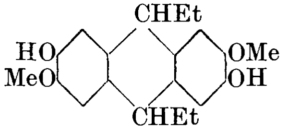
CLXXXII.—*The Structure of Di*iso*eugenol.*

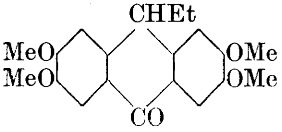
By ROBERT DOWNS HAWORTH and CECIL ROBERT MAVIN.

DI*iso*EUGENOL has been prepared by Puxeddu (*Gazzetta*, 1909, **39**, i, 136) by the action of hydrogen chloride on an alcoholic or ethereal solution of *iso*eugenol. On methylation, dimethyl*iso*eugenol, m. p. 106°, was obtained, and this could also be prepared by the action of alcoholic or ethereal hydrogen chloride on methyl*iso*eugenol (Szeki, *Ber.*, 1906, **39**, 2422; Francesconi and Puxeddu, *Gazzetta*, 1909, **39**, i, 208). According to the latter authors dimethyl*iso*eugenol is oxidised by cold potassium permanganate and gives a monobromo-substitution derivative; hence it may be considered as an unsaturated substance of unsymmetrical structure. Later work on analogous compounds (Mayer, *Atti R. Accad. Lincei*, 1914, **23**, 358; Puxeddu, *Gazzetta*, 1916, **46**, ii, 169, 177) showed these compounds to be saturated and a *cyclo*butane formula was suggested.

Our experiments confirm the view that dimethyl*iso*eugenol is saturated. It is not oxidised by potassium permanganate in acetone solution and it has been shown that di*iso*eugenol is 2 : 6-*dihydroxy*-3 : 7-*dimethoxy*-9 : 10-*diethyl*-9 : 10-*dihydroanthracene* (I). When dimethyl*iso*eugenol was oxidised with chromic acid in acetic acid solution, two products were obtained. One of these is probably 2 : 3 : 6 : 7-*tetramethoxy*-9-*ethylanthranol* (II). The other has been proved to be 2 : 3 : 6 : 7-*tetramethoxyanthraquinone* (III) by an independent synthesis from *m*-hemipinic anhydride and veratrole; these reacted in the presence of aluminium chloride to give 4 : 5 : 3′ : 4′-*tetramethoxy*-2-*benzoylbenzoic acid* (IV), which was converted into (III) by the action of 80% sulphuric acid. The formula (I, with OMe for both OH groups) suggested for dimethyl*iso*eugenol will accommodate a second stereoisomeric form of this substance, and Ciamician and Silber (*Ber.*, 1906, **39**, 1390) have isolated a dimethyl*iso*eugenol, m. p. 96°, by the action of iodine on methyl-*iso*eugenol in the presence of light.

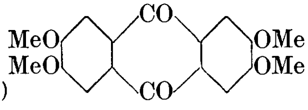
(I.)

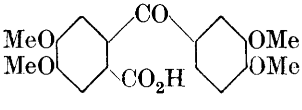




(II.)

(III.)





(IV.)

It would appear that this facile formation of anthracene derivatives is dependent on the presence of reactive hydrogen atoms in the nucleus of the propenylbenzene derivative. Anethole under similar conditions does not yield an anthracene derivative (Goodall and Haworth, J., 1930, 2483), but *iso*safrole polymerises to a crystalline dimeric form, for which a dihydroanthracene structure has already been suggested (Robinson, J., 1915, **107**, 267).

EXPERIMENTAL.

*Di*iso*eugenol* (I).—*iso*Eugenol (50 g.) and $5N$-methyl-alcoholic hydrogen chloride were heated under reflux for 4·5 hours. Most of the alcohol was removed, the dark coloured fluorescent residue diluted with water, and the solid collected and crystallised from methyl alcohol, colourless needles (35 g.), m. p. 179—180°, being obtained (Found: C, 73·1; H, 7·4; *M*, 325. Calc. for $C_{20}H_{24}O_4$: C, 73·2; H, 7·3%; *M*, 328). The mother-liquor yielded a further small quantity of di*iso*eugenol and a viscous dark-coloured oil (12 g.).

*Dimethyl*isoeugenol (I, with OMe for both OH groups).—(*a*) Di*iso*eugenol (10 g.) was methylated with methyl sulphate and potassium hydroxide in methyl-alcoholic solution in the usual manner. The product was extracted with ether and dried with potassium carbonate, and the ether allowed to evaporate; colourless needles (9 g.), m. p. 104—106°, raised to 105—106° by crystallisation from aqueous acetic acid, were obtained. (*b*) Methyl*iso*eugenol (10 g.), refluxed with 5*N*-methyl-alcoholic hydrogen chloride (200 c.c.), yielded a product identical with that obtained by method (*a*) (Found: C, 74·2; H, 7·9. Calc. for $C_{22}H_{28}O_4$: C, 74·2; H, 7·8%). Dimethyl*iso*eugenol was recovered unchanged after being boiled with potassium permanganate in acetone solution for 6 hours.

2 : 3 : 6 : 7-*Tetramethoxy*-9-*ethylanthranol* (II).—A solution of chromic acid (17 g.) in glacial acetic acid (60 c.c.) was added during 2·5 hours to a boiling solution of dimethyl*iso*eugenol (10 g.) in glacial acetic acid (150 c.c.). The product was poured into water (1000 c.c.), and the brown solid (6·7 g.) collected, washed with water and crystallised twice from alcohol, slender red prisms, m. p. 193°, being obtained (Found: C, 70·0; H, 6·5. $C_{20}H_{22}O_5$ requires C, 70·2; H, 6·4%).

2 : 3 : 6 : 7-*Tetramethoxyanthraquinone* (III).—(*a*) Dimethyl*iso*eugenol (5 g.) was oxidised by chromic acid (40 g.) as described. The solid (2 g.) was collected and dried. (*b*) 4 : 5 : 3′ : 4′-Tetramethoxy-2-benzoylbenzoic acid (IV) (0·7 g.) and sulphuric acid (7 c.c. of 80%) were heated in a water-bath. A deep red solution was obtained, from which crystals rapidly separated. After 10 minutes, water was added, and the solid collected and dried (0·6 g.).

2 : 3 : 6 : 7-*Tetramethoxyanthraquinone* (III) is sparingly soluble in the usual organic solvents, and it was purified either by sublimation or by crystallisation from boiling nitrobenzene, long yellow needles being obtained. The products obtained by methods (*a*) and (*b*), alone or mixed, melted at 344° (Found: C, 65·8; H, 4·8. $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%).

4 : 5 : 3′ : 4′-*Tetramethoxy*-2-*benzoylbenzoic Acid* (IV).—*m*-Hemipinic anhydride (6 g.), veratrole (5 g.), aluminium chloride (2 g.), and carbon disulphide (50 c.c.) were heated under reflux for 36 hours. After steam distillation the residue was extracted with ether, the ether removed, and the residual solid dissolved in sodium bicarbonate

solution, treated with charcoal, and filtered. The filtrate, acidified with hydrochloric acid, precipitated a solid which crystallised from methyl alcohol in colourless stout prisms (1·5 g.), m. p. 222—223° (Found : C, 62·2 ; H, 5·3. $C_{18}H_{18}O_7$ requires C, 62·4 ; H, 5·2%).

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