The Chemistry of Extractives from Hardwoods. Part XVI. Coumarin Constituents of* Fagara macrophylla, Zanthoxylum flavum, *and* Chloroxylon swietenia.

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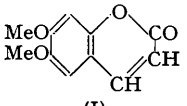
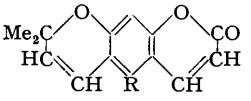
[Reprint Order No. 4932.]

The principal crystalline heartwood extractives of *Fagara macrophylla* (olon), of *Zanthoxylum flavum* (alternatively *Fagara flava*) (West Indian satinwood), and of a third species *Chloroxylon swietenia* (East Indian satinwood) also believed to be of the same family, Rutaceae, are coumarins, some of them already known as products of other *Zanthoxylum* species. 6 : 7-Dimethoxycoumarin (æsculetin dimethyl ether) and 6 : 7 : 8-trimethoxycoumarin are present in olon; suberosin (7-methoxy-6-*iso*pent-2′-enylcoumarin) and psoralene [furano(2′ : 3′-6 : 7)coumarin] have been found in W. Indian satinwood; and E. Indian satinwood contains xanthyletin [2′ : 2′-dimethylpyrano(5′ : 6′-6 : 7)coumarin], xanthoxyletin (5-methoxyxanthyletin), and the related but previously unknown phenol, 7-demethylsuberosin.

THE genus *Zanthoxylum* (family Rutaceae) with the sub-genus *Fagara* (regarded as synonymous in the Bentham and Hooker classification) consist approximately of 150—200 species of shrubs and trees, including a few well-known as a source of furniture woods. Chemical investigations on some 30 species have been reported in the literature but they chiefly concern constituents of the bark, roots, leaves, or fruit. The principal compounds so far isolated are alkaloids, *e.g.*, skimmianine and berberine, and coumarin derivatives. Among the latter are 6 : 7-dimethoxycoumarin (æsculetin dimethyl ether) (I) found in the leaves of *Z. setosum* (Araki and Miyashita, *J. Pharm. Soc. Japan*, 1928, **48**, 437), and those present in the bark of *Z. americanum*, namely, xanthyletin (II; R = H), xanthoxyletin (II; R = OMe), and *allo*xanthoxyletin, of which the structures were determined by



(I)



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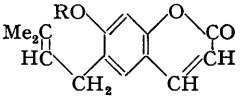


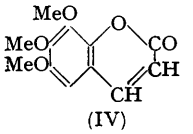
(III)

Robertson and his collaborators (Bell, Robertson, and Subramaniam, *J.*, 1936, 627; Bell and Robertson, *J.*, 1936, 1828; Robertson and Subramaniam, *J.*, 1937, 286; Bell, Bridge, and Robertson, *J.*, 1937, 1542). Closely related to xanthyletin is the 7-methoxy-6-*iso*pent-2′-enylcoumarin, suberosin (III; R = Me), recently isolated from the bark of *Z. suberosum* (Ewing, Hughes, and Ritchie, *Austral. J. Sci. Res.*, 1950, **3**, *A*, 342).

Previous investigations on woods of *Zanthoxylum* species appear to have been limited to West Indian satinwood (*Z. flavum*) from which were isolated two unidentified lactones, $C_{11}H_{10}O_3$, m. p. 124—126°, and $C_{14}H_{12}O_3$, m. p. 133° (Auld and Pickles, *J.*, 1912, **101**, 1052). Once readily available, *e.g.*, from Cuba, Jamaica, Puerto Rico, this valuable decorative wood has been almost entirely eliminated from these W. Indian islands (personal communication from Mr. F. H. Wadsworth, Forestry Service, U.S. Department of Agriculture), but sufficient was ultimately procured to enable a re-examination of the heartwood extractives to be undertaken. The extractable constituents of the somewhat similar W. African timber olon (*Fagara macrophylla*) and of East Indian satinwood (*Chloroxylon swietenia*) have also been studied since it was of interest to ascertain the existence of any chemical relation between these species in view of uncertainties about the classification of *C. swietenia* with respect to the families Rutaceae and Meliaceae (cf. Metcalfe and Chalk, "Anatomy of the Dicotyledons," Clarendon Press, Oxford, 1950, pp. 356, 357). All three timbers are said to be resistant to decay and to the attack of termites (personal communication from Mr. B. J. Rendle, D.S.I.R. Forest Products Research Laboratory).

* Part XV, *J.*, 1953, 4158.

Extraction of coarsely powdered olon with boiling light petroleum yielded a mixture of a crystalline solid and an involatile oil. A further quantity of the solid was obtained from the subsequent ether-extraction and it was resolved by crystallisation into 6 : 7-dimethoxycoumarin (I) and 6 : 7 : 8-trimethoxycoumarin (IV), the latter not formerly known as a natural product. The coumarin (I) was also isolated from the succeeding acetone extract, and the total yield amounted to 2·3% of the wood. The average content of the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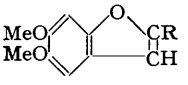
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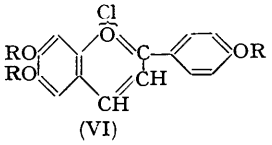
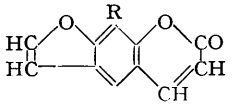
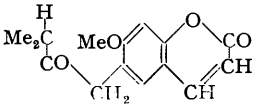

(VI)

trimethoxycoumarin (IV) was 0·18%; it has m. p. 104° and may be identical with the unidentified substance, m. p. 104°, obtained together with (I) from *Z. setosum* by Araki and Miyashita (*loc. cit.*). A compound $C_{15}H_{13}O_2{\cdot}OMe$ and an alkaloid $C_{20}H_{21}O_7N$, isolated as hydrochloride, were also found in the extracts but were present in amounts too small for detailed investigation.

