X-ray powder diffraction data for the *N*-acylamino acids: *ortho, meta*, and *para*-methyl hippuric acids

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N-acylamino acid isomers: *ortho, meta*, and *para*-methylhippuric acids, are specific xylene metabolites. Here, we report X-ray powder diffraction data, unit-cell parameters, and space groups for the three isomer ($C_{10}H_{11}NO_3$), [*ortho*-methylhippuric acid 2 mHA, monoclinic $P2_1/n$ cell, $a = 8.522(1)$, $b = 10.443(1)$, $c = 10.734(1)$ Å, $\beta = 92.43(1)°$, $V = 954.5(1)$ Å^3; *meta*-methylhippuric acid 3 mHA, monoclinic $C2/c$ cell $a = 20.0951(2)$, $b = 10.485(1)$, $c = 10.074(2)$ Å, $\beta = 119.08(1)°$, $V = 1933.9(1)$ Å^3; *para*-methylhippuric acid 4 mHA, orthorhombic $P2_12_12_1$ cell, $a = 5.1794(7)$, $b = 8.279(1)$, $c = 22.276(2)$ Å, $V = 955.2(2)$ Å^3], space group. In each case, all measured diffraction peaks were indexed and are consistent with the corresponding space group. © *2016 International Centre for Diffraction Data*. [doi:10.1017/S0885715616000312]

Key words: X-ray powder diffraction data, *N*-acylamino acids, hippuric acid derivatives, BTX metabolites

I. INTRODUCTION

Benzene, toluene, and xylene (BTX) are common organic solvent widely used in the chemical industry. It has been reported that exposure to high concentrations of volatile organic compounds such as BTX will lead to a series of diseases, causing acute and chronic respiratory effects, functional alterations of the central nervous system, mucous and skin irritations, and, in extreme cases, chromosome aberrations (Bilban, 2004; Celik and Akbas, 2005). Hippuric acid (HA) and methylhippuric acids (mHA) are metabolites of toluene and xylene produce in the human body, since they are found as physiological components of the human urine if toluene or xylene was inhaled. Thus, quantification of HA and mHA in urine is actually used as a diagnostic marker of exposure to toluene and xylene (Sperlingová *et al*., 2007; Antunes *et al*., 2013).

A search in the Cambridge Structural Database (CSD, v 5.36, February 2015) (Allen, 2002) and PDF-ICDD database (ICDD, 2011) showed no entries for these HA derivatives. The aim of this work is to report the X-ray powder diffraction data of the three *N*-acylamino acids derivatives of the HA; 2, 3, and 4-methylhippuric acids (Figure 1), which are the specific metabolites of the 2, 3, and 4-xylene solvent contaminants.

II. EXPERIMENTAL

A. Specimen preparations

For the X-ray analysis, small quantities of *ortho, meta*, and *para*-methylhippuric acids at 99% of purity (obtained from commercial source, Aldrich) were ground mechanically in an agate mortar and pestle. The resulting fine powders, sieved to 106 μm, were mounted on a flat zero-background holder covered with a thin layer of petroleum jelly.

B. Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) characterization

Melting points were measured in an electro thermal apparatus. The FTIR absorption spectra were obtained as KBr pellet using a Perkin-Elmer 1600 spectrometer. ^{1}H-NMR spectra were recorded on a Bruker Avance 400 model spectrometer in DMSO-d_6 solution.

2 mHA: mp 164–165 °C, FTIR (cm^{-1}); C–H 749.9, 727.9, N–H 3479.3, O–H 3296.8, ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm); 11.0 (*s*, COO**H**), 7.45 (*s*, CON**H**), 7,44 (*d*, H5), 7.32 (*t*, H7), 7.19 (*d*, H8), 7.23 (*t*, H6), 4.11 (*s*, C**H**$_2$), 2.43 (*s*, C**H**$_3$).

3 mHA: mp 138–140 °C, FTIR (cm^{-1}); C–H 809.4, N–H 3450.6, O–H 3356.0, ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm); 11.1 (*s*, COO**H**), 8.1 (*s*, CON**H**), 7.84 (*s*, H5), 7.74 (*d*, H9), 7.48 (*t*, H7), 7.37 (*d*, H6), 3.94 (*s*, |C**H**$_2$), 2.35 (*s*, C**H**$_3$).

