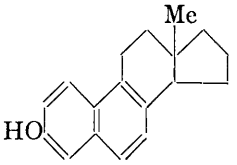
137. *The Synthesis of Compounds Related to the Sterols, Bile Acids, and Œstrus-producing Hormones. Part III. 7-Methoxy-1 : 2-cyclopentenophenanthrene, a Dehydrogenation Product of Œstrin and Equilenin.*

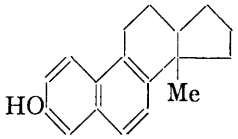
By A. COHEN, J. W. COOK, C. L. HEWETT, and (in part) A. GIRARD.

THE selenium dehydrogenation of methoxyœstratriene * to a compound giving analytical data in agreement with a methoxy*cyclo*pentenophenanthrene has already been reported (Cook and Girard, *Nature*, 1934, **133**, 377), and it has now been found that the *methyl* ether of " desoxo "-equilenin is dehydrogenated to the same substance. Hence equilenin, which forms a considerable proportion of the œstrogenic substances present in mares' urine during the later stages of pregnancy (Sandulesco, Tchung, and Girard, *Compt. rend.*, 1933, **196**, 137), contains the same ring system as œstrone, with the hydroxyl group in the same position. Moreover, 7-*methoxy*-1 : 2-cyclo*pentenophenanthrene* (VIII) has now been synthesised and found to be identical with this dehydrogenation product of the hormone derivatives. This, therefore, provides conclusive proof that the ring system of œstrin and equilenin is the same as that of the sterols and bile acids, and that the hydroxyl group is attached to the same position in this ring system as the hydroxyl group of cholesterol. It also follows that it is ring I of œstrone and œstriol which is aromatic, a conclusion reached by Danielli, Marrian, and Haslewood (*Biochem. J.*, 1933, **27**, 311) on the basis of surface-film measurements. The elegant conversion of œstriol into 1 : 2-dimethylphenanthrene by Butenandt, Weidlich, and Thompson (*Ber.*, 1933, **66**, 601) had already demonstrated the presence of the phenanthrene ring system in œstrone and œstriol, but did not rigidly define the position of attachment of the additional five-membered ring, a limitation which these authors recognised.

Analyses of the *methyl* ethers of both equilenin and its " desoxo "-derivative, and of the *picrate* of the latter substance, were all in good agreement with the formulation, $C_{18}H_{18}O_2$, assigned to equilenin by its discoverers (Girard, Sandulesco, Fridenson, and Rutgers, *Compt. rend.*, 1932, **195**, 981), and so the formation of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene from equilenin, as also from œstrone, involves the loss of a methyl group during selenium dehydrogenation. This points strongly to the attachment of this methyl group to a quaternary carbon atom, from which it follows that there are only two possible structures (I and II) for " desoxo "-equilenin, since equilenin is a saturated substance which forms a stable picrate (Girard *et al.*, *loc. cit.*).

(I.)



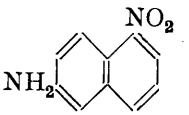


(II.)

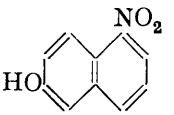
* For the nomenclature of œstrin derivatives, see Adam *et al.* (*Nature*, 1933, **132**, 205).

The methyl ether of a compound represented by structure (II) * was isolated in the penultimate stage of the synthesis of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene, and was found to be different from the methyl ether of " desoxo "-equilenin. However, this does not exclude structure (II) for the natural product, as there would be *cis*- and *trans*-isomerides (both resolvable) of (II).

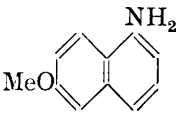
For the synthesis of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene by the type of method elaborated for the parent hydrocarbon (Cook and Hewett, J., 1933, 1098) it was necessary first to devise a method for the preparation of 1-bromo-6-methoxynaphthalene. 1-Naphthylamine-6-sulphonic acid (Cleve's acid) was readily converted by the Sandmeyer reaction into *1-bromonaphthalene-6-sulphonic acid*, in which the sulphonic acid group could not be replaced without displacement of bromine. The conversion of 6-hydroxy-1-naphthylamine (Sachs, *Ber.*, 1906, **39**, 3016) into *6-methoxy-1-naphthylamine* (V) by acetylation of the amino-group, methylation of the hydroxyl group, and finally hydrolytic removal of acetyl was readily accomplished on a small scale, but was unsuitable as a preparative method on account of the facility with which the aminonaphthol undergoes aerial oxidation. As the starting point in our eleven-stage synthesis of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene we ultimately used 5-nitro-2-naphthylamine (III), which Friedländer and Szymanski (*Ber.*, 1892, **25**, 2076) obtained, together with the 8-nitro-compound, by addition of β-naphthylamine nitrate to concentrated sulphuric acid below 0°. The 5-nitro-compound was converted into 5-nitro-2-naphthol (IV), which was methylated with methyl *p*-toluenesulphonate, and the product was reduced to 6-methoxy-1-naphthylamine (V).



