Studies in Terpenoids. Part XXXI.[1] Synthesis of Pyrocurzerenone, a Furosesquiterpenoid from *Curcuma zedoaria* †

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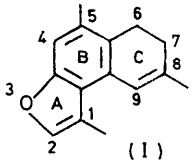
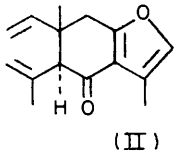
7-Acetonyloxy-5-methyl-α-tetralone (Vc) was cyclodehydrated to 7,8-dihydro-1,5-dimethylnaphtho[2,1-*b*]-furan-9(6*H*)-one (VIa), the structure of which was established by an independent synthesis from methyl 4-(4-acetonyloxy-2-methylphenyl)butyrate (IXd). Similarly, 7-acetonyloxy-2,5-dimethyl-α-tetralone (Vf), synthesized *via* 4-(5-isopropyl-4-methoxy-2-methylphenyl)-2-methylbutyric acid (XIIb) and 7-methoxy-2,5-dimethyl-α-tetralone (Vd), was cyclodehydrated to 7,8-dihydro-1,5,8-trimethylnaphtho[2,1-*b*]furan-9(6*H*)-one (VIb), which on reduction and dehydration furnished pyrocurzerenone (6,7-dihydro-1,5,8-trimethylnaphtho[2,1-*b*]furan) (I). The deisopropylation and cyclodehydration of (XIIb) to (Vd) were effected in one step by treatment with polyphosphoric acid.

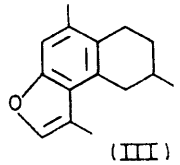
PYROCURZERENONE (6,7-dihydro-1,5,8-trimethylnaphtho[2,1-*b*]furan) (I), claimed to be the first furocadinane to be isolated [2] from a natural source, occurs in *Curcuma zedoaria* Roscoe. Its structure was deduced [2] mainly on the basis of its n.m.r. spectrum and an interesting pyrolytic transformation involving a double Cope rearrangement by which curzerenone (II) and its epimer, both natural products, gave pyrocurzerenone (I). This paper reports the synthesis of pyrocurzerenone (I) and its pyrolytic disproportionation products [(III) and (IV)] and fully supports the structural assignments made by Hikino *et al.*[2] A related furocadinane, brachyl oxide, which can be regarded as octahydropyrocurzerenone [(I) with reduced rings A and B] has recently been isolated.[3]



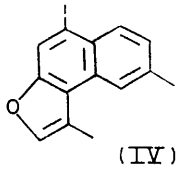
(I)



(II)



(III)



(IV)

We envisaged a synthesis of pyrocurzerenone (I) proceeding *via* 7-acetonyloxy-2,5-dimethyl-α-tetralone (Vf). Cyclodehydration of (Vf) to the naphthofuranone (VIb), reduction to the alcohol (VII), and finally dehydration would give pyrocurzerenone (I). In view of the ready availability of the related tetralone (Va),[4] we tested the projected route (Va) ⟶ (Vb) ⟶ (Vc) ⟶ (VIa) (see Experimental section). Although we expected [5a] the acetonyloxytetralone (Vc) to cyclodehydrate to give the naphthofuranone (VIa), a comparison of the aromatic proton signals [(Vc) 6-H at δ 7·07 and 8-H at 7·37; product ArH at δ 7·37) pointed to the possibility of the cyclodehydrated product possessing the isomeric structure (VIII) (which retains the lower field aromatic proton *peri* to the carbonyl). It thus became necessary to confirm the structure (VIa). The known arylbutyric acid (IXa) [6] was demethylated to (IXb). The acetonyl derivative (IXd) of the methyl ester (IXc) on cyclodehydration with concentrated sulphuric acid [5] gave the benzofuran ester (Xa). The ester and its corresponding acid (Xb) showed in their n.m.r. spectra two aromatic *para*-protons of the benzene ring. Alternative ring closure to (XI) would have been distinguished by the AB coupling of the *ortho* aromatic protons. The benzofuran acid (Xb) on cyclisation gave the naphthofuranone (VIa), identical with the material obtained by the cyclodehydration of the acetonyloxytetralone (Vc), thus ruling out the alternative mode of cyclization of (Vc) to (VIII).

