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HUMIC ACID—III

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Abstract—The effect of KOH fusion, pyrolysis, and hydriodic acid on acid boiled humic acid (ABHA) has been studied.

As many of the products of the KOH fusion of ABHA are obtained similarly from the "polymers" of *o*- or *p*-benzoquinone or furfural, it is probable that the fusion products shed little, if any, light on the constitution of HA.

A few of the polycyclic aromatic hydrocarbons detected amongst the zinc distillation products of ABHA or the quinone "polymers" may possibly be secondary products but it is unlikely that the majority of the complex hydrocarbons arise in this way.

Additional evidence supporting the polycyclic nature of ABHA has been obtained by reduction with hydriodic acid and phosphorus, which gives an oil G containing a complex mixture of aliphatic (or alicyclic) hydrocarbons of mol wts above 190. Dehydrogenation of oil G or of fractions separated either by distillation or chromatography yields products in which pyrene, a methylpyrene and perylene have been detected by UV and mass spectral methods.

PREVIOUS workers[1] have reported the formation in high yields of phenolic degradation products by the alkaline fusion of HA. The water soluble acidic product now obtained in 30% yields by fusion of ABHA with KOH at 280° was separated into a small amount of unidentified steam volatile acids, a mixture of phenols containing resorcinol, orcinol and phloroglucinol and a carboxylic acid fraction from which oxalic acid was isolated. Paper chromatographic examination of this carboxylic acid fraction showed the presence of 3,4- and 3,5-dihydroxybenzoic acids together with 14 unidentified non-phenolic fluorescent substances. The acid fraction was also separated by counter-current distribution followed by paper chromatography, and mass spectral comparison of some of the fractions with authentic samples confirmed the presence of the dihydroxybenzoic acids and suggested in addition the presence of hydroxybenzene dicarboxylic acids. The black amorphous products‡ obtained by the alkaline "polymerization" of *o*- or *p*-benzoquinones have been subjected to alkaline fusion and the products analysed by the same techniques. 2,5- and 3,5-Dihydroxybenzoic acids were detected in the products from the *p*-benzoquinone "polymer" whilst the *o*-benzoquinone "polymer" yielded 3,4- and 3,5-dihydroxybenzoic acids. The alkaline fusion of the black amorphous product obtained from the acid "polymerization" of furfural, rather unexpectedly gave an

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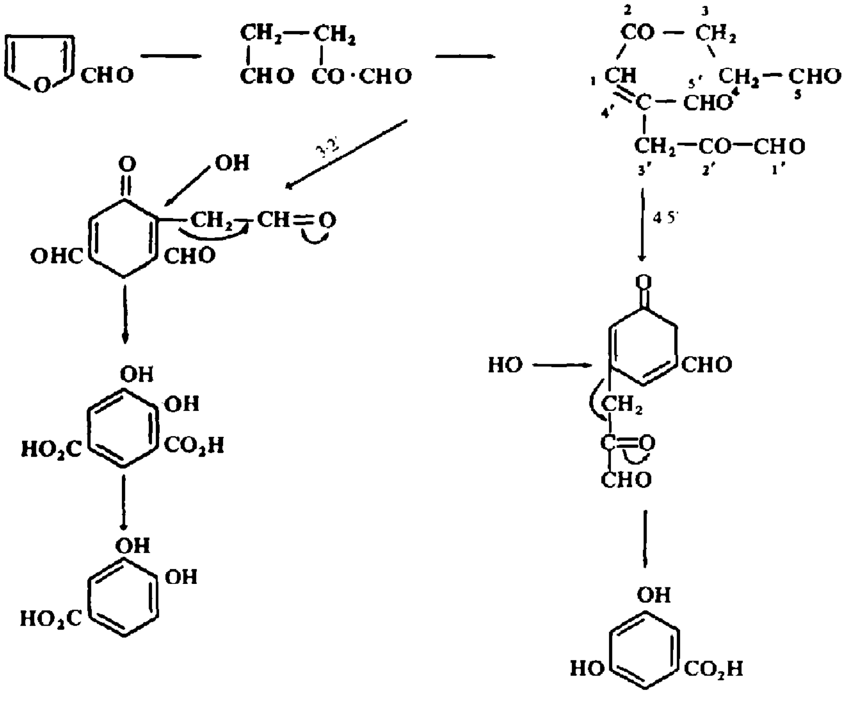
‡ The black amorphous products are conveniently referred to as "polymers", although the analytical data for the products from the benzoquinones indicate that some oxidation occurs during the "polymerization".

acid fraction which was shown by paper chromatography to contain 3,4- and 3,5-dihydroxybenzoic acids, and many of the non-phenolic fluorescent substances obtained from ABHA were also produced by the fusion of the synthetic benzoquinone and furfural "polymers" as shown in Table 2. The products of the KOH fusion are probably not diagnostic of the structure of humic acid or of the synthetic "polymers" and we prefer to regard them as secondary substances resulting from the breakdown of the complex products into relatively simple units which recombine under the fusion conditions. Numerous acceptable schemes may be devised to illustrate the formation of 3,4- and 3,5-dihydroxybenzoic acids from *o*- and *p*-benzoquinones and the following, suggested by Professor W. D. Ollis, outlines reactions by which the acids could be derived from furfural:



The detection of numerous aromatic substances from the distillation of ABHA with zinc dust[2] was taken as evidence of the presence of a polycyclic aromatic core, although it was conceded that some of the aromatic hydrocarbons might have been produced by secondary reactions.