The structure of the major constituent (I) was confirmed by its conversion with methyl sulphate and alkali into 2 : 4 : 5-trimethoxycinnamic acid and by its formation of 2-acetoxy-4 : 5-dimethoxycinnamic acid. Similarly, the trimethoxycoumarin (IV) yielded 2 : 3 : 4 : 5-tetramethoxycinnamic acid, oxidised to 2 : 3 : 4 : 5-tetramethoxybenzoic acid (Wessely and Demmer, *Ber.*, 1928, **61**, 1279). Bromination of 6 : 7-dimethoxycoumarin led invariably to the 3-bromo-derivative and not to the dibromocoumarin described by Araki and Miyashita (*loc. cit.*). The action of aqueous hot alkali on the 3-bromo-compound gave 5 : 6-dimethoxycoumarone-2-carboxylic acid (V; R = CO_2H), which was decarboxylated in quinoline to 5 : 6-dimethoxycoumarone (V; R = H) (Tanaka, *J. Amer. Chem. Soc.*, 1951, **73**, 872). From the coumarin (I) and *p*-methoxyphenylmagnesium bromide 6 : 7 : 4′-trimethoxyflavylium chloride (VI; R = Me) was prepared and hence the salt (VI; R = H).

The principal crystalline component of the viscous oil dissolved by boiling petroleum from W. Indian satinwood was suberosin (III; R = Me); it crystallised from methanol, and from the remaining solution a small amount of psoralene (VII; R = H) was obtained. Further limited quantities of both compounds were derived from the succeeding extraction with ether [total yields, of (III; R = Me) 0·85%, of (VII; R = H) 0·055%], and traces

(VII) 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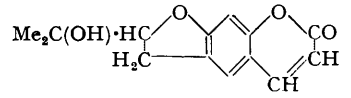
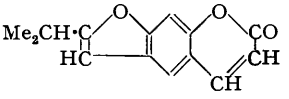
of a coumarin believed to be xanthotoxin (VII; R = OMe). Minute quantities of other unrecognised products were found, but none corresponding to either of the lactones reported by Auld and Pickles (*loc. cit.*).

Various compounds already described were prepared from the coumarin (III; R = Me), *e.g.*, 2 : 4-dimethoxy-5-*iso*pent-2′-enylcinnamic acid (methyl suberosinic acid; Ewing *et al.*, *loc. cit.*); it was oxidised to acetone and 7-methoxycoumarin-6-aldehyde (Ewing, *et al.*, *loc. cit.*) and was cyclised to dihydroxanthyletin when heated with hydrobromic acid. A tribromo-derivative, believed to be 3 : 2′ : 3′-tribromosuberosin, and an epoxide were prepared; in view of the failure of coumarin to react with monoperphthalic acid (Dean, *Fortschritte der Chemie Organischer Naturstoffe*, 1952, **9**, 231), the epoxide is regarded as the 2′ : 3′-compound. With boiling oxalic acid, the oxide was hydrated to a crystalline diol; with boiling dilute sulphuric acid it isomerised to the 2′-keto-compound (VIII). The 2′ : 2′-dimethylchromen synthesised from suberosin and excess of methylmagnesium iodide was an oil.

The light petroleum and ether extracts of E. Indian satinwood consisted of viscous liquids from which appreciable quantities of crystalline compounds were isolated, *i.e.*, xanthyletin (II; R = H) (3·3%), xanthoxyletin (II; R = OMe) (0·1%), and a phenolic coumarin $C_{14}H_{14}O_3$ (1·3%). Further small amounts of (II; R = H) and of the phenolic

constituent from the later acetone treatment of the wood have been included in the percentage yields. Xanthyletin and xanthoxyletin were identified by mixed m. p. with specimens kindly provided by Professor A. Robertson, F.R.S., and by the preparation of the dihydro-derivatives. Dihydroxanthyletin gave a 3-bromo-derivative converted

(IX)   (X)

by alkalis into 2′ : 2′-dimethyldihydropyrano(5′ : 6′-5 : 6)benzofuran-2-carboxylic acid, which was decarboxylated to the corresponding dihydrodimethylpyranobenzofuran.

The new phenolic coumarin gave suberosin (III; R = Me) when methylated with diazomethane, and dihydroxanthyletin under catalysis with hot dilute hydrochloric acid, and it was thereby recognised as 7-demethylsuberosin (III; R = H). Through the action of monoperphthalic acid demethylsuberosin undergoes oxidation at the 2′-position and cyclisation to a compound (IX) which is therefore the racemic form of the natural products (−)-nodakenetin and (+)-marmesin (Chatterjee and Mitra, *J. Amer. Chem. Soc.*, 1949, **71**, 606). As with marmesin, the structure (IX) is confirmed by dehydration with phosphoric oxide to deoxyoreosolone (X).

Experimental

Light absorption data refer to solutions in ethanol.

