LIIV.—*The Tannin of the Canadian Hemlock* (*Tsuga Canadensis*, Carr.).

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ALTHOUGH the chemistry of the pyrogallol tannins, of which gallotannin is the best known representative, has progressed during the last fifteen years, little or nothing has been published on the catechol (phlobaphen-producing) tannins, to which group nearly all the technically important vegetable tanning materials belong. We have investigated hemlock tannin, a representative of this group, in view of its colonial importance, and have accumulated observations during the three and a-half years this work has been in progress which we describe in this paper, without, however, attempting to draw any conclusions as to the probable constitution of hemlock tannin. Those who are acquainted with the literature on gallotannin (compare Dekker, "De Looistoffen," 1906; Nierenstein, "Chemie der Gerbstoffe," 1910; Dekker, "Die Gerbstoffe," 1913; Perkin and Everest, "The Natural Organic Colouring Matters," 1918) will be struck by the numerous formulæ which have been suggested for gallotannin, and the contradictory results that have been obtained. This is due to the amorphous character of gallotannin in particular and the tannins in general, and it is for this reason that we give our results on hemlock tannin without committing ourselves at this juncture to any theoretical discussion on the subject.

Böttlinger's Bromo-hemlock Tannin.

Böttlinger (*Ber.*, 1884, 17, 1041) examined the action of bromine on tannin extracts, and determined the percentage of bromine contained in the precipitated bromo-compounds. On the basis of the bromo-compounds obtained from mangrove, hemlock, quebracho, mimosa, chestnut, *Terra japonica*, and spruce, he proposed formulæ for these tannins which are more or less generally accepted. Böttlinger's formula for hemlock tannin is $C_{20}H_{18}O_{10}$; he deduced this from his bromo-derivative, $C_{20}H_{14}O_{10}Br_4$, from which he also prepared the acetyl derivative, $C_{20}H_9O_{10}Br_4Ac_5$. We have made a careful re-investigation of Böttlinger's work on hemlock tannin, with the following results:

(1) Böttlinger's bromination method does not always yield the same product, $C_{20}H_{14}O_{10}Br_4$, which requires $Br=43.60$ per cent.,

but a series of compounds in which the bromine content varies from 40 to 49 per cent. The analyses of eleven preparations gave:

Br = 41.28, 47.56, 43.88, 40.12, 43.20, 47.29, 44.56, 41.74, 48.48, 41.56, and 43.26 per cent.

(2) If Böttinger's product is obtained, it can be fractionated into a number of compounds in which the bromine content varies from 40 to 48 per cent. The fractionation method employed by us consisted in dissolving the bromo-compound in acetone and fractionally precipitating by the addition of chloroform. Three such experiments were made, and the results were:

Experiment I.—Bromine content of product, 43.12 per cent.

Fractions:	I.	II.	III.	IV.	V.
Br =	43.56	45.63	46.82	46.96	48.09 per cent.

Experiment II.—Bromine content of product, 43.88 per cent.

Fractions:	I.	II.	III.	IV.	V.
Br =	40.22	42.84	44.22	47.86	48.56 per cent.

Experiment III.—Bromine content of product, 43.98 per cent

Fractions:	I.	II.	III.
Br =	41.98	44.56	46.22 per cent.

(3) If hemlock tannin is prepared and fractionated by the method described later, and the different fractions are brominated separately, a series of bromo-compounds is obtained in which the bromine content increases as the phlobaphen content decreases.

<i>Brominated Phlobaphens.</i>			<i>Brominated Hemlock Tannin.</i>			
Frac- tions:	I.	II.	Frac- tions:	I.	III.	V.
Br =	38.59	42.33%	Br =	43.56	46.82	47.40%
Br =	39.14	41.56%	Br =	—	46.77	48.09%
Br =	40.11	42.82%	Br =	—	46.96	48.22%
Br =	—	—	Br =	—	—	49.56%

Our results suggest that Böttinger's formula for hemlock tannin and bromo-hemlock tannin must be disregarded, which conclusion, probably, also applies to the other bromo-tannins mentioned.

Alkali Hydrolysis of Bromo-hemlock Tannin.