Having successfully converted the acetonyloxytetralone (Vc) into the naphthofuranone (VIa), we now required (Vf) for cyclodehydration to (VIb). For this we used the arylbutyric acid [7] (XIIb) which was available in large quantity.[8] We noted that the lower homologue of (XIIb), *i.e.* (XIIa) on cyclization with polyphosphoric acid (PPA) gave the deisopropyltetralone (Va) in attractive yield (68%).[9] Similar treatment of (XIIb) furnished a mixture of the required deisopropyltetralone (Vd) [7a] together with the isopropyl-migrated tetralone (XIIIa) [9] in the ratio 2 : 1. Demethylation of this mixture by pyridine hydrochloride gave the corresponding mixture of hydroxytetralones (Ve) and (XIIIb) which could be readily separated by fractional crystallization. The required hydroxytetralone (Ve) on condensation [10] with bromoacetone [11]

† This work was presented at the Symposium in Organic Chemistry, University of Madras, Abstracts, January 1973, p. 3.

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[4] A. S. Dreiding and W. J. Pummer, *J. Amer. Chem. Soc.*, 1953, **75**, 3162.

[5] (*a*) R. Stoermer, *Annalen*, 1900, **312**, 237; (*b*) R. Stoermer and R. Wehln, *Ber.*, 1902, **35**, 3549.

[6] R. D. Desai and M. A. Wali, *Proc. Indian Acad. Sci.*, Series (A), 1937, **6**, 144 (*Chem. Abs.*, 1938, **23**, 509).

[7] (*a*) R. G. Lindahl, *Ann. Acad. Sci. Fennicae*, Series A II, 1953, **48**, 7 (*Chem. Abs.*, 1955, **49**, 8223); (*b*) P. B. Talukdar, *J. Org. Chem.*, 1956, **21**, 506.

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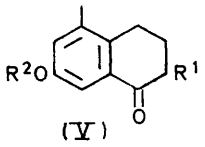
[9] K. Yamada, S. Takada, Y. Hayakawa, and Y. Hirata, *Bull. Chem. Soc. (Japan)*. 1969, **42**, 3011.

[10] H. N. Grant, V. Prelog, and R. P. A. Sneeden, *Helv. Chim. Acta*, 1963, **46**, 415.

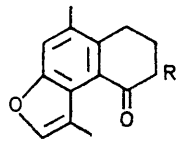
[11] P. A. Levene, *Org. Synth.*, Coll. Vol. II, 1950, p. 88.

gave the acetonyloxytetralone (Vf). Its cyclodehydration with sulphuric acid [5] as described for (Vc) and (IXd) gave the naphthofuranone (VIb). It was reduced by sodium borohydride to the naphthofuranol (VII), which on dehydration with toluene-*p*-sulphonic acid gave pyrocurzerenone (I), m.p. 77—78° (lit.,[2] 76·5—77·5°), i.r. spectrum identical with that of authentic material,[2] and u.v. and n.m.r. data in agreement with those published.[2] Hydrogenation of the synthetic pyrocurzerenone (I) gave dihydropyrocurzerenone (III), m.p. 72·5—73·5° (lit.,[2] 72—73°), and dehydrogenation with sulphur furnished the furocadalene (IV), m.p. 97—100° (lit.,[2] 98—100°). The i.r., n.m.r., and u.v. spectra of (III) and (IV) tallied in all respects with those of authentic material.



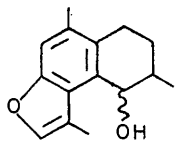
(V)

a; R^1 = H, R^2 = Me
b; R^1 = R^2 = H
c; R^1 = H, R^2 = CH_2COCH_3
d; R^1 = R^2 = Me
e; R^1 = Me, R^2 = H
f; R^1 = Me, R^2 = CH_2COCH_3

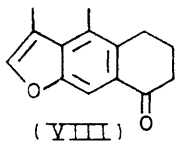


(VI)

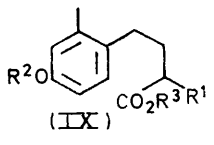
a; R = H
b; R = Me



(VII)

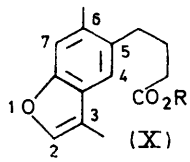


(VIII)