Extraction of Olon (Fagara macrophylla).—The coarsely ground wood (3·5 kg.) was extracted for 18 hr. with boiling light petroleum (b. p. 60—80°). Crystalline solid was collected from the cold solution, and a further crop was obtained by triturating with ether (50 c.c.) the syrupy residue obtained by evaporation of the petroleum filtrate. Crystallisation of the combined solids from methanol gave first 6 : 7-dimethoxycoumarin (I) (23—24 g.) and then 6 : 7 : 8-trimethoxycoumarin (IV) (5·3 g.). The material left in the ether was a pale orange oil (11 g.) neutral and unsaponifiable, and resolved by chromatography on alumina into several fractions of which one (eluted with benzene) crystallised from benzene–light petroleum in *needles* (0·2 g.), m. p. 122—123° (Found: C, 75·2; H, 6·6; OMe, 12·6. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3; OMe, 12·1%); light absorption: max., 226 mμ; log ε 3·95.

Subsequent treatment of the wood with boiling ether extracted a gummy solid from which the coumarins (I) (6·6 g.) and (IV) (1 g.) were isolated by crystallisation from methanol. Chromatographic fractionation of the residue (3 g.) yielded a further amount (0·1 g.) of the substance, m. p. 122—123°.

From the petroleum- and ether-extracted wood boiling acetone removed a resin (*ca.* 100 g.) which when triturated with cold methanol gave a further quantity (51 g.) of the coumarin (I) (total yield 81 g., 2·3%). Finally, extraction with boiling ethanol afforded a brittle dark brown resin (30 g.) from which no homogeneous substance was obtained.

The residue from the acetone-soluble portion of the wood was in one case extracted with boiling water (3 × 350 c.c.). Concentration of the aqueous solution to 500 c.c. and treatment with concentrated hydrochloric acid (10 c.c.) precipitated a yellow crystalline *hydrochloride* (0·2 g.) which crystallised from methanol in needles, m. p. 276° (decomp.) (Found: C, 56·5; H, 5·4; N, 3·3; Cl, 8·7; OMe, 9·0; NMe, 9·74. $C_{20}H_{21}O_7N$,HCl requires C, 56·7; H, 5·2; N, 3·3; Cl, 8·4; 1OMe, 7·3; 1NMe, 6·8%). The amorphous base gave precipitates with the usual alkaloid reagents and with gallic acid in concentrated sulphuric acid a turquoise blue colour indicative of a methylenedioxy-group.

6 : 7-*Dimethoxycoumarin* (I).—The coumarin (I) crystallised in colourless needles, m. p. 143—143·5°, its alcoholic solution exhibiting a strong blue-violet fluorescence (Found: C, 63·7; H, 4·8; OMe, 30·8. Calc. for $C_{11}H_{10}O_4$: C, 64·1; H, 4·9; 2OMe, 30·0%); light absorption: max., 229, 294 and 342 mμ; log ε 4·23, 3·76, 4·1. With boiling aqueous potassium hydroxide the coumarin gave *trans*-2-hydroxy-4 : 5-dimethoxycinnamic acid, yellow prisms (from methanol), m. p. 197—198° (Araki and Miyashita, *loc. cit.*, give m. p. 197—198°); this gave an acetate, needles (from methanol), m. p. 210—211° (*idem, loc. cit.*, give m. p. 210—211°) (Found: C, 58·2; H, 5·2; OMe, 25·3. Calc. for $C_{13}H_{14}O_6$: C, 58·6; H, 5·3; 2OMe, 23·3%), and methyl ether, yellow prisms (from ethanol), m. p. 168° (*idem, ibid.*, 1929, **49**, 736, give m. p. 168°) (Found: C, 60·3; H, 5·7; OMe, 41·3. Calc. for $C_{12}H_{14}O_5$: C, 60·5; H, 5·9;

3OMe, 39·1%). Bromination of the coumarin in cold acetic acid, benzene, or chloroform gave the monobromo-derivative, needles (from ethanol), m. p. 178—179° (*idem, ibid.*, 1928, **48**, 437, give m. p. 176°) (Found: C, 46·1; H, 2·9; Br, 26·1. Calc. for $C_{11}H_9O_4Br$: C, 46·3; H, 3·2; Br, 28·0%); light absorption: max., 234, 258, 306, 356 mμ; log ε 4·17, 3·83, 3·83, 4·2. Demethylation of the coumarin with boiling hydrobromic acid in acetic acid gave æsculetin, prisms (from ethanol), m. p. 268—269° (Glaser and Kraus, *Biochem. Z.*, 1923, **138**, 183, give m. p. 270°) (Found: C, 60·6; H, 3·8. Calc. for $C_9H_6O_4$: C, 60·7; H, 3·4%).

5 : 6-*Dimethoxycoumarone-2-carboxylic Acid* (V; R = CO_2H).—3-Bromo-6 : 7-dimethoxycoumarin (3·0 g.) was treated with aqueous potassium hydroxide (10%; 150 c.c.) at the b. p. for 1 hr. and the resulting orange solution poured into excess of hydrochloric acid (5N). The precipitated 5 : 6-dimethoxycoumarone-2-carboxylic acid (2·25 g., 97%) after two precipitations from a solution in sodium hydrogen carbonate separated from ethanol in colourless needles, m. p. 242—244° (decomp.) (Found: C, 59·1; H, 4·5; OMe, 28·3. Calc. for $C_{11}H_{10}O_5$: C, 59·5; H, 4·5; 2OMe, 27·9%) [Tanaka, *loc. cit.*, gives m. p. 245° (decomp.)]. Esterification with methanol–hydrogen chloride gave the *methyl ester*, needles (from methanol), m. p. 140—142° (Found: C, 60·7; H, 5·0; OMe, 38·1. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1; 3OMe, 39·4%).

