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THE STRUCTURES OF GARCINONES A, B AND C: THREE NEW XANTHONES FROM *GARCINIA MANGOSTANA*

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Key Word Index—*Garcinia mangostana*; Guttiferae; xanthones; 1, 3, 6-trihydroxy-2, 4-*bis*(3-methylbut-2-enyl)-9H-xanthen-9-one; 5, 9, 11-trihydroxy-10-(3-methylbut-2-enyl)-3, 3-dimethyl-3H, 12H-pyrano[3,2-*a*]xanthen-12-one; 1, 3, 6, 7-tetrahydroxy-2-(3-methylbut-2-enyl)-8-(3-hydroxy-3-methylbutanyl)-9H-xanthen-9-one.

Abstract—Three new tetraoxygenated xanthones (garcinones A, B and C), each disubstituted with C_5-units, have been isolated from the chloroform extract of the fruit-hulls of *Garcinia mangostana*. Their structures were established by a combination of spectral interpretation and chemical correlation.

INTRODUCTION

Our previous investigations on the minor constituents from *Garcinia mangostana* L. yielded three polyoxygenated xanthones [1, 2], in addition to the five reported earlier [3]. The chloroform extract on chromatographic separation and further purification produced three new additional minor xanthones, i.e. garcinones A, B and C. The isolation of these compounds has already been reported in a preliminary communication [4]. The present paper details the evidence leading to their structures.

RESULTS AND DISCUSSION

Garcinone A (**1a**), $C_{23}H_{24}O_5$ ($[M]^+$ 380), mp 224–225°, had IR and UV spectra reminiscent of polyoxygenated xanthones. The IR spectrum showed bands at 3380 and 1635 cm^{-1} characteristic of a xanthone with a hydroxyl group(s) chelated to the carbonyl group. Acetylation (Ac_2O–Py) gave a triacetate (**1b**), $C_{29}H_{30}O_8$ ($[M]^+$ 506), mp 115–117°, which confirmed the presence of three hydroxyl functions. In the mass spectrum of **1a**, the presence of characteristic peaks at *m/z* 337, 324, 311, 283, 269 and 257, in addition to the $[M]^+$ peak, strongly suggested [5, 6] **1a** was a trihydroxy xanthone with two 3,3-dimethylallyl substituents *ortho* to hydroxyl groups. In the ^1H NMR spectrum of **1b** in $CDCl_3$, the benzylic protons of both the side-chains appeared as broad doublets ($J = 6$ Hz) at δ 3.31 indicating their substitutions on carbons other than C-1 or C-8. In the aromatic region, the spectrum showed a one-proton quartet at δ 8.15 which was readily assigned to H-8 and since the proton showed a normal *ortho* coupling ($J = 9$ Hz) the C-7 position was also unsubstituted. The complex two-proton multiplet centred at δ 7.35 was assigned to H-7 and H-5 of the same ring. The xanthone showed a negative $Pb(OAc)_2$ test [7] while the absence of a shift of the UV maxima [8] with NaOAc–H_3BO_3 eliminated the possibility of two *ortho* hydroxyl substitutions. Moreover, the negative Gossypetone reaction [9] excluded a *para* quinol structure in **1a**. Finally, the larger NaOAc induced bathochromic shift (of the higher wavelength band in the UV spectrum) in comparison to the xanthone with a single hydroxyl substitution, *para* to the carbonyl group, the negative Gibb's test [10, 11] shown by **1a** and the smaller coupling constant (1 Hz) of the H-8 quartet in the ^1H NMR spectrum of **1b** indicative of *meta* or *para* coupling, led directly to the structure **1a** for garcinone A.