(III.)



(IV.)

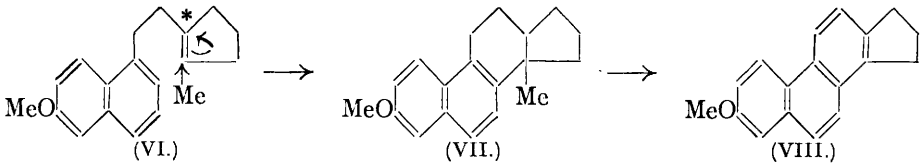


(V.)

By the Sandmeyer reaction, (V) was converted into *1-bromo-6-methoxynaphthalene*, but the yield was only 4%, and no better result was obtained by the Gattermann method. However, the equally useful *1-iodo-6-methoxynaphthalene* was obtained from (V) in yields of 45% and greater. The Grignard compound of this iodonerolin condensed with ethylene oxide to give β-*6-methoxy-1-naphthylethyl alcohol*, which was then converted into the *chloride*.

For two reasons we used 2-methyl*cyclo*pentanone and not *cyclo*pentanone for interaction with the Grignard solution prepared from this chloride. In the first place, we wished to prepare the compound (VII) for comparison with its isomeride obtained from equilenin (see above). Secondly, it was shown in previous communications (Cook and Hewett, J., 1933, 1108; this vol., p. 365) that the cyclisation of 1-(β-1′-naphthylethyl)-Δ^1-*cyclo*pentene gives, in addition to *cyclo*pentanotetrahydrophenanthrene, considerable amounts of isomeric spirans; for example, the pure picrate of 7 : 8-dihydrophenalyl*spirocyclo*pentane was isolated in 28% yield. We inferred from experiments recorded by Harper, Kon, and Ruzicka (this vol., p. 124) that spiran formation is lessened and perhaps completely avoided when a methyl group is attached to carbon atom 2 of the *cyclo*pentene ring, although these authors cited no evidence of the homogeneity of their cyclisation product. On theoretical grounds also, we anticipated that cyclisation of 1-(β-*6′-methoxy*-1′-*naphthylethyl*)-2-*methyl*-Δ^1-cyclo*pentene* (VI) would give less unwanted spirans than the analogous compound without the methyl group. Actually, we isolated 97% of the distilled cyclisation product of (VI) in the form of the homogeneous *picrate* of *7-methoxy-1-methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene* (VII).

* (*Added in proof.*) The free hydroxy-compound (II) has been obtained by demethylation of the synthetic methoxy-compound (VII) and was found to produce a strong œstrous response in castrated mice when injected in doses of 10 mg. These biological experiments were carried out by Mr. I. Hieger and are being continued in order to determine the minimum dose which suffices for œstrogenic activity.



(VI.) (VII.) (VIII.)

The absence of spiran formation in this reaction is clearly conditioned by the methyl group's electron-repelling influence, of which it is an interesting illustration. For, the + *I* effect of this methyl group will tend to set up an electromeric change in the sense shown in formula (VI), so that a proton from the naphthalene nucleus will be attracted to the position denoted by an asterisk, and hence cyclisation must proceed as shown. Spiran formation would require attachment of the anionoid carbon atom 2′ or 8′ of the naphthalene nucleus to position 1 of the *cyclo*pentene ring. The methoxy-group at 6′ (VI) would, of course, exert no appreciable influence on the reactivity of the meta-position 8′.

Selenium dehydrogenation of (VII) gave 7-methoxy-1 : 2-*cyclo*pentenophenanthrene (VIII) in 50% yield. That the quaternary methyl group has undergone elimination and not migration during this process, as also in the analogous dehydrogenations of the hormone derivatives, is clearly demonstrated by the consistent analytical figures given by the well-crystallised, constant-melting methoxy*cyclo*pentenophenanthrene and two derivatives (*picrate* and s-*trinitrobenzene complex*).

