922. *The Chemistry of Extractives from Hardwoods. Part XXIX.* Eusiderin, a Possible By-product of Lignin Synthesis in* Eusideroxylon zwageri.

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Eusiderin is a neutral compound $C_{22}H_{26}O_6$ occurring in the wood of *Eusideroxylon zwageri*. It contains a *C*-methyl, an allyl, and four methoxyl groups, and its recognisable degradation products are pyrogallol derivatives. Under demethylation conditions the dihydro-compound gives 5-n-propylpyrogallol indicating that eusiderin arises from the oxidative coupling through oxygen of two C_6–C_3 phenols of the type associated with lignin synthesis.

Eusideroxylon zwageri (family Lauraceæ) occurs in Borneo and Indonesia and yields a dense red-brown durable wood, of which limited amounts are imported into the United Kingdom as " belian " (" billian ").[1] Fractionation of the oily material extracted from the shredded timber with boiling light petroleum gave a small quantity (0·05—0·08%) of a crystalline lævorotatory solid, $C_{22}H_{26}O_6$. This new product, eusiderin, was unaffected by phenolic and carbonylic reagents, but Zeisel determinations indicated four methoxyl groups in the molecule. In view of their inertness, the remaining oxygen atoms were attributed to aryl ether linkages, possibly cyclic.

Catalytic reduction led to a dihydro-derivative resistant to further hydrogenation. Whereas the Kuhn–Roth estimation revealed one *C*-methyl group in eusiderin, dihydroeusiderin contained two. This indication of a terminal methylene group in eusiderin is in agreement with the formation of formaldehyde on ozonolysis, which was isolated as the 2,4-dinitrophenylhydrazone and dimedone compound. The resemblance between the light absorption of eusiderin and of its dihydro-compound showed that the unsaturated linkage is not in conjugation with the aromatic system.

The non-volatile oily ozonolysis product (amorphous 2,4-dinitrophenylhydrazone) was readily oxidised by permanganate, with loss of a further carbon atom to eusideric acid, characterised as its methyl ester and amide. Its light absorption resembled that of an aromatic acid, and like eusiderin it was optically active and contained a *C*-methyl group. Eusideric acid was decarboxylated (copper–quinoline) in good yield to a neutral product, $C_{19}H_{22}O_6$, which from the occurrence of the system $H_2C{:}CH{\cdot}CH_2{\cdot}$ in eusiderin, was designated deallyleusiderin.

Dehydrogenation experiments on dihydroeusiderin and deallyleusiderin with palladised charcoal or selenium were either without effect or yielded unpurifiable products; oxidation with selenium dioxide or lead tetra-acetate was likewise unsuccessful. Bromination of eusiderin and of its derivatives gave only one crystalline product, a tribromodihydroeusiderin, which like the parent compound was stable to 3% methanolic potash. The Clemmensen reduction also was without action on eusiderin, whereas it effects reductive scission of the dihydrofuran ring of homopterocarpin,[2] a compound which appeared to have some resemblance to deallyleusiderin. Catalytic reduction in acetic acid–perchloric acid with palladised charcoal, which is effective in the hydrogenolysis of certain benzyl ethers,[3] failed with dihydroeusiderin.