Garcinone B (**2a**), $C_{23}H_{22}O_6$ ($[M]^+$ 394), mp 190–192°, gave UV and IR spectra characteristic of 1,3,6,7-tetraoxygenated xanthones [1]. The presence of three hydroxyl groups in the molecule, one of which is chelated, was directly confirmed by the formation of a triacetate (**2b**) and a di-O–Me ether (**2c**). In the ^1H NMR spectrum of **2a**, signals for all the 22 protons were clearly discernible. The presence of a 3,3-dimethylallyl substituent was confirmed by two singlets at δ 1.65 and 1.75 for the vinyl methyls and a triplet at δ 5.20 (1H) for the vinylic proton. The signal for the benzylic protons was obscured by the solvent signal, but it could be clearly observed as a doublet at δ 3.25 in the NMR spectrum of **2b**. The signals at δ 1.45 (6H, *s*) 5.95 (1H, *d*) and 7.95 (1H, *d*) in the spectrum of **2a** were indicative of a 2,2-dimethyl-2H-pyran ring. The characteristic downfield shift of one of the vinylic proton doublets at δ 7.95 of the chromene ring strongly suggested [12] the chromene ring to be angularly cyclized and also adjacent to the xanthone carbonyl group. The angular position of the pyran ring was further suggested by the absence of any UV absorption band in the region 280–290 nm, as contrasted to those xanthones with only a linearly cyclized pyran ring [1, 13, 14]. Additional support for the angular arrangement of the

pyran ring was obtained from the absence of any appreciable diamagnetic shift for the vinyl proton signals in the NMR spectrum of **2b** which is typical [15] of linearly fused pyrano xanthones. Two aromatic proton singlets were observed at δ 6.83 and 6.40, the upfield position of the latter being characteristic [1] of H-8 and the other being assigned to H-6. The mass spectrum of **2a** showed the typical fragment ion peaks at m/z 379, 351, 339 and 323 in addition to $[M]^+$ suggesting it was a pyrano-xanthone with a 3,3-dimethylallyl side-chain *ortho* to a hydroxyl group(s), i.e. at C-10 similar to mangostin (**3a**) and γ-mangostin (**3b**). The structure **2a** was finally confirmed by the oxidative cyclization of **2a** and **3b** with DDQ in C_6H_6 for 3 hr and 45 min, respectively, to afford 5, 13-dihydroxy-3, 3, 10, 10-tetramethyl-3H, 10H, 14H-dipyrano [3,2-*a*: 2′, 3′: *i*] xanthen-14-one (**4**) and 5, 9, 11-trihydroxy-10-(3-methylbut-2-enyl)-3, 3-dimethyl-3H, 12H-pyrano [3, 2-*a*] xanthen-12-one, respectively, the latter compound being identical to the natural xanthone (**2a**).

Garcinone C (**5a**), $C_{23}H_{26}O_7$ ($[M]^+$ 414), mp 216–218°, had IR and UV spectra characteristic of a partially methylated polyhydroxy xanthone with a 1, 3, 6, 7-tetraoxygenation pattern. On acetylation (Ac_2O–Py) it yielded a penta-*O*-acetyl derivative (**5b**) which proved the presence of five hydroxyl groups in the molecule. The mass spectrum of **5a** showed the presence of a characteristic peak at m/z 396, in addition to the $[M]^+$ peak. The former was formed by loss of 18 amu from the $[M]^+$ and suggested the presence of an alcoholic hydroxyl group in the side-chain. Furthermore, the mass spectrum after the loss of 18 amu from the $[M]^+$ was almost identical to that of γ-mangostin (**3b**). That the two compounds differ only with respect to the C_5 side-chain which is 3, 3-dimethylallyl in **3b** and the corresponding hydrated form, 3-hydroxy-3-methyl butanyl, in **5a** became evident from a consideration of the ^1H NMR of **5a** and **5b**. The spectrum of **5a** showed a signal at δ 1.20 (6H, *s*) consistent with the presence of a $C(OH)Me_2$ grouping, in addition to the signals at δ 1.63 (3H, *s*) and 1.72 (3H, *s*) for the two vinyl Me groups of the dimethylallyl substituent. The benzylic protons of both the side-chains appeared at δ 3.27 in the NMR of **5a** and was superimposed on the H_2O signal, whereas in the NMR spectrum of **5b** these protons appeared as a four-proton multiplet at δ 3.31 suggesting that the 3-hydroxy-3-methylbutanyl side-chain was *ortho* to the xanthone carbonyl group and that the 3, 3-dimethylallyl substituent was at some other position as in **5a**. The aromatic proton singlets at δ 6.33 and 6.74 in the NMR spectrum of **5a** were readily assigned to H-4 and H-5 respectively, the former being shifted upfield due to its location in the phloroglucinol ring. The presence of a D_2O exchangeable signal at δ 13.98 (1H, *s*) provided direct evidence for the hydroxyl group on C-1. Thus, the structure of garcinone C was established as **5a**.

