122. *The Chemistry of Extractives from Hardwoods. Part IV. Okanin and* iso*Okanin, the Isomeric 2 : 3 : 4 : 3′ : 4′-Pentahydroxychalkones.*

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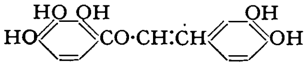
Two colouring matters, okanin and *iso*okanin, have been isolated from the yellowish-brown heartwood of the West African tree *Cylicodiscus gabunensis* Harms., okanin being identified as 2 : 3 : 4 : 3′ : 4′-pentahydroxychalkone by comparison with a synthetic specimen. The formation of distinct phenylhydrazones, converted on heating into a common pyrazoline, indicates that the two pigments are geometrical isomers.

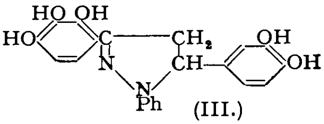
Cylicodiscus gabunensis Harms., one of the largest trees in West Africa, is the source of a hard and dense wood known commercially as okan or African greenheart. A tendency to check and become distorted on seasoning renders it somewhat unsuitable for furniture manufacture, but owing to its high durability the timber is often used in its country of origin for heavy constructional work. In view of its classification as very resistant to decay, okan was included among a number of timbers of which extracts are now undergoing chemical examination. We are greatly indebted to Mr. W. O. Woodward, Director, The Nottingham Mills Co., for help in obtaining samples of okan.

The heartwood, which varies in colour from yellow to brown and is sometimes tinted green, is readily distinguished from the pinkish sapwood. A small-scale extraction of the heartwood gave only a negligible petroleum-soluble fraction, but the material (1·3%) removed by boiling ether appeared to be largely composed of the characteristic colouring matters of the timber, and a further quantity was found among the tannins which constitute the bulk of the considerable alcoholic extract (10—12%). These preliminary experiments enabled a simple procedure to be devised for the isolation of the pigments, consisting in boiling the powdered wood with alcohol and exhaustively extracting the resultant brown brittle resin with cold ether. The gummy ether-soluble portion hardened when stirred with water and was then readily fractionated by dissolving it in boiling 50% acetic acid. The portion crystallising when the solution was cooled amounted to 1·3% of the timber and was an orange compound, $C_{15}H_{12}O_6$, m. p. 235—240° (decomp.), which has been named okanin. By evaporation of the remaining solution and crystallisation of the solid residue from water, the yellow hydrated *iso*okanin, $C_{15}H_{12}O_6,1\frac{1}{2}H_2O$, m. p. 140° (efferv.), comprising approximately 1·8% of the wood, was obtained.



(I; *trans.*) Okanin

(II; *cis.*) *iso*Okanin



(III.)

Okanin dissolved in aqueous alkalis to deep-orange solutions from which it was recovered unchanged on acidification. It formed a deep red 2 : 4-dinitrophenylhydrazone typical of the αβ-unsaturated ketones and gave an intense ferric reaction and a purple colour on reduction with magnesium and alcoholic hydrogen chloride. These observations together with the molecular formula were suggestive of a pentahydroxychalkone structure, and it was then noticed that the melting point of okanin was similar to that of 2 : 3 : 4 : 3′ : 4′-pentahydroxychalkone (Russell and Todd, *J.*, 1934, 1506; Kurth, *J. Amer. Chem. Soc.*, 1939, **61**, 861). The identity of the two compounds appeared to be confirmed by the ultra-violet absorption of okanin which was in close agreement with the spectrum of the pentahydroxychalkone as determined by Russell, Todd, and Wilson (*J.*, 1934, 1940) but, whereas the pentabenzoate of the synthetic chalkone, its sole recorded derivative, is described as a solid, m. p. 85° (Russell and Todd, *loc. cit.*), the corresponding benzoate of okanin could not be obtained crystalline. However, a specimen of 2 : 3 : 4 : 3′ : 4′-pentahydroxychalkone which was then prepared from protocatechualdehyde and gallacetophenone by Kurth's method (*loc. cit.*) was indistinguishable from the natural compound, and their readily crystallisable penta-acetates were proved identical by the mixed melting point test.

