891. *The Chemistry of Extractives from Hardwoods. Part IX.* Constituents of the Heartwood of* Ferreirea spectabilis.

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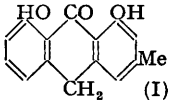
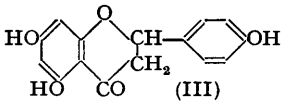
Two new phenols, ferreirin, $C_{16}H_{14}O_6$, and homoferreirin, $C_{17}H_{16}O_6$, and an alcohol, ferreol, $C_{30}H_{50}O$ or $C_{30}H_{52}O$, have been isolated from the heartwood of *Ferreirea spectabilis*. In addition, the timber contains *n*-pentacosane, $C_{25}H_{52}$, 5 : 7 : 4′-trihydroxyflavanone (naringenin), 5 : 7-dihydroxy-4′-methoxy*iso*flavone (biochanin-A), and 1 : 8-dihydroxy-3-methyl-9-anthrone (chrysophanic acid anthrone).

Ferreirea spectabilis, a large tree found in central South America, yields a hard dense wood with a waxy surface which when freshly cut is brownish-yellow with streaks of darker shade. The timber is reported to be highly resistant to decay, and is occasionally imported into the United Kingdom under the name sucupira, a description sometimes applied, however, to wood from other sources, *e.g.*, *Bowdichia* species.

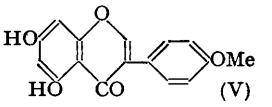
A light petroleum extract of the powdered timber deposited crystalline material which was resolved by ether into a sparingly soluble bright yellow compound (I), $C_{15}H_{12}O_3$, and an easily dissolved phenol (II), $C_{17}H_{16}O_6$, purified *via* its acetate. Treatment of the wood was continued with boiling ether which removed a phenol (III), $C_{15}H_{12}O_5$, but the yields of these compounds were insufficient to allow of their detailed examination. Approximately 200 kg. of timber were therefore extracted, and we are indebted to Messrs. Boots Pure Drug Co., Ltd., Nottingham, and to Messrs. T. and H. Smith, Ltd., Edinburgh for this assistance. The evaporated benzene extract from 100 kg. was partly crystalline owing to the presence of two further phenols, (IV), $C_{16}H_{14}O_6$, and (V), $C_{16}H_{12}O_5$, not observed during the trial experiments. Phenol (II) was found in solutions remaining from the crystallisation of these products, being isolated as before through its diacetate, but although indications of the colouring matter (I) were observed, compound (III) obtained in the preliminary work by ether-extraction, did not appear to be present. Further crystalline material was obtained by concentration of both the petroleum- and benzene-soluble residues and this consisted of mixed esters which on hydrolysis afforded a monohydric alcohol, approximating in composition to the formula $C_{30}H_{50}O$ or $C_{30}H_{52}O$. Finally, distillation of the most soluble portion of the extracts gave a hydrocarbon having the properties of *n*-pentacosane.



(I)



(III)



(V)

The yellow colouring matter (I), $C_{15}H_{12}O_3$, was dihydroxylic and formed red solutions with aqueous alkalis. It was readily oxidised to a compound, $C_{15}H_{10}O_4$, and was reduced by zinc dust distillation to 2-methylanthracene. (I) was therefore recognised as 1 : 8-dihydroxy-3-methyl-9-anthrone, its oxidation product being chrysophanic acid. It is one of the principal constituents of commercial Goa and Araroba powders (Jowett and Potter, *J.*, 1902, **81**, 1575) found in the stem cavities of several Brazilian *Andira* species, notably *A. araroba*, and it is also present in wood of the S. American genus *Tecoma* (Freise, *Chem. Abstr.*, 1938, **32**, 4243) and in Tagasayan wood, *Cassia siamea* (Iwakawa, *Arch. Exp. Path. Pharm.*, 1911, **65**, 315).

