

327. *The Constitution of Tannins. Part III. Hemlock Tannin. Synthesis of Bis-(7 : 8 : 3' : 4'-tetrahydroxy)flavpinacol.*

By ALFRED RUSSELL and JOHN TODD.

THE hemlock is a conifer widely distributed through the North American Continent and the bark contains upwards of 10% of a water-soluble phlobatannin. Hemlock extracts find extensive use in North America for tanning purposes; elsewhere, their use is limited because they give leathers having the deep red colour of the solutions.

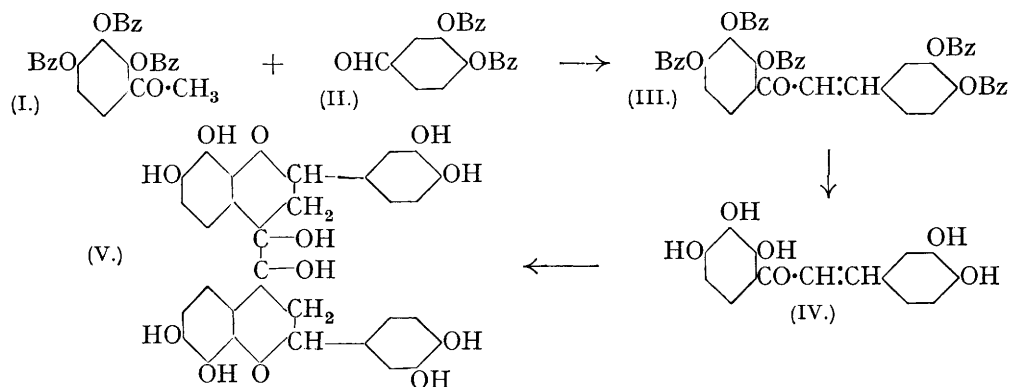
The tannin has been isolated on several occasions (see Perkin and Everest, "Natural Organic Colouring Matters"), but the results reported are confusing. A complete empirical re-examination of the tannin, newly extracted from hemlock bark, has therefore been made; it has the usual appearance of tannins but is somewhat darker. Treatment of the cruder specimens with boiling dilute mineral acids produced a phlobaphene and traces of glucose (identified by its osazone) but, after purification through its lead salt, the tannin was free from sugar. By fission with fused alkali, pyrogallol and protocatechuic acid (and pyrocatechol by decarboxylation of this acid) were obtained. The very close qualitative resemblance between hemlock tannin and bis-(5 : 7 : 3' : 4'-tetrahydroxy)flavpinacol led to repeated examinations of the fission products for phloroglucinol residue, but none could be found.

In accordance with the views now being examined (this vol., pp. 218, 1066), hemlock tannin appears to be a flavpinacol hydroxylated on the pattern of bis-(7 : 8 : 3' : 4'-tetrahydroxy)flavpinacol (V) or even identical with it. So far as can be found, hemlock tannin is the only phlobatannin that gives pyrogallol as its phenolic component, and it is likely that its unusually deep red solutions and ready conversion into phlobaphene are due to

this departure from the usual phloroglucinol or resorcinol pattern. Moreover, it is known that polyhydroxy-chalkones are more highly coloured when their structure contains phenolic hydroxyl groups ortho to each other, particularly in the 3 : 4-position, than when these groups are otherwise distributed. This deepening of colour has become very evident during the progress of this research.

The synthesis of *bis*-(7 : 8 : 3' : 4'-tetrahydroxy)flavpinacol has now been accomplished. It gives the typical qualitative tests for phlobatannins, and bears a close quantitative resemblance to natural hemlock tannin. The parent 2 : 3 : 4 : 3' : 4'-pentahydroxy-chalkone, which precipitates gelatin in aqueous solution, is readily distinguishable from the flavpinacol by its crystalline nature and by its colour reactions with ferric chloride (dark chocolate-brown) and lead acetate (deep red). The results indicate, even in the unlikely event of phloroglucinol having been overlooked amongst the fission products of hemlock tannin, that flavpinacols hydroxylated on the 7 : 8 : 3' : 4'-pattern are phlobatannins.

Gallacetophenone tribenzoate (I) condensed at 0° with protocatechualdehyde dibenzoate (II) in presence of anhydrous hydrogen chloride in dry ethyl acetate to give 2 : 3 : 4 : 3' : 4'-pentabenzoyloxychalkone (III), from which, by hydrolysis with alkali, resulted 2 : 3 : 4 : 3' : 4'-pentahydroxychalkone (IV), and this, by reduction with zinc dust and alcoholic hydrogen chloride, gave the required flavpinacol (V). The use of alcoholic hydrogen chloride is necessary owing to the strongly acidic character of the chalkone (gallaldehyde is more strongly acidic than acetic acid; Rosenmund and Zetzsche, *Ber.*, 1918, **51**, 594).



The solubilities of the synthetic product are in exact agreement with those of hemlock tannin. Both are readily soluble in water, alcohols, ethyl acetate, and acetone, giving red solutions, and insoluble in chloroform and its homologues and in hydrocarbons. The synthetic product is, like hemlock tannin, rapidly and quantitatively absorbed by hide powder, and it rapidly tans small pieces of sheep-skin, giving a leather which is considerably lighter in colour than that obtained with the natural product.

The properties of the synthetic and the natural product are compared in the following table, the colour reactions being identical except where colours are given in parentheses, in which case these refer to the natural tannin. Both substances were used in $\frac{1}{2}\%$ aqueous solution, both solutions being light yellow.