The accompanying isomeric yellow pigment was found to be closely related to okanin, a solution of the former in dilute acid kept at 100° gradually depositing the less-soluble pentahydroxychalkone. Moreover, the derivative obtained from *iso*okanin and 2 : 4-dinitrophenylhydrazine in boiling 2N-hydrochloric acid was identical in its colour change at higher temperature and in decomposition point with okanin 2 : 4-dinitrophenylhydrazone. *iso*Okanin thus appeared to be the corresponding tetrahydroxyflavanone, but the acetylation of *iso*okanin to a penta-acetate which, moreover, was different from okanin penta-acetate, decisively excluded the possibility. It was thus evident that the two colouring matters were geometrical isomers, a conclusion strengthened by the quantitative formation of okanin when its isomer was heated above the melting point. The greater stability, higher melting point, etc., of okanin and its formation by synthesis all point to the *trans*-configuration (I) for this isomer, *iso*okanin therefore being the *cis*-modification (II). Instances of *cis–trans*-isomerism in the chalkone series have already been reported, *e.g.*, ω-benzylidene-4-*p*-tolylacetophenone (Badoche, *Bull. Soc. chim.*, 1928, **43**, 337) and α-bromo-β-methoxystyryl phenyl ketone (Dufraisse and Gillet, *Ann. Chim.*, 1929, **11**, 5), although the phenomenon is often confused with polymorphism (see Weygand and Hennig, *Ber.*, 1927, **60**, 2428), but we know of no previous example among the naturally-occurring chalkones.

An attempt was made to reduce the isomeric chalkones to the identical saturated ketone and thus obtain further proof of their *cis-trans*-relationship. Catalytic reduction of okanin resulted in the rapid absorption of one mole of hydrogen, and then slowly of a second, the reaction being interrupted without difficulty and the required ketone isolated as its 2 : 4-dinitrophenylhydrazone. *iso*Okanin, on the other hand, rapidly absorbed two moles of hydrogen at constant rate but, in presence of sodium hydroxide, the absorption was much slower and virtually ceased with the uptake of one mole, a 2 : 4-dinitrophenylhydrazone being obtained which was identical in appearance with that from dihydro-okanin. A comparison by the melting point method was unreliable, the two samples having indefinite decomposition points, but their identity was rigidly established by *X*-ray powder-diffraction photographs kindly prepared by Mr. S. C. Wallwork.

Catalytic reduction of the okanin and *iso*okanin penta-acetates also showed unexpected variation, the former rapidly consuming two moles of hydrogen, while absorption of the second equivalent by the *iso*okanin derivative occurred only very slowly.

The relationship of the two compounds was unambiguously established by a study of their phenylhydrazones. As with the 2 : 4-dinitrophenylhydrazones, the rates of reaction of the two isomeric chalkones with phenylhydrazine differed considerably. With okanin the reaction was extremely slow at room temperature, but was apparently complete after heating at 100°, although the product could not be obtained solid. *iso*Okanin, however, readily gave a crystalline phenylhydrazone at room temperature. Heating with acetic acid, a reagent known to cause ring-closure of chalkone phenylhydrazones to pyrazolines (cf. Raiford and Peterson, *J. Org. Chem.*, 1939, **1**, 524), resulted in the formation from both derivatives of the identical crystalline product, 5-(3 : 4-dihydroxyphenyl)-3-(2 : 3 : 4-trihydroxyphenyl)-1-phenyl-Δ^2-pyrazoline (III). This pyrazoline was also obtained when *iso*okanin phenylhydrazone was heated in ethanol, or from the reaction of the chalkone and phenylhydrazine on a steam-bath.

EXPERIMENTAL.

Okanin and iso*Okanin.*—Finely divided okan (200 g.) was twice heated in boiling ethanol (1·5 l.) for 5 hours and the filtered extracts were combined and evaporated to dryness on a steam-bath under reduced pressure. The chocolate-brown resin (27 g.) was readily broken up and removed from the flask, but it liquefied in contact with hot ether and was therefore triturated with small portions (50 c.c.) of the solvent in a mortar until the extracts were no longer coloured (total, 1 l.). The solution, after treatment with charcoal, was evaporated and thus gave a thick gummy residue, which on trituration with water (50 c.c.) solidified and was collected.

