FURTHER OBSERVATIONS ON THE LEAD TETRAACETATE OXIDATION OF REDUCING DISACCHARIDES[1]

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ABSTRACT

Evidence is presented which supports an earlier suggestion that the linkage-position in a reducing disaccharide may be determined readily by lead tetraacetate oxidation. Compounds examined include aldose and ketose disaccharides and aldobiuronic acids. Two types of reaction—one catalyzed by potassium acetate and the other non-catalyzed—are employed jointly to illustrate oxidation patterns which clearly differentiate each position of the biose linkage. Partial degradation of reducing disaccharides by lead tetraacetate oxidation is illustrated by the preparation of 2-*O*-α- and 2-*O*-β-D-glucopyranosyl-D-erythritol and 4-*O*-β-D-galactopyranosyl-D-erythritol. In turn, 2-*O*-β-D-glucopyranosyl-D-erythritol is degraded to 2-*O*-β-D-glucopyranosyl-glycerol.

A previous publication (16) described some oxidations of reducing disaccharides by lead tetraacetate. The reactions were carried out in aqueous acetic acid (2) using potassium acetate, which promoted catalysis of the carbohydrate oxidations and also permitted estimation of the formic acid released (15). Each position of the biose linkage was found to be associated with a distinctive oxidation pattern which readily differentiated it from other possible positions. It was therefore suggested that lead tetraacetate oxidation might be useful for determining the position of the linkage in a reducing disaccharide. The study has now been extended to include additional reducing disaccharides and some aldobiuronic acids which recently have become available to us. Other aspects of the lead tetraacetate oxidation of bioses are also considered in the light of recent findings with the normal (non-catalyzed) oxidation of monosaccharides (17).

The current results on structure determination are consistent with those obtained earlier (16), and the linkage-position determined for each compound is the same as that assigned by other investigators through the use of accepted methods. The data are summarized in Fig. 1 and Table I. As found previously, 1,6-aldohexopyranose disaccharides are degraded to a much greater extent than other linkage types, yielding about five moles of formic acid and consuming about six moles of oxidant. In contrast, 1,3- and 1,4-disaccharides yield little more than one mole of formic acid, most of which appears to be derived slowly from the non-reducing end-units. The latter two linkage types, however, are clearly distinguishable from each other in that the reducing end-unit of the former is cleaved only at the 1,2-hemiacetal glycol group to yield a pentose (monoformate), whereas that of the 1,4-compound is oxidized additionally at the 2,3-glycol group to give a tetrose (diformate).

These data are paralleled by results obtained from the structurally related 3-, 4-, and 6-mono-*O*-methyl-D-glucoses, allowance being made for the absence

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of a glycosidic non-reducing end-unit, which are virtually identical with the results reported previously for mono-*O*-methyl-D-galactoses. The behavior of 2-*O*-methyl sugars suggests that a disaccharide possessing a 1,2-linkage should be unique in readily yielding a mole of formaldehyde, since the primary alcohol group of the reducing end-unit would not be protected from oxidation either by the presence of a glycosidic linkage or by a formate ester group. This expectation has now been confirmed by lead tetraacetate oxidation of a known 1,2-disaccharide (7).

Two compounds, 4-*O*-β-D-mannopyranosyl-D-glucose and 4-*O*-β-D-mannopyranosyl-D-mannose, exhibit the only instances encountered of oxidation behavior which differs significantly from that expected. The reducing end-units of other 1,4-disaccharides examined—maltose, lactose, cellobiose, and 4-*O*-α-D-glucopyranosyl-D-mannose—are found to consume approximately two moles of oxidant within the first 15 min. reaction time (Table I and Ref. 16, Table I). This value, which is consistent with production of a tetrose from the reducing end-unit, is obtained by subtracting from the total consumption the quantity of lead tetraacetate consumed by the appropriate methyl monose glycoside. The latter quantity is assumed to approximate to the consumption of oxidant by the non-reducing end-unit. On the same basis, the reducing end-units of the mannosido-mannose and mannosido-glucose are found to consume only about one mole of oxidant, which corresponds to production of a pentose unit rather than the tetrose actually found. All other data (Fig. 1 and Table I), moreover, clearly indicate that the compounds should be assigned, correctly, a 1,4-linkage. In contrast, the reducing end-units of 3- and 6-*O*-α-D-mannopyranosyl-D-mannose are found to consume the predicted one mole and three moles of lead tetraacetate, respectively, by assuming that the α-mannopyranose non-reducing end-units are oxidized at the same rate as is methyl α-D-mannopyranoside. Since methyl α- and β-D-mannopyranosides are oxidized rapidly at about the same rate, the β-mannopyranose units of the two 1,4-disaccharides appear to possess an unusual ring conformation in solution, which is not easily attacked by lead tetraacetate.