During his investigations on bromo-quebracho tannin, Nierenstein (*Collegium*, 1905, 69) obtained on hydrolysis with alcoholic potassium hydroxide (1) *isovanillic* acid, and (2) a substance, $C_3H_7O_4Br$, to which he assigned provisionally the name monobromo-quebrachilic acid. The latter crystallised from chloroform in small needles melting at 119–120°. We have extended these investi-

gations to bromo-hemlock tannin, but were only able to isolate a substance, $C_8H_7O_4Br$, which apparently is closely allied to monobromoquebrachilic acid, and is provisionally called *monobromotsuginic acid*. For comparison, the melting points of these two substances and of their derivatives are tabulated.

Monobromoquebrachilic Acid.

Free acid ...	m. p. 119—120°
Methyl ester ...	m. p. 96—98°
Ethyl ester...	m. p. 93—94°

Monobromotsuginic Acid.

Free acid ...	m. p. 143—145°
Methyl ester ...	m. p. 108—111°
Ethyl ester ...	m. p. 100—102°

Nierenstein (*loc. cit.*) obtained from monobromoquebrachilic acid on further hydrolysis monobromoresorcinol, but we have failed to isolate any definite disintegration product from monobromotsuginic acid.

Alkali Hydrolysis.—About 10 grams of bromo-hemlock tannin containing 44.56 per cent. of bromine were heated under reflux on a water-bath with 100 c.c. of 20 per cent. alcoholic potassium hydroxide for six hours, and the solution was filtered after dilution with water. The filtrate was evaporated to dryness and extracted with acidified boiling alcohol. After several days, a crop of needles (about 0.1 gram) was obtained, which was collected and recrystallised from alcohol and benzene. Repetition of the hydrolysis gave amounts of crude monobromotsuginic acid varying from 0.7 to 1.2 per cent. of the weight of bromo-hemlock tannin.

Monobromotsuginic acid crystallises from alcohol and benzene in small, sharp needles which melt at 143—145°, carbon dioxide being evolved.

Found: C=38.75; H=3.42; Br=31.62. M.W.=251.

$C_8H_7O_4Br$ requires C=38.87; H=2.87; Br=32.39 per cent.
M.W.=247.

The *methyl* ester, prepared by the hydrochloric acid method, crystallises from chloroform in silky needles melting at 108—111°.

Found: C=41.95; H=3.67.

$C_9H_9O_4Br$ requires C=41.38; H=3.44 per cent.

The *ethyl* ester crystallises from alcohol in needles melting at 100—102°

Found: C=43.22; H=4.58.

$C_{10}H_{11}O_4Br$ requires C=43.63; H=4.00 per cent.

The *acetyl* derivative is prepared by digesting monobromotsuginic acid with acetic anhydride for several hours, the excess of, acetic anhydride being removed in a vacuum. It separates from

alcohol in small, cubic crystals melting at 124--126°, carbon dioxide being evolved.

Found: C=41.22; H=3.64.

$C_{10}H_9O_5Br$ requires C=41.52; H=3.12 per cent.

Attempts to prepare carbethoxy- and benzoyl derivatives failed, as the products did not crystallise.

So far as it is possible to deduce from the above data, monobromotsuginic acid may be regarded as having the constitution $CO_2H \cdot C_7H_5OBr \cdot OH$.

Much work, however, is still required before it will be possible to decide on a definite constitution for this fission product, which in time may prove of importance to the chemistry of hemlock tannin in particular and the catechol tannins in general.

Preparation of Hemlock Tannin.

The finely sieved hemlock bark (about 8 kilos. were used each time) was extracted repeatedly with acetone. The extraction must always be carried out in the cold, on account of the ease with which hemlock tannin is oxidised to phlobaphens. The united acetone solutions were evaporated to one-third of their bulk under diminished pressure at about 55°. In this and in the succeeding operations, great care must be taken to keep the temperature as low as possible, as otherwise a considerable loss of hemlock tannin occurs through the formation of phlobaphen.