The crude product (8·0 g., 4%) was dissolved in boiling acetic acid (100 c.c. of 50%) from which the *okanin* separated in rosettes of bright orange crystals (2·6 g.) which when recrystallised from aqueous acetic acid or aqueous alcohol appeared as flat orange leaflets, m. p. 235—240° (decomp.) (Found, in an air-dried sample : C, 59·3; H, 4·7. $C_{15}H_{12}O_6,H_2O$ requires C, 58·8; H, 4·6. Found, after drying at 150° : C, 62·7; H, 4·2. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%). A specimen of the synthetic chalkone was identical in appearance and also had m. p. 235—240°. Russell and Todd (*loc. cit.*) give m. p. 233° (decomp.); Kurth (*loc. cit.*), m. p. 249°. The alcoholic ferric reaction of both specimens was chocolate-brown.

Evaporation of the mother-liquor from the first crystallisation of okanin left a yellow-brown residue which crystallised from water (100 c.c.; charcoal) as lemon-yellow needles (3·7 g.) of iso*okanin* sesquihydrate, m. p. 140° (efferv.) (Found, in an air-dried sample : C, 57·8; H, 4·7. $C_{15}H_{12}O_6,1\frac{1}{2}H_2O$ requires C, 57·2; H, 4·7%. Found, after drying at 120° : C, 62·2; H, 4·45%). The pure *iso*okanin was easily soluble in hot water and the ordinary organic solvents, and readily dissolved in alkali to an orange solution from which it was precipitated on acidification. The ferric chloride reaction in alcohol was brownish-green. On digestion of a strong solution of the compound in 2% aqueous hydrochloric acid at 100° the liquid darkened and the less-soluble *trans*-pentahydroxychalkone separated; after 2 hours 35% had been converted into the orange modification. *iso*Okanin, heated to 180°, quickly re-solidified to an orange product identified through its acetyl derivative (see below) as the *trans*-isomeride.

trans-2 : 3 : 4 : 3′ : 4′-*Penta-acetoxychalkone.*—The natural chalkone (0·5 g.) was heated with anhydrous sodium acetate (1 g.) in acetic anhydride (3 c.c.) for 1 hour at 100°. When the mixture was poured into water, a pale brown oil separated and rapidly solidified, which when crystallised from ethanol gave the *chalkone penta-acetate* (0·67 g., 81%) in colourless needles, m. p. 141°, alone or mixed with synthetic penta-acetoxychalkone (Found : C, 59·4; H, 4·6. $C_{25}H_{22}O_{11},\frac{1}{2}H_2O$ requires C, 59·2; H, 4·55%. Found after drying at 120° : C, 60·1; H, 4·7. $C_{25}H_{22}O_{11}$ requires C, 60·2; H, 4·4%).

cis-2 : 3 : 4 : 3′ : 4′-*Penta-acetoxychalkone.*—*iso*Okanin (0·5 g.) was acetylated as in the case of the *trans*-isomer, and the cis-*penta-acetate* (0·65 g., 83%) obtained as colourless needles, m. p. 113° (Found : C, 60·1; H, 4·5%). Unlike the parent hydroxy-compound it could not be converted into the *trans*-isomer by heating, decomposition occurring to give phenolic products.

trans-2 : 3 : 4 : 3′ : 4′-*Pentahydroxychalkone* 2 : 4-*Dinitrophenylhydrazone.*—(i) A solution of okanin (0·2 g.) in ethanol (1 c.c.) was treated with 2 : 4-dinitrophenylhydrazine (0·15 g.) dissolved in boiling hydrochloric acid (50 c.c.; 2N.). After 5 minutes' boiling, a copious dark red precipitate of the 2 : 4-*dinitrophenylhydrazone* suddenly appeared. This was collected and dissolved in boiling methanol (50 c.c.) from which a crystalline precipitate again appeared after 5 minutes' heating. The product was a scarlet powder (0·25 g.), m. p. 253° (decomp.), which became maroon when heated alone or on attempted crystallisation from high-boiling solvents such as acetic acid or xylene, characteristic very sparingly soluble dark shining platelets being formed (Found : C, 53·7; H, 3·5. $C_{21}H_{16}O_9N_4$ requires C, 53·8; H, 3·4%).