5 : 6-*Dimethoxycoumarone* (V; R = H).—The above acid (V; R = CO_2H) (1·9 g.) was heated at 220° in quinoline (10 c.c.) with copper powder (0·4 g.) until the evolution of carbon dioxide ceased (30 min.). The cooled mixture was poured into ether and filtered and, after the quinoline had been removed by dilute hydrochloric acid, the ethereal layer was washed with water, dried, and evaporated. The residue was a straw-yellow oil which, purified by passage down an alumina column in light petroleum (b. p. 40—60°) solution, crystallised from light petroleum (b. p. 40—60°) giving the coumarone (V; R = H) as colourless needles (0·9 g., 60%), m. p. 54—55° (Found: C, 67·3; H, 5·8; OMe, 32·8. Calc. for $C_{10}H_{10}O_3$: C, 67·4; H, 5·7; 2OMe, 34·8%) (Tanaka *loc. cit.*, gives m. p. 53—54°).

6 : 7 : 4′-*Trimethoxyflavylium Chloride* (VI; R = Me).—6 : 7-Dimethoxycoumarin (2·5 g.) in dry benzene (250 c.c.) was slowly added to a stirred solution of *p*-methoxyphenylmagnesium bromide prepared from excess of *p*-bromoanisole (7·5 g.) in ether (20 c.c.). After 1 hr. the mixture was treated with concentrated hydrochloric acid (6 c.c.), and the dark green deposit collected and washed successively with benzene, ether, and dilute hydrochloric acid. The dried residue (3·8 g., 95%) was crystallised from 1% aqueous hydrochloric acid, giving the *flavylium chloride* (VI; R = Me) as a brown mass of microscopic orange needles with a green lustre, m. p. 158° (decomp.) (Found: C, 58·8; H, 6·1. $C_{18}H_{17}O_4Cl,2H_2O$ requires C, 58·6; H, 5·7. Found, after drying at 100° in a vacuum: C, 65·4; H, 5·9; loss, 9·2. $C_{18}H_{17}O_4Cl$ requires C, 65·0; H, 5·1; loss, 9·8%). Solutions of the flavylium salt in dilute aqueous acid have a very intense green fluorescence.

Demethylation of the compound with hydriodic acid followed by conversion of the product into the chloride (cf. Willstätter, Zechmeister, and Kindler, *Ber.*, 1924, **57**, 1938) gave 6 : 7 : 4′-*trihydroxyflavylium chloride* (VI; R = H) (64%) as vermilion microscopic plates (from methanolic hydrochloric acid), m. p. 290° (decomp.), sinters at 250° (Found: C, 60·3; H, 4·3. $C_{15}H_{11}O_4Cl,\frac{1}{2}H_2O$ requires C, 60·1; H, 4·0%) (Hoyashi, *Acta Phytochim.*, Tokyo, 1935, **8**, 179, gives m. p. 284, sinters at 250°, but apparently no analysis). Solutions of the salt in mineral acid are orange-red, becoming carmine-red on the addition of alkali and then fading, after 24 hr., to yellow. With sodium acetate, solutions of the flavylium salt give a bright red precipitate. The ferric reaction of the salt in ethanol is red-brown.

6 : 7 : 8-*Trimethoxycoumarin* (IV).—The coumarin (total yield, 0·18%) crystallised from methanol or benzene–light petroleum in large thick colourless prisms, m. p. 104° (Wessely and Demmer, *loc. cit.* give m. p. 104°) [Found: C, 60·7; H, 5·1; OMe, 40·5%; *M* (Rast), 232. Calc. for $C_{12}H_{12}O_5$: C, 61·0; H, 5·1; 3OMe, 39·4%; *M*, 236].

2 : 3 : 4 : 5-*Tetramethoxycinnamic Acid*.—Alkaline hydrolysis of the trimethoxycoumarin (IV) and methylation with methyl sulphate by the method of Wessely and Demmer (*loc. cit.*) gave 2 : 3 : 4 : 5-*tetramethoxycinnamic acid* not isolated by these authors, which crystallised in needles from aqueous ethanol, m. p. 81—82° (Found: C, 58·3; H, 6·4; OMe, 45·9. $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0; 4OMe, 46·2%). Oxidation of this acid with alkaline permanganate gave 2 : 3 : 4 : 5-tetramethoxybenzoic acid, m. p. 85—85·5° (*idem, loc. cit.*, give m. p. 85°) (Found: C, 54·7; H, 5·7; OMe, 50·1. Calc. for $C_{11}H_{14}O_6$: C, 54·5; H, 5·8; 4OMe, 51·2%).

