m 1598 vc	v(CC) 8b	1598 vs	1614 m	1592 vs	1603 sh	1592 vs	13.86	1625	1613 m	1600 vs	12.96	1626	1616 m	1603 vs	19.96	1624	1634 m
1054 m 1024 13.00 1050 vs 1015 m 1020 12.00 1000 vs 1015 m 1025 13.00 1352 vs 1015 m 1328 vs 1014 m 1356 vs	v.(COO)	1553 w	1545 vs	1547 w	1578 s	1547 w	307.73	1547	1545 vs	1000 v3	525 11	1555	1560 vs	1005 V3	482.26	1531	1557 vs
150 vs 1546 112 79 1522 w 1520 m 1539 122 41 1518 w 1520 sh 1536 230 95 1534 w 1508 s 1539 w 1520 m	v(CC) 19a	1555 W	1520 m	1539 w	1508 s	1534 w	230.95	1536	1520 sh	1518 w	122.41	1539	1520 m	1522 w	112.79	1546	1524 s
1464 m 1506 40.84 1460 m 1507 42.30 1467 sh 1466 m 1507 41.68 1486 w 1456 m 1485 w 1466 m	$\delta_{rr}(CH_2)$		1466 m	1485 w	1456 m	1486 w	41.68	1507	1466 m	1467 sh	42.30	1507	1460 m	1022 11	40.84	1506	1464 m
1504 33.64 1505 33.86 1505 33.30	Cas(Cr.5)		1100 111	1100 11	1 100 111	1100 11	33.30	1505	1100	1 107 511	33.86	1505	1100 111		33.64	1504	1 10 1 111
1491 10.47 1452 m 1491 10.71 1448 m 1491 11.94 1450 m 1450 m 1453 m	$\delta_{as}(CH_3)$	1453 m		1450 m		1450 m	11.94	1491		1448 m	10.71	1491		1452 m	10.47	1491	
1490 8.16 1490 6.95 1490 5.78							5.78	1490			6.95	1490			8.16	1490	
1485 3.54 1485 2.97 1485 1.90	$\delta_s(CH_3)$						1.90	1485			2.97	1485			3.54	1485	
1484 25.80 1482 3.84 1483 7.83							7.83	1483			3.84	1482			25.80	1484	
1445 17.80 1414 s 1422 sh 1447 30.87 1446 27.58 1410 w 1410 vw 1418 w	v(CC) 19b	1418 w		1410 vw		1410 w	27.58	1446			30.87	1447	1422 sh	1414 s	17.80	1445	
1395 vs 1423 724.53 1392 m 1395 vs 1397 778.15 1398 s 1398 vs 1400 767.19 1385 sh 1385 vs 1382 sh 1398 vs 1398 sh	v _s (COO)	1398 sh	1398 vs	1382 sh	1385 vs	1385 sh	767.19	1400	1398 vs	1398 s	778.15	1397	1395 vs	1392 m	724.53	1423	1395 vs
1319 m 1321 m 1315 m 1315 m 1312 sh 1313 sh 1312 sh 1311 m 1314 sh 1313 w	$\delta_s(CH_3)$	1313 w	1314 sh	1311 m	1312 sh	1313 sh			1312 sh	1315 m			1315 m	1321 m			1319 m
1277 m 1406 364.65 1288 w 1277 s 1409 194.71 1277 w 1279 m 1411 371.61 1283 sh 1277 m 1270 w	$\nu(CC)$ + βC -(OH) _{ar} 14	1270 w	1277 m		1283 sh		371.61	1411	1279 m	1277 w	194.71	1409	1277 s	1288 w	364.65	1406	1277 m
1240 m 1338 32.94 1247 w 1238 s 1335 25.70 1237 m 1238 s 1336 33.25 1222 s 1223 vs 1222 m 1236 m 1229 m	v(CH) 2	1229 m	1236 m	1222 m	1223 vs	1222 s	33.25	1336	1238 s	1237 m	25.70	1335	1238 s	1247 w	32.94	1338	1240 m
1296 89.56 1296 92.50 1296 96.55	$\beta(OH)_{ar}$						96.55	1296			92.50	1296			89.56	1296	
1209 s 1263 77.90 1210 vw 1211 s 1259 76.92 1210 vw 1213 s 1258 77.66 1202 w 1203 s 1202 w 1213 s 1212 w	v(C-O)	1212 w	1213 s	1202 w	1203 s	1202 w	77.66	1258	1213 s	1210 vw	76.92	1259	1211 s	1210 vw	77.90	1263	1209 s
1228 257.62 1228 249.53 1228 249.71	$\beta(CH) = 3$						245.71	1228			249.63	1228			257.62	1228	
1210; 12.40; 1211; 11.90; 1211; 11.77;	$p(CH_3)$						11.77;	1211;			11.90;	1211;			12.46;	1210;	
1201 1.55 1202 2.10 1202 2.55 1171 0.45 1171 0.42 1171 0.42	$o(CH_{\tau})$						2.55	1202			2.10	1202			1.55	1201	