In order to precipitate the phlobaphens, the concentrated acetone solution was poured into twice its bulk of water and allowed to remain overnight. The phlobaphens, which appeared as a bulky, dark red mass, were collected, washed, and dried in a desiccator. The filtrate, which contained the hemlock tannin and always a certain amount of unprecipitated phlobaphens, was evaporated to a viscid mass in a vacuum at a temperature not exceeding 55°. This was dissolved in 570 c.c. of alcohol, and if still rich in phlobaphens gave a further precipitation if diluted with an equal amount of water. Usually, only a small portion of the alcoholic solution was tested, so as to avoid loss through oxidation. If, then, on adding water to a test portion little or no precipitation of phlobaphens took place, the whole alcoholic solution was evaporated to dryness under diminished pressure at 55°. On the other hand, if much phlobaphen was precipitated, the solution was diluted with an equal amount of water, and the preceding operations were repeated. The resultant mass (about 300 grams) was

carefully dried, and appeared then as a dark red, brittle substance, evidently still rich in phlobaphens.

The crude hemlock tannin (100 grams) was extracted with 750 c.c. of carefully dried acetone. The acetone was added in several portions and filtered before each fresh addition. The residue insoluble in acetone appeared, when carefully washed with light petroleum and dried in a vacuum at 70°, as a pale brown powder, which weighed about 5 grams. The dark red acetone solution was treated with portions of 50, 100, and 400 c.c. of chloroform, as used by Nierenstein in the purification of gallo-tannin (*Annalen*, 1912, **388**, 243). The first two fractions were dark and inclined to be viscid. The third fraction was pink. When washed with light petroleum and dried in a vacuum, they weighed respectively 8, 12, and 35 grams. The filtrate from fraction III was evaporated to dryness under diminished pressure at 55°, and the residue dissolved in 150 c.c. of ethyl acetate, which when poured into 200 c.c. of chloroform yielded 26 grams of a light-coloured precipitate. The filtrate was again evaporated to dryness, the residue dissolved in 100 c.c. of ethyl acetate, and fractions V and VI were precipitated by successive addition of 100 c.c. of chloroform. Fraction V (10 grams) was faintly pink, whilst fraction VI (2 grams) was creamy-white.

Found:

Fraction III.—C=61.58, 61.86; H=5.05, 5.29.

Fraction IV.—C=63.52, 63.30; H=5.31, 5.33.

Fraction V.—C=64.09; H=5.41.

Fraction VI.—C=64.24, 64.06, 64.33; H=4.88, 5.08, 5.23 per cent.

The amorphous character of the products and also the variations in the composition of the different fractions show how undesirable it is to calculate an empirical formula for hemlock tannin, as is also the case with gallotannin (compare Nierenstein, *Annalen*, 1912, **388**, 243). In addition to this, hemlock tannin also contains traces of a methoxy-compound, from which we have not succeeded in freeing it. We found that even the purest fraction (VI) contained OMe=0.80, whilst some of the other fractions gave as much as 3.56 per cent. of methoxyl.*

* During these investigations, experiments were also made to see if some of the methoxyl in the hemlock tannin showed resistance towards hydriodic acid, and we therefore re-heated the Perkin-Zeisel apparatus on the following day after the methoxy-estimations had been carried out, as described by Herzig (*Monatsh.*, 1905, **25**, 603; 1908, **29**, 263) during his investigation of ellagic acid. We were thus able to observe an increase in the methoxy-content which, however, could be accounted for by the formation of a

Purified hemlock tannin is a pink, amorphous powder which does not melt when heated above 300°, but begins to decompose at about 260—275°. It is soluble in alcohol, acetone, ethyl acetate, or water, in which it forms deep red solutions. When hydrolysed according to Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915) for the estimation of sugar in gallotannin, it was found that hemlock tannin does not contain any kind of sugar. With iron chloride it gives a deep green coloration, especially in alcoholic solution. Hemlock tannin is precipitated by gelatin or alkaloids, and is quantitatively absorbed by caseinogen (compare Körner and Nierenstein, *Chem. Zeit.*, 1911, **36**, 31; Nierenstein, *Annalen*, 1912, **388**, 224; Spiers, *J. Agric. Sci.*, 1919, **6**, 77).

Alkali Hydrolysis of Hemlock Tannin.

(1) *Alcoholic Potassium Hydroxide.*—The only definite fission product obtained by this method was protocatechuic acid, crystallising from water in small needles melting at 191—194°, carbon dioxide being evolved. When mixed with protocatechuic acid, no depression (m. p. 193—194°) was observed.