The 1,4-ketohexose disaccharides, maltulose and lactulose, each liberate one mole of formic acid and consume three moles of lead tetraacetate. These results are consistent with those obtained with the aldose disaccharides and with the fact that ketose sugars yield esters of glycolic acid (17). Accordingly, the reducing end-units apparently consume only one mole of oxidant and are degraded to a glycolate ester of D-erythrose, and the non-reducing end-units yield formic acid at rates characteristic of other glucosides or galactosides. The 1,3-ketose disaccharide, turanose, shows behavior similar to that of the 2-substituted aldoses, being overoxidized by lead tetraacetate and yielding a mole of formaldehyde. These ketose disaccharides are thus comparable to aldose disaccharides in which the reducing end-unit is a pentose (compare 3-*O*-D-glucopyranosyl-D-arabinose with maltulose), differing in that the ester formed by cleavage of the hemiacetal glycol group is a glycolate, rather than a formate, ester.

Since the oxidation characteristics which distinguish a given linkage position

TABLE I

LEAD TETRAACETATE OXIDATION OF REDUCING DISACCHARIDES

Compound	$Pb(OAc)_4$ consumed[1]		Oxidation products		
	Total[2]	Reducing end[3]	Pentose[4]	Tetrose	Formaldehyde[4]
3-*O*-α-D-Mannopyranosyl-D-mannose	—	0.9,	Arabinose (1.0)	0	—
3-*O*-α-D-Glucopyranosyl-D-glucose	—		Arabinose (0.8)	0	—
3-*O*-Methyl-D-glucose	1.1	1.0	—	—	—
4-*O*-β-D-Mannopyranosyl-D-mannose	4.3	1.2	0	Erythrose	0
4-*O*-β-D-Mannopyranosyl-D-glucose	4.1	1.1	0	Erythrose	0
4-*O*-β-D-Glucopyranosyl-D-mannose	4.1	2.2	0	Erythrose	0
4-*O*-β-D-Glucopyranosyl-D-glucose	4.0	2.1	0	Erythrose	0
4-*O*-D-Glucuronopyranosyl-D-galactose	4.9	—	0	Threose	Trace
4-*O*-(4-*O*-Methyl-D-glucuronopyranosyl)-D-galactose	2.7	—	0	Threose	Trace
4-*O*-Methyl-D-glucose	2.0	—	—	—	0
6-*O*-β-D-Glucopyranosyl-D-glucose	5.7	—	—	—	—
6-*O*-α-D-Mannopyranosyl-D-mannose	6.4	3.2	—	—	—
6-*O*-Methyl-D-glucose	4.3	3.0	—	—	—
2-*O*-Methyl-D-glucose	5.0	—	—	—	1.0
3-*O*-α-D-Glucopyranosyl-D-fructose	6.1	—	—	—	1.1
4-*O*-β-D-Galactopyranosyl-D-fructose	3.0	—	0	Erythrose	—
4-*O*-α-D-Glucopyranosyl-D-fructose	3.0	—	0	Erythrose	—
3-*O*-α-D-Glucopyranosyl-D-arabinose	3.2	—	0	Erythrose	—