Dr. J. D. Bernal has very kindly made a crystallographic comparison, by optical and also *X*-ray methods, of our three samples of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene prepared by synthesis and by dehydrogenation of the two hormones. He reports that they are crystallographically identical.

Experimental.

(Micro analyses by Dr. A. Schoeller are marked with an asterisk; all m. p.'s are corrected.)

Derivatives of Equilenin (with A. Girard).

The equilenin used in these experiments was isolated from the urine of pregnant mares, and was separated from œstrone by making use of the fact that, unlike œstrone, equilenin forms a stable picrate.

Methyl Ether of Equilenin.—A mixture of equilenin (1 g.), 10% aqueous potassium hydroxide (4 c.c.), and methyl *p*-toluenesulphonate (1·3 g.) was heated on the steam-bath for 2½ hours, more 10% potassium hydroxide solution (5 c.c.) being added after 1½ hours. The crude *methyl* ether was moderately pure; a sample (50 mg.) was twice recrystallised from alcohol (charcoal), forming colourless slender needles, m. p. 195·5—197·5° (to a pink liquid) in a pre-heated bath (*Found : C, 81·3; H, 7·2. $C_{19}H_{20}O_2$ requires C, 81·4; H, 7·2%).

Kishner–Wolff Reduction.—The remainder of the crude methoxy-compound was dissolved in boiling alcohol (100 c.c.), and the solution treated with semicarbazide hydrochloride (1 g.) and sodium acetate (1 g.) dissolved in water (15 c.c.). The whole was set aside at room temperature for 24 hours; the amorphous semicarbazone was then collected and washed; it had m. p. 273—275° (uncorr.; decomp.) and was very sparingly soluble in the usual media. The semicarbazone was suspended in sodium ethoxide solution (from 1 g. of sodium and 20 c.c. of alcohol) and heated at 180° for 20 hours. The reduction was accompanied by complete demethylation, the product being an uncrystallisable gum, soluble in dilute alkali. This was re-methylated by the procedure already described, and the solid methyl ether was recrystallised from alcohol (yield, 0·55 g.). This *methyl* ether (I or II) crystallised from methyl alcohol in long colourless needles, m. p. 121—122° (*Found : C, 85·5; H, 8·2. $C_{19}H_{22}O$ requires C, 85·6; H, 8·3%). The *picrate* crystallised from alcohol in well-formed, bright red needles, m. p. 128—129° (*Found : C, 60·8; H, 5·1. $C_{19}H_{22}O,C_6H_3O_7N_3$ requires C, 60·6; H, 5·1%).

Dehydrogenation.—The methyl ether (I or II) (0·35 g.) was heated with selenium (0·5 g.) at 300—320° for 8 hours (examination of the product suggested that the period of heating had been too short). After extraction with ether and removal of the solvent, the material was distilled over sodium at 0·2 mm. (bath temperature slowly raised to 180°). The higher fractions of the distillate crystallised immediately; the whole was dissolved in hot alcohol, and the solution allowed to crystallise. The resulting methoxy*cyclo*pentenophenanthrene (70 mg.), recrystallised

from alcohol, formed colourless leaflets, m. p. 134·5—135·5° (*Found: C, 86·8; H, 6·4. Calc.: C, 87·05; H, 6·5%). This substance, its picrate (m. p. 137—137·5°), and its *s*-trinitrobenzene complex (m. p. 161—162°) did not depress the m. p.'s of the corresponding compounds prepared from œstrone (Cook and Girard, *loc. cit.*).

Sodium 1-*Bromonaphthalene*-6-*sulphonate.*

A solution of sodium 1-naphthylamine-6-sulphonate (24·5 g.) in water (150 c.c.) and hydrobromic acid (*d* 1·4; 40 c.c.) was diazotised at 0° with a solution of sodium nitrite (7·25 g. in 50 c.c.). The diazo-solution was gradually added to cuprous bromide (14·4 g.) in hydrobromic acid (*d* 1·4; 100 c.c.), the temperature being maintained at 75—80°. After ½ hour the solution was cooled to 0°, and the crystalline product collected, dried (11 g.), and recrystallised twice from dilute sodium hydroxide solution, and finally from water. *Sodium* 1-*bromonaphthalene*-6-*sulphonate* formed colourless leaflets containing 1 mol. of water of crystallisation which was lost at 100° (Found: Br, 25·65. $C_{10}H_6O_3BrSNa$ requires Br, 25·9%).