11/1, 0.43, 11/1, 0.42, 11/1, 0.43, 11/1, 0.43, 11/1, 0.43, 11/1, 0.43, 11/2, 0.71	p(CH ₃)						0.45,	11/1,			0.42,	11/1,			0.45,	11/1,	
1144 343 24 1145 347 46 1145 349 20	$vO = (CH_{a})$						349.20	1145			347.46	1145			343 24	1144	
1130 3625 1131 4092 1129 4430	ко (сн.) в(СН) 18b						44 30	1129			40.92	1131			36.25	1130	
1069 2.67 1184 m 1072 2.65 1185 vw 1184 m 1072 2.53 1191 w 1190 w	$vO-(CH_2)$			1190 w		1191 w	2.53	1072	1184 m	1185 vw	2.65	1072	1184 m		2.67	1069	
1119 vs 967 4.30 1121 w 1111 vs 962 2.88 1111 w 1111 vs 961 0.39 1114 m 1111 vs 1114 m 1107 vs 1111 w	v(CH) 13	1111 w	1107 vs	1114 m	1111 vs	1114 m	0.39	961	1111 vs	1111w	2.88	962	1111 vs	1121 w	4.30	967	1119 vs
1042 m 1041 m 1040 m 1042 m 1040 m 1033 s 1034 m 1033 s 1034 m 1038 m	$\delta_{as}(CH_3)$	1038 m	1034 m	1033 s	1034 m	1033 s			1040 m	1042 m			1040 m	1041 m			1042 m
959 w 779 139.44 961 w 955 w 768 98.43 954 m 955 w 782 156.46 947 m 950 vw 945 m 949 w 949 w	β _s (COO)	949 w	949 w	945 m	950 vw	947 m	156.46	782	955 w	954 m	98.43	768	955 w	961 w	139.44	779	959 w
910 m 922 10.87 910 w 912 m 921 12.53 914 w 912 m 921 11.04 915 w 901 m 915 w 907 m 911 w	v(CH) 7b	911 w	907 m	915 w	901 m	915 w	11.04	921	912 m	914 w	12.53	921	912 m	910 w	10.87	922	910 m
883 m 890 16.66 885 vw 874 m 892 16.71 875 vw 874 m 898 15.30 873 w 880 m 867 w 881 m ??	γ(CH) 11	??	881 m	867 w	880 m	873 w	15.30	898	874 m	875 vw	16.71	892	874 m	885 vw	16.66	890	883 m
869 sh 878 0.98 856 w 881 1.98 856 w 881 0.98 866 w ??	γ(CH)	??	866 w				0.98	881	856 w		1.98	881	856 w		0.98	878	869 sh
833 w 831 3.60 818 w 818 w 823 0.39 818 m 810 sh 831 16.99 807 m 831 w 806 m 845 w 836 w	v(CH) 7a	836 w	845 w	806 m	831 w	807 m	16.99	831	810 sh	818 m	0.39	823	818 w	818 w	3.60	831	833 w
793 s 801 w 785 s 785 s 790 m 793 s 795 m 795 s 806 w	$\alpha(CCC)$ 12	806 w	795 s	795 m	793 s	790 m			785 s				785 s	801 w			793 s
762 2.29 763 1.69 769 1.89	γ(CH) 5						1.89	769			1.69	763			2.29	762	
755 s 798 45.56 759 s 754 s 800 42.10 755 m 756 s 805 40.96 754 w 750 m 754 w 750 s 749 w	$\gamma_{\rm s}({\rm COO})$	749 w	750 s	754 w	750 m	754 w	40.96	805	756 s	755 m	42.10	800	754 s	759 s	45.56	798	755 s
675 m 595 0.02 677 w 671 m 596 0.06 689 w 673 m 597 0.05 685 w 679 w 681 w 677 m 677 w	φ(CC) 4	677 w	677 m	681 w	679 w	685 w	0.05	597	673 m	689 w	0.06	596	671 m	677 w	0.02	595	675 m
550 w 566 0.11 550 w 546 m 565 0.04 546 w 546 w 564 0.01 546 m 546 m 545 m 544 w	φ(CC) 16b		544 w	545 m	546 m	546 m	0.01	564	546 w	546 w	0.04	565	546 m	550 w	0.11	566	550 w
555 3.01 517 w 554 2.60 517 w 514 w 521 w	$\alpha(CCC)$ 6b			521 w		514 w				517 w	2.60	554		517 w	3.01	555	
494 w 505 7.93 491 w 488 w 490 0.67 498 w 490 w 527 6.74 498 w 498 w 496 w 498 w 492 m	$\beta_{as}(COO)$	492 m	498 w	496 w	498 w	498 w	6.74	527	490 w	498 w	0.67	490	488 w	491 w	7.93	505	494 w
413 vw 416 w 416 w 417 w 411 vw 449 90 95 442 90 58 443 91 71	$\phi(CC)$ $\gamma(OH)_{2r}$			411 vw	417 w		91 71	443	416 w		90 58	442	416 w		90 95	449	413 vw