[1]*Corrected by the amount consumed in oxidation of formic acid to* CO_2.
[2]*Five hours' reaction time.*
[3]*Fifteen minutes' reaction time; total consumption less the consumption by the corresponding methyl glycoside.*
[4]*Moles per mole.*

are associated chiefly with the reducing end of the disaccharide, the reactions described should also be of use with aldobiuronic acids, in which the non-reducing end-units are easily overoxidized by glycol-cleavage agents owing to the formation of an intermediate active methylene group (12). Thus, the oxidation of 6-*O*-β-D-glucuronopyranosyl-D-galactose at the outset resembles that of the 1,6-hexose disaccharides (Fig. 1), despite an eventual pronounced overoxidation. Paralleling the low acid yield from 1,4-hexose disaccharides, 4-*O*-D-glucuronopyranosyl-D-galactose gives much less acid than the 1,6-compound. Oxidation of the methoxyaldobiuronic acid, 4-*O*-(4-*O*-methyl-D-

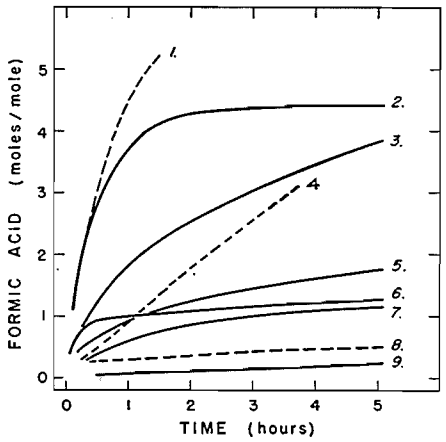

FIG. 1. Production of formic acid (evolution of carbon dioxide) during the lead tetraacetate oxidation of reducing disaccharides and aldobiuronic acids. (Compounds grouped together give identical or approximately the same rate curve; the data shown are for the first-named compound.)

1. 6-*O*-D-Glucuronopyranosyl-D-galactose
2. 6-*O*-α-D-Mannopyranosyl-D-mannose
   6-*O*-β-D-Glucopyranosyl-D-glucose
3. 3-*O*-α-D-Glucopyranosyl-D-fructose
4. 4-*O*-D-Glucuronopyranosyl-D-galactose
5. 3-*O*-D-Mannopyranosyl-D-mannose
6. 4-*O*-β-D-Galactopyranosyl-D-fructose
7. 4-*O*-D-Mannopyranosyl-D-glucose
   4-*O*-D-Mannopyranosyl-D-mannose
   4-*O*-β-D-Glucopyranosyl-D-mannose
   3-*O*-α-D-Glucopyranosyl-D-arabinose
   4-*O*-α-D-Glucopyranosyl-D-fructose
8. 4-*O*-(4-*O*-Methyl-D-glucuronopyranosyl)-D-galactose
9. 4-*O*-Methyl-D-glucose

glucuronopyranosyl)-D-galactose, illustrates more clearly the behavior of the reducing end-unit since the non-reducing end-unit of this compound does not yield formic acid and is not prone to overoxidation. Thus the formic acid production is only slightly greater than that from 4-*O*-methyl monoses, but the three moles of oxidant consumed correspond to formation of a tetrose diformate at the reducing end and cleavage of the 2,3-glycol group of the non-reducing end-unit. In agreement with these data, both 1,4-compounds yield threose (identified chromatographically) after oxidation and hydrolysis. A 1,3-linked aldobiuronic acid would be expected, accordingly, to yield one mole of pentose, and a 1,2-compound to give a mole of formaldehyde. The assignment of linkage position in aldobiuronic acids may be facilitated further by use of the oxidizing conditions considered below, in which complications due to overoxidation of the non-reducing end-unit are eliminated.

Studies on the reactions of monoses with lead tetraacetate have shown that aldoses and ketoses are degraded in a stepwise fashion, being attacked first at the hemiacetal glycol group (17). Since the rates of reaction of these compounds relative to those of glycosides (9, 15) are extremely rapid, it was to be expected that the reducing end-unit of a disaccharide should be degraded selectively under similar conditions, i.e., without potassium acetate and in the presence of only 1 to 2% of water. The rates of oxidation given in Fig. 2 are in agreement with this expectation. Aldose disaccharides possessing a 1,3-linkage quickly consume one mole of oxidant and further reaction is slow; the related 1,4-ketoses also consume one mole of oxidant rapidly. The aldose