Synthesis of 7-*Methoxy*-1 : 2-cyclo*pentenophenanthrene.*

5-*Nitro*-2-*naphthylamine* (III).—β-Naphthylamine (900 g.) was added to a boiling solution of urea (15 g.) in water (6 l.) and concentrated nitric acid (450 c.c.). The nitrate (1230 g.) was dried, powdered, and added gradually to well-stirred concentrated sulphuric acid (8 l.), the temperature being maintained at — 5°. The resulting solution was poured into water (60 l.), the whole was boiled and filtered, and the sulphates which crystallised were treated with excess of boiling dilute aqueous ammonia. The bases were recrystallised from alcohol and then from benzene, yielding 185 g. of pure 5-nitro-2-naphthylamine, m. p. 144·5°.

5-*Nitro*-2-*naphthol* (IV).—A mixture of concentrated sulphuric acid (130 c.c.) and water (130 c.c.) was added to a fine suspension of 5-nitro-2-naphthylamine (65 g.) in glacial acetic acid (260 c.c.), and the product diazotised at 10° with sodium nitrite (26 g. in 100 c.c. of water) (compare Veselý and Dvořák, *Bull. Soc. chim.*, 1923, **33**, 324). Urea (3·5 g.) was then added, and the clear solution slowly run into boiling 5% sulphuric acid (8 l.). The whole was filtered while still boiling, and the dark coloured residue repeatedly extracted with boiling acidified water until extraction of the nitronaphthol was complete (about 8 l. in all). 5-Nitro-2-naphthol (49 g.) crystallised in orange needles, m. p. 147—149° (lit., 147°).

1-*Nitro*-6-*methoxynaphthalene.*—A mixture of the aforesaid nitronaphthol (121 g.), 10% aqueous potassium hydroxide (420 c.c.), and methyl *p*-toluenesulphonate (147 g.) was heated on the steam-bath for 3 hours, more potassium hydroxide (140 c.c.) being added after 1½ hours. After cooling, the product was collected and recrystallised from methyl alcohol, giving 115 g. of 1-*nitro*-6-*methoxynaphthalene*. A sample crystallised from *cyclo*hexane in pale yellow, microscopic plates, m. p. 74·5—75·5° (Found: C, 65·3; H, 4·5. $C_{11}H_9O_3N$ requires C, 65·0; H, 4·5%).

6-*Methoxy*-1-*naphthylamine* (V).—Reduction of the nitronerolin (110 g.) was effected by West's method (J., 1925, **127**, 494) and gave 75 g. of 6-*methoxy*-1-*naphthylamine*, b. p. 190°/13—14 mm. A sample of the distilled amine crystallised from light petroleum in colourless needles, m. p. 73—74° (Found: C, 76·2; H, 6·4. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·4%). The acetyl derivative had m. p. 142·5—143·5° alone or mixed with a sample prepared as described by Sachs (*loc. cit.*), and the *benzoyl* derivative crystallised from alcohol in pinkish needles, m. p. 184—185° (Found: N, 5·2. $C_{18}H_{15}O_2N$ requires N, 5·05%).

Hydrolysis of the acetamidonerolin (0·5 g.) prepared from Schäffer's acid by the method of Sachs was effected by heating on the steam-bath for an hour with sulphuric acid (1 c.c.) in alcohol (10 c.c.). The same methoxynaphthylamine was obtained, identification being completed by conversion into the benzoyl derivative just described.

1-*Bromo*-6-*methoxynaphthalene.*—A diazo-solution prepared from the aminonerolin (V) was added to a solution of cuprous bromide in 48% hydrobromic acid at 70—80°, and the product isolated and distilled at 0·05 mm. (bath at 110°). The liquid distillate (yield, 4%) gave the *picrate* of 1-bromo-6-methoxynaphthalene, which crystallised from alcohol in orange needles, m. p. 105—106° (Found: Br, 16·8. $C_{11}H_9OBr,C_6H_3O_7N_3$ requires Br, 17·1%).