The ^{13}C NMR chemical shifts for the two new xanthones, garcinone B (**2a**) and C(**5a**), are presented in Table 1, along with those of mangostin (**3a**) and γ-mangostin or normangostin (**3b**). The assignments were done by SFORD, PRFT and selective heterodecoupling measurements of all the four xanthones and finally by comparison with the ^{13}C NMR data of these xanthones with each other and those reported [16–19] for other xanthones and related compounds with the application of known substituent shifts [20, 21].

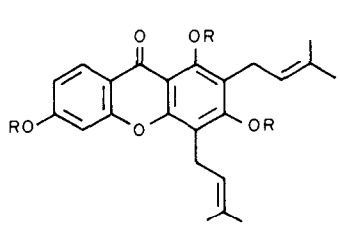
Table 1. ^{13}C NMR chemical shifts of **2a**, **5a**, **3a** and **3b** in ppm (±0.05) downfield from TMS in DMSO-d_6 solution

Carbon	**3a**	**3b**	**5a**	Carbon	**2a**
1	159.9	159.9	160.0	11	159.7
2	109.7	109.4	109.3	10	109.7
3	162.3	162.1	162.0	9	162.4
4	92.3	92.1	92.1	8	92.4
4a	154.2	154.3	154.3	7a	154.3
5	101.8	100.2	100.1	6	102.7
6	156.9	152.5	152.5	5	153.2
7	143.4	140.8	140.8	4a	138.1
8	136.4	127.7	129.9	12b	119.7
8a	110.1	110.1	110.3	12a	106.8
9	181.3	181.6	181.7	12	181.5
9a	101.9	102.1	102.0	11a	102.1
10a	154.6	152.0	152.1	6a	152.3
11	21.0	21.2	21.1	15	21.0
12	122.7	122.7	122.7	16	122.5
13	130.3	130.3	130.4	17	130.4
14	25.6	25.7	25.6	18	25.6
15	17.7	17.8	17.8	19	17.8
16	25.8	25.5	22.1	1	120.4
17	123.8	123.8	NO*	2	132.6
18	130.3	130.1	69.4	3	75.1
19	25.6	25.7	29.2	13	26.8
20	18.1	18.2	29.2	14	26.8
7-OMe	60.2				

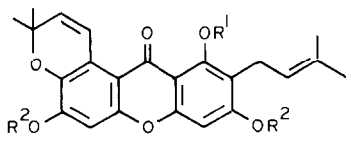
*NO: not observed (coincides with a solvent peak).

Signal intensities in PRFT spectra were very useful in the differentiation of the quaternary aromatic carbons from each other. The alkoxyl-bearing aromatic carbons and the non-oxygenated C-8a and C-9a (C-12a and C-11a in **2a**) showed smaller signal intensities than the hydroxyl-bearing aromatic carbons and non-oxygenated C-2 and C-8 (C-10 and C-12b in **2a**) when 1.2 sec pulse repetition was used. The former carbons have fewer protons in their vicinity or the protons are more distant than in the case of the latter carbon atoms and thus the ^{13}C–^1H dipolar relaxation rate of the former is decreased [22]. Diagnostically, the signal of C-8a was the weakest, the corresponding C-12a in **2a** being almost unobservable with a 1.2 sec pulse repetition. Interestingly, the methylene carbons of the 3, 3-dimethylallyl substituents also gave weak signals. The side-chains apparently have a low barrier of rotation about the Ar–CH_2 bond, leading to increased motion and decreased relaxation rate for the methylene carbon [22].