unit of a 1,6-compound behaves similarly to an unsubstituted aldose, rapidly taking up two moles of lead tetraacetate. In contrast, aldohexopyranose disaccharides or aldobiuronic acids having 1,4-linkages are oxidized more slowly, possibly because they are unable to assume furanose ring forms (17), glucose units being less readily attacked than galactose units. The data obtained with the corresponding monomethyl aldohexoses are virtually identical, clearly indicating that the non-reducing end-units of the bioses are not attacked appreciably during the reaction period studied. This latter point is pertinent particularly for locating the linkage in aldobiuronic acids which, as noted above, may be overoxidized in the catalyzed reaction. Since the hemiacetal group of the 2-substituted sugars is blocked, these compounds are oxidized by lead tetraacetate at a relatively slow rate. The results therefore suggest that the non-catalyzed lead tetraacetate reaction may provide useful information, complementary to that obtained with the catalyzed reaction, for differentiating the various linkage types in disaccharides and aldobiuronic acids.

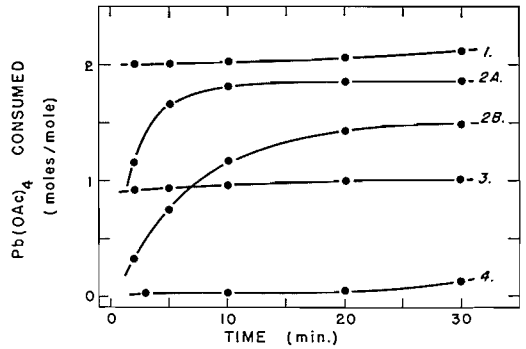

FIG. 2. Rates of lead tetraacetate consumption for reducing disaccharides, aldobiuronic acids, and mono-*O*-methyl hexoses. (Compounds grouped together give identical or approximately the same rate curve; the data shown are for the first-named compound.)

1. 6-*O*-D-Glucuronopyranosyl-D-galactose
6-*O*-D-Galactopyranosyl-D-glucose
6-*O*-Methyl-D-glucose

2A. 4-*O*-D-Glucuronopyranosyl-D-galactose
4-*O*-(4-*O*-Methyl-D-glucuronopyranosyl)-D-galactose
4-*O*-Methyl-D-galactose

2B. 4-*O*-α-D-Glucopyranosyl-D-glucose
4-*O*-Methyl-D-glucose

3. 3-*O*-α-D-Glucopyranosyl-D-arabinose
3-*O*-D-Mannopyranosyl-D-mannose
3-*O*-β-D-Glucopyranosyl-D-glucose
3-*O*-α-D-Glucopyranosyl-D-glucose
3-*O*-D-Galactopyranosyl-D-galactose
4-*O*-β-D-Galactopyranosyl-D-fructose
3-*O*-Methyl-D-glucose

4. 2-*O*-Methyl-D-glucose
2-*O*-Methyl-D-galactose

In addition to its value for the determination of structure, lead tetraacetate oxidation may be employed also for the preparation of some disaccharides by stepwise degradation of other disaccharides, in a manner already demonstrated with monosaccharides (17). To illustrate these possibilities melibiose, maltose, and cellobiose have been oxidized to give in high yields 4-*O*-α-D-galactopyranosyl-D-erythrose, and 2-*O*-α- and 2-*O*-β-D-glucopyranosyl-D-erythrose, respectively. The disaccharides were characterized as the crystalline glycosyl-erythritols. These reactions are equivalent to two successive single degradations by other procedures for descending the sugar series (6). Another possibility examined

was that of effecting a further controlled degradation starting from the glycosyl-erythritol. For the latter purpose, the fact that a polyol is more rapidly oxidized than a glycoside (8, 9) was utilized to degrade 2-*O*-β-D-glucopyranosyl-D-erythritol to 2-*O*-β-D-glucopyranosyl-L-glyceraldehyde which was reduced in turn, affording the known 2-*O*-β-D-glucopyranosyl-glycerol. This compound has been synthesized by Carter (4) from the intermediate formed by the Koenigs–Knorr reaction using tetraacetyl glucosyl bromide and 1,3-*O*-benzylidene-glycerol. The reaction sequence described therefore provides a possible synthetic pathway for glycosyl-erythritols and -glycerols, some of which are of natural occurrence (3, 13, 18) and, as noted elsewhere (5), may afford a definitive method for determining the configuration of the biose linkage in reducing disaccharides.