^a Ref. [8,18].

^b s – strong; m – medium; w – weak; v – very.

^c The symbol "ν" denotes stretching vibrations. "β" denotes in-plane bending modes. "γ" designates out-of-plane bending modes; " ϕ (CCC)" denotes the aromatic ring out-of-plane bending modes. and " α (CCC)" designates the aromatic ring in-plane bending modes.

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Table 3 The experimental and calculated chemical shifts of protons in the ¹H NMR and carbons in the ¹³C NMR spectra of syringic acid and alkali metal syringates, δ (ppm).

Atom position ^a	n ^a Syringic acid			Syringates										
				Li			Na			К			Rb	Cs
	Exp.	Calc. ^b	Calc. ^c	Exp.	Calc. ^b	Calc. ^c	Exp.	Calc. ^b	Calc. ^c	Exp.	Calc. ^b	Calc. ^c	Exp.	Exp.
H1	12.61	5.42	6.04	-	-	-	-	-	-	-	-	-	-	-
H2	7.22	7.13	7.30	7.25	7.35	7.44	7.24	7.40	7.42	7.18	7.35	7.42	7.16	7.14
H3a,3b,5a,5b	3.80	3.69	3.84	3.73	3.68	3.81	3.74	3.67	3.80	3.76	3.71	3.82	3.74	3.72
H3c,5c	3.80	4.10	4.25	8.32	4.04	4.21	8.34	4.01	4.18	-	4.03	4.20	8.34	8.38
H4	9.19	5.61	6.09	3.73	5.37	5.75	3.74	5.25	5.67	3.76	5.26	5.68	3.74	3.72
H6	7.22	7.28	7.37	7.25	7.44	7.46	7.24	7.40	7.44	7.18	7.35	7.42	7.16	7.14
C1	120.52	122.39	122.30	128.83	128.33	129.27	129.66	130.39	131.49	127.10	131.55	132.07	129.89	131.85
C2	107.01	110.25	110.61	107.03	110.04	108.80	106.89	110.11	108.52	106.68	109.40	108.15	106.60	106.58
C3	147.57	152.57	152.29	146.88	152.34	151.93	146.84	152.06	151.56	146.93	151.97	151.71	146.74	146.68
C4	140.34	148.06	147.60	137.89	146.24	144.74	137.14	145.06	143.74	137.79	145.06	143.84	136.82	136.25
C5	147.57	151.21	152.19	146.88	150.42	151.54	146.84	150.32	151.79	146.93	150.20	151.44	146.74	146.68
C6	107.01	107.62	108.23	107.03	106.59	106.69	106.89	106.76	106.57	106.68	106.07	106.18	106.60	106.58
C7	167.39	170.04	171.99	170.50	189.01	187.83	170.48	182.80	182.58	168.29	184.03	183.28	168.37	168.57
C8	56.09	55.14	55.76	55.77	55.06	55.67	55.79	54.92	55.56	55.78	54.97	55.60	55.71	55.68
C9	56.09	55.62	56.22	55.77	55.25	55.80	55.79	55.04	55.62	55.78	55.07	55.64	55.71	55.68