(2) *Alcoholic Barium Hydroxide.*—We originally used aqueous barium hydroxide with some success, but later employed the methyl-alcoholic solution (compare Müller, T., 1915, **107**, 874). This hydrolysis yielded protocatechuic acid, 2:3-dihydroxybenzoic acid, and a new substance, $C_{10}H_8O_3$, which was apparently an *aldehyde*.

The hydrolysis was carried out by heating about 10 grams of hemlock tannin with an excess of methyl-alcoholic barium hydroxide for eight to ten hours under reflux. The alcohol was then removed on the water-bath, and the residue diluted with water and acidified with dilute sulphuric acid. The liquid, and also the barium sulphate precipitate, were extracted several times with ether, and the ethereal solution (solution A) treated with sodium hydrogen carbonate solution saturated with carbon dioxide. The aqueous part thus obtained was acidified and extracted with ether (solution B), and both ethereal solutions were investigated separately.

Ethereal Solution A.—The solution left, on evaporation, a tarry precipitate of silver iodide when hydriodic acid and acetic anhydride are left for twenty-four hours and then heated (Manning and Nierenstein, *Ber.*, 1913, **46**, 3983. Critics of this note (compare G. Goldschmiedt, *Ber.*, 1914, **47**, 389; A. G. Perkin and Oesch, T., 1914, **105**, 2352) appear to have overlooked the necessity of allowing the mixture to remain for at least a day before any precipitation of silver iodide can be obtained.

mass, which became solid on rubbing and kneading with light petroleum. The dry solid was then extracted in a Soxhlet apparatus with benzene, when the greater part of the product dissolved, leaving a tarry residue in the thimble. The benzene was evaporated to dryness, and the residue (about 0.8 gram) crystallised from alcohol and benzene, from which it separated in small, silky plates melting at 125---126°. It is also soluble in alcohol or much benzene or toluene, from which solutions it crystallises in needles (m. p. 125---126°) after strong concentration of the solvents.

Found: C=68.45; H=4.83. M.W.=160, 166.

$C_{10}H_8O_3$ requires C=68.18; H=4.54 per cent. M.W.=176.

With phenylhydrazine it forms a *phenylhydrazone*, which crystallises from glacial acetic acid in dark brown needles melting and decomposing at 191°.

Found: N=17.91, 17.49.

$C_{16}H_9O_2N_2$ requires N=17.27 per cent.

When oxidised on the water-bath with potassium permanganate in alkaline suspension, it yields the *acid*, $C_9H_7O_2 \cdot CO_2H$, which crystallises from water in long, prismatic needles melting at 214---216°, carbon dioxide being evolved.

Found: C=62.42; H=4.60.

$C_{10}H_8O_4$ requires C=62.50; H=4.20 per cent.

The *sodium* and *potassium* salts were prepared and crystallised from water.

Found: Na=11.12; K=20.86.

Calculated: Na=10.74; K=20.40 per cent.

Diazomethane yields the *methyl* ester, which crystallises from benzene in silky needles melting at 152---153°.

Found: C=64.24; H=4.82.

$C_{11}H_{10}O_4$ requires C=64.18; H=4.62 per cent.

Ethereal Solution B.—The residue which was left on evaporation of the ether crystallised from water in small needles melting indefinitely between 145° and 168°, although the product was recrystallised several times from that solvent. The only definite colour reactions obtained were those of protocatechuic acid, and the analytical data also agreed for a dihydroxybenzoic acid. (Found: C=54.12; H=4.22. $C_7H_6O_4$ requires C=54.52; H=3.94 per cent.) Attempts were made to separate the mixture by fractional crystallisation, but no fraction of a definite melting point was obtained. The product when heated with soda-lime only gave, so far as could be ascertained, catechol (small needles from

benzene, m. p. 102—103°), from which we concluded that the mixture consisted probably of protocatechuic acid (m. p. 198—199°) and 2:3-dihydroxybenzoic acid (m. p. 204°) (compare Praxmarer, *Monatsh.*, 1906, **27**, 1199; also abstract of this paper, A., 1907, **92**, i, 216, where the melting point is wrongly given as 240°). The product was therefore treated in ethereal solution with diazomethane and converted into the methyl esters of veratric acid (m. p. 59—60°) and 2:3-dimethoxybenzoic acid (m. p. 57—58°) (compare Praxmarer, *loc. cit.*), and the mixture fractionated under diminished pressure. Sixteen grams of the methyl esters gave the following fractions, which crystallised from benzene on subsequent solidification:

Fraction I.—1.84 Grams, b. p. 124—127°/10—11 mm., m. p. 47—53°.