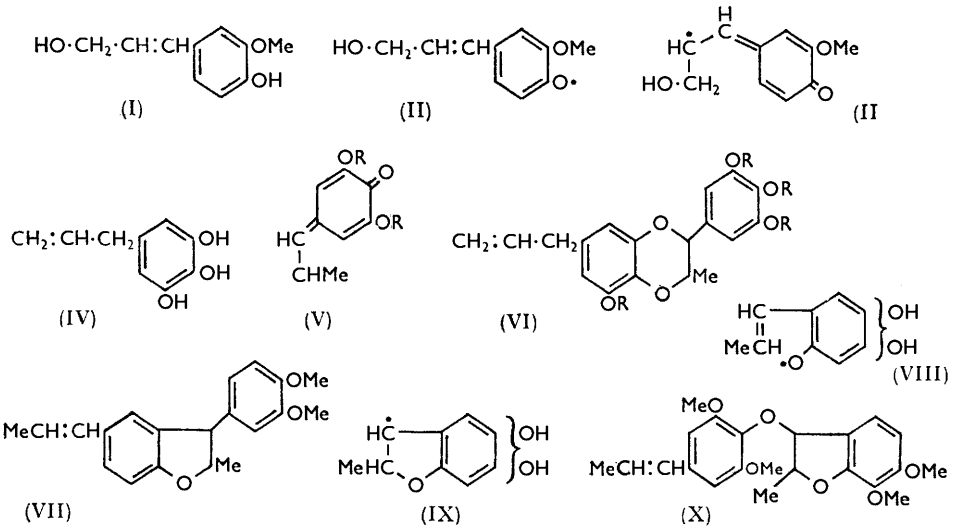
The type of phenol present in eusiderin was revealed by the action of hydriodic acid on its deallyl derivative followed by acetylation; pyrogallol triacetate was then obtained. Reductive cleavage with sodium in liquid ammonia as applied to various aryl and alkylaryl

* Part XXVIII, *J.*, 1956, 4477.

[1] Hart, " Timbers of South East Asia," Timber Development Association, London, 1955, p. 10.
[2] McGookin, Robertson, and Whalley, *J.*, 1940, 787.
[3] Hartung and Simonoff, *Org. Reactions*, 1953, **7**, 263; Baker, Cornell, and Cron, *J. Amer. Chem. Soc.*, 1948, **70**, 1490.

ethers degraded deallyleusiderin to 1-methylpyrogallol, isolated as diacetate and compared with a synthetic specimen. Phenolic material was also obtained by this method from dihydroeusiderin but neither the product nor its derivatives were purifiable. Sodium–alcohol reduction, which is known to reduce pyrogallol ethers to resorcinol derivatives,[4] failed to give any recognisable product from deallyleusiderin.

Demethylation conditions (hydriodic acid–acetic acid) applied to dihydroeusiderin resulted in formation of a compound isolated as a triacetate, $C_{12}H_{18}O_6$, m. p. 49—51°, and duly identified by synthesis as the 1,2,3-triacetoxy-5-propylbenzene. It was prepared by acetylation of the Clemmensen reduction product of 3,4,5-trihydroxypropiophenone and had m. p. and mixed m. p. 51°, whereas the compound correspondingly prepared from 2,3,4-trimethoxypropiophenone had m. p. 109°.



It follows that eusiderin contains a 5-allylpyrogallol residue with its three hydroxyl functions either methylated or otherwise combined in ether linkages. The existence of four methoxyl groups in the parent compound, which is therefore derived from a tetrahydric phenol $C_{18}H_{18}O_6$, points to the presence of a second phenolic constituent and although this is not necessarily based on pyrogallol it is significant that no phenolic degradation products have been observed other than pyrogallol compounds.

In view of the near simple factorial relation between the molecular formula of the tetrademethyleusiderin $C_{18}H_{18}O_6$ and that of the largest authenticated degradation product *viz* 5-allylpyrogallol, $C_9H_{10}O_3$, it is probable that the C_{18} nucleus arises from the oxidative coupling of two alkylpyrogallol molecules. This hypothesis suggests a connection with the lignans and lignins which are generally regarded as oxidation (dehydrogenation) products of either coniferyl or sinapyl alcohol, the latter predominating in the lignins of hardwood species.

An essential step in lignan synthesis and apparently also in the formation of the more complex molecules of lignins is the union of the three-carbon side-chains by oxidative coupling at the respective β-carbon atoms, with secondary condensations involving the alcoholic and phenolic hydroxyl groups. The process has been given a mechanistic interpretation by Erdtman,[5] the primary phase being the dehydrogenation of monomer (I) to a phenoxide radical (II), the resulting free-radical activity at the side-chain β-position (III) leading to the characteristic ββ-carbon linking.

[4] Thoms and Siebeling, *Ber.*, 1911, **44**, 2135; Sonn and Scheffler, *Ber.*, 1924, **57**, 960; Asahina, *Ber.*, 1936, **69**, 1043.