4 mHA: mp 163–165 °C, FTIR (cm^{-1}); C–H 832.7, N–H 3458.6, O–H 3354.4, ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm); 11.8 (*s*, COO**H**), 7.99 (*s*, CON**H**), 7.82 (*d*, H5, H9), 7.27 (*d*, H6, H8), 4.12 (*s*, C**H**$_2$), 2.37 (*s*, C**H**$_3$).

C. Powder diffraction data collection

X-ray powder diffraction patterns were collected at room temperature in a Philips PW-1150/25 diffractometer with Bragg–Brentano geometry using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å; 30 KV, 15 mA) and a diffracted beam graphite

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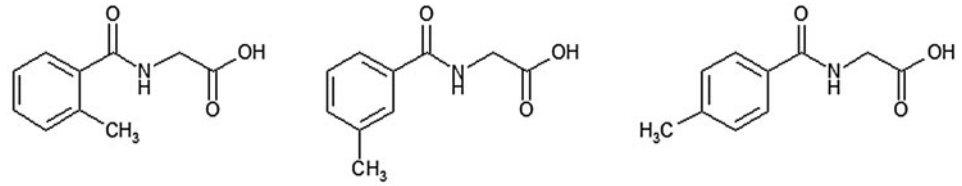

ortho-methylhippuric acid (2mHA) | *meta*-methylhippuric acid (3mHA) | *para*-methylhippuric acid (4mHA)

Figure 1. Structural diagram of the *ortho, meta*, and *para*-methylhippuric acids.

TABLE I. X-ray powder diffraction data of *ortho*-methylhippuric acid (2 mHA).

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
11.824	7.4783	10	0	1	1	11.818	7.4819	−0.006
11.824	7.4783	10	0	1	1	11.818	7.4819	−0.006
12.980	6.8145	4	−1	0	1	12.988	6.8103	0.008
13.537	6.5353	100	1	0	1	13.538	6.5351	0.001
15.988	5.5386	33	1	1	1	15.984	5.5398	−0.004
16.517	5.3625	9	0	0	2	16.518	5.3622	0.001
16.956	5.2244	4	0	2	0	16.965	5.2217	0.009
18.592	4.7684	24	0	1	2	18.585	4.7701	−0.007
19.930	4.4510	4	1	2	0	19.929	4.4513	−0.001
20.844	4.2579	27	2	0	0	20.847	4.2573	0.003
21.680	4.0956	21	1	1	2	21.676	4.0963	−0.004
22.541	3.9411	28	−2	1	0	22.534	3.9423	−0.007
24.344	3.6532	10	2	1	1	24.337	3.6541	−0.006
25.697	3.4637	25	−1	2	2	25.704	3.4628	0.007
26.289	3.3870	28	1	2	2	26.279	3.3883	−0.010
			0	1	3	26.328	3.3821	
26.906	3.3108	6	0	3	1	26.904	3.3111	−0.002
27.277	3.2667	18	2	0	2	27.269	3.2675	−0.007
28.553	3.1234	5	2	2	1	28.538	3.1250	−0.015
			2	1	2	28.600	3.1185	
30.599	2.9191	18	0	3	2	30.592	2.9198	−0.007
31.716	2.8188	3	−1	2	3	31.727	2.8178	0.011
			−3	0	1	32.255	2.7729	
32.298	2.7693	15	2	2	2	32.291	2.7699	−0.007
			0	0	4	33.392	2.6811	
33.404	2.6801	6	−3	1	1	33.405	2.6801	0.001
34.064	2.6297	4	−2	3	1	34.055	2.6304	−0.009
			3	1	1	34.086	2.6281	
35.695	2.5131	3	−1	1	4	35.700	2.5128	0.005
36.895	2.4341	3	−2	3	2	36.894	2.4342	−0.001
37.440	2.4000	6	3	1	2	37.444	2.3997	0.004
37.855	2.3746	5	1	3	3	37.855	2.3746	0.000
38.297	2.3482	3	0	4	2	38.311	2.3474	0.014
38.792	2.3194	4	−1	2	4	38.790	2.3195	−0.001
39.664	2.2704	3	−3	0	3	39.669	2.2701	0.005
			3	2	2	40.420	2.2296	
40.467	2.2271	3	2	0	4	40.478	2.2266	0.011
			2	4	0	40.495	2.2256	
41.422	2.1780	6	3	0	3	41.414	2.1784	−0.007
			2	1	4	41.429	2.1776	
42.491	2.1256	10	2	3	3	42.510	2.1247	0.019
			0	3	4	42.523	2.1241	
45.701	1.9835	3	0	2	5	45.689	1.9840	−0.012
46.010	1.9709	3	−4	2	0	46.004	1.9712	−0.007
			−4	1	2	45.990	1.9717	
46.485	1.9519	4	−4	2	1	46.473	1.9523	−0.012
			4	0	2	46.523	1.9503	
47.283	1.9208	4	−3	4	0	47.264	1.9215	−0.019
48.614	1.8712	4	2	4	3	48.623	1.8709	0.010
			0	4	4	48.635	1.8705	
49.284	1.8473	3	3	3	3	49.305	1.8466	0.021
			3	2	4	50.883	1.7930	