(ii) *iso*Okanin (0·2 g.) was added to a boiling solution of 2 : 4-dinitrophenylhydrazine in hydrochloric acid (50 c.c.; 2N.) whereupon an immediate dark red precipitate was obtained, which in boiling acetic acid or xylene gave glistening plates indistinguishable from those obtained as in (i) (Found : C, 53·6; H, 3·7%).

2 : 3 : 4-*Trihydroxyphenyl* 2-(3 : 4-*Dihydroxyphenyl*)*ethyl Ketone.*—(i) Okanin (21·9 mg.) in ethanol (5 c.c.) was hydrogenated at room temperature and pressure, a palladised charcoal catalyst being used. One mol. of hydrogen (1·85 c.c.) was absorbed during 8 minutes, and a further similar quantity in 90 minutes. Crystalline products could not be isolated either after complete hydrogenation or from the material isolated when reduction was interrupted at the dihydro-stage. However, from the latter a plum-coloured 2 : 4-*dinitrophenylhydrazone* of the dihydrochalkone was obtained as a crystalline powder, m. p. 260° (decomp.) with much previous darkening (Found : C, 51·4; H, 4·6. $C_{21}H_{18}O_9N_4,H_2O$ requires C, 51·6; H, 4·1%).

(ii) When *iso*okanin (27·4 mg.) was reduced as in (i) two mols. of hydrogen (4·4 c.c.) were steadily absorbed, the absorption–time plot being a continuous curve. In the presence of sodium hydroxide (0·1 c.c. of 2N., *ca.* 2 equivs.) reduction was much slower and had nearly ceased after the uptake of one mol. The product was converted into a 2 : 4-dinitrophenylhydrazone identical in appearance, decomposition point, and *X*-ray diffraction pattern with that prepared from the *trans*-isomer (Found : C, 51·1; H, 4·1%).

5-(3 : 4-*Dihydroxyphenyl*)-3-(2 : 3 : 4-*trihydroxyphenyl*)-1-*phenyl*-Δ^2-*pyrazoline* (III).—(i) Okanin (0·15 g.) was heated with phenylhydrazine (0·07 g., 1·25 mols.) in boiling ethanol (5 c.c.) for 2 hours. The addition of water precipitated an oil which was separated by decantation, dissolved in alcohol (1 c.c.), and reprecipitated with water. No crystalline material could be obtained from the resulting product but, after it had been heated at 100° with acetic acid (1 c.c.) for 1 hour, the addition of water gave the solid *pyrazoline* (III) (79 mg., 40%) which crystallised from aqueous ethanol in small, very pale straw-coloured tablets, m. p. 157° (Found, in an air-dried sample : C, 63·3; H, 5·4; N, 7·6. $C_{21}H_{18}O_5N_2,H_2O$ requires C, 63·6; H, 5·05; N, 7·1. Found, after drying at 120° : C, 66·4; H, 4·4; loss, 5·4. $C_{21}H_{18}O_5N_2$ requires C, 66·7; H, 4·7; loss, 4·6%).

(ii) A solution of *iso*okanin (0·2 g.) and phenylhydrazine (0·1 g., 1·3 mols.) in ethanol (2 c.c.) was kept for 24 hours at 0°. The cis-2 : 3 : 4 : 3′ : 4′-*pentahydroxychalkone phenylhydrazone* precipitated by adding water crystallised on scratching and gentle warming. It separated as a hemihydrate from cold aqueous ethanol as minute cream-coloured prisms (91 mg., 35%), darkening on exposure to air and light, m. p. 175° (Found, in air-dried sample : C, 65·3; H, 4·7; N, 6·8. $C_{21}H_{18}O_5N_2,\frac{1}{2}H_2O$ requires C, 65·1; H, 4·9; N, 7·2. Found, after drying at 70° *in vacuo* : C, 66·9; H, 5·0. $C_{21}H_{18}O_5N_2$ requires C, 66·7; H, 4·7%). When heated with acetic acid, or in ethanol at 100° for 30 minutes, the phenylhydrazone was converted into the pyrazoline, m. p. 157°, identical with that prepared from okanin. The pyrazoline was also the sole product when *iso*okanin and phenylhydrazine reacted at 100°.

Determinations of ultra-violet spectra were made with a Unicam spectrophotometer generously provided by Imperial Chemical Industries Limited.

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