Extraction of West Indian Satinwood (Zanthoxylum flavum).—Extraction of the ground wood (4 kg.) with boiling light petroleum for 18 hr. and evaporation gave a viscous orange oil (140 g.) having a strong coconut odour. After several hours at 0° the oil was decanted from the portion which had solidified, and the solid separated by crystallisation from methanol into

suberosin (III; R = Me) (29 g.) and the more-soluble psoralene (VII; R = H) (0·8 g.). The residual oil contained no detectable amount of steam-volatile material and only traces of alkali-soluble products, *e.g.*, suberosin (0·7 g.), which was extracted with 8% aqueous sodium hydroxide. In chromatography on alumina, 97% was eluted with light petroleum. After refluxing with excess of 1% methanolic potassium hydroxide and removal of the gummy acid fraction (2 g.), the neutral oil (64 g.) gave suberosin (1 g.) and a crystalline alcohol (0·3 g.), needles (from light petroleum), m. p. 107—109°, $[\alpha]_D^{20}$ +56° in $CHCl_3$ (Liebermann–Burchard reaction, red, fluorescing green) (Found, after drying at 120°: C, 84·2; H, 11·8. $C_{30}H_{50}O$ requires C, 84·6; H, 11·8%). Finally, distillation of the oil (27 g.) gave two fractions (*a*) b. p. (from sodium) 140—150°/0·05 mm. (1·3 g.) (Found: C, 75·7; H, 10·8%) and (*b*) b. p. 158—172°/0·05 mm. (0·25 g.) consisting of suberosin.

Further extraction of the wood with ether and evaporation of the solution gave a viscous red oil (40 g.) which, after 3 days at 0°, deposited a solid separated by crystallisation from methanol into suberosin (0·8 g.), psoralene (1·4 g.), and a third coumarin (0·026 g.) regarded as xanthotoxin and separating from light petroleum as needles, m. p. 144—145° [Found: C, 66·5; H, 3·9; OMe, 14·1%; *M* (Rast), 213. Calc. for $C_{12}H_8O_4$: C, 66·7; H, 3·7; 1OMe, 14·3%; *M*, 216]. Xanthotoxin has m. p. 145—146° (Thoms, *Ber.*, 1911, **44**, 3325). Treatment of the non-crystalline part of the extract by alkali-extraction, chromatography, hydrolysis, and distillation failed to yield any further pure material. The acetone extract mainly consisted of a dark phenolic resin (160 g.) from the neutral part of which suberosin (3·1 g.) was obtained by crystallisation from a small volume of acetone. Extraction of the wood with ethanol gave only resinous material (20 g.).

Suberosin (*7-Methoxy-6-isopent-2′-enylcoumarin*) (III; R = Me).—Suberosin (total yield 34·1 g., 0·85%) crystallised in large rhombic prisms, m. p. 87—88°, from methanol (Ewing *et al.*, *loc. cit.*, give m. p. 87·5°) [Found: C, 73·5; H, 6·9; OMe, 14·5%; *M* (Rast), 231. Calc. for $C_{15}H_{16}O_3$: C, 73·7; H, 6·6; 1OMe, 12·7%; *M*, 244]; light absorption: max. 224, 253, 332 mμ; log ε, 4·34, 3·76, 4·18. Hot aqueous sodium hydroxide and methyl sulphate gave methylsuberosinic acid, yellow prisms, m. p. 134—135°, from aqueous ethanol (*idem*, *loc. cit.*, give m. p. 134—135°) (Found: C, 69·4; H, 7·3; OMe, 21·3. Calc. for $C_{16}H_{20}O_4$: C, 69·5; H, 7·3; 2OMe, 22·5%) which gave an oily methyl ester. The oxidation of suberosin with chromic acid in acetic acid at room temperature gave acetone, identified as the 2 : 4-dinitrophenylhydrazone, and 7-methoxycoumarin-6-aldehyde, m. p. 252—253° (*idem*, *loc. cit.*, give m. p. 252—253°) (Found: C, 63·9; H, 4·1; OMe, 13·9. Calc. for $C_{11}H_8O_4$: C, 64·7; H, 4·0; OMe, 15·2%). The dibromide prepared by bromination at room temperature in benzene crystallised from ethanol as plates, m. p. 148° (*idem*, *loc. cit.*, give m. p. 148°) (Found: C, 44·6; H, 4·3; Br, 40·1. Calc. for $C_{15}H_{16}O_3Br_2$: C, 44·6; H, 4·0; Br, 39·6%); light absorption: max., 222, 326 mμ; log ε, 3·93, 3·75.

Dihydroxanthyletin.—Suberosin (2 g.) was refluxed for 1 hr. with aqueous hydrobromic acid (150 c.c.; *d* 1·49) containing red phosphorus (1 g.), and the resulting solution poured on ice and extracted with ether. The alkali-insoluble portion of the ethereal extract crystallised from light petroleum (b. p. 60—80°) in elongated plates (0·2 g.), m. p. 122—124° alone and mixed with an authentic specimen of dihydroxanthyletin (Found: C, 72·9; H, 6·2. Calc. for $C_{14}H_{14}O_3$: C, 73·0; H, 6·1%).

Tribromosuberosin.—Suberosin (1 g.) in glacial acetic acid (5 c.c.) was treated with a solution of bromine (1·32 g., 2 mols.) in acetic acid (10 c.c.). After 1 hr. the solvent was removed under reduced pressure, the residue of *tribromosuberosin* crystallising from ethanol in colourless prisms, m. p. 170° (Found: C, 37·6; H, 3·5; Br, 49·5. $C_{15}H_{15}O_3Br_3$ requires C, 37·3; H, 3·1; Br, 49·7%); light absorption: max., 226, 340 mμ; log ε 4·24, 4·26. Solutions of the compound show a blue-violet fluorescence.