EXPERIMENTAL

The following compounds were obtained from the sources indicated in brackets: 3- and 6-*O*-α-D-mannopyranosyl-D-mannose (Prof. J. K. N. Jones); the barium salt of 4-*O*-(4-*O*-methyl-D-glucuronopyranosyl)-D-galactose (Dr. J. R. Nunn); nigerose (Dr. J. H. Pazur); 4-*O*-β-D-glucopyranosyl-D-mannose and 4-*O*-β-D-mannopyranosyl-D-glucose (Prof. F. Smith); the barium salt of 4-*O*-D-glucuronopyranosyl-D-galactose (Dr. A. M. Stephen); 4-*O*-β-D-mannopyranosyl-D-mannose (Prof. R. L. Whistler).

Other compounds were prepared by methods chosen from the literature or were obtained commercially.

The procedures used for determination of formic acid, lead tetraacetate consumption, pentose, and formaldehyde have been described previously (16).

Paper chromatography of the alcohols obtained from the degradation of disaccharides was carried out on Whatman No. 1 filter paper using butanol–ethanol–water (40: 11: 19 v/v) (11) as solvent and ammoniacal silver nitrate as spray reagent (14). The term R_{gal} denotes the rate of movement of the spots produced relative to galactose.

Solutions were concentrated at 40°C. *in vacuo*.

Examination of the Oxidation Products for Pentose or Tetrose Units

This was carried out as illustrated by the following example: 1.02 mgm. of 3-*O*-D-mannopyranosyl-D-mannose in 0.01 ml. of water was taken up in 0.1 ml. of acetic acid. Lead tetraacetate (4.0 mgm., 3 molar equivalents) in 0.4 ml. of acetic acid was added. Aliquots (0.05 ml.) of the solution were withdrawn at intervals for estimation of pentose; found: 1.06 moles (10 min.), 1.06 moles per mole (45 min.). Oxalic acid (10 mgm.) in acetic acid was added with stirring to the solution remaining, and 30 min. later the precipitate of lead oxalate was removed on the centrifuge. The acetic acid was evaporated off, the residue taken up in 0.2 ml. of water and heated in a sealed tube for three hours on the boiling water bath. The hydrolyzate, on examination by paper chromatography with various solvents, was found to contain only arabinose and mannose (aniline oxalate spray (10)) which, visually, were present in approximately equal amounts.

Measurement of Oxidation Rates in the Non-catalyzed Reaction

In a typical experiment 10 mgm. of maltose, dissolved in 0.2 ml. of water, was taken up in 10 ml. of acetic acid. Lead tetraacetate (200 mgm.), dissolved in 10 ml. of acetic acid, was added to the sugar solution. Aliquots (2 ml.) of the reaction mixture were removed at chosen intervals for the determination of lead tetraacetate consumed. The data are presented in Fig. 2.

*4-O-α-*D*-Galactopyranosyl-*D*-erythritol*

Lead tetraacetate (4.8 gm.) was added to a vigorously stirred solution of melibiose hydrate (1.8 gm.) in acetic acid (450 ml.) containing water (8.0 ml.). After six minutes' reaction time the solution gave a negative starch–iodide test. Oxalic acid dihydrate (0.5 gm.) in acetic acid (5 ml.) was then added, stirring being continued for an additional 30 min.; the lead oxalate was filtered off and the filtrate concentrated to dryness. The residue was taken up in water (30 ml.) and the solution was filtered, shaken with Amberlite IR–120 resin, and stored at 3°C. for 18 hr. The solution was deionized with a mixed-bed resin and concentrated, yielding a sirup (1.6 gm.). The latter, which did not crystallize and which streaked heavily on a paper chromatogram, was dissolved in water (30 ml.) and treated with sodium borohydride (400 mgm.) (1, 19). The resulting solution was kept at room temperature for 12 hr., then it was acidified with acetic acid, cations were removed with Amberlite IR–120 resin, the solution was concentrated to dryness, and boric acid was removed by repeated addition and distillation of methanol. After being taken up in methanol–ethanol the reduced product crystallized (0.9 gm.) and after one recrystallization from the same solvent had m.p. 133°C. and $[\alpha]_D^{25}$ +134° (*c*, 2, water). The compound (R_{gal}, 0.83) gave galactose and erythritol on acid hydrolysis (paper chromatographic identification). Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.11%; H, 6.99%.