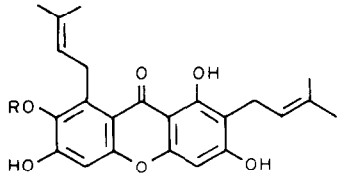
The chemical shift of C-8 (C-12b in **2a**) can be used as a probe for the substitution pattern of this ring in C-7 oxygenated, C-8 alkylated xanthones. Thus, the shift of C-8 in mangostin (**3a**) again shows the same unusually high, in fact total, suppression of the *ortho* shielding effect of the C-7 methoxy group, due to its flanking by two *ortho* substituents, as we previously reported for the related pyranoxanthones [1]. The resulting large downfield shift of C-8 (about 20 ppm) in these C-7 methoxylated and C-6 oxygenated xan-



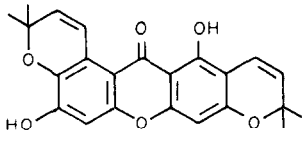
1a R = H
1b R = Ac



	R^1	R^2
2a	H	H
2b	Ac	Ac
2c	H	Me



3a R = Me
3b R = H



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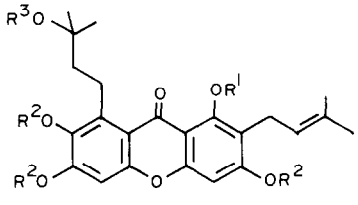
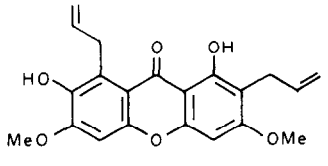


	R^1	R^2	R^3
5a	H	H	H
5b	Ac	Ac	Ac
5c	H	Me	H



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thones and a smaller downfield shift (about 10 ppm) in **3b**, **5a** and **6** (C-8 at δ 125.5 in $CDCl_3$) [18], which have a C-7 hydroxyl group instead of a methoxyl group, can be partially explained by the reduced electron density in the ring which is in turn caused by a steric perturbation of the resonance interaction of the C-7 methoxyl/hydroxyl oxygen with the aromatic ring [1]. The C-4a alkoxy group in **2a** is more coplanar with the xanthone nucleus and the resonance interaction is not so much perturbed. In consequence, the C-12b signal at δ 119.7 is shifted upfield and is nearer the predicted value.

It is interesting to note that C-7 and C-8a (C-4a and C-12a in **2a**), but not C-10a, C-5 nor C-6 (C-6a, C-6 and C-5 in **2a**), appear increasingly downfield in the series **2a** to **3b**, **5a** to **3a**, indicating the decreased electron density at C-7, C-8 and C-8a and a preferred electron release route by the C-7 oxygen via C-8a toward the γ-pyrone carbonyl group [19].

EXPERIMENTAL

Mps: uncorr, IR: Nujol; MS: 70 eV; ^{1}H NMR: 90 and 59.8 MHz, $CDCl_3$–DMSO-d_6, TMS as int. standard; ^{13}C NMR: made with a Fourier transform accessory and signal multiplicity was determined by off-resonance decoupling after proton noise decoupling. The solvent D_2O provided the lock signal, chemical shifts are accurate to within ±0.02 ppm.

Isolation. The fruit hulls, after extraction with petrol (bp 60–80°) [2], were further extracted with $CHCl_3$ followed by absolute EtOH. The $CHCl_3$ extract (10 g), after removal of the solvent, was chromatographed over Si gel (500 g). Fractions eluted with C_6H_6, C_6H_6–$CHCl_3$ (3:1), (1:1) and (1:3) respectively, were rechromatographed and further purified by prep. TLC to yield mangostin (3.2 g); garcinone A (25 mg) and garcinone B (120 mg); γ-mangostin (150 mg) and garcinone C (100 mg) with another minor xanthone of yet unknown structure respectively.

Garcinone A (**1a**) was recrystallized ($CHCl_3$–MeOH) as fine yellow crystals (25 mg), mp 224–225°; UV λ_{max}^{EtOH} nm (log ϵ): 245 (4.5), 260 (4.0), 289 (4.0), 323 (4.1) and 370 (3.5); $\lambda_{max}^{EtOH-NaOAc}$ nm (log ϵ): 244 (4.4), 295 (3.9), 326 (4.0) and 369 (4.3); IR ν_{max}^{Nujol} cm^{-1}: 3380 (chelated OH) and 1635 (γ-pyrone C=O); MS *m/z* (rel. int.): 380 $[M]^+$ (25), 337 $[M-43]^+$ (5), 324 $[M-56]^+$ (7), 323 (5), 311 $[M-69]^+$ (63), 295 (17), 283 (5), 269 (16) and 257 (100). (Found: C, 72.55; H, 6.41%. $C_{23}H_{24}O_5$ requires: C, 72.61; H, 6.36%.) The triacetate (**1b**) crystallized from MeOH as fine colourless needles, mp 115–117°; IR ν_{max}^{Nujol} cm^{-1}: 1715 and 1225 (acetate); MS *m/z* (rel. int.): 506 $[M]^+$ (40), 464 $[M-42]^+$ (35), 422 $[M-2\times42]^+$ (10), 380 [M –