Complex of Suberosin and 2 : 4-Dinitrophenylhydrazine Sulphate.—Suberosin dissolved in the minimum amount of methanol and treated with an excess of saturated methanolic 2 : 4-dinitrophenylhydrazine sulphate gave a *complex* (95%), m. p. 167—168°, crystallising from ethanol or acetic acid in yellow plates (Found: C, 46·1; H, 4·5; N, 10·2; S, 5·2. $C_{15}H_{16}O_3,C_6H_6O_4N_4,H_2SO_4$ requires C, 46·5; H, 4·5; N, 10·4; S, 5·9%). The complex was resolved into its components on an alumina column, light petroleum eluting the coumarin and benzene the remaining hydrazine sulphate. The light absorptions of the complex and of equimolecular solutions of the coumarin and the hydrazine sulphate in separate cells placed in series in the spectrophotometer were indistinguishable.

Suberosin 2′ : 3′-Epoxide.—Suberosin (2 g.) in dry ether (75 c.c.) was treated with a solution of monoperphthalic acid (1·6 g.) in dry ether (25 c.c.) at 0° for 24 hr. After being washed with

aqueous sodium hydrogen carbonate, the ethereal solution was dried and evaporated, the residue (1·8 g.) of *epoxide* crystallising from benzene in prisms, m. p. 114—114·5° (Found: C, 68·7; H, 6·1; OMe, 12·0. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2; OMe, 11·9%). The compound gave an orange-coloured solution with a violet fluorescence in concentrated sulphuric acid.

Dihydro-2′ : 3′-dihydroxysuberosin.—Suberosin epoxide (0·52 g.) was treated with boiling aqueous oxalic acid (1%) for 1 hr. (cf. Böhme and Pietsch, *Ber.*, 1939, **72**, 773) and the resulting *diol* crystallised from chloroform–light petroleum as small cubic prisms, m. p. 136—137° (Found: C, 64·6; H, 6·4. $C_{15}H_{18}O_5$ requires C, 64·7; H, 6·5%). Rapid precipitation after boiling in chloroform solution for 5 min. gave elongated yellow prisms, m. p. 129—131°, which reverted to the colourless form after several days at room temperature. The compound in concentrated sulphuric acid gave a bright red solution with a violet fluorescence.

Dihydro-2′-oxosuberosin (VIII).—Suberosin epoxide (0·8 g.) was heated with dilute sulphuric acid (20%) for 4 hr. (cf. *idem, loc. cit.*); the product then crystallised from chloroform–light petroleum as colourless plates, m. p. 92—93°, consisting of *dihydro-2′-oxosuberosin* (0·7 g.) (Found: C, 69·5; H, 6·3. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%). The *oxime* formed colourless needles, m. p. 169—170°, from aqueous ethanol (Found: C, 65·7; H, 6·1; N, 4·7. $C_{15}H_{17}O_4N$ requires C, 65·4; H, 6·2; N, 5·1%).

7-Methoxy-2 : 2-dimethyl-6-isopent-2′-enylbenzopyran.—Suberosin (2 g.) in ether (200 c.c.) was added slowly to a solution of excess of methylmagnesium iodide (from 6·5 g. of methyl iodide) in ether (100 c.c.). The solution was boiled for 3 hr. and then treated with dilute hydrochloric acid. The product was isolated with ether in the usual way, distillation affording the *benzopyran* as an oil (1 g.), b. p. 90—92°/0·05 mm., n_D^{20} 1·5493 (Found: C, 78·7; H, 8·3; OMe, 10·5. $C_{17}H_{22}O_2$ requires C, 79·0; H, 8·6; OMe, 12·0%).

Psoralene (VII; R = H).—Crystallised from benzene–light petroleum or methanol psoralene formed large colourless needles, m. p. 161—162° (Jois, Manjunath, and Rao, *J. Indian Chem. Soc.*, 1933, **10**, 41, give m. p. 161—162°) [Found: C, 70·5; H, 3·3%; *M* (Rast), 189. Calc. for $C_{11}H_6O_3$: C, 71·0; H, 3·3%; *M*, 186]. Treatment with potassium hydroxide–methyl sulphate in the usual way converted psoralene into β-(6-methoxy-5-coumaronyl)acrylic acid which separated as pale yellow needles, m. p. 163—165°, from benzene–light petroleum or aqueous ethanol (Jois and Manjunath, *Ber.*, 1937, **70**, 434, give m. p. 163—165°) (Found: C, 66·2; H, 4·5; OMe, 14·2. Calc. for $C_{12}H_{10}O_4$: C, 66·1; H, 4·6; 1OMe, 14·1%).

Extraction of East Indian Satinwood (Chloroxylon swietenia).—The coarsely ground wood (3·6 kg.) was extracted for 120 hr. with boiling light petroleum (b. p. 40—60°). The cooled solution was decanted from the semi-crystalline deposit which gave xanthyletin (79·6 g.) by crystallisation from methanol. The contents of the residual methanolic solution and of the light petroleum solution were separated by 8% aqueous sodium hydroxide into phenolic (65 g.) and neutral (35 g.) fractions. The neutral fraction when crystallised from methanol gave xanthyletin (8·4 g.) and the xanthyletin–xanthoxyletin complex (8·5 g.), m. p. 99—104°, previously described by Robertson and Subramaniam (*J.*, 1937, 1549). Treatment of the mother-liquors from this fraction with 60% aqueous alkali at 100° (10 min.) followed by dilution and extraction with ether left an aqueous solution from which carbon dioxide precipitated a solid separated by methanol into xanthoxyletin (3·85 g.) and a further amount (8·5 g.) of the above complex.