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TABLE I. Continued

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
50.914	1.7920	3	3	4	2	50.894	1.7926	−0.020
51.538	1.7717	4	2	2	5	51.531	1.7719	−0.007
			−1	5	3	51.531	1.7720	
			4	1	3	51.596	1.7699	
52.835	1.7313	3	−2	4	4	52.829	1.7314	−0.005
53.825	1.7017	3	4	3	2	53.833	1.7015	0.008
			−2	3	5	53.865	1.7006	
54.801	1.6737	3	3	3	4	54.795	1.6739	−0.006
			−2	0	6	54.808	1.6735	
			−2	5	3	54.810	1.6735	
			3	4	3	54.839	1.6726	

TABLE II. X-ray powder diffraction data of *meta*-methylhippuric acid (3 mHA).

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
9.647	9.1601	25	2	0	0	9.653	9.1548	0.006
9.716	9.0956	50	−1	1	0	9.713	9.0985	−0.003
12.177	7.2621	1	−1	1	1	12.174	7.2641	−0.003
15.521	5.7041	1	−3	1	1	15.526	5.7024	0.005
16.895	5.2434	35	0	2	0	16.898	5.2423	0.003
17.586	5.0387	82	−2	0	2	17.593	5.0368	0.007
19.377	4.5769	32	4	0	0	19.375	4.5774	−0.002
19.660	4.5116	43	−2	2	1	19.666	4.5102	0.006
			0	2	1	19.692	4.5043	
			−3	1	2	20.108	4.4122	
20.149	4.4033	2	0	0	2	20.155	4.4019	0.006
			−1	1	2	20.159	4.4011	
22.981	3.8666	6	3	1	1	22.990	3.8651	0.009
23.999	3.7049	100	−4	2	1	24.005	3.7039	0.006
24.474	3.6340	22	1	1	2	24.478	3.6334	0.005
			−2	2	2	24.487	3.6321	
25.745	3.4574	52	−5	1	0	25.747	3.4571	0.002
26.325	3.3826	15	−4	2	2	26.337	3.3811	0.012
			2	0	2	26.365	3.3775	
26.986	3.3012	20	−1	3	1	26.980	3.3018	−0.006
			−3	3	1	28.699	3.1079	
28.730	3.1046	3	1	3	1	28.735	3.1040	0.006
29.240	3.0516	37	6	0	0	29.240	3.0516	0.001
29.616	3.0137	5	−1	1	3	29.617	3.0136	0.001
31.002	2.8820	9	−6	2	1	31.015	2.8809	0.013
31.439	2.8430	4	3	1	2	31.441	2.8428	0.002
			2	2	2	31.482	2.8392	
31.729	2.8176	7	−7	1	1	31.728	2.8178	−0.001
33.390	2.6812	3	−5	3	1	33.401	2.6804	0.011
33.948	2.6384	29	−6	2	0	33.962	2.6373	0.015
34.526	2.5956	7	1	3	2	34.536	2.5948	0.011
35.483	2.5277	12	−5	3	0	35.475	2.5282	−0.007
36.926	2.4322	4	−6	0	4	36.930	2.4319	0.004
			−5	1	4	36.976	2.4290	
			−2	0	4	37.047	2.4245	
37.109	2.4206	4	−3	3	3	37.097	2.4214	−0.013
			2	4	1	38.416	2.3412	
38.476	2.3377	14	−1	3	3	38.464	2.3384	−0.012
39.441	2.2827		−8	2	1	39.445	2.2825	0.004
39.780	2.2640	4	−7	3	2	39.793	2.2633	0.013
			5	1	2	39.832	2.2612	
40.357	2.2330	4	2	2	3	40.364	2.2326	0.007
			0	0	4	40.970	2.2009	
40.981	2.2004	2	−2	2	4	40.978	2.2006	−0.003
42.274	2.1360	2	1	3	3	42.263	2.1365	−0.011
43.101	2.0969	3	8	2	0	43.089	2.0975	−0.013
43.500	2.0786	8	6	0	2	43.492	2.0790	−0.008
			−3	3	4	44.609	2.0295	