Compound (II) is a dihydric phenol and on methylation gives a dimethyl ether identical with the trimethyl ether of (IV). (IV) and (II), which have been designated ferreirin and homoferreirin respectively, are *iso*flavanones; their constitutions are discussed in a later paper.

Phenol (III) exhibited the characteristic colour tests of a flavanone. Under mild conditions of methylation, an alkali-insoluble dimethyl ether with a marked ferric reaction

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was formed, thereby indicating the presence of a 5-hydroxyl group. Alkaline hydrolysis gave *p*-hydroxy-benzoic or -cinnamic acid and so led to the recognition of (III) as naringenin, 5 : 7 : 4′-trihydroxyflavanone. Apart from its occurrence in several *Prunus* species as the 7-rhamnoglucoside naringin (see, however, Rabaté, *Bull. Soc. Chim. biol.*, 1934, **17**, 314) and as salipurposide (naringenin 5-D-glucoside) in *Salix purpurea*, naringenin has been found in the bark of *Prunus persica* (Shinoda and Uyeda, *Chem. Zentr.*, 1929, **100**, 1547) and in the heartwood of the South American tree *Nothofagus dombeyi* (Pew, *Chem. Abstr.*, 1948, **42**, 8191).

The usual colour reactions denoted a flavone or *iso*flavone structure for phenol (V), and its behaviour on acetylation and alkylation disclosed two hydroxyl groups, one having diminished reactivity owing to chelation. From its oxidation with nitric acid to 4-methoxy-3-nitrobenzoic acid and degradation by alkali to 4-methoxybenzyl 2 : 4 : 6-trihydroxyphenyl ketone and formic acid, (V) was identified as biochanin-A, 5 : 7-dihydroxy-4′-methoxy*iso*flavone, previously isolated from germinated chana grain by Siddiqui (*J. Sci. Ind. Res. India*, 1945, **4**, 68; Bose and Siddiqui, *ibid.*, p. 231).

Differences in the nature of the constituents isolated in the laboratory and the large-scale extractions were at first attributed to the substitution of benzene for the solvents used in the preliminary experiments, but the extraction of a second 100 kg. of the wood by successive treatment with light petroleum and then ether gave further somewhat divergent results, which seemed to imply a variation in the wood species under examination. By means of the bright red alkali reaction of the anthrone and of the pink colour given by naringenin in the presence of magnesium and hydrochloric acid it was possible rapidly to ascertain the distribution of these two constituents in the available specimens of wood without the necessity of carrying out solvent extractions. An analysis of fourteen boards of sucupira by means of these colour tests revealed that they were divisible into two groups, one exhibiting strong anthrone and flavanone colours and the other responding only feebly to these reactions. When the fourteen samples were examined in the Wood Structure Section of the Forest Products Research Laboratory all were identified as the wood of *F. spectabilis*, but whereas the group having a low anthrone (I) and naringenin (III) content also gave positive starch tests and showed signs of pin-hole borer attack, thereby indicating their probable derivation from the exterior heartwood, the remaining specimens containing a high proportion of the constituents (I) and (III) were free from starch and pin-hole borer damage and evidently consisted of interior heartwood. These fluctuations in the content of at least two highly characterised constituents of the heartwood offer a particularly clear example of the well-known variation in distribution and, even, nature of timber extractives with respect to the original location of the wood within the stem of the tree.

Experimental

Extraction of Constituents of Ferreirea spectabilis *Heartwood.*—(i) The finely ground timber (600 g.) was extracted (Soxhlet) with boiling light petroleum (b. p. 60—80°), and the resulting solution kept at 0° for 2 days. The solid deposit was collected and triturated with ether, and the insoluble portion recrystallised from light petroleum, giving yellow rhombs of the anthrone (I) (yield >0·05%), m. p. 188—194°. From the evaporated ethereal solution a brown semi-solid material (0·75 g.) was obtained, which was heated with acetic anhydride and sodium acetate on a steam-bath. The product was crystallised from ethanol, and after contact with 2N-sodium hydroxide at room temperature for 24 hours yielded homoferreirin (II) (0·05%), m. p. 165·5—168°.