^a Atom numbering in Fig. 1.

^b Calculations for isolated molecules.

^c Calculations for the molecules in the solvent (DMSO).

(IR), 1261 cm⁻¹ (R), 1379 cm⁻¹ (theoret.) and v(OH): 3374 cm⁻¹ (IR), 3776 cm^{-1} (theoret.). Deformation in plane vibration bands β (C=O): 737 cm⁻¹ (IR), 734 cm⁻¹ (R), 665 cm⁻¹ (theoret) and deformation out of plane vibration bands γ (C=O): 671 cm⁻¹ (IR), 676 cm⁻¹ (R), 776 cm⁻¹ (theoret.). Moreover, in the spectra of acid the bands of lower intensity are present, originating from deformation vibrations $\beta(OH)$ located at 1206 cm⁻¹ (IR), 1198 cm⁻¹ (R), 1329 cm⁻¹ (theoret.) and $\gamma(OH)$ 581 cm⁻¹ (IR), 581 cm⁻¹ (R), 580 cm^{-1} (theoret.) were also observed. In the spectrum of the syringic acid also bands from the aromatic ring and functional groups of the ring (hydroxyl –OH_{ar} and methoxy –OCH₃ groups) were present, which were also visible in the spectra of salt. Comparison of the spectrum of acid with those of its alkali metal salts revealed, first of all, the disappearance of stretching vibrations band (C=O). Instead, bands related to the stretching and deformation vibrations of (COO⁻) groups (v_{as} 1578–1545 cm⁻¹, v_s 1398–1385 cm⁻¹, β_s 959–949 cm⁻¹, β_{as} 498–488 cm⁻¹) were found in the spectra of complexes. The wavenumbers of symmetric in-plane deformations $\beta_{as}(COO)$ decreased in the following series Li \rightarrow Na = K \rightarrow Rb \rightarrow Cs. The values of $\Delta\beta = \beta_s(COO) - \beta_{as}(COO)$ increased in the spectra along the series: $Rb \rightarrow Cs \rightarrow K = Li \rightarrow Na$ syringates and they are respectively: 451, 452, 465, 467 cm^{-1} . The wavenumbers as well as intensities of the aromatic ring vibration bands did not significantly change. The IR spectra of metal syringates is presented in Fig. 2, where the shift of particular bands along the mentioned above series may be observed.