On oxidation with lead tetraacetate – potassium acetate in acetic acid the compound yielded 1.9 moles of formic acid and consumed 5.8 moles of oxidant. Calculated for 4-*O*-α-D-galactopyranosyl-D-erythritol: formic acid, 2.0; lead tetraacetate consumption, 6.0 moles.

*2-O-α-*D*-Glucopyranosyl-*D*-erythritol*

Maltose (3.4 gm.), dissolved in water (8 ml.), was taken up in acetic acid (450 ml.) and treated with lead tetraacetate (9.2 gm.) for three hours. The addition of oxalic acid (2 gm.) in acetic acid (20 ml.) destroyed the excess lead tetraacetate and precipitated most of the divalent lead ions. The product was worked up and reduced with sodium borohydride (1 gm.) as described above. Yield, 2.8 gm. (R_{gal}, 0.90). Crystallization took place in methanol–ethanol, and after recrystallization from the same solvent the product had m.p. 147°–148°C. and $[\alpha]_D$ +130° (*c*, 1.8, water). Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.10%; H, 7.11%.

The compound (0.3 gm.) was acetylated by warming with acetic anhydride (2 ml.) and pyridine (0.8 ml.). The excess acetic anhydride was decomposed with ice water yielding a sirup which slowly crystallized. The acetate was

recrystallized from ethanol (yield 0.4 gm.), m.p. 97–98°C., $[\alpha]_D$ +105° (*c*, 1.2, chloroform). Calculated for $C_{24}H_{34}O_{16}$: C, 49.82%; H, 5.92%; acetyl, 52.1%. Found: C, 49.74%; H, 5.98%; acetyl, 52.2%.

2-O-β-D-Glucopyranosyl-D-erythritol

Cellobiose (3.4 gm.) was oxidized with lead tetraacetate (9.2 gm.) in acetic acid (600 ml.) containing water (10 ml.) for four hours. The product was worked up and reduced by the method described previously yielding a solid product (2.7 gm.) which was recrystallized from aqueous methanol (R_{gal}, 0.90); m.p. 185°–187°C., $[\alpha]_D$ −17° (*c*, 2.0, water). Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.38%; H, 7.10%. Oxidation with lead tetraacetate – potassium acetate in acetic acid—found: formic acid, 1.0 mole; lead tetraacetate consumption, 3.8 moles. Calculated for $C_{10}H_{20}O_9$: formic acid, 1.0 mole; lead tetraacetate consumption, 4.0 moles.

The heptaacetate of the disaccharide was prepared by the acetic anhydride – pyridine method. After recrystallization from ethanol it had m.p. 116°C. and $[\alpha]_D$ −1.4° (*c*, 1.6, chloroform). Calculated for $C_{24}H_{34}O_{16}$: C, 49.82%; H, 5.92%; acetyl, 52.1%. Found: C, 50.04%; H, 5.98%; acetyl, 51.8%.

2-O-β-D-Glucopyranosyl-glycerol

Lead tetraacetate (0.49 gm.) was added to a vigorously stirred solution of 2-*O*-β-D-glucopyranosyl-D-erythritol (0.31 gm.) in acetic acid (60 ml.) containing water (1 ml.). The solution was stirred for six hours and the product was isolated by the procedure described above. The sirup obtained (0.27 gm.) was dissolved in water (10 ml.) and reduced with sodium borohydride (0.1 gm.). The reduced product (0.26 gm.) was crystallized from methanol–ethanol. A paper chromatogram showed a major spot (R_{gal}, 1.33) and a faint spot (R_{gal}, 0.90). On acid hydrolysis, glucose and glycerol were produced (identified by paper chromatography). After recrystallization from methanol–ethanol the material had m.p. 163°C. and $[\alpha]_D$ −30.2° (*c*, 1.2, water). Calculated for $C_9H_{18}O_8$: C, 42.52%; H, 7.14%. Found: C, 42.78%; H, 7.13%. Carter reports m.p. 165°C. and $[\alpha]_D^{20}$ −30.1° for 2-*O*-β-D-glucopyranosyl-glycerol (4).

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