The wood was then extracted with boiling ether for several hours and the solution concentrated to small bulk. The crystalline solid thus obtained consisted of naringenin (III) (0·07%), m. p. 228°. Later, when large-scale experiments had indicated the occurrence in the wood of biochanin-A (V), evaporation of the ether-concentrate from which naringenin had been separated, and crystallisation of the residue from methanol, gave the crude *iso*flavone (V) (0·1%), m. p. *ca.* 200°. The presence of ferreirin (IV) was not observed during laboratory extraction although it was probably present in the crude homoferreirin; being liquid, triacetyl-ferreirin would have been lost in the purification of homoferreirin by recrystallisation of its acetate.

(ii) Treatment of 100 kg. of the powdered wood with boiling benzene yielded 4·3 kg. of a

brown syrupy mass containing colourless crystalline material. The latter was isolated by mixing the extract with a small volume of benzene, the solid being collected and refluxed with chloroform to remove coloured impurities. The resultant product (290 g.) was crystallised from methanol, thereby yielding biochanin-A (V) (110 g.) in needles, m. p. 215—216°. From the methanol filtrate ferreirin (IV) was precipitated with water, and when crystallised from ethyl acetate–light petroleum the compound (93 g.) had m. p. 210—212°. Homoferreirin was obtained from the ethyl acetate–petroleum filtrate by acetylation of its contents and hydrolysis of the recrystallised acetate. The crystalline anthrone (I) was not encountered, but aqueous sodium hydroxide washings of the crude extracts exhibited the characteristic red colour of its alkali salts. Naringenin, which is sparingly soluble in benzene, did not appear to be present.

(iii) A further quantity of the wood (100 kg.), treated with boiling light petroleum and then with boiling ether, gave respectively 1·2 and 1·3 kg. of extractives. From the former the anthrone (I) was again isolated, but the phenols (II) and (IV) were not obtained from this fraction.

The ether-soluble product (1·3 kg.) was dissolved in boiling methanol from which biochanin-A (100 g.) crystallised during 24 hours at 0—2°. The filtrate was evaporated and from the dark oily residue a mixture of ferreirin and homoferreirin was obtained by repeated extraction with benzene. Crystallisation of the mixture from ethyl acetate–light petroleum yielded ferreirin (IV), (II) being obtained from the mother-liquors by purification *via* the diacetate. The benzene-insoluble residue consisting of crude naringenin was best purified by trituration with cold ether and crystallisation from aqueous methanol (charcoal).

1 : 8-*Dihydroxy*-3-*methyl*-9-*anthrone* (I).—Recrystallised from chloroform or ethyl acetate the anthrone (I) (yield from centre heartwood, 0·47%) formed bright yellow, square, glistening plates, m. p. 208—209° (Naylor and Gardner, *J. Amer. Chem. Soc.*, 1931, **53**, 4114, give m. p. 204°) (Found: C, 74·8; H, 5·1%; *M*, 236. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%; *M*, 240). For the molecular-weight determination we are indebted to Dr. S. C. Wallwork who found unit cell, 945·4. The triacetate had m. p. 236—237° (Found: C, 68·5; H. 4·7. Calc. for $C_{21}H_{18}O_6$: C, 68·8; H, 4·95%), and the *dimethyl ether* 142·5—143·5° (Found: C, 76·3; H, 6·3; OMe, 23·5. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0; 2OMe, 23·1%).

The orange sublimate from zinc dust distillation of the anthrone was purified in benzene solution by chromatography on alumina, and the eluate resublimed *in vacuo* to give 2-methylanthracene, m. p. 203—204° (Found: C, 93·2; H, 6·4. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·3%). Oxidation of the anthrone (1 g.) with excess of concentrated nitric acid gave 1 : 8-dihydroxy-3-methyl-2 : 4 : 5 : 7-tetranitroanthraquinone (1·05 g.), long orange needles (from acetic acid), decomp. 300° (Found: C, 41·9; H, 1·9; N, 12·9. Calc. for $C_{15}H_6O_{12}N_4$: C, 41·5; H, 1·4; N, 12·9%).