Crystallisation of the phenolic fraction from benzene gave *7-demethylsuberosin* (24·0 g.), a further quantity being isolated from the mother-liquor as the acetate (26 g.).

The following ether-extract, an orange oil (98 g.), was also separated into phenolic and non-phenolic fractions. The neutral fraction treated as above with alkali gave xanthyletin (15 g.) and the xanthyletin–xanthoxyletin complex (11 g.). The phenolic portion of the extract when crystallised gave 7-demethylsuberosin (16 g.), a further quantity being isolated as acetate (23 g.).

Further extraction of the wood with acetone gave a resinous mass (143 g.) of which some 50% was ether-soluble, and was separated into phenolic and non-phenolic fractions. The former gave 7-demethylsuberosin (8·1 g.) when crystallised from benzene, and from a methanol solution of the neutral portion xanthyletin (16·7 g.) was obtained.

Xanthyletin (II; R = H).—Xanthyletin (total yield 120 g., 3·3% approx.) crystallised from methanol in elongated flat prisms, m. p. and mixed m. p. 126—127° [Found: C, 73·4; H, 5·5%; *M* (Rast), 235. Calc. for $C_{14}H_{12}O_3$: C, 73·7; H, 5·3%; *M*, 228]; light absorption: max., 266, 348 mμ; log ε 4·34, 4·15. The dihydro-derivative prepared by reduction in ethanol with palladium at normal temperature and pressure formed elongated plates, m. p. 122—124°, from benzene–light petroleum (Bell and Robertson, *loc. cit.*, give m. p. 124—125°) (Found: C, 72·9; H, 6·2. Calc. for $C_{14}H_{14}O_3$: C, 73·0; H, 6·1%). Hot alkali and methyl sulphate

converted xanthyletin into *O*-methylxanthyletenic acid, yellow prisms (from methanol), m. p. 191—192° (decomp.) [*idem, loc. cit.*, give m. p. 193—194° (decomp.)] (Found : C, 69·4; H, 6·3; OMe, 12·7. Calc. for $C_{15}H_{16}O_4$: C, 69·2; H, 6·2; OMe, 11·9%). Alkaline hydrolysis of xanthyletin, in addition to acetone and resorcinol (Bell and Robertson, *loc. cit.*), gave acetaldehyde. The aqueous distillate from the hydrolysis mixture was treated with aqueous dimedone, acetaldehyde–dimedone complex being collected after 24 hr. and identified by comparison with an authentic specimen. Acetone isolated by distillation from the mother-liquors was identified as 2 : 4-dinitrophenylhydrazone.

Xanthoxyletin (II; R = OMe).—Xanthoxyletin (total yield 0·1% approx.) crystallised from methanol in colourless elongated prisms, m. p. and mixed m. p. 132—133° [Found : C, 69·5; H, 5·6; OMe, 12·2%; *M* (Rast), 259. Calc. for $C_{15}H_{14}O_4$: C, 69·7; H, 5·5; OMe, 12·0%; *M*, 258]. Dihydroxanthoxyletin, obtained by reduction with palladium and hydrogen, had m. p. 143—144° (*idem, loc. cit.*, give m. p. 144·5—145·5°) (Found : C, 69·3; H, 6·5; OMe, 11·9. Calc. for $C_{15}H_{16}O_4$: C, 69·2; H, 6·2; 1OMe, 11·9%).

3-*Bromodihydroxanthyletin.*—Dihydroxanthyletin (12 g.) in glacial acetic acid (200 c.c.) was treated with bromine (8·5 g., 1 mol.) in acetic acid (30 c.c.). After 2 hr. the solvent was removed under reduced pressure and the residue of 3-*bromodihydroxanthyletin* (16 g.) crystallised from benzene as flat elongated prisms, m. p. 163—164° (Found : C, 54·5; H, 4·5; Br, 25·8. $C_{14}H_{13}O_3Br$ requires C, 54·4; H, 4·2; Br, 25·8%).

Dihydro-2′ : 2′-dimethylpyrano(5′ : 6′-5 : 6)coumarone-2-carboxylic Acid.—3-Bromodihydroxanthyletin (15 g.) in aqueous potassium hydroxide (250 c.c., 10%) was heated under reflux for 1 hr. The cooled solution was poured into excess of hydrochloric acid, and the precipitate was collected and crystallised from methanol, the *acid* separating as glistening plates (6·5 g.), m. p. 242—244° (decomp.) (Found : C, 68·5; H, 5·3. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%). The *methyl ester* prepared in methanol–hydrogen chloride crystallised from light petroleum as elongated flat prisms, m. p. 105—106° (Found : C, 69·0; H, 6·1. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%).

Dihydro-2′ : 2′-dimethylpyrano(5′ : 6′-5 : 6)coumarone.—The coumarone-carboxylic acid (6·2 g.) was heated in boiling quinoline (20 c.c.) containing copper powder (0·5 g.) for 12 min. The cooled solution was poured into ether, and the quinoline removed from the filtered solution by dilute hydrochloric acid. The ethereal solution was dried, and decolourised by passing it through alumina. Distillation gave a fraction (2·6 g., 51%), b. p. 153—155°/13 mm., which crystallised from a small volume of light petroleum (b. p. 40—60°) at 0°, the *coumarone* separating in large prisms, m. p. 39—41° (Found : C, 77·2; H, 6·8. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). Its solution in concentrated sulphuric acid was orange changing to brown, red, purple, and finally blue. The *picrate* prepared in methanol, separated in bright red needles, m. p. 88—89° (Found : C, 53·1; H, 3·7; N, 9·7. $C_{13}H_{14}O_2,C_6H_3O_7N_3$ requires, C, 52·9; H, 4·0; N, 9·7%).