Peaks at 3073–2977 cm⁻¹ can be assigned to the C–H stretching modes of aromatic ring. The typical four peaks that occur in the spectra of aromatic compounds were present in the region 1686–1410 cm⁻¹. In the IR and Raman spectra of studied compounds these bands are located at about 1660 cm⁻¹ (8a), 1620 cm⁻¹ (8b), 1520 cm⁻¹ (19a) and 1420 cm⁻¹ (19b). Stretching vibrations bands $v_{as}(CH_3)$ that occur in the ranges: 2955–2938 cm⁻¹ (IR, Raman) and $v_s(CH_3)$ in the ranges: 2847–2833 cm⁻¹ (IR, Raman). The $\delta_{as}(CH_3)$ (in plane bending) give the bands in the ranges: 1468–1444, 1042–1033 cm⁻¹ (IR, Raman), and $\delta_s(CH_3)$ in the range: 1484–1312 cm⁻¹ (IR). The bands of the vO–(CH₃) vibrations are located in the range 1190–1154 cm⁻¹.

The wavenumbers of aromatic bands numbered as 8a, 8b, 7a, 7b, 11, 12 and 16b in IR as well as in Raman spectra increase in comparison to free acid.

The correlation between calculated and experimentally obtained wavenumbers in IR spectra of syringic acid and lithium, sodium, potassium syringates were studied and generally good agreement was found. The correlation coefficient *R* for 4-hydroxy-3,5-dimethoxybenzoic acid spectra is 0.9962 and lithium, sodium and potassium salts amount to 0.9973; 0.9964; 0.9975, respectively.



Fig. 1. Structures of: syringic acid (a) and sodium syringate (b).



Fig. 2. Experimental FT-Raman spectra (a), FT-IR spectra (b) of syringic acid and the FT-IR spectra of salts: lithium (c), sodium (d), potassium (e), rubidium (f) and cesium syringates (g).

NMR spectra

One of the most important factors that affect the chemical shift is the electron density. Increasing the electron density causes a higher field intensity and the decrease – lower field strength. Theoretically as well as experimentally obtained ¹H NMR and ¹³C NMR chemical shifts of syringic acid and alkali metal syringates are presented in Table 3. The numbering of atoms is shown in Fig. 1. The experimental proton (¹H) and carbon (¹³C) NMR spectra of syringic acid are presented in Figs. 3 and 4.

Data for the last two salts were only experimentally obtained. Almost all protons in salts were shifted diamagnetically in comparison to acid. This tendency suggests that introduction of alkali metal atoms causes the decrease in the ring current intensity. The largest changes of chemical shifts were observed at H4 atom. It indicates a decrease in the electronic charge density around this nucleus and a decrease in the screening effect. The differences between chemical shifts of proton atoms along metal series are small and irregular. Theoretical an experimental signals from carbons no. 2, 3, 4, 5, 6, 8, and 9 were shifted downfield in comparison to the appropriate signals in the spectrum of



Fig. 3. The experimental proton (¹H) NMR spectra of syringic acid.



ligand, whereas the signals from carbons no. 1 and 7 were shifted upfield.

The linear correlation was observed between carbon NMR theoretical and experimental data of studied compounds. The correlation coefficient (R) for ¹³C NMR spectra are amount to 0.999 (calculations for isolated molecules); 0,999 (calculations for the molecules in DMSO) for acid, 0.995; 0,996 for lithium, 0,998; 0,998 for sodium and 0,997; 0,998 for potassium syringates.

Table 4

Dipole moments (Debye) and total energy (Hartree, 1 hartree = 2625.5 kJ/mol) calculated using B3LYP/6-311++G^{**} method.

	Syringic acid	Syringates					
		Li	Na	К			
Dipole moment Energy	0.314 -725.308	5.088 -732.306	8.000 -887.067	7.372 -132.469			

Table 5

The bond lengths and angles of the structures of syringic acid and its alkali metal salts calculated in B3LYP/6-311++G^{**} level (atom numbering on Fig. 1).