1 : 8-*Dihydroxy*-3-*methylanthraquinone* (*Chrysophanic Acid*).—An attempted ozonolysis of the anthrone (1 g.) in chloroform gave, after washing of the solution with aqueous sodium carbonate and evaporation, chrysophanic acid (0·3 g.), golden plates (from benzene–light petroleum), m. p. 194—195° (Found: C, 70·9; H, 4·0. Calc. for $C_{15}H_{12}O_4$: C, 70·8; H, 4·0%), identical with the alkaline hydrogen peroxide oxidation product. A *monoacetate*, prepared with acetic anhydride–perchloric acid and crystallising in golden needles from acetone–methanol, had m. p. 188—190° and was thus different from the acetate, m. p. 155°, described by Hesse (*Annalen*, 1899, **309**, 32) (Found: C, 69·2; H, 3·8. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%). It gave a brown ferric reaction and a red solution in aqueous sodium hydroxide.

Ferreirin (IV) *and Homoferreirin* (II).—*Ferreirin* crystallised from aqueous methanol or ethyl acetate–light petroleum in prisms, m. p. 210—212° (Found: C, 63·7; H, 4·8; OMe, 10·5. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·7; 1OMe, 10·3%). Its solution in alkalis is yellow, in nitric acid red, and its ferric reaction brown-violet. When ferreirin was reduced with sodium amalgam the subsequently acidified solution became pink. *Homoferreirin* (maximum yield 0·05%) separated from benzene–light petroleum or aqueous methanol in rectangular plates, m. p. 168—169° (Found: C, 64·7; H, 5·3; OMe, 19·2. $C_{17}H_{16}O_6$ requires C, 64·55; H, 5·1; 2OMe, 19·4%). Its colour reactions resembled those of ferreirin. With acetic anhydride–sodium acetate *diacetylhomoferreirin* was obtained, which crystallised from ethanol in long needles, m. p. 132—133° (Found: C, 63·0; H, 4·7; OMe, 14·6. $C_{21}H_{20}O_8$ requires C, 63·0; H, 5·0; 2OMe, 15·5%).

5 : 7 : 4′-*Trihydroxyflavanone* (*Naringenin*) (III).—The product (III) (yield from centre heartwood, 1%) gave an intense brown-violet ferric reaction, and cherry-red solutions on reduction both with magnesium in hydrochloric acid and with sodium amalgam when followed by acidification. It crystallised from aqueous methanol in long glistening needles, m. p. 250—

251° (Asahina and Inubuse, *Ber.*, 1928, **61**, 1514, found m. p. 251°) (Found : C, 66·3; H, 4·6. Calc. for $C_{15}H_{12}O_5$: C, 66·2; H, 4·4%). Triacetylnaringenin, prepared by the action of acetic anhydride and 2 drops of 60% perchloric acid at room temperature, crystallised from ethyl acetate–light petroleum in needles, m. p. 91—92°. Its analyses were satisfactory only after drying at 100° (Found : C, 63·0; H, 4·7; OAc, 35·4. Calc. for $C_{21}H_{18}O_8$: C, 63·3; H, 4·55; 3OAc, 32·4%). Asahina and Inubuse (*loc. cit.*) give, however, m. p. 53—55°. 7 : 4′-Dimethylnaringenin, prepared with diazomethane, formed needles (from aqueous methanol), m. p. 118—119° (Found : C, 67·6; H, 5·5; OMe, 20·1. Calc. for $C_{17}H_{16}O_5$: C, 68·0; H, 5·4; 2OMe, 20·7%). Asahina and Inubuse record m. p. 115—116°. Naringenin oxime consisted of needles, m. p. 229—230° (lit., 231—232°) (Found : C, 59·5; H, 5·0; N, 4·9. Calc. for $C_{15}H_{13}O_5N,H_2O$: C, 59·0; H, 4·95; N, 5·6%).