7-*Demethylsuberosin* (III; R = H).—7-Demethylsuberosin (yield 1·3%) crystallised from benzene in flat elongated prisms, m. p. 133·5—134° [Found : C, 73·3; H, 6·3%; *M* (Rast), 227. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%; *M*, 230]; light absorption : max., 226, 334 mμ; log ε 4·12, 4·21. The compound is readily soluble in dilute alkali to a yellow solution with a blue fluorescence; in sulphuric acid it gives a pale straw-yellow colour with a blue-violet fluorescence. It is very soluble in methanol and acetone, moderately soluble in benzene, chloroform, and ethyl acetate, and very sparingly soluble in light petroleum. Methylation at 0° for 18 hr. in ether with an excess of diazomethane gave suberosin, m. p. and mixed m. p. 87—88° (Found : C, 74·3; H, 6·8; OMe, 13·7. Calc. for $C_{15}H_{16}O_3$: C, 73·8; H, 6·6; 1OMe, 12·7%). When 7-demethylsuberosin was boiled in aqueous-alcoholic hydrochloric acid (0·2N) for 3 hr. and the solution diluted, dihydroxanthyletin was obtained (yield, 90%), m. p. and mixed m. p. 122—124° (Found : C, 73·5; H, 6·3. Calc. for $C_{14}H_{14}O_3$: C, 73·0; H, 6·1%). The *acetate* (acetic anhydride–pyridine) separated from aqueous ethanol in elongated prisms or from benzene in shining plates, m. p. 98—100° (Found : C, 70·9; H, 5·6; CH_3·CO, 16·6. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9; 1CH_3·CO, 15·8%). The *benzoate* crystallised in needles from aqueous alcohol, m. p. 124—125° (Found : C, 75·7; H, 5·5. $C_{21}H_{18}O_4$ requires C, 75·4; H, 5·4%). The *dibromo*-derivative, prepared with bromine (1 mol.) in cold benzene, crystallised from methanol in needles, m. p. 185—186°; light absorption : max., 207, 222, 331 mμ; log ε 4·42, 4·17, 4·17 (Found : C, 43·2; H, 3·8; Br, 40·1. $C_{14}H_{14}O_3Br_2$ requires C, 43·1; H, 3·6; Br, 41·0%). The *tribromo*-derivative prepared in acetic acid crystallised from methanol in plates, m. p. 176—178° (Found : C, 35·6; H, 3·0; Br, 50·8. $C_{14}H_{13}O_3Br_3$ requires C, 35·8; H, 2·8; Br, 51·1%); light absorption : max., 207, 224, 345 mμ; log ε 4·52, 3·91, 4·20.

7-*Demethyldihydrosuberosin.*—7-Demethylsuberosin (0·8 g.), shaken in ethanol (100 c.c.)

with palladium chloride (0·05 g.), absorbed hydrogen (1 mol.) at room temperature and pressure in 80 min. *7-Demethyldihydrosuberosin* separated in colourless needles, m. p. 106—108°, from benzene (Found : C, 72·4; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

(±)*Nodakenetin* [(±)-*Marmesin*] (IX).—An ethereal solution of excess of monoperphthalic acid (3·3 g.) containing 7-demethylsuberosin (4 g.) was kept at 0° for 24 hr. Acidic material was then extracted with aqueous sodium hydrogen carbonate, and the residual solution was dried and evaporated. The residue of (±)-*nodakenetin* crystallised from benzene in glistening plates (2·4 g., 56%), m. p. 152—153° (Chatterjee and Mitra, *loc. cit.*, give the m. p. of an equimolecular mixture of nodakenetin and marmesin as *ca.* 155°) (Found : C, 68·3; H, 5·6. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%). The compound was insoluble in cold alkalis, and unaffected by methylation with diazomethane or methyl sulphate–potassium carbonate, and by boiling with 20% sulphuric acid. The *acetate* (sodium acetate–acetic anhydride) crystallised from aqueous ethanol in elongated plates, m. p. 124—126° (*idem, loc. cit.*, give m. p. 130° for the acetates of the optically active compounds) (Found : C, 66·6; H, 5·3. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%).

Deoxyoreosolone (X).—(±)-Nodakenetin (0·25 g.) was heated with phosphoric oxide in benzene at the b. p. for 5 hr. and the benzene solution decanted, washed, and evaporated. The residual deoxyoreosolone (0·08 g.) crystallised from light petroleum (b. p. 60—80°) as plates, m. p. 136—137° (*idem, loc. cit.*, give m. p. 138—140°) (Found : C, 73·3; H, 5·4. Calc. for $C_{14}H_{12}O_3$: C, 73·7; H, 5·3%).

The authors thank Messrs. Marrs, Cross and Wilfrid Fairbairns, London, for obtaining the three wood species used in this investigation, and Mr. D. B. Irvin, Director, Messrs. Irvin and Sellers, Liverpool, for a gift of W. Indian satinwood. One of the authors (J. R. H.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Allowance.

THE UNIVERSITY, NOTTINGHAM. [*Received, December 28th,* 1953.]