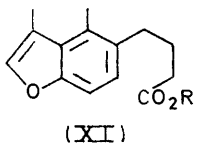
(IX)

a; R^1 = R^3 = H, R^2 = Me
b; R^1 = R^2 = R^3 = H
c; R^1 = R^2 = H, R^3 = Me
d; R^1 = H, R^2 = CH_2COCH_3, R^3 = Me



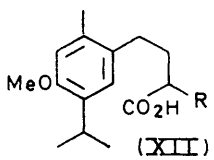
(X)

a; R = Me
b; R = H



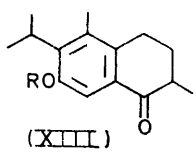
(XI)

R = H or Me



(XII)

a; R = H
b; R = Me



(XIII)

a; R = Me
b; R = H

EXPERIMENTAL

For general experimental directions, see Part XXX [1] in this series.

7-Hydroxy-5-methyl-α-tetralone (Vb).—7-Methoxy-5-methyl-α-tetralone [4] (Va) (3·2 g) was heated with pyridine hydrochloride (20 g) at 185—190° for 2 h. The mixture was poured into ice–water, when the *hydroxytetralone* (Vb) separated as a pale yellow precipitate, m.p. 164—166° (from benzene) (1·75 g); $\nu_{max.}$ (Nujol) 3225 (OH) and 1655 cm^{-1} (C=O) (Found: C, 74·9; H, 7·0. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%).

7-Acetonyloxy-5-methyl-α-tetralone (Vc).—A mixture of the hydroxytetralone (Vb) (1·7 g), bromoacetone [11] (1·5 g), powdered, anhydrous potassium carbonate (1·3 g), and dry acetone (30 ml) was refluxed with stirring for 16 h. Acetone was removed under reduced pressure and the residue was diluted with water and extracted with ether. The ethereal extract was washed with sodium hydroxide (10%; 5 × 40 ml). Removal of the solvent gave the *acetonyloxytetralone* (Vc) as a black viscous liquid, which solidified on cooling, m.p. 83—85° (from benzene–light petroleum) (1·4 g); $\nu_{max.}$ (Nujol) 1725 (saturated C=O) and 1669 cm^{-1} (tetralone C=O); δ ($CDCl_3$) 2·28 and 2·32 (each 3H, s, 5-Me and COMe), 2·0—3·0 (6H, $[CH_2]_3$), 4·62 (2H, s, OCH_2-CO), 7·07 (1H, d, *J* 2 Hz, 6-H), and 7·37 (1H, d, *J* 2 Hz, 8-H) (Found: C, 72·0; H, 7·1. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

1,5-Dimethyl-7,8-dihydronaphtho[2,1-b]*furan-9*(6H)*-one* (VIa).—To polyphosphoric acid [prepared from phosphorus pentoxide (15·6 g) and phosphoric acid (10·4 ml)] the acetonyloxytetralone (Vc) (0·5 g) was added at room temperature [10] with stirring. After 1 h the mixture was decomposed with crushed ice. By extraction with ether a green oil (0·55 g) was obtained which was chromatographed on a column of silica gel (40 g). Elution with hexane–benzene (1 : 1) gave an oil (0·18 g) which on sublimation (130—140° and 2 mmHg) solidified to give the *naphthofuranone* (VIa) (46 mg), m.p. 59—61° (from light petroleum); $\nu_{max.}$ (Nujol) 1685 cm^{-1} (C=O); δ (CCl_4) 2·37—2·40 (6H, d, *J* 1 Hz and s, 1-Me and 5-Me), 2·0—3·0 (6H, m, $[CH_2]_3$), and 7·37br (2H, s, $W_{\frac{1}{2}}$ 3 Hz, 2-H and 4-H) (Found: C, 78·8; H, 7·0. $C_{14}H_{14}O_2$ requires C, 78·5: H, 6·6%).

4-(4-Hydroxy-2-methylphenyl)butyric Acid (IXb).—The methoxy-acid [6] (IXa) (12 g) was heated with pyridine hydrochloride (30 g) at 185—190° for 6 h. The mixture was poured into ice–dilute hydrochloric acid (1 : 1) The usual work-up afforded the *hydroxy-acid* (IXb) (7 g); m.p. 111—113° (from benzene); $\nu_{max.}$ (Nujol) 3350 (OH of phenol), and 1725 and 1710 cm^{-1} (C=O) (Found: C, 68·2; H, 7·7. $C_{11}H_{14}O_3$ requires C, 68·2; H, 7·6%).