$3\times42]^+$ (8), 352 (75), 328 (30), 313 (25), 205 (80), 155 (60) and 150 (100); ^{1}H NMR (90 MHz, $CDCl_3$): δ 8.15 (1H, *dd*, $J = 9$, 1 Hz), 7.25–7.45 (2H, *m*), 5.06 (2H, *t*, $J = 6$ Hz), 3.31 (4H, *d*, $J = 6$ Hz), 1.60 (3H, *s*), 1.66 (3H, *s*), 1.75 (3H, *s*) and 1.99 (3H, *s*).

Garcinone B (**2a**) was crystallized (C_6H_6–MeOH) as a dull yellow solid (120 mg), mp 190–192°; UV λ_{max}^{EtOH} nm (log ϵ): 247 (4.4), 267 (4.4), 339 (4.1) and 390 sh (4.0); $\lambda_{max}^{EtOH-NaOAc}$ nm: (log ϵ) 247 (4.4), 267 (4.4) and 377 (4.2); IR ν_{max}^{Nujol} cm^{-1}: 3480 (OH) and 1650 (CO); MS *m/z* (rel. int.): 394 $[M]^+$ (84), 379 $[M-Me]^+$ (83), 351 $[M-43]^+$ (53), 339 $[M-55]^+$ (100) and 323 $[M-Me\text{-}56]^+$ (34); ^{1}H NMR (90 MHz, DMSO-d_6): δ 13.73 (1H, *s*), 7.95 (1H, *d*, $J = 10$ Hz), 6.83 (1H, *s*), 6.40 (1H, *s*), 5.95 (1H, *d*, $J = 10$ Hz), 5.20 (1H, *t*, $J = 6$ Hz), 3.20–3.60 (2H, masked by H_2O signals), 1.75 (3H, *s*), 1.65 (3H, *s*) and 1.45 (6H, *s*). (Found: C, 69.95; H, 5.66%. $C_{23}H_{22}O_6$ requires: C, 70.04; H, 5.62%.) The triacetate (**2b**) crystallized ($CHCl_3$–MeOH) as pale yellow needles, mp 191–192°; MS *m/z* (rel. int.): 520 $[M]^+$ (53), 505 $[M-Me]^+$ (55), 478 $[M-42]^+$ (76), 436 $[M-2\times42]^+$ (47), and 394 $[M-3\times42]^+$ (41); ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.93 (1H, *d*, $J = 10$ Hz), 7.16 (1H, *s*), 7.63 (1H, *s*), 5.83 (1H, *d*, $J = 10$ Hz), 5.05 (1H, *t*, $J = 6.5$ Hz), 3.25 (2H, *d*, $J = 6.5$ Hz), 2.46 (6H, *s*), 2.33 (3H, *s*), 1.75 (3H, *s*), 1.69 (3H, *s*) and 1.43 (6H, *s*).

Di-O-Me *ether of* **2a**. Xanthone **2a** (10 mg) on methylation (CH_2N_2–Et_2O) afforded **2c** as bright yellow needles (hexane), mp 196–198°; UV λ_{max}^{MeOH} nm (log ϵ): 244 (4.0), 270 (4.1), 323 (3.8) and 364 (3.4); MS *m/z* (rel. int.): 422 $[M]^+$ (68), 407 $[M-Me]^+$ (100), 379 $[M-43]^+$ (60) and 367 $[M-55]^+$ (80).