Reagent.	Reaction.	Reagent.	Reaction.
Alc. FeCl_3	Dark vivid green colour.	Na_2SO_3	Faint green (pink) colour.
Aq. FeCl_3	Dark vivid green colour; dark ppt. on standing.	HNO_2	Immediate brown ppt.
Gelatin	Dirty white ppt.	CuSO_4	Faint green colour.
$\text{Pb}(\text{OAc})_2$	Light coloured ppt., sol. in HOAc .	$\text{CuSO}_4 + \text{NH}_3 \text{ aq.}$	Heavy dark ppt.
Boiling 5% HCl	Soln. darkens to deep red and red insol. ppt. separates.	$\text{NH}_3 \text{ aq.}$	Soln. darkens slowly.
$\text{Br}_2 \text{ aq.}$	Immediate heavy orange (yellow) ppt.	$\text{CH}_3\text{O} + \text{HCl}$	Ppt. on warming.
$\text{Cu}(\text{OH})_2$	Faint red (pink) colour, light red (pink) ppt.	$\text{K}_2\text{Cr}_2\text{O}_7 \text{ aq.}$	Immediate brown ppt.
		$\text{K}_3\text{Fe}(\text{CN})_6 + \text{NH}_3 \text{ aq.}$	Deep red colour.

EXPERIMENTAL.

Extraction of Hemlock Tannin.—The crushed and dried bark was extracted with cold water, and the filtered aqueous extract treated with salt, the tannin being precipitated as a light-coloured amorphous mass. The mixture of tannin and salt was collected, dried, and extracted with acetone (Soxhlet). The acetone was removed by evaporation on the water-bath till the extract was syrupy; it was now transferred to a vacuum desiccator, and the tannin rapidly swelled and dried. It was purified, when necessary, through its lead salt and formed a light red, amorphous substance retaining traces of solvents obstinately.

2 : 3 : 4 : 3' : 4'-Pentahydroxychalkone.—Gallacetophenone tribenzoate (9.6 g.; 1 mol.) and protocatchualdehyde dibenzoate (7 g.; 1 mol.) were dissolved in dry ethyl acetate (80 c.c.). The ice-cold solution, when saturated with anhydrous hydrogen chloride for 60 hours, became yellow, orange, and finally, clear light red. The ethyl acetate was removed by evaporation, and the clear red residual syrup boiled with alcohol (50 c.c.), cooled, and the alcohol decanted from the light yellow *2 : 3 : 4 : 3' : 4'-pentabenzoyloxychalkone*. This was washed with cold alcohol, and then crystallised from much alcohol in transparent light yellow nodules, which were not definitely crystalline (did not transmit polarised light); m. p. 85° after sintering at a lower temperature (Found: C, 72.7; H, 4.1. $C_{50}H_{32}O_{11}$ requires C, 74.2; H, 4.0%. $C_{50}H_{32}O_{11}$, EtOH requires C, 73.0; H, 4.45%). It (11 g.) was dissolved with difficulty in boiling alcohol (300 c.c.), and to the solution was added dropwise (nitrogen atmosphere) aqueous potassium hydroxide (28 g. in 300 c.c.), the alcohol distilling off at an equal rate. The solution slowly became clear dark orange-red; after 4 hours, it was cooled in ice, acidified (hydrochloric acid), and removed from the nitrogen atmosphere. The precipitated benzoic acid and chalkone were collected, and extraction of the filtrate with ethyl acetate, after saturation with sodium chloride, yielded a further quantity of chalkone. The *chalkone* was freed from benzoic acid by washing with benzene (Soxhlet), and finally obtained as a deep orange-red, microcrystalline solid (3 g.), m. p. 233° (Found: C, 61.9; H, 4.4. $C_{15}H_{12}O_6$ requires C, 62.5; H, 4.2%). That complete hydrolysis had been effected was ascertained by collecting and weighing the benzoic acid produced.

Bis-(7 : 8 : 3' : 4'-tetrahydroxy)flavpinacol.—The above chalkone (2 g.) was dissolved in alcohol (60 c.c.), and to the boiling solution was added, portionwise (12 mins.), saturated alcoholic hydrogen chloride (3 c.c.) and zinc dust (10 g.). The opaque red solution became clear and very light brown but, after filtration, it darkened somewhat; it was cooled rapidly, diluted largely with water (300 c.c.), saturated with sodium chloride, and extracted with ethyl acetate (60 c.c.). The extract was washed with water till free from halogen (5×30 c.c.), dried (sodium sulphate), and evaporated several times with acetone to remove most of the ethyl acetate. Finally, the hot syrupy residue was dried in a vacuum, the product swelling to a vitreous golden-red mass. On grinding, a light red, amorphous solid resulted, which retained traces of solvents obstinately and, for analysis, was dried over sodium hydroxide at 110° and 15 mm. for 8 hours (Found: C, 62.0; H, 4.55. $C_{30}H_{26}O_{12}$ requires C, 62.2; H, 4.5%).

The following analyses of natural hemlock tannin are added for comparison: Crude natural hemlock tannin, extracted as described and dried over sodium hydroxide at 120° and 15 mm. for 24 hours (Found: C, 61.7, 62.7; H, 4.9, 5.0%); natural hemlock tannin, purified through its lead salt and dried as above (Found: C, 62.1; H, 4.4%); lead (hemlock) tannate (Found: Pb, 27.3, 28.2. Calc. for $C_{30}H_{24}O_{12}Pb$: Pb, 27.6%); methylated hemlock tannin (methyl sulphate and alkali) [Found: C, 66.5; H, 6.15; OMe, 31.8, 32.6. Calc. for $C_{30}H_{18}O_4(OMe)_8$: C, 66.1; H, 6.1; OMe, 36.0%].

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THE UNIVERSITY, GLASGOW.

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