Syringic acid		Syringates					
		Li	Na	K			
	Calc.	Calc.	Calc.	Calc.			
Bond lengths (Å) ^a							
C1-C2	1 400	1 398	1 397	1 397			
(2-(3))	1 394	1 388	1 394	1 395			
C3-C4	1 405	1 403	1 403	1 403			
C4-C5	1.404	1.404	1.402	1.402			
C5-C6	1.387	1.394	1.389	1.389			
C1-C6	1.399	1.398	1.397	1.397			
C1C7	1.478	1.490	1.501	1.502			
C7-01	1.362	1.277	1.270	1.271			
C7—02	1.212	1.276	1.272	1.272			
01-H1/M	0.968	1.851	2.204	2.203			
02—M	-	1.850	2.203	2.203			
C2—H2	1.079	1.080	1.080	1.080			
C3-03	1.359	1.376	1.364	1.364			
O3–C8	1.422	1.423	1.419	1.419			
C4-04	1.353	1.357	1.360	1.300			
04—H4	0.968	0.967	0.967	0.967			
C5-05	1.372	1.362	1.378	1.378			
05—С9	1.426	1.421	1.422	1.422			
C6—H6	1.081	1.080	1.080	1.080			
Angles (°)							
C1-C2-C3	120.13	118.90	119.02	120.44			
C2-C3-C4	119.41	121.09	121.17	119.46			
C3-C4-C5	119.77	119.66	119.50	119.50			
C4-C5-C6	120.98	119.37	119.46	121.17			
C5-C6-C1	118.94	120.32	120.44	119.02			
C2-C1-C6	120.77	120.67	120.43	120.43			
C1-C7-01	113.29	119.72	118.45	118.53			
C1-C7-02	125.31	119.83	118.53	118.45			
01	121.40	120.45	123.01	123.01			
C7-01-H1/M	106.36	82.96	88.00	88.03			
C7-02-M	-	83.05	87.03	88.00			
C1-C2-H2	119.12	118.68	118.51	117.86			
C2-C3-O3	125.10	125.72	125.66	125.04			
C3-03-C8	118.25	118.28	118.20	117.92			
C3-C4-04	119.67	120.57	120.60	119.91			
C4-04-H4	107.37	107.12	106.97	106.97			
C4C505	113.19	115.54	113.19	113.17			
С5—О5—С9	118.46	117.99	118.21	118.20			
C5-C6-H6	122.27	121.66	122.47	122.47			

^a 1 Å = 10^{-10} m

Corresponding values of correlation coefficient of ¹H NMR were found lower.

Calculated data

Optimized geometrical structures of syringic acid and lithium, sodium, potassium syringates were calculated using B3LYP/6- $311++G^{**}$ method [16]. The bond lengths and the angles between

Table 6

The calculated aromaticity indices for syringic acid and syringates lithium, sodium and potassium.

Aromaticity indices	Syringic acid	Syringates		
		Li	Na	К
HOMA	0.9636	0.9692	0.9734	0.9728
I_6	94.8130	95.4470	96.40277	96.1029
A _i	0.9956	0.9966	0.9974	0.9975
BAC	0.9158	0.9273	0.9377	0.9399
$\Delta(CC)^{a}$	0.018	0.016	0.014	0.014

^a Differences between the longest and the shortest bonds in the ring.

bonds in studied molecules are presented in Table 5. The atoms numbering is shown in Fig. 1. Substitution of metal cation in a place of carboxylic group hydrogen of syringic acid does not cause significant changes in the electronic charge distribution of the ring. The significant increase of C7–O1, C1–C7, O1–M, O2–M bond lengths is observed in the series acid \rightarrow lithium \rightarrow sodium = potassium. The bond lengths of C7–O2 insignificantly decrease in the above order. In the case of angles, the increase was observed, C1–C6–C7, C1–C7–O2, C7–O1–M, C7–O2–M but decrease was noticed for: C1–C2–C7, C1–C7–O1, C3–O3–C8, O1–M–O2, C7–M–O1.