It has now been established that polycyclic hydrocarbons are present in the neutral distillates obtained by the zinc dust distillation of relatively simple phenols and phenolic acids at 550°. Thus 3,4- and 3,5-dihydroxybenzoic acids gave small yields of a neutral distillate which was shown by UV and mass spectrometry to contain anthracene and 9-phenylfluorene; phoroglucinol gave a distillate containing phenanthrene, pyrene and possibly triphenylene.

It has also been observed that zinc dust distillation of ABHA at 400° gives the same products in the same yields as observed previously[2] at 550° but at this lower temperature, however, 3,4- and 3,5-dihydroxybenzoic acids give very small yields of distillates composed entirely of anthracene. The furfural and the *o*- and *p*-benzoquinone "polymers" did not yield any aromatic hydrocarbons when distilled with zinc dust at 400°, but similar treatment of the quinone "polymers" at 500° gave neutral oils in which anthracene, pyrene, benzofluorenes and 1,2- and 3,4-benzopyrene were detected by UV and mass spectrometry.

Pyrolysis of ABHA in a stream of hydrogen at 550°, and in the absence of zinc dust, led to the formation of carbon dioxide (13% of the weight of ABHA), water (30%), a dark brown ether-soluble distillate (3%) and a black residue (54%) which gave an amorphous X-ray powder diagram. The neutral portion of the ether-soluble distillate was separated by TLC into a number of fractions, the UV spectra of which indicated that small amounts of anthracene, pyrene and benzofluorenes were formed during the pyrolysis. The *p*-benzoquinone "polymer" behaved similarly losing water (13%) and carbon dioxide (13%) on pyrolysis in a hydrogen steam at 550° but polycyclic aromatic substances were not detected.

As ABHA gave complex hydrocarbons under conditions where simple phenols and the synthetic "polymers" did not yield anything more complex than anthracene and as perylene and coronene have not been detected in experiments with simple phenols or quinone "polymers" it is concluded that at least some of the products obtained from ABHA were probably primary products.

Further evidence in favour of a polycyclic structure for ABHA has been obtained by reduction with hydriodic acid and red phosphorus at 250°. The neutral ether-soluble product gave, on steam distillation, a steam volatile oil X and a non-volatile oil G in yields of 3 and 18% respectively.

The steam volatile oil X, after separation from iodoform by TLC, had b.p. 135–145°/25 mm, an aliphatic UV spectrum, and showed no doubly charged ions in the mass spectrum. Dehydrogenation with Pd–C followed by TLC separated a fraction containing unchanged aliphatic material and a small fraction showing a typical anthracene UV spectrum and mass spectrum indicating the presence of anthracene and methylanthracene.

The non-volatile oil G was shown by VPC to contain at least 21 components and the IR spectrum of the mixture revealed only aliphatic CH absorption. Dehydrogenation of oil G with Pd–C yielded a neutral product giving by TLC a major fraction which was shown to be largely unchanged when examined by IR spectroscopy and VPC, together with a number of minor fractions showing M^+ in the range *m/e* 216–286. Dehydrogenation of one of these minor fractions with sulphur followed by TLC gave a fraction with a typical pyrene UV spectrum and the mass spectrum indicated the presence of pyrene (*m/e* 202; high resolution confirmed $C_{16}H_{10}$), and a methylpyrene (*m/e* 216). This latter assignment, indicated by the presence of a strong M-1 fragment ion, was supported by the synthesis of 3-methylpyrene by a slight modification of the method described by Vollmann *et al.*[3] which also showed M^+ at *m/e* 216, and a strong M-1 fragment ion.

After these preliminary experiments oil G was examined by distillation and chromatographic methods. Distillation under reduced pressure gave two main hydrocarbon fractions in 20 and 60% yield respectively. Each fraction was mainly aliphatic in character and did not show doubly charged ions in the mass spectrum but the UV spectrum showed very weak peaks indicative of of some unsaturation. The lower boiling fraction, which gave a mass spectrum with M^+ in the range *m/e* 174–246, was dehydrogenated with Pd–C; separation by TLC into a number of fractions yielded largely unchanged material together with a fraction in which pyrene and a methylpyrene were identified as described above. The higher boiling fraction gave a mass spectrum showing M^+ in the range *m/e* 258–300, and the M^+ at *m/e* 272 was shown by high resolution to be $C_{20}H_{32}$ which would be consistent with a perhydroperylene structure. This fraction was dehydrogenated and separated into 7 fractions, the first two of which resembled unchanged material and were largely aliphatic in character, the third and fourth fractions contained pyrene and a methylpyrene (UV and mass spectral data) and the fifth fraction was shown by the UV and mass spectra to be largely composed of perylene (*m/e* 252). More complex hydrocarbons are probably present in higher fractions but reliable assignments could not be made.