1-*Iodo*-6-*methoxynaphthalene.*—A solution of 6-methoxy-1-naphthylamine sulphate (62 g.) in hot 2*N*-sulphuric acid (425 c.c.) was cooled to 0°, and the suspension diazotised with sodium nitrite (20 g. in 100 c.c. of water). Excess of nitrous acid was destroyed with urea, and the solution was gradually added to a solution of potassium iodide (85 g.) in 2*N*-sulphuric acid (380 c.c.). After being kept at room temperature for an hour, the whole was heated on the steam-bath for 15 minutes (more prolonged heating is undesirable), cooled, and extracted with

ether. The ethereal extract was washed, first with sodium bisulphite solution, then with dilute alkali, and finally water, and was dried and the ether removed. The residue distilled at 135—140°/0·2 mm. and gave a brownish-yellow oil (35·5 g.) which eventually crystallised. After recrystallisation from light petroleum, 1-*iodo*-6-*methoxynaphthalene* formed an almost colourless, crystalline powder, m. p. 33—33·5° (Found : I, 44·4. $C_{11}H_9OI$ requires I, 44·7%). Its *picrate* formed orange needles, m. p. 98—99° (Found : I, 24·65. $C_{11}H_9OI,C_6H_3O_7N_3$ requires I, 24·7%).

β-6-*Methoxy*-1-*naphthylethyl Alcohol*.—A Grignard solution prepared from 1-iodo-6-methoxynaphthalene (34 g.) and magnesium turnings (3·2 g.), activated with methylmagnesium iodide, in anhydrous ether (135 c.c.) was treated with ethylene oxide (7·5 g.) exactly as for the preparation of β-1-naphthylethyl alcohol (J., 1933, 1107). The resulting methoxynaphthylethyl alcohol formed a viscous yellowish liquid (12·5 g.), b. p. 160—165°/0·3 mm. The 3 : 5-*dinitrobenzoate*, obtained by brief heating at 100° with 3 : 5-dinitrobenzoyl chloride in pyridine, crystallised from benzene in yellow needles, m. p. 177·5—178°, which lost their lustre when dried at 90° (*Found : C, 60·6; H, 4·1. $C_{20}H_{16}O_7N_2$ requires C, 60·6; H, 4·1%). β-6-*Methoxy*-1-*naphthylethyl alcohol*, obtained by hydrolysis of the pure ester and distilled at 0·2 mm., from an air-bath heated at 120—130°, formed an almost colourless, viscous gum (Found : C, 77·0; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). After some weeks this crystallised (m. p. 35—36°).

β-6-*Methoxy*-1-*naphthylethyl Chloride*.—An ice-cold solution of the aforesaid carbinol (14 g.) in dimethylaniline (9 c.c.) was treated in the usual way with thionyl chloride (5·2 c.c.), and the chloride distilled at 0·2 mm. (oil-bath at 160—165°). There were obtained 12·4 g. of a pale yellow, somewhat viscous liquid, the *picrate* of which separated from alcohol as an orange powder, m. p. 74—76° (Found : Cl, 7·8. $C_{13}H_{13}OCl,C_6H_3O_7N_3$ requires Cl, 7·9%).

1-(β-6′-*Methoxy*-1′-*naphthylethyl*)-2-*methyl*-Δ^1-cyclo*pentene* (VI).—The 2-methyl*cyclo*pentanone required for this was obtained in good yield by the method of Cornubert and Borrel (*Bull. Soc. chim.*, 1930, **47**, 301), no modification being necessary (contrast Kon, J., 1933, 1085).

To an ice-cold Grignard solution prepared from methoxynaphthylethyl chloride (12 g.), magnesium turnings (1·4 g.), and anhydrous ether (40 c.c.) was slowly added 2-methyl*cyclo*pentanone (6 g.). The whole was kept at room temperature for an hour, and was finally warmed for ½ hour. The product was decomposed with ice and ammonium chloride, and was then washed and fractionated. The carbinol fraction, b. p. 185—190°/0·15 mm., formed a very viscous, yellowish liquid (6 g.), which was dehydrated by heating for an hour at 160—165° with potassium hydrogen sulphate (9 g.). The *cyclo*pentene derivative (VI) formed a somewhat viscous, pale yellow liquid (5·15 g.), b. p. about 157°/0·15 mm. Its *picrate* crystallised from alcohol in pale orange, microscopic needles, m. p. 90—91° (not clear below 96°) (*Found : C, 60·15; H, 5·0. $C_{19}H_{22}O,C_6H_3O_7N_3$ requires C, 60·6; H, 5·1%).