[5] Erdtman, *Research*, 1950, **3**, 63; see also Smith, *Ann. Reports*, 1956, **53**, 277.

An allyl side-chain, however, as in the pyrogallol (IV), does not admit of C_β free-radical formation *via* the phenoxide, although it is feasible in the isomeric propenyl compound to give the compound (V). The union of (IV) (or of the corresponding phenoxide radical) with (V), followed by *o*-hydroxyl addition to the quinone-methine system, would lead to structure (VI; R=H). Assuming methylation of the remaining oxygen substituents, *i.e.*, OR = OMe, structure (VI), and its isomer (VIa) with the benzodioxan substituents reversed, have all the known features of eusiderin. Both (VI) and (VIa) are derived from identical C_9 units, have four methoxyl groups, an allyl side-chain and a *C*-methyl group, and both are asymmetric. The validity of the assumption that only 5-substituted pyrogallol units are involved being accepted, there is no alternative formula. Oxidative coupling in any other way—for example to a dihydrobenzofuran similar to the product (VII) obtained by Erdtman from isoeugenol,[6] would require carbon–carbon linkage of the two nuclei. This not only creates a difficulty with regard to the number of methoxyl groups in the final structure, but it would also preclude hydrolytic degradation to a simple alkylpyrogallol, as observed with dihydroeusiderin. On the other hand, a dihydrobenzofuran structure cannot be excluded if an *ortho*-alkylphenol also is involved in the biosynthesis of eusiderin. With the preliminary cyclisation of an *ortho*-substituted phenoxide radical (VIII) to (IX), a dihydrobenzofuran would readily be evolved by its condensation with the pyrogallol (IV). The resulting structure, *e.g.*, (X), has all the observed attributes of eusiderin, the non-appearance of hydrolytic products other than pyrogallol derivatives being attributable to the instability under strongly acid conditions of the β-hydroxydihydrofuran primarily formed.

On the other hand, the resistance of eusiderin to dehydrogenation reagents creates a difficulty. Both of the structures (VI) and (X) are theoretically capable of losing hydrogen from their heterocyclic nuclei, although the behaviour of the system Ar·O·CH:CHMe·O· and of its possible products under dehydrogenation conditions is speculative. Secondary changes during biosynthesis in which the *C*-methyl group migrates to the adjoining position cannot be entirely excluded and by producing a quaternary carbon would inhibit the loss of hydrogen. There seems, however, little doubt that this newly isolated natural product arises from C_9 units of the type generally associated with the formation of hardwood lignin and its occurrence in this environment very strongly suggests that it is closely related to the fundamental units involved in lignin synthesis of which it is a by-product.

Experimental

The Extraction of E. zwageri.—The shredded wood was extracted in batches (*ca.* 5·5 kg.) with boiling light petroleum (b. p. 60—80°; 6 l.) for 40 hr. Evaporation of the extract to 400 c.c. and cooling resulted in the deposition of wax (26 g., 0·48%) which was not investigated. Further concentration to 70 c.c. precipitated an oil, which yielded a solid (A) (2·4 g., 0·044%) when triturated with methanol. Finally, evaporation gave an orange oil which was heated with alcoholic sodium hydroxide (5%; 150 c.c.). The unsaponifiable portion was heated under diminished pressure thereby giving a liquid fraction (9 g., 0·16%), b. p. 55—85°/0·1 mm.

This fraction (9 g.) was chromatographed on alumina and from a light petroleum–benzene eluate (4 : 1) more A (1·7 g., 0·03%) was obtained. Continued elution with benzene and benzene–ether yielded a product (B) (0·55 g., 0·01%), m. p. 134°.

The oil, b. p. 55—85°/0·1 mm., was redistilled from sodium; the fraction (7·7 g., 0·18%) of b. p. 63—64°/0·2 mm. then had the composition of a sesquiterpene hydrocarbon (Found: C, 88·5; H, 12·0. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%). Light absorption: max. 205, 248 mμ; log ε 3·88, 2·61. It failed to give any crystalline product with hydrogen chloride in ether or acetic acid. Dehydrogenation with palladised charcoal at 250—280° (15 hr.) or with selenium (20 hr.) at 300—330° and chromatography on alumina gave oils from which 1,3,5-trinitrobenzene or picric acid adducts were not isolable.