Alkali Hydrolysis of Naringenin.—(i) Hydrolysis of naringenin with 50% aqueous potassium hydroxide at 160° gave *p*-hydroxycinnamic acid, m. p. 215° (decomp.) (Found : C, 65·6; H, 4·8. Calc. for $C_9H_8O_3$: C, 65·85; H, 4·9%). The acetate, prisms (from ethyl acetate–light petroleum), had m. p. 205—207° (Found : C, 64·2; H, 4·8. Calc. for $C_{11}H_{10}O_4$: C, 64·1; H, 4·9%).

(ii) Naringenin (2 g.) was slowly added to a melt of potassium hydroxide (10 g.) and water (2 g.) at 220°. After 10 minutes the mixture was cooled and dissolved in water, and the solution acidified. The acid extracted by ether crystallised from water in prisms (0·5 g.), m. p. 213—214° alone or mixed with *p*-hydroxybenzoic acid (Found : C, 60·8; H, 4·2. Calc. for $C_7H_6O_3$: C, 60·9; H, 4·4%). Its acetate had m. p. and mixed m. p. 188—189°.

5 : 7-*Dihydroxy-4′-methoxy*isoflavone (*Biochanin-A*).—The phenol (V) crystallised from methanol or ethyl acetate–light petroleum in needles, m. p. 215—216°. Biochanin-A has m. p. 215° (Bose and Siddiqui, *loc. cit.*) (Found : C, 67·7; H, 4·4; OMe, 11·4. Calc. for $C_{16}H_{12}O_5$: C, 67·6; H, 4·3; 1OMe, 10·9%). Its ferric reaction was intense brown-violet. Acidification of a solution reduced by sodium amalgam gave a pink colour.

Treatment of (V) with sodium acetate and acetic anhydride at 100° gave 5 : 7-diacetoxy-4′-methoxy*iso*flavone crystallising from methanol in needles, m. p. 188—189° (lit., 190°) (Found : C, 65·2; H, 4·3. Calc. for $C_{20}H_{16}O_7$: C, 65·2; H, 4·4%). By 5 minutes' heating at 100° 7-*acetoxy-5-hydroxy-4′-methoxy*isoflavone was obtained, which crystallised from methanol in rectangular plates, m. p. 155—156° (Found : C, 66·1; H, 4·3; OMe, 9·1. $C_{18}H_{14}O_6$ requires C, 66·25; H, 4·3; OMe, 9·5%). The intense brown-violet ferric reaction indicated the free 5-hydroxyl group.

When 3 : 5-dinitrobenzoyl chloride was added to biochanin-A in pyridine, the 7-(3 : 5-*dinitrobenzoyl*)-5-*hydroxy*-4′-*methoxy*isoflavone separated, and crystallised from dioxan in bright yellow prisms, m. p. 265—266° (Found : C, 58·1; H, 3·2; N, 6·2. $C_{23}H_{14}O_{10}N_2$ requires C, 57·7; H, 2·9; N, 5·9%). With diazomethane, (V) gave 7 : 4′-dimethoxy-5-hydroxy*iso*flavone, m. p. 141—142° (Found : C, 68·3; H, 4·6; OMe, 20·4. Calc. for $C_{17}H_{14}O_5$: C, 68·5; H, 4·7; 2OMe, 20·8%), and on prolonged treatment with methyl sulphate and potassium carbonate in acetone the trimethoxy*iso*flavone, m. p. 162—163° (Found : C, 69·6; H, 5·5; OMe, 30·2. Calc. for $C_{18}H_{18}O_5$: C, 69·2; H, 5·2; 3OMe, 27·3%).

When biochanin-A (1 g.), or its dimethyl ether, was heated with concentrated nitric acid (16 c.c.) on a steam-bath for ½ hour and the solution poured into water, 4-methoxy-3-nitrobenzoic acid separated in needles, m. p. and mixed m. p. 192—193°.