The foregoing hydroxy-acid was esterified with methanol and sulphuric acid to furnish the *methyl ester* (IXc), m.p. 62—63° (from benzene–light petroleum); $\nu_{max.}$ (Nujol) 3405 (OH) and 1720 cm^{-1} (ester C=O); δ ($CDCl_3$) 2·23 (3H,

s, Ar*Me*), 1·8—2·8 (6H, m, $[CH_2]_3$), 3·67 (3H, s, CO_2Me), 5·5 (1H, s, OH), 6·58 (1H, dd, *J* 1·5 and 6 Hz, aromatic 5-H), 6·63 (1H, s, aromatic 3-H), and 6·92 (1H, dd, *J* 1·5 and 6Hz, aromatic 6-H) (Found: C, 69·4; H, 7·8. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%).

Methyl 4-(4-*Acetonyloxy*-2-*methylphenyl*)*butyrate* (IXd).—A mixture of the foregoing phenolic ester (IXc) (6·2 g), anhydrous potassium carbonate (4·2 g), bromoacetone (5 g), and acetone (100 ml) was refluxed for 18 h. From the mixture the *acetonyloxy-ester* (IXd) (7 g) was obtained as a yellow, mobile liquid, using the work-up as described for (Vc). An analytical sample was prepared by chromatography (silica gel column) and sublimation (120° at 1 mmHg); $\nu_{max.}$ (film) 1740br cm^{-1} (ester and ketone C=O); δ ($CDCl_3$) 2·2 (3H, s, Ar*Me*), 3·63 (3H, s, CO_2Me), 4·43 (2H, s, OCH_2CO), 6·63 (2H, merged dd, *J* 8 Hz, aromatic 3-H and 5-H), and 7·05 (1H, dd, *J* 8 Hz, aromatic 6-H) (Found: C, 68·3; H, 7·8. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%).

4-(3,6-*Dimethylbenzofuran*-5-*yl*)*butyric Acid* (Xb) *and its Cyclization to* (VIa).—The preceding acetonyloxy-ester (IXd) (2 g) and concentrated sulphuric acid (28 ml) were stirred together at −10° for 15 min and then at room temperature for 1·5 min. The mixture was re-cooled to −10° and was then decomposed with crushed ice. The product was extracted with ether. After washing with aqueous sodium hydrogen carbonate, evaporation gave the benzofuran ester (Xa), which was sublimed (105° at 2 mmHg) after passing through a column of silica gel (light petroleum–benzene, 1 : 2); $\nu_{max.}$ (neat) 1740 cm^{-1} (ester C=O); δ(CCl_4) 2·17 (3H, d, *J* 1·5 Hz, 3-Me), 2·40 (3H, s, 6-Me), 3·6 (3H, s, CO_2Me), 7·10 (2H, s, 4-H and 7-H), and 7·17 (1H, d, *J* 1·5 Hz, 2-H). The ester (Xa) on saponification with alcoholic potassium hydroxide (6%; 25 ml; 1 h) afforded the *benzofuran acid* (Xb) which on sublimation (160—170° at 2 mmHg) solidified, m.p. 143—145° (from benzene) (0·3 g); $\nu_{max.}$ (Nujol) 1710 cm^{-1} (acid C=O); δ [$(CD_3)_2SO$] 2·20 (3H, d, *J* 1·5 Hz, 3-Me), 2·38 (3H, s, 6-Me), 7·38 (2H, s, 4-H and 7-H), and 7·69 (1H, d, *J* 1·5 Hz, 2-H) (Found: C, 72·3; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

The benzofuran acid (Xb) (0·2 g) in benzene (30 ml) was added dropwise to phosphorus pentachloride (0·25 g) in benzene (10 ml) with stirring. The mixture was heated at 45° for 15 min. To the cooled solution tin(IV) chloride (0·6 g) in benzene (25 ml) was added keeping the temperature below 5° and stirring continued for 1 h more. Ice–dilute hydrochloric acid (1 : 1) was added below 10° and the product worked up as usual. A solution of the resulting yellow solid was passed through a column of silica gel. Elution with light petroleum gave the *naphthofuranone* (VIa) as a white solid (0·09 g), m.p. 59—61° (from aqueous ethanol), identical (mixed m.p., i.r., and n.m.r.) with the compound obtained from (Vc) (see above).