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TABLE II. Continued

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
44.618	2.0291	3	0	2	4	44.612	2.0293	−0.006
45.363	1.9975	3	−9	1	0	45.371	1.9971	0.009
45.718	1.9828	3	3	5	0	45.710	1.9832	−0.009
46.404	1.9551	3	0	4	3	46.408	1.9549	0.004
			−3	1	5	47.003	1.9315	
47.044	1.9300	4	5	3	2	47.033	1.9304	−0.011
49.121	1.8531	5	7	1	2	49.129	1.8528	0.008
			−8	4	2	49.154	1.8519	
49.906	1.8258	4	−10	2	4	49.897	1.8261	−0.009
			−6	4	4	51.195	1.7828	
51.203	1.7825	3	3	1	4	51.205	1.7825	0.002
52.933	1.7283	3	−10	2	0	52.924	1.7286	−0.009
54.274	1.6887	1	4	0	4	54.273	1.6887	−0.001

TABLE III. X-ray powder diffraction data of *para*-methylhippuric acid (4 mHA).

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
7.931	11.1383	12	0	0	2	7.931	11.1379	0.000
11.401	7.7548	2	0	1	1	11.392	7.7605	−0.008
13.304	6.6495	82	0	1	2	13.314	6.6445	0.010
15.891	5.5722	25	0	0	4	15.900	5.5690	0.009
17.571	5.0429	12	1	0	1	17.564	5.0449	−0.007
18.865	4.6998	2	1	0	2	18.879	4.6965	0.013
19.183	4.6228	4	0	1	4	19.191	4.6209	0.008
20.193	4.3937	8	1	1	0	20.206	4.3910	0.013
20.600	4.3079	37	1	1	1	20.599	4.3081	−0.001
20.885	4.2498	14	1	0	3	20.893	4.2481	0.008
21.458	4.1375	30	0	2	0	21.447	4.1396	−0.011
21.722	4.0878	95	1	1	2	21.737	4.0850	0.015
22.911	3.8783	50	0	2	2	22.899	3.8802	−0.011
23.510	3.7808	37	1	1	3	23.518	3.7796	0.008
24.610	3.6143	13	0	2	3	24.600	3.6156	−0.009
25.802	3.4498	5	1	1	4	25.816	3.4481	0.013
26.815	3.3218	3	0	2	4	26.811	3.3223	−0.004
27.552	3.2346	14	1	2	0	27.560	3.2337	0.008
27.840	3.2018	100	1	2	1	27.855	3.2001	0.015
28.729	3.1047	29	1	2	2	28.722	3.1054	−0.007
29.436	3.0317	9	0	2	5	29.428	3.0326	−0.008
30.062	2.9700	10	0	1	7	30.058	2.9704	−0.004
31.538	2.8343	4	1	1	6	31.529	2.8351	−0.009
32.121	2.7842	1	0	0	8	32.118	2.7845	−0.003
33.004	2.7117	1	1	0	7	33.008	2.7114	0.003
33.953	2.6380	2	0	1	8	33.937	2.6392	−0.016
34.234	2.6170	2	1	2	5	34.234	2.6170	0.000
34.854	2.5718	6	2	0	1	34.846	2.5724	−0.008
			0	2	7	35.552	2.5229	
35.563	2.5222	1	2	0	2	35.559	2.5224	−0.003
			0	3	4	36.299	2.4727	
36.321	2.4713	6	2	1	0	36.316	2.4716	−0.005
36.605	2.4528	4	1	0	8	36.609	2.4525	0.004
36.825	2.4386	10	1	2	6	36.828	2.4384	0.003
			1	3	0	36.873	2.4356	
37.247	2.4119	12	2	1	2	37.231	2.4129	−0.016
37.927	2.3702		0	1	9	37.908	2.3714	−0.019
			0	3	5	38.333	2.3461	
38.362	2.3444	5	2	1	3	38.349	2.3451	−0.013
40.345	2.2336	2	1	0	9	40.352	2.2332	0.008
			1	3	4	40.385	2.2315	
41.285	2.1849	1	2	2	1	41.285	2.1849	−0.001
41.954	2.1516	2	0	1	10	41.964	2.1511	0.010
42.801	2.1109	3	1	2	8	42.821	2.1100	0.020
43.990	2.0566	2	2	1	6	43.972	2.0574	−0.018