Dipole moments, energies and geometric aromaticity indices, were calculated and also shown in Tables 4 and 6. Comparing the values of dipole moment for molecule of 4-hydroxy-3,5-dimeth-oxybenzoic acid and its salts one can observe an increasing tendency: 0.314 D for free acid; 5.088 D for lithium salt; 7.372 D for potassium; for sodium salt 8.000 D. Values of energy decrease in the series: $K \rightarrow H \rightarrow Li \rightarrow Na$. Almost all aromaticity indices increase in the following order: acid \rightarrow lithium \rightarrow sodium \rightarrow potassium. The aromaticity indexes calculated for benzoic acid [17] (HOMA = 0.982; A_j = 0.998; BAC = 0.950; I_6 = 96.89) are higher than those obtained for syringic acid (HOMA = 0.964; A_j = 0.996; BAC = 0.916; I_6 = 94.81). This suggest that the syringic acid molecule.

Atomic charges on the atoms of 4-hydroxy-3,5-dimethoxybenzoic acid molecule and its alkali metal salts were calculated by Mulliken, APT (atomic polar tensor), NBO/NPA (natural bond orbital/ natural population analysis) methods (Table 7). The electron density around C1 atom increased for lithium and sodium, and then decreased for potassium syringate. Growing electron density around the metal atoms was observed in a series of acid \rightarrow lithium \rightarrow sodium \rightarrow potassium. The decrease of the charge around atoms C6, C1, O2 was observed.

The correlation between theoretical and experimental data was studied. The correlation between atomic charges on hydrogen atoms (obtained by Mulliken, APT and NBO/NPA methods) and the appropriate experimental chemical shifts (¹H NMR) were calculated. The correlation coefficients *R* amount to 0.482; 0.892; 0.916, respectively (Fig. 5). From these data one could draw following conclusion: NBO/NPA method shows the best correlation with experimental results. The total charges on the aromatic ring as well as on COO⁻ group were calculated. The increase of total charge of carboxylate group are observed in the order Li < Na < K when APT method was used for calculation. Using NBO/NPA method no changes were observed in above series. The total charge in aromatic ring is not changed in the series of alkali metal syringates irrespective of used method.

Table 7	
The atomic charge (e ^a) calculated by B3LYP/6-311++G** method for syringic acid and lithium, sodium and potassium syring	gates.

Atom	tom Syringic acid			Syringates								
	_			Li			Na			К		
	Mulliken	ATP	NBO/NPA	Mulliken	ATP	NBO/NPA	Mulliken	ATP	NBO/NPA	Mulliken	ATP	NBO/NPA
C1	1.481	-0.308	-0.164	2.480	-0.282	-0.148	2.650	-0.226	-0.141	1.796	-0.251	-0.140
C2	-0.329	-0.087	-0.255	-0.389	-0.116	-0.256	-0.357	-0.142	-0.262	-0.299	-0.142	-0.261
C3	-0.552	0.506	0.287	-0.565	0.522	0.284	-0.506	0.535	0.283	-0.598	0.536	0.283
C4	-0.504	0.472	0.277	-0.523	0.445	0.266	-0.652	0.424	0.258	-0.582	0.426	0.258
C5	-0.456	0.460	0.265	-0.449	0.468	0.261	-0.444	0.481	0.260	-0.509	0.482	0.260
C6	-0.149	-0.101	-0.251	-0.302	-0.122	-0.259	-0.271	-0.147	-0.266	-0.199	-0.148	-0.265
C7	0.277	1.472	0.788	-0.179	1.429	0.766	-0.337	1.374	0.766	-0.086	1.410	0.765
C8	-0.297	0.525	-0.206	-0.293	0.525	-0.204	-0.294	0.527	-0.203	-0.294	0.527	-0.203
C9	-0.298	0.519	-0.201	-0.299	0.522	-0.200	-0.298	0.524	-0.199	-0.300	0.523	-0.199
01	-0.207	-0.775	-0.696	-0.339	-1.036	-0.825	-0.469	-1.018	-0.824	-0.461	-1.074	-0.824
02	-0.307	-0.874	-0.615	-0.341	-1.037	-0.828	-0.469	-1.019	-0.826	-0.466	-1.075	-0.826
03	-0.172	-0.877	-0.526	-0.176	-0.881	-0.530	-0.177	-0.885	-0.532	-0.177	-0.885	-0.532
04	-0.253	-0.768	-0.651	-0.262	-0.766	-0.659	-0.269	-0.762	-0.664	-0.268	-0.764	-0.663
05	-0.267	-0.890	-0.571	-0.168	-0.895	-0.575	-0.268	-0.900	-0.577	-0.268	-0.899	-0.577
H1/M	0.299	0.304	0.484	0.190	0.829	0.886	0.442	0.854	0.917	1.017	0.950	0.915
H2	0.210	0.093	0.232	0.214	0.097	0.236	0.223	0.099	0.235	0.208	0.099	0.234
H3a	0.155	-0.034	0.170	0.151	-0.035	0.169	0.149	-0.037	0.168	0.150	-0.037	0.168
H3b	0.155	-0.034	0.170	0.151	-0.035	0.169	0.149	-0.037	0.168	0.150	-0.037	0.168
H3c	0.195	0.004	0.193	0.190	-0.002	0.189	0.187	-0.006	0.187	0.186	-0.006	0.188
H4	0.304	0.336	0.488	0.301	0.331	0.486	0.300	0.327	0.485	0.299	0.328	0.485
H5a	0.166	-0.023	0.176	0.161	-0.027	0.173	0.159	-0.029	0.172	0.159	-0.029	0.172
H5b	0.166	-0.023	0.176	0.161	-0.027	0.173	0.159	-0.029	0.172	0.159	-0.029	0.172
H5c	0.182	0.006	0.192	0.177	-0.001	0.189	0.174	-0.005	0.187	0.173	-0.004	0.187
H6	0.200	0.097	0.237	0.211	0.096	0.236	0.219	0.097	0.235	0.207	0.098	0.234