7-*Methoxy*-2,5-*dimethyl*-α-*tetralone* (Vd).—To polyphosphoric acid [from phosphorus pentoxide (202 g) and phosphoric acid (120 ml)] 2-methyl-4-(5-isopropyl-4-methoxy-2-methylphenyl)butyric acid [7] (XIIb) (20 g) was added at 97° with stirring. After 0·5 h the product was worked up in the usual manner to give neutral material (b.p. 140—160° at 3 mmHg) (13·9 g). G.l.c. showed the presence of two compounds in the ratio 2 : 1. A solution of a portion (*ca.* 0·5 g) in light petroleum on refrigeration gave the major component, the *methoxytetralone* (Vd) as white needles, m.p. 51—52° (from aqueous methanol); $\nu_{max.}$ (Nujol) 1685 cm^{-1} (C=O); δ (CCl_4) 1·2 (3H, d, *J* 7 Hz, 2-Me), 2·23 (3H, s, 5-Me), 3·78 (3H, s, OMe), 6·80 (1H, d, *J* 3 Hz, 6-H), and 7·26 (1H, d, *J* 5 Hz, 8-H) (Found: C, 76·5; H, 7·8. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%).

The minor component was inferred to be the isopropyl-migrated methoxytetralone (XIIIa) from the following experiment.

7-*Hydroxy*-2,5-*dimethyl*-α-*tetralone* (Ve).—The preceding cyclodehydrated material (13·4 g) was heated with pyridine hydrochloride (37 g) at 200—210° for 9 h. The hot solution was poured into dilute hydrochloric acid, and the solid which separated was filtered off. T.l.c. showed two spots. Two crystallizations from benzene gave the *hydroxytetralone* (Ve) (4·7 g), m.p. 171—172°; $\nu_{max.}$ (Nujol) 3410 (OH and 1675 cm^{-1} (C=O). The specimen was identical (mixed m.p. and i.r.) with the product of demethylation of (Vd) (Found: C, 75·8; H, 7·5. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

7-*Hydroxy*-6-*isopropyl*-2,5-*dimethyl*-α-*tetralone* (XIIIb).—The combined mother liquors from the fractional crystallization of (Ve) were evaporated to dryness. The residue was stirred with aqueous sodium hydroxide (3%; 30 ml) for 0·5 h and filtered. Crystallization of the residue from benzene gave the isopropyl-migrated *tetralone* (XIIIb) as small needles, m.p. 189—192° (2 g); $\nu_{max.}$ (Nujol) 3425 (OH) and 1675 cm^{-1} (C=O); δ ($CDCl_3$) 1·2—1·37 (9H, merged, 2-Me and 6-CH*Me*$_2$), 2·27 (3H, s, 5-Me), 6·4 (1H, s, OH), and 7·61 (1H, s, 8-H) (Found: C, 77·6; H, 8·7. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·7%).

The alkaline solution on acidification gave the hydroxytetralone (Ve), m.p. 168—171° (0·8 g).

7-*Acetonyloxy*-2,5-*dimethyl*-α-*tetralone* (Vf).—A mixture of the hydroxytetralone (Ve) (4·4 g), bromoacetone (3·6 g), powdered, anhydrous potassium carbonate (3·2 g), and dry acetone (15 ml) was refluxed with stirring for 16 h. Work-up as described for (Vc) gave the *acetonyloxytetralone* (Vf), m.p. 72—73° (from light petroleum); $\nu_{max.}$ (Nujol) 1730 (saturated C=O) and 1675 cm^{-1} (tetralone C=O); δ (CCl_4) 1·22 (3H, d, *J* 7 Hz, 2-Me), 2·23 and 2·28 (each 3H, s, 5-Me and COMe), 4·47 (2H, s, OCH_2CO), 6·92 (1H, d, *J* 3 Hz, 6-H), and 7·23 (1H, d, *J* 3 Hz, 8-H) (Found: C, 73·1; H, 7·6. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%).