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TABLE III. Continued

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
45.623	1.9867	6	1	1	10	45.627	1.9866	0.003
46.122	1.9664	3	0	1	11	46.104	1.9671	−0.018
			1	2	9	46.145	1.9654	
46.926	1.9345	2	1	3	7	46.937	1.9341	0.011
47.437	1.9149		1	4	1	47.437	1.9149	0.000
47.995	1.8939	7	1	4	2	47.993	1.8940	−0.003
48.341	1.8811	2	2	3	1	48.326	1.8817	−0.015
			2	3	2	48.874	1.8619	
48.914	1.8605	5	1	4	3	48.908	1.8607	−0.006
49.756	1.8309	5	2	3	3	49.778	1.8302	0.021
50.152	1.8174	1	1	4	4	50.168	1.8168	0.016
			0	1	12	50.331	1.8113	
			0	4	6	50.436	1.8078	
50.477	1.8064	1	2	2	7	50.457	1.8071	−0.021
			2	0	9	50.995	1.7893	
51.025	1.7883	2	2	3	4	51.022	1.7884	−0.002
52.272	1.7486	3	2	1	9	52.260	1.7489	−0.012
			1	0	12	52.307	1.7475	
53.651	1.7068	1	1	4	6	53.651	1.7068	0.000
			3	0	2	53.675	1.7061	
			2	3	6	54.465	1.6832	
54.514	1.6818	3	3	0	3	54.521	1.6816	0.007

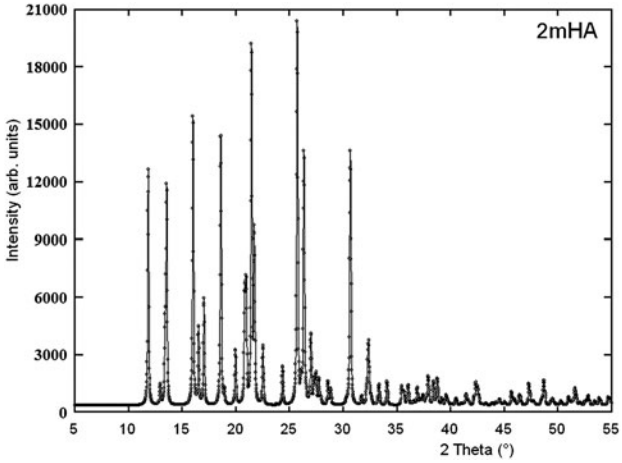

Figure 2. X-ray powder diffraction pattern of *ortho*-methylhippuric acid.