The residue from the distillation of the above carbinol was dissolved in hot benzene. On standing, the cold solution deposited αδ-*di*-(6-*methoxy*-1-*naphthyl*)*butane*, colourless microscopic needles, m. p. 150—150·5° (*Found : C, 84·3; H, 7·0; *M*, Rast method, 334, 340. $C_{26}H_{26}O_2$ requires C, 84·3; H, 7·1%; *M*, 370).

7-*Methoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene* (VII).—Finely powdered anhydrous aluminium chloride (6 g.) was gradually added to an ice-cold solution of the *cyclo*pentene derivative (VI) (4·8 g.) in carbon disulphide (50 c.c.). After being kept in ice for 7 hours with occasional shaking, the clear solution was decanted from the aluminium chloride sludge (the latter was not examined, as in analogous cases this fraction gave only polymeric substances) and was shaken with dilute hydrochloric acid and then with water. After removal of the solvent the product was distilled at 0·2 mm. (bath temperature, 195—200°), and the viscous distillate (3·35 g.) was treated with picric acid (4 g.) in alcohol. The resulting *picrate* (5·62 g.) of 7-*methoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene* formed bright red needles, m. p. 89·5—90° (*Found : C, 60·7; H, 5·0. $C_{19}H_{22}O,C_6H_3O_7N_3$ requires C, 60·6; H, 5·1%). The material recovered from the alcoholic liquors after removal of picric acid was treated with *s*-trinitrobenzene, and gave 0·45 g. of the complex described below.

The *methoxy*-compound (VII), regenerated from the pure picrate, formed a thick yellowish gum which refused to crystallise (Found : C, 85·7; H, 8·1. $C_{19}H_{22}O$ requires C, 85·6; H, 8·3%); it gave a s-*trinitrobenzene complex* which separated from methyl alcohol in long scarlet needles, m. p. 110—110·5° (*Found : C, 62·7; H, 5·2; N, 8·5. $C_{19}H_{22}O,C_6H_3O_6N_3$ requires C, 62·6; H, 5·3; N, 8·8%).

7-*Methoxy*-1 : 2-cyclo*pentenophenanthrene* (VIII).—The tetracyclic methoxy-compound (VII) (1 g.) was heated with selenium (1·5 g.) at 300—320° for 21½ hours. The product, which crystallised on cooling, was extracted with ether, the ether removed from the filtered solution, and the

residue recrystallised from alcohol. The resulting greyish solid (0·43 g.) was heated with sodium (40 mg.) at 170° for a few minutes, and then sublimed at 140—150°/0·05 mm. The white sublimate (0·36 g.) was twice recrystallised from alcohol and then formed colourless leaflets, m. p. 136—137° (*Found: C, 87·3; H, 6·3; OMe, 12·3. $C_{18}H_{16}O$ requires C, 87·05; H, 6·5; OMe, 12·5%). This synthetic 7-*methoxy*-1 : 2-cyclo*pentenophenanthrene* (VIII), like the specimens obtained from œstrone and equilenin, gave a magenta solution in concentrated sulphuric acid, which rapidly faded to orange-yellow. After an hour or so the colour became green and a dark red fluorescence developed. A further 0·1 g. of this methoxy-compound was isolated by vacuum distillation of the residue from the alcoholic liquors from which the original crude material had separated.

The *picrate* of (VIII) crystallised from alcohol in light red needles, m. p. 136·5—137·5° (*Found: C, 60·3; H, 4·0. $C_{18}H_{16}O,C_6H_3O_7N_3$ requires C, 60·4; H, 4·0%). This picrate was easily dissociated, for dilute solutions slowly deposited colourless crystals of the methoxy-compound, even in presence of excess of picric acid.

The s-*trinitrobenzene complex* of (VIII) formed golden-orange needles, m. p. 161—161·5° (*Found: C, 62·5; H, 4·1. $C_{18}H_{16}O,C_6H_3O_6N_3$ requires C, 62·4; H, 4·15%).

There were no depressions of m. p.'s when the three substances last described were mixed with the corresponding compounds prepared by dehydrogenation of methoxyœstratriene. The m. p. of 1 : 2-*cyclo*pentenophenanthrene (135°) was depressed 20—30° by the 7-methoxy-compound.

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