Fraction II.—4.26 Grams., b. p. 124—126°/10—12 mm., m. p. 52—54°.

Fraction III.—4.47 Grams, b. p. 125—127°/10—12 mm., m. p. 55—56°.

Fraction IV.—2.12 Grams, b. p. 126—129°/10—11 mm., m. p. 58—59°.

Each fraction was hydrolysed on the water-bath with alkali, and the free methoxy-acids were crystallised from dilute alcohol. These fractions melted as follows:

Fraction I.—M. p. 162—168°.

Fraction II.—M. p. 178—180°. Mixed m. p. with veratric acid, 178—180°; mixed m. p. with 2:3-methoxybenzoic acid, 158—164°.

Fraction III.—M. p. 176—183°. Mixed m. p. with veratric acid, 164—171°; mixed m. p. with 2:3-dimethoxybenzoic acid, 172—178°.

Fraction IV.—M. p. 184—186°. Mixed m. p. with veratric acid, 168—174°; mixed m. p. with 2:3-dimethoxybenzoic acid, m. p. 183—185°.

The melting point of veratric acid is given as 181° (compare Freund and Niederhofheim, *Ber.*, 1896, **29**, 858; Kostanecki and Tambor, *Ber.*, 1907, **39**, 4022). There is, however, no reference to 2:3-dimethoxybenzoic acid. This was therefore prepared by the action of diazomethane on 2:3-dihydroxybenzoic acid prepared according to Praxmarer's method (*loc. cit.*); the ester was subsequently hydrolysed and the methoxy-acid crystallised from dilute alcohol, from which it separated in needles melting at 187—188°, carbon dioxide being evolved. (Found: C=59.14; H=5.72. $C_9H_{10}O_4$ requires C=59.31; H=5.54 per cent.)

From the above data, it is probable that fraction II consisted mainly of veratric acid (Found: C=59.12; H=5.78. Calc.: C=59.31; H=5.54 per cent.), whereas fraction IV consisted of 2:3-dimethoxybenzoic acid (Found: C=58.92; H=5.46. Calc.: C=59.31; H=5.54 per cent.), from which we conclude that proto-catechuic and 2:3-dihydroxybenzoic acids are formed during the hydrolysis of hemlock tannin.

Methylated Hemlock Tannin.

Hemlock tannin was methylated with diazomethane in ethereal suspensions, fractions IV, V, and VI only being used for the methylation. The dry tannin was suspended in ether, as used in the Grignard reaction (compare Clibbens and Nierenstein, T., 1915, **107**, 1491), and an excess of diazomethane allowed to act on it for about twelve hours. In the case of fraction IV there was always a residue, after methylation, insoluble in ether [similar observations were made by Herzig (*Monatsh.*, 1912, **33**, 843), and Fischer and Freudenberg (*Ber.*, 1912, **45**, 2723), during the methylation of gallotannin with diazomethane]. Fraction V also left a small residue, but fraction VI on methylation dissolved completely in ether.

The ethereal solution was filtered and the ether removed under diminished pressure. The residue was purified by dissolving in a little alcohol and pouring into water. It frequently happened that the methylated product did not separate out readily, in which case the liquid was shaken vigorously to coagulate the precipitate and allowed to remain for a time. The precipitate was then collected, carefully washed, and dried in a desiccator.

Methylated hemlock tannin obtained in this way after several precipitations was a white, amorphous product with a more or less distinctly yellow tint; it was readily soluble in alcohol, ether, acetone, benzene, carbon tetrachloride, or *s*-tetrachloroethane, but insoluble in light petroleum. The product had no definite melting point; it sintered at 74—79° and melted at 134—141°.

Found: C=65.69, 65.25, 64.82, 65.12; H=5.58, 5.46, 5.82, 5.27; OMe=26.48, 25.65, 25.84 per cent. M.W. (in chloroform)=620, 561, 552, 574.