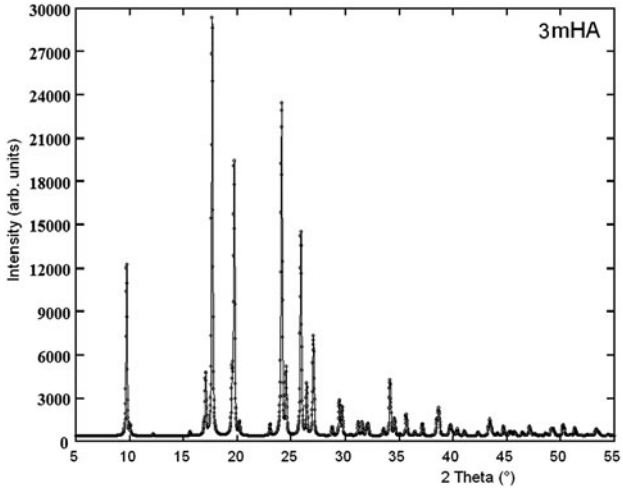

Figure 3. X-ray powder diffraction pattern of *meta*-methylhippuric acid.

monochromator. The specimens were scanned from 5 to 55° 2θ, with a step size of 0.02 and counting time of 10 s. Silicon (SRM 640) was used as an external standard. The analytical software package HIGHSCORE PLUS v2.0 (PANalytical, Almelo, The Netherlands) was used to establish the positions of the peaks from the α_1 component, strip mathematically the α_2 component from each reflection, and to determine the peak intensities of the diffraction peaks (Tables I–III).

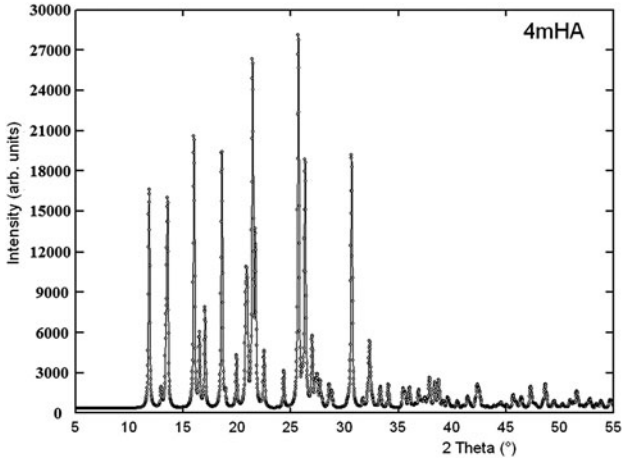

Figure 4. X-ray powder diffraction pattern of *para*-methylhippuric acid.

III. RESULTS AND DISCUSSION

The experimental powder diffraction patterns are depicted in Figures 2–4. Automatic indexing of the experimental X-ray diffraction patterns were done using DICVOL06 (Boultif and Louër, 2004), which gave unique solutions in monoclinic (2 mHA, 3 mHA) and orthorhombic (4 mHA) cells. These results are consistent with the space groups $P2_1/n$ (2 mHA), $C2/$

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TABLE IV. X-ray crystal structural data for the mHA isomers.

System	2-methylhippuric (2 mHA) Monoclinic	3-methylhippuric (3 mHA) Monoclinic	4-methylhippuric (4 mHA) Orthorhombic
Space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_12_12_1$ (No. 19)
Z (Z')	4(1)	8(1)	4(1)
T (K)	295	295	295
D_{cal} (g cm^{-3})	1.343	1.338	1.345
Unit-cell parameters (Å, °)	a = 8.522(1)	a = 20.951(2)	a = 5.1794(7)
	b = 10.443(1)	b = 10.485(1)	b = 8.279(1)
	c = 10.734(1)	c = 10.074(2)	c = 22.276(2)
	β = 92.43(1)	β = 119.08(1)	
Vol (Å^3)	954.5(1)	1933.9(1)	955.2(2)
$M_{(20)}$	39.8	46.7	38.7
$F_{(30)}$	57.3 (0.0058, 90)	51.8 (0.0064, 90)	76.8 (0.0080, 49)

c (3 mHA), and $P2_12_12_1$ (4 mHA) obtained in a single-crystal analysis, which will be published elsewhere.

The complete powder diffraction dataset were reviewed in the mentioned space groups, using the program NBS*AIDS83 (Mighell *et al*., 1981). The X-ray powder diffraction patterns of three *N*-acylamino acids are given in Tables I–III. The crystal data and indexing figures of merit M_N (de Wolff, 1968) and F_N (Smith and Snyder, 1979) for the three compounds are shown in Table IV.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at http://dx.doi.org/10.1017/S0885715616000312.

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