1,5,8-*Trimethyl*-7,8-*tetrahydronaphtho*[2,1-b]*furan*-9(6H)-*one* (VIb).—The foregoing acetonyloxytetralone (Vf) (2 g) and concentrated sulphuric acid (26 ml) were precooled separately in an ice–salt bath. The tetralone was added to the acid with stirring during 10 min. After 18 h at 0°, the mixture was decomposed with ice, when a pale yellow powder separated (1·6 g), which was purified by chromatography. Elution with light petroleum from a column of silica gel (60 g) gave the *naphthofuranone* (VIb), m.p. 78—79° (from aqueous methanol) (0·4 g); $\nu_{max.}$ (Nujol) 1695 cm^{-1} (C=O); δ(CCl_4) 1·23 (3H, d, *J* 7 Hz, 8-Me), 2·35 (3H, s, 5-Me), 2·37 (3H, d, *J* 1·5 Hz, 1-Me), and 7·35 (2H, s, 2- and 4-H) (Found: C, 78·5; 7·3. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%).

1,5,8-*Trimethyl*-6,7-*dihydronaphtho*[2,1-b]*furan* (*Pyrocurzerenone*) (I).—A mixture of the tetralone (VIb) (0·4 g), sodium borohydride (0·4 g), and ethanol (15 ml) was left overnight. Ethanol was removed under reduced pressure and the residue was diluted with ice-cold water and acidified with glacial acetic acid. Work-up furnished the naphthofuranol (VII) as a semi-solid mass (0·38 g); $\nu_{max.}$ (Nujol) 3325 cm^{-1} (OH). A benzene solution (15 ml) of (VII) was refluxed with toluene-*p*-sulphonic acid (0·1 g) for 0·5 h.

The solution was cooled, diluted with ether, and washed with aqueous sodium hydrogen carbonate. The solvent was removed and the brownish gum was sublimed (105° at 3 mmHg) to give *pyrocurzerenone* (I), m.p. 77—78°, as needles (from methanol) (0·14 g); $\lambda_{max.}$ (ethanol) 235sh (log ε 4·05), 242 (4·2), 250 (4·2), 282sh, and 292 nm (4·2); δ (CCl_4) 1·97br (3H, s, 8-Me), 2·31 (3H, s, 5-Me), 2·36 (3H, d, *J* 1·5 Hz, 1-Me), 6·71 (1H, q, 9-H), 6·95 (1H, s, 4-H), and 7·14 (1H, d, *J* 1·5 Hz, 2-H). The i.r. spectrum was identical with that of authentic material (Found: C, 84·6; H, 7·9. $C_{15}H_{16}O$ requires C, 84·9; H, 7·6%).

The synthetic pyrocurzerenone (I) (80 mg) was hydrogenated over platinum oxide (Adams catalyst) (7 mg) in methanol (25 ml) until 1 mol. equiv. of hydrogen was absorbed. The usual work-up furnished *dihydropyrocurzerenone* (III), m.p. 72·5—73·5 (from methanol); $\lambda_{max.}$ (ethanol) 216 (log ε 4·4), 2·48sh (4·0), 251 (4·1), 260sh (4·0), 280 (3·5), and 290 nm (3·5); δ (CCl_4) 1·09 (3H, d, *J* 6 Hz, 8-Me), 2·23 (3H, s, 5-Me), 2·35 (3H, d, *J* 1·5 Hz, 1-Me), 6·96 (1H, s, 4-H), and 7·11 (1H, d, *J* 1·5 Hz, 2-H). The i.r. spectrum was identical with that of an authentic specimen (Found: C, 83·6; H, 8·7. $C_{15}H_{18}O$ requires C, 84·1; H, 8·5%).

The synthetic pyrocurzerenone (I) (0·2 g) was heated with sulphur (0·04 g) at 235—245° for 2 h. The unchanged sulphur was removed by the addition of sodium borohydride (0·1 g) and rectified spirit (10 ml) to the mixture, which was refluxed for 2 h.[12] The solvent was removed and the residue sublimed (110° at 2 mmHg), to give 1,5,8-*trimethylnaphtho*[2,1-b]*furan* (IV) as a white solid, m.p. 97—100° (from aqueous ethanol). Its i.r. and n.m.r. spectra tallied with those of the authentic material.

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