The chromatographic separation method, which avoids the high temperatures associated with the distillation techniques described above, gave however very similar results. Oil G was separated by column chromatography into five fractions and the main fraction, which showed no absorption above 230 mμ in the UV and only aliphatic CH in the IR spectra, gave a mass spectrum with M^+ in the range *m/e* 192–274. This fraction was dehydrogenated with Pd–C and the product, separated by TLC, yielded a fraction with unchanged UV spectrum and a mass spectrum showing M^+ in the range *m/e* 190–260, a second fraction containing pyrene (*m/e* 202) and a methylpyrene (*m/e* 216, 215) and a third fraction containing perylene (*m/e* 252).

The detection of pyrene, methylpyrene and perylene in the dehydrogenation products of the high molecular weight substances in oil G constitutes powerful evidence in support of a polycyclic structure for ABHA. These aromatic hydrocarbons must arise from the perhydro precursors in oil G and no evidence has been obtained of the presence of simple cyclic compounds either in oil G or in the dehydrogenation products. No analogies can be traced for the conversion of simple benzenoid substances into complex polycyclic compounds during reduction with hydriodic acid and red phosphorus and the most rational interpretation of the reactions described in this communication must postulate the presence of a polycyclic core in ABHA.

EXPERIMENTAL

The ABHA used was isolated from Ringinglow I peat as described in Part I.[4]

UV and mass spectra were determined as described previously[2] and the same symbols are employed in reporting the results with the addition of m* for metastable ions.

Unless otherwise stated the VPC was done on a Griffin & George D.6 gas density balance using a silicone rubber SE.30 column of 6 ft. length at 150° and a flow rate of 60 ml/min of N_2.

The phenolic and acidic fractions obtained from KOH fusion were examined by two-dimensional paper chromatography using (a) 6% AcOH and (b) benzene–AcOH–water (125:72:3) for development unless otherwise stated; spots were detected by exposure to UV light followed by spraying with tetrazotized benzidine and/or Gibbs reagent.

Chromatographic separation of the P and HI and Zn dust distillation products was accomplished using silica gel plates and pet. ether (b.p. 40–60°) as solvent unless otherwise stated. The fractions were detected either as fluorescent bands under UV light or by spraying the edges of the plates with 2% ceric sulphate in 2N H_2SO_4.

Dehydrogenation of the products from P and HI experiments was accomplished by heating with 10% Pd–C (0·5 parts) in a sealed tube at 350° for 4 hr unless otherwise stated. The mixture was repeatedly extracted with ether and the extract was washed successively with 2N NaOH, 2N HCl and water, dried and the solvent removed.

"Polymers" of o- and p-benzoquinone. A slow stream of air was drawn through a soln of the quinone (10 g) in 3N NaOH (100 ml) for 24 hr. The soln was acidified and the ppt collected in a centrifuge, washed and dried. The solid (6 g) was then boiled with 6N HCl (180 ml) for 24 hr and the product (4·7 g) was collected, washed and dried (Found for *p*-benzoquinone "polymer": C, 59·6; H, 2·7%. Found for *o*-benzoquinone "polymer"; C, 58·65; H, 3·3%).

A mixed "polymer" (Table 2) was prepared as above from an equimolecular mixture of *o*- and *p*-benzoquinone.

"Polymer" of furfural. Freshly distilled furfural (20 g) was boiled with 6N HCl (300 ml) for 3 hr. The cooled soln was filtered and the residue (17 g) was well washed with water and dried (Found: C, 65·9; H, 4·5%).

KOH *fusion.* ABHA or the synthetic polymer from *o*- or *p*-benzoquinone or from furfural (12 g) was fused with KOH (120 g) at 280–290° for 4 hr with occasional stirring. The mixture was cooled, dissolved in water, and a trace of insoluble material removed by centrifuging; acidification of the solution yielded a ppt (Table 1).

In the case of the fusion of ABHA the aqueous soln was steam distilled and ether extraction of the distillate gave an acidic product (0·4 g) which reduced Tollens reagent but the constituents could not be identified by paper chromatography or TLC.

The aqueous solution was continuously extracted with ether and the acids and phenols (Table 1) were removed in $NaHCO_3$ and NaOH respectively and recovered by ether extraction. The yields are tabulated below.

TABLE 1

Product	Precipitate	Acid fraction	Phenol fraction
ABHA	3·7 g	3·09 g	0·13 g
o-Benzoquinone "polymer"	3·5 g	3·8 g	0·37 g
p-Benzoquinone "polymer"	3·94 g	3·88 g	0·55 g
Furfural "polymer"	5·45 g