The solid A consisted of *eusiderin*, needles (from methanol), m. p. 94°, $[\alpha]_D^{19}$ −25·4° (*c* 1·80) [Found: C, 68·8; H, 6·7; OMe, 30·8; *C*-Me, 4·0%; *M*, 386 (Rast), 376 (*X*-ray). $C_{22}H_{26}O_6$ requires C, 68·4; H, 6·8; 4OMe, 32·1; 1*C*-Me, 2·9%; *M*, 386). Light absorption: max. 211,

[6] Erdtman, *Annalen*, 1933, **503**, 283.

272 mμ; log ε 4·89. 3·36]. Eusiderin is easily soluble in most organic solvents except light petroleum; it gave no colour with alcoholic ferric chloride and a red-brown colour with concentrated sulphuric acid.

Product B formed silky needles, m. p. 137°, $[\alpha]_D$ −34° (*c* 2·04), from ethyl acetate–methanol, consisting of β-sitosterol (Found: C, 83·7; H, 12·3. Calc. for $C_{29}H_{50}O$: C, 84·0; H, 12·2%). The acetate had m. p. and mixed m. p. 125—127°, $[\alpha]_D$ −38° (*c* 0·71), and the benzoate, m. p. and mixed m. p. 141—144°.

Dihydroeusiderin.—A solution of eusiderin (0·5 g.) in ethanol (50 c.c.) reduced in presence of Adams's catalyst (0·05 g.) was saturated in 15 min. after absorbing 35 c.c. (1·1 mols.) of hydrogen.

Dihydroeusiderin was obtained by evaporating the filtered solution, and it crystallised from aqueous methanol as prismatic needles (0·46 g.), m. p. 68° [Found: C, 67·9; H, 7·2; OMe, 30·4; *C*-Me, 6·7%; *M*, 343 (Rast). $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·3; 4OMe, 32·0; 2*C*-Me, 7·7%; *M*, 388). Light absorption: max. 210, 272 mμ; log ε 4·89, 3·73].

The reduction of eusiderin (0·036 g.) over palladium–charcoal (12%) in glacial acetic acid (7 c.c.) containing perchloric acid (60%; 2·5%) gave similar results. Dihydroeusiderin was unattacked by potassium permanganate in boiling acetone. It was recovered unchanged after being heated in refluxing diphenyl ether for 3 hr. with 30% palladised charcoal. Treatment of 0·5 g. with selenium at 260—280° for 22 hr. and extraction with chloroform which was then passed through alumina, gave on distillation (*a*) 0·08 g., b. p. <140° (bath)/0·05 mm., strongly smelling of selenides, which was discarded, and (*b*) 0·11 g., b. p. 140—160° (bath)/0·05 mm., with only benzenoid light absorption: max. 211, 271 mμ; $E^{1\%}_{1\,cm.}$ 1220, 190.

Tribromodihydroeusiderin.—Hydrogen bromide was evolved when a solution of dihydroeusiderin (0·041 g.) in chloroform (2 c.c.) was treated at room temperature with a slight excess of bromine in chloroform (5%; v/v). After 1 hr., the solution was evaporated at 25° under reduced pressure. The residue of *tribromodihydroeusiderin* crystallised from methanol as silky needles, m. p. 120° (Found: C, 42·5; H, 4·1; Br, 37·4; OMe, 18·1. $C_{22}H_{25}O_6Br_3$ requires C, 42·2; H, 4·0; Br, 38·5; 4OMe, 19·8%). The treatment of eusiderin and methyl eusiderate with bromine in chloroform or acetic acid under the above conditions gave intractable gums.