Cyclodehydrogenation of **2a**. Xanthone **2a** (50 mg) in dry C_6H_6 (20 ml) was refluxed with DDQ (70 mg) for 3 hr. Usual work-up and chromatographic purification afforded **4** as greenish yellow needles (30 mg) from C_6H_6, mp 218–219°; UV λ_{max}^{EtOH} nm (log ϵ): 282 (4.7), 303 sh (4.6), 333 (4.4) and 385 (4.4); IR ν_{max}^{Nujol} cm^{-1}: 3500 (OH) and 1650 (CO); MS *m/z* (rel. int.): 392 $[M]^+$ (31), 377 $[M-Me]^+$ (100), 359 (5) and 347 (5); ^{1}H NMR (90 MHz, $CDCl_3$): δ 13.66 (1H, *s*), 8.05 (1H, *d*, $J = 10.5$ Hz), 6.85 (1H, *s*), 6.75 (1H, *d*, $J = 10.5$ Hz), 6.26 (1H, *s*), 6.22 (1H, *s*), 5.83 (1H, *d*, $J = 10.5$ Hz), 5.57 (1H, *d*, $J = 10.5$ Hz) and 1.48 (12H, *s*). (Found: C, 70.28; H, 5.22%. $C_{23}H_{20}O_6$ requires C, 70.40; H, 5.14%.)

Partial cyclodehydrogenation of **3b**. Xanthone **3b** (200 mg) in dry C_6H_6 (50 ml) was refluxed with DDQ (80 mg) with subsequent monitoring by TLC. After 45 min the hot reaction mixture was filtered off. The filtrate after evaporation and chromatographic purification afforded 5, 9, 11-trihydroxy-10-(3-methylbut-2-enyl)-3, 3-dimethyl-3H, 12H-pyrano-[3, 2-*a*]xanthen-12-one as fine yellow cubes (60 mg) from C_6H_6, mp 189–190° and was found to be identical with **2a** by mmp, Co-TLC and superimposable IR.

Garcinone C (**5a**) was crystallized from MeOH as a yellow solid (100 mg), mp 216–218°; UV λ_{max}^{EtOH} nm: (log ϵ) 243 (4.5), 260 (4.4) and 370 (4.3); IR ν_{max}^{Nujol} cm^{-1}: 3550 (OH), 3440 and 3150 (chelated OH) and 1640 (CO); MS *m/z* (rel. int.): 414 $[M]^+$ (10), 396 $[M-18]^+$ (80), 381 $[M-18\text{-}15]^+$ (15), 379 (30), 353 $[M-61]^+$ (70), 341 $[M-18-55]^+$ (100), 340 $[M-18-56]^+$ (50), 325 (90), 299 (30), 297 (92) and 285 (52); ^{1}H NMR (59.8 MHz, DMSO-d_6): δ 13.98 (1H, *s*), 6.74 (1H, *s*), 6.33 (1H, *s*), 5.18 (1H, *t*, $J = 6.5$ Hz), 3.27 (4H, masked by H_2O signal), 1.72 (3H, *s*), 1.62 (3H, *s*) and 1.20 (6H, *s*). (Found: C, 66.42; H, 6.39%. $C_{23}H_{26}O_7$ requires: C, 66.65; H, 6.32%.) The penta-acetate (**5b**), prepared by treatment of **5a** with Ac_2O–Py in a boiling water-bath for 10 hr, was crystallized from C_6H_6 as fine colourless needles, mp 150–152°; UV λ_{max}^{MeOH} nm (log ϵ): 244 (4.6), 270 sh (4.2) and 345 (4.0); IR ν_{max}^{Nujol} cm^{-1}: 1770 and 1255 (acetate); MS *m/z* (rel. int.): 624 $[M]^+$ (2), 564 $[M-60]^+$ (25), 522 $[M-60-42]^+$ (58), 480 $[M-60-2\times42]^+$ (56), 438 $[M-60-3\times42]^+$ (62), 396 $[M-60-4\times42]^+$ (65), 353 (62), 341 (88) and 339 (100); ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.35 (1H, *s*), 7.32 (1H, *s*), 5.08 (1H, *t*, $J = 6$ Hz), 3.31 (4H, *m*), 2.46 (3H, *s*), 2.40 (3H, *s*), 2.30 (3H, *s*), 2.05 (3H, *s*), 1.95–2.10 (2H, *m*), 1.77 (3H, *s*), 1.70 (3H, *s*) and 1.60 (6H, *s*).

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