^a $e = 1.6021892 \times 10^{-19}$ C.



Fig. 5. The correlation between calculated atomic charges (Mulliken, APT, NBO/NPA methods) on hydrogen atoms and the appropriate experimental chemical shifts (¹H NMR).

Conclusions

The theoretical parameters were compared to the experimental characteristics of studied compounds. Good correlation between experimental and calculated IR and NMR spectra was noted. The correlation coefficients (*R*) for IR spectra for syringic acid, lithium, sodium, and potassium syringates amount to 0.9962; 0.9973; 0.9964; 0.9975, respectively. The corresponding values for ¹³C NMR spectra are in the range 0.995 – 0.999. The calculated energy decreases in order: $K \rightarrow H \rightarrow Li \rightarrow Na$. Experimental studies (FT-IR, FT-Raman) showed that alkali metal ions affect the electronic charge distribution in the aromatic ring. The intensity and wavenumbers in the case of bands number as 20a, 2, 4, 16b, 19a (IR), 20b, 19b, 2, 13, 4 (*R*) decrease in comparison to free acid, which shows disorder of the electron ligand. In the ¹H NMR spectra of syringates the signals from all protons are shifted upfield in com-

parison to appropriate signals in the spectrum of acid. The chemical shifts of protons H3, H4 and H5 decrease in the series: $Li \rightarrow Na \rightarrow K \rightarrow Rb \rightarrow Cs$ syringates as consequence of the circular current weakening and therefore an increase in the screening of aromatic protons. This is an evidence that alkali metal perturb the aromatic system of the molecule.

The highest correlation coefficients were obtained for experimental and theoretical data calculated by the NBO/NPA method.

Spectral characteristic of the alkali metal syringates was performed. Replacement of carboxylic group hydrogen with alkali metal ions brought about some characteristic changes in molecular spectra as well as in geometrical structure of studied molecules. Obtained data of total energy indicated that stabilization of studied molecules increases along the series: $K \rightarrow H \rightarrow Li \rightarrow Na$. The values of dipole moment show an increasing tendency in series: syringic acid $\rightarrow K$ syringate. HOMA, A_j , BAC and I_6 aromaticity indices show that the salts possess higher aromaticity character then the acid molecule. Good agreement was obtained between the experimental and calculated infrared spectra.

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