5 : 7-*Diethoxy-4′-methoxy*isoflavone.—Biochanin-A (5 g.), ethyl sulphate (10 c.c.), and excess potassium carbonate in acetone were heated under reflux for 24 hours. From the filtered and evaporated solution the *diethyl ether* was obtained, which crystallised from benzene–light petroleum in stout prisms, m. p. 130—131° (Found : C, 70·4; H, 6·2. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

Alkali Hydrolysis of Biochanin-A.—Hydrolysis of (V) (1 g.) with potassium hydroxide (5·5 g.) in 50% aqueous alcohol (50 c.c.) at 100° for 15 minutes gave 4-methoxybenzyl 2 : 4 : 6-trihydroxyphenyl ketone which when crystallised from aqueous methanol had m. p. 195° (Found : C, 62·0; H, 5·3. Calc. for $C_{15}H_{14}O_5,H_2O$: C, 61·6; H, 5·5%). Acidification of the aqueous residue to Congo-red and distillation afforded a solution which contained formic acid. Hydrolysis with 5% aqueous-alcoholic potassium hydroxide for 10 hours gave *p*-methoxyphenylacetic acid, m. p. and mixed m. p. 85—86° (Found : C, 65·0; H, 6·1. Calc. for $C_9H_{10}O_3$: C, 65·05; H, 6·1%).

Ferreol.—The evaporated light petroleum extract from which the anthrone (I) had been separated gradually deposited crystalline solid (yield 0·05%), m. p. 65—70°. The neutral material obtained after hydrolysis of the crude product with alcoholic potassium hydroxide

(300 c.c.; 10%) was then fractionated in light petroleum solution on an alumina column (60 × 2 cm.). After development with light petroleum (2 l.), elution was carried out with benzene and then ether. Earlier fractions were not homogeneous (m. p.s 128° to 132°) but later portions crystallised from acetone–methanol, giving *ferreol* in plates, m. p. 178—179°, $[\alpha]_D^{22}$ +11° [Found, after drying at 150°: C, 83·1; H, 12·1%; *M* (Rast), 417. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%; *M*, 427. $C_{30}H_{52}O$ requires C, 84·0; H, 12·2%]. The triterpene gave a yellow colour with tetranitromethane.

The *acetate* crystallised from acetone–methanol in needles, m. p. 138—139°, $[\alpha]_D^{21}$ +26° (Found: C, 82·0, 82·4; H, 11·6, 11·3. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%). The *benzoate*, needles from acetone–methanol, had m. p. 174°, $[\alpha]_D^{24}$ +53° (Found: C, 83·7; H, 10·5. $C_{37}H_{54}O_2$ requires C, 83·7; H, 10·25. $C_{37}H_{56}O_2$ requires C, 83·4; H, 10·6%), and the 3 : 5-*dinitrobenzoate*, glistening plates from acetone–methanol, m. p. 226—227°, $[\alpha]_D^{22}$ +27·5° (Found: C, 71·1; H, 8·5; N, 4·5. $C_{37}H_{52}O_6N_2$ requires C, 71·6; H, 8·4; N, 4·5. $C_{37}H_{54}O_6N_2$ requires C, 71·3; H, 8·8; N, 4·5%).

n-*Pentacosane*.—A portion of the light petroleum-soluble material from the large-scale benzene extraction of sucupira was distilled (bath-temp. 150—160°/0·05 mm.), the distillate forming plates, m. p. 53°, from acetone (Heilbron and Bunbury, "Dictionary of Organic Compounds," London 1943, gives for *n*-pentacosane m. p.s 53·3—54°, 54°, 55·5—56°) [Found: C, 85·3; H, 14·6%; *M* (Rast), 348. Calc. for $C_{25}H_{52}$: C, 85·2; H, 14·8%; *M*, 352]. The hydrocarbon was unattacked in the Kuhn–Röth *C*-methyl determination.

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