The methoxy-estimations were carried out in a Zeisel-Perkin apparatus, acetic anhydride being added. If the latter was replaced by phenol (compare Weishut, *Monatsh.*, 1913, **33**, 1165), the same result was obtained (OMe=25.76 per cent.). In view of the experiences of W. Richter (*Diss.*, Erlangen, 1902, 44), who found that eutannin is more fully methylated with diazomethane

in an acetone solution than in an ethereal one, we also used the former as a solvent, without, however, increasing the methoxy-content. (Found: OMe=25.89 per cent.). For similar reasons, we also used methyl alcohol as a solvent (compare Geake and Nierenstein, *Biochem. J.*, 1914, **8**, 292), the result being the same (Found: OMe=25.43 per cent.).

Methylated hemlock tannin was found to be optically active: $[\alpha]_D^{25} -41^\circ$ (in chloroform), -24.7° (in *s*-tetrachloroethane), 50.1° (in alcohol), and -16.9° (in acetone).

Alkali Hydrolysis of Methylated Hemlock Tannin.

Methylated hemlock tannin (about 5—10 grams) was hydrolysed by boiling with a 10 per cent. solution of alcoholic potassium hydroxide for about three hours. The alcohol was then evaporated, and the residue extracted with boiling water and filtered from any incompletely hydrolysed or tarry substance. On acidifying with dilute sulphuric acid, the filtrate gave a bulky precipitate (precipitate A), which was collected, washed, and dried in a desiccator. The filtrate was extracted with ether several times, and the ethereal extract treated with a 5 per cent. solution of sodium hydrogen carbonate saturated with carbon dioxide. Nothing was found to remain in the ether. The sodium hydrogen carbonate solution was acidified with dilute sulphuric acid and extracted with ether. On evaporation of the ether, a residue was obtained which was crystallised several times from water with the addition of animal charcoal, when small crystals were obtained melting at 208° . They proved to be vanillic acid, and gave no depression of the melting point when mixed with vanillic acid. (Found: C=57.02; H=5.08. Calc.: C=57.11; H=4.81 per cent.)

Precipitate A.—The product was purified by dissolving several times in alcohol and precipitating with water.

Found: C=67.14, 66.83; H=6.49, 6.22; OMe=28.18 per cent.

When oxidised with potassium permanganate in alkaline solution, hemipinic acid was produced. The following method of oxidation gave the best results. 1.5 Grams of the substance were heated on a water-bath for six to eight hours with 75 c.c. of 2*N*-potassium hydroxide and 3 grams of potassium permanganate dissolved in about 50 c.c. of water, which were added in two portions. The solution was acidified, filtered, and extracted with ether. The residue left on evaporation crystallised from water in small needles, which melted when slowly heated at 170 — 173° (compare Nierenstein, *Annalen*, 1913, **396**, 198; Pschorr and

Samuleanu, *Ber.*, 1899, **32**, 3411), which melting point was not depressed when mixed with hemipinic acid prepared from opianic acid. (Found: C=53.33; H=5.09. Calc.: C=53.07; H=4.47 per cent.)

Mild hydrolysis of precipitate A furnished opianic acid, which was obtained on warming 2 grams of the substance with 20 c.c. of 2*N*-alcoholic potassium hydroxide for several hours on the water-bath under reflux at a temperature not higher than 60°. The alcohol was evaporated, the residue acidified, and extracted with ether. The ethereal extract was shaken with sodium hydrogen carbonate solution saturated with carbon dioxide, and the aqueous part, after acidification with dilute sulphuric acid, extracted with ether. The carefully dried residue which was left on evaporation of the ether deposited, from benzene, thin, prismatic needles melting at 147—149°. When mixed with opianic acid, no depression of the melting point was observed. (Found: C=56.82, 56.78; H=5.12, 4.94. Calc.: C=57.11; H=4.81 per cent.) A small amount was converted into the oxime, crystallising in small needles melting at 81°, which is in the vicinity of the melting point 82—83°, as found by W. H. Perkin, jun. (*T.*, 1890, **57**, 1071). There was not enough material for a combustion.

The fact that the methylated hemlock tannin yields opianic acid (I) suggests the possible existence of noropianic acid (II) in hemlock tannin, which probably explains the formation of hemipinic acid (III) and veratric acid (IV) from methylated hemlock tannin and protocatechuic acid (V) and 2:3-dihydroxybenzoic acid (VI) from hemlock tannin:

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