Ozonolysis of Eusiderin.—A solution of eusiderin (0·2 g.) in ethyl acetate (10 c.c.) was treated at −40° for 5½ min. with ozonised oxygen (1·2 mol.). After dilution with ethyl acetate (15 c.c.), the solution was shaken with hydrogen and palladised charcoal (0·2 g., 5%) until absorption ceased. The filtered solution and washings (40 c.c.) were shaken with water (4 × 10 c.c.) and aqueous 2,4-dinitrophenylhydrazine (50 c.c.) was added to the aqueous solution. Crystallisation from methanol of the precipitate (0·05 g.) gave orange-yellow flakes of formaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 164—165°. Similarly, formaldehyde dimedone derivative, m. p. and mixed m. p. 189°, was obtained from the ozonolysis.

The main ozonolysis product remaining in the ethyl acetate solution was liquid and gave no crystalline derivatives. Oxidation at room temperature with potassium permanganate in acetone afforded eusideric acid, m. p. 238°.

Eusideric Acid.—A solution of eusiderin (1·0 g.) in acetone (80 c.c.) was refluxed with the addition of potassium permanganate (2·4 g.) in small portions during 2 hr., followed by heating for a further hour. After filtration, the acetone solution was heated for 1 hr. with additional potassium permanganate (0·5 g.), and the manganese dioxide again collected. The combined precipitates were extracted with hot water (3 × 40 c.c.), and the aqueous extracts acidified to yield *eusideric acid* (0·79 g., 78%), which crystallised from aqueous methanol as needles, m. p. 238° alone or mixed with the acid from the ozonolysis product, $[\alpha]_D$ −26·1° (*c* 0·729) [Found: C, 61·5; H, 5·6; OMe, 29·5%; *M*, 358 (Rast); equiv., 387. $C_{20}H_{22}O_8$ requires C, 61·5; H, 5·7; 4OMe, 32·8%; *M*, 390. Light absorption: max. 209, 270 mμ; log ε 4·81, 4·11].

When eusiderin (0·2 g.) in acetone (50 c.c.) was shaken with potassium permanganate (0·5 g.) at room temperature for 18 hr., eusideric acid (0·11 g.), m. p. and mixed m. p. 238°, was again isolated.

The *methyl ester*, prepared with ethereal diazomethane, crystallised from methanol as needles, m. p. 168°, $[\alpha]_D$ = −26·5° (*c* 1·21) (Found: C, 62·2; H, 6·0; OMe, 38·2; *C*-Me, 4·5. $C_{21}H_{24}O_8$ requires C, 62·4; H, 6·0; 5OMe, 38·3; 1*O*-Me, 3·7%. Light absorption: max. 209, 273 mμ; log ε 4·79, 4·15).

Eusideric acid (0·072 g.) was refluxed for 3 hr. with thionyl chloride (1 c.c.) and the excess of reagent removed under reduced pressure. Ammonia was passed through a solution of the

pale brown residue in benzene (3 c.c.) at 5°, and the product obtained by evaporation of the washed benzene solution was crystallised from aqueous methanol to give *eusideramide* as needles, m. p. 192° (Found: C, 61·5; H, 5·9; N, 3·4; OMe, 28·6. $C_{20}H_{23}O_7N$ requires C, 61·7; H, 5·9; N, 3·6; 4OMe, 31·9%). The amide (0·2 g.) in dioxan (4 c.c.) was recovered unchanged from a solution of sodium hypochlorite [from 0·1 g. of chlorine and sodium hydroxide (6%; 5 c.c.) at 0°].

Deallyleusiderin.—A solution of the acid (0·23 g.) in redistilled quinoline (4 c.c.) containing copper bronze (0·25 g.) was refluxed for 30 min., then cooled and diluted with ether (20 c.c.). After successive washings with hydrochloric acid (5%; 8 × 10 c.c.), water (20 c.c.), aqueous sodium carbonate (5%; 2 × 10 c.c.), and water (20 c.c.), the dried evaporated extract was dissolved in chloroform and filtered through alumina (10 cm. × 1 cm.). Evaporation gave *deallyleusiderin* (0·14 g.) which crystallised from chloroform–methanol as needles, m. p. 135°, $[\alpha]_D$ −18·9° (*c* 0·95) (Found: C, 65·8; H, 6·4; OMe, 32·8. $C_{19}H_{22}O_6$ requires C, 65·9; H, 6·4; 4OMe, 35·8%). Light absorption: max. 214, 269 mμ; log ε 4·53, 3·24.

A mixture of deallyleusiderin (0·29 g.) and selenium (0·6 g.) was heated at 250—260° for 6 hr., and the product isolated with chloroform (50 c.c.). After percolation through alumina (20 g.) and evaporation, a residue of deallyleusiderin (0·19 g.) was the recognisable product. With selenium at 280—290° for 8 hr., the product was an intractable tar.

Deallyleusiderin (0·2 g.) was heated to 70° for 15 min. in glacial acetic acid (10 c.c.) with lead tetra-acetate (0·6 g.). The gum (0·11 g.) obtained on working up partly crystallised, with the recovery of deallyleusiderin (0·07 g.).

Similar results were obtained with dihydroeusiderin.

No deposition of selenium occurred when deallyleusiderin (0·005 g.) was refluxed for 24 hr. with fresh selenium dioxide (0·005 g.) in ethyl acetate (2 c.c.), acetic acid (95%; 2 c.c.), or pentyl alcohol (2 c.c.). Dihydroeusiderin under similar conditions appeared to undergo reaction (selenium deposited) but only dihydroeusiderin, isolated as its tribromo-derivative (0·08 g.), was obtained.

Deallyleusiderin was recovered after being shaken overnight with aluminium chloride (0·078 g., 2 mol.) in benzene (3 c.c.) and ether (5 c.c.), followed by heating under reflux for 5 hr. The phenolic gum (0·06 g.) obtained from deallyleusiderin (0·076 g.) by refluxing it for 4 hr. with aluminium chloride (0·094 g., 3 mol.) in dry benzene (5 c.c.), etc., was heated at 100° with benzoyl chloride (0·2 c.c.) and pyridine (2 c.c.). Isolation in the usual manner gave an oil, b. p. 140—160° (bath)/0·1 mm. (Found: C, 76·7; H, 5·4; OMe, 9·7%).

Hydriodic Acid Cleavage.—(*A*) *Of deallyleusiderin.* The deallyl compound (0·2 g.) was refluxed for 30 min. with hydriodic acid (68%; 2 c.c.), acetic acid (3 c.c.), and red phosphorus (0·2 g.) in an atmosphere of nitrogen, and the brown mixture evaporated under reduced pressure, and treated with water (20 c.c.). The solution extracted with ether (4 × 20 c.c.) containing sulphur dioxide, dried, and evaporated under nitrogen yielded a red-brown gum (0·08 g.) which was treated with acetic anhydride (1 c.c.) and pyridine (2 c.c.) at 100° for 1 hr. The reagents were then removed *in vacuo*, water (10 c.c.) was added, and the mixture was extracted with ether (4 × 5 c.c.). Evaporation of the dried extract left a brown gum (0·13 g.) which sublimed at 120—150° (bath)/0·2 mm. The cream solid (0·026 g.) thus obtained crystallised from methanol as needles, m. p. 161—163°, alone or mixed with pyrogallol triacetate [Found: C, 57·5; H, 5·1; OAc, 50·8%; *M*, 225 (Rast). Calc. for $C_{12}H_{12}O_6$: C, 57·1; H, 4·8; 3OAc, 51·2%; *M*, 252].

(*B*) *Of dihydroeusiderin.* The dihydro-derivative (0·2 g.) was refluxed for 1 hr. with acetic acid (1·5 c.c.) and hydriodic acid (68%; 1·5 c.c.) containing red phosphorus (0·2 g.), and the mixture evaporated at 100° *in vacuo*. The residue was dissolved in water (6 c.c.), and the gum isolated from it with ether (8 × 5 c.c.) was heated at 100° for 2 hr. with acetic anhydride (1 c.c.) and pyridine (1 c.c.). The product, isolated as in the previous experiment, was sublimed at 0·1 mm. to yield fractions, (i) (0·08 g.), b. p. 120—140°, (ii) (0·06 g.), b. p. 140—180°; (iii) (0·02 g.), b. p. 180—200°, and (iv) (0·01 g.), b. p. 200—240° (temp. are bath). Fraction (i) was redistilled at 120—140° (bath)/0·1 mm., to yield an oil (0·04 g.) which slowly crystallised. The *acetate* separated from methanol as prisms, m. p. 49—51° undepressed by 1,2,3-triacetoxy-5-n-propylbenzene (Found: C, 61·1; H, 5·7; OAc, 46·1. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·2; 3OAc, 43·9%). Fraction (ii) redistilled as an uncrystallisable gum (Found: C, 61·9; H, 6·1; OAc, 39·5%). No homogeneous products were isolated from fractions (iii) and (iv).

With boiling aqueous hydrobromic acid (48%; 3 c.c.) and acetic acid (3 c.c.) for 3 hr., and

working up in the manner of (*A*), dihydroeusiderin (0·2 g.) gave an uncrystallisable brown oil (0·14 g.), which after 15 hours' refluxing in acetone (10 c.c.) with dimethyl sulphate (0·3 g.) and potassium carbonate (0·5 g.) gave a non-phenolic oil (0·11 g.). Chromatography of this on alumina (20 g.) failed to give any crystalline fraction.

(*C*) *Of eusideric acid.* The acid (0·18 g.), hydriodic acid (1 c.c.), acetic acid (1·5 c.c.), and red phosphorus (0·2 g.) were heated for 30 min., and the product isolated by evaporation was treated with aqueous sodium carbonate (5%; 10 c.c.) and extracted with ether (4 × 10 c.c.) (extract A). The acidified aqueous phase was further extracted with ether (8 × 10 c.c.), giving extract (B).

Acetylation (as above) of the contents (0·06 g.) of extract (A) gave no material volatile at 200°/0·1 mm. (bath). Extract (B) contained a brown gum (0·05 g.) which gave a green colour followed by a black precipitate with alcoholic ferric chloride. It yielded no characterisable acetylation products.

Sodium–Liquid Ammonia Cleavage.—(*A*) *Of deallyleusiderin.* A solution in benzene (5 c.c.) of deallyleusiderin (0·31 g.) was poured into liquid ammonia (30 c.c.), then sodium (0·46 g.), was added in small portions with stirring during 1 hr., and the solution left for 12 hr. Water (5 c.c.) was then introduced and the ammonia allowed to evaporate; after which more water (30 c.c.) was added and the solution washed with ether (2 × 50 c.c.). Extraction with ether (6 × 25 c.c.) and ethyl acetate (4 × 25 c.c.) of the acidified, blue aqueous solution yielded on evaporation a brown gum which was treated with acetic anhydride (1 c.c.) and pyridine (1 c.c.). Sublimation of the product gave a light-red oil (0·03 g.), b. p. 120—160° (bath)/0·05 mm., which crystallised in prisms from benzene–light petroleum (b. p. 40—60°) to yield a solid (0·016 g.), m. p. after resublimation 91°, undepressed by 2,3-diacetoxyanisole. The identity of the two specimens was also apparent from the infrared spectra.

The reduction of deallyleusiderin (0·32 g.) with sodium (1·1 g.) added to its alcoholic solution (15 c.c.) gave an oil (0·22 g.) (mainly alkali-insoluble) which gave an amorphous precipitate with Brady's reagent.

(*B*) *Of dihydroeusiderin.* Dihydroeusiderin (0·47 g.) in ether (10 c.c.) was added to liquid ammonia (60 c.c.) containing sodium (0·26 g.), and the mixture left with occasional stirring for 7 hr. Isolation as above yielded a phenolic oil (0·11 g.) which gave a green colour with alcoholic ferric chloride, but neither the oil nor its acetylation product could be crystallised. The non-phenolic portion (0·21 g.) was a pale yellow gum containing dihydroeusiderin (0·1 g.) and gave an amorphous 2,4-dinitrophenylhydrazone.

1,2,3-*Triacetoxy*-4-*propylbenzene.*—2,3,4-Trihydroxypropiophenone (4·8 g.), prepared as by Campbell and Copenger, was refluxed with zinc amalgam (5%; 20 g.) and hydrochloric acid (6N; 30 c.c.) for 6 hr., additional hydrochloric acid (concentrated; 1 c.c.) being added hourly. The solid remaining was 1,2,3-trihydroxy-4-propylbenzene (95%; 4·2 g.), needles (from benzene), m. p. 110° (lit., m. p. 110—111°). With acetic anhydride and pyridine it gave 1,2,3-*triacetoxy*-4-*propylbenzene* (1·4 g.), prisms (from methanol), m. p. 109° (Found: C, 61·2; H, 6·1; OAc, 47·8. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·2; 3OAc, 43·9%).

1,2,3-*Triacetoxy*-5-*propylbenzene.*—A solution of 3,4,5-trimethoxypropiophenone (2 g.) in ethanol (10 c.c.) was refluxed for 8 hr. with amalgamated zinc (5%; 5 g.) and hydrochloric acid (concentrated; 10 c.c.), with further amounts of acid (2 c.c.) added every 2 hr. The product, b. p. 130—160° (bath)/12 mm., was heated for 30 min. with boiling hydriodic acid (5 c.c.). The mixture was concentrated under reduced pressure, diluted with water (15 c.c.), and extracted with ether (4 × 10 c.c.) containing sulphur dioxide. The phenolic product thus isolated was acetylated as above, and the acetate twice distilled giving an oil, b. p. 140—150° (bath)/0·1 mm., which slowly solidified. Crystallisation from methanol gave 1,2,3-*triacetoxy*-5-*propylbenzene* as prismatic needles, m. p. and mixed m. p. 51—52°.

2,3-*Diacetoxyanisole.*—*o*-Vanillin (15·2 g.) was converted by the Dakin reaction into 2,3-dihydroxyanisole (10·7 g., b. p. 127—129°/14 mm.), and acetylation (1 g.) with acetic anhydride (5 c.c.) and pyridine (5 c.c.) yielded the diacetate. After recrystallisation from methanol and vacuum sublimation, it formed rectangular prisms, m. p. 91° (lit., m. p. 91°) (Found: C, 59·2; H, 5·3; OMe, 14·6; OAc, 41·7. Calc. for $C_{11}H_{12}O_5$: C, 58·9; H, 5·4; 1OMe, 13·8; 2OAc, 38·4%).

Eusiderohydrazide.—Methyl eusiderate (0·2 g.) was refluxed for 12 hr. with hydrazine hydrate (90%; 2 c.c.) and ethanol (5 c.c.). The *hydrazide* separated on cooling and crystallised from ethanol as long silky needles (0·18 g.), m. p. 212° (Found: C, 59·5; H, 6·3; N, 6·7; OMe, 30·9. $C_{20}H_{24}O_7N_2$ requires C, 59·5; H, 6·0; N, 6·9; 4OMe, 30·7%).

A solution of the hydrazide (0·15 g.) in hydrochloric acid (12%; 8 c.c.) treated at −5° with sodium nitrite (0·07 g.) in water (0·4 c.c.) and then raised to 10°, gave a white solid which was heated in slowly distilling ethanol (10 c.c.) and benzene (5 c.c.) for 4 hr., ethanol (8 c.c.) being added to maintain a constant volume. The non-crystalline residue obtained by evaporation was refluxed for 18 hr. with hydrochloric acid (3 c.c.) and acetic acid (2 c.c.), the solution evaporated under reduced pressure, and the residue shaken with aqueous ammonia (5%; 5 c.c.) and ether. Trituration with methanol gave purple-tinged prisms (0·05 g.), m. p. 183—186° (Found: C, 59·0; H, 6·6; N, 3·1; OMe, 25·4. $C_{22}H_{27}O_8N$ requires C, 60·9; H, 6·2; N, 3·2; 4OMe, 28·6%). Eusideroyl chloride did not react with freshly activated sodium azide in boiling dry benzene.

A solution of eusideric acid (0·2 g.) in sulphuric acid (concentrated; 0·4 c.c.) was treated at 30° with hydrazoic acid (0·05 g.) in chloroform (1 c.c.), but addition of the red solution to aqueous sodium carbonate (10%; 10 c.c.) and crushed ice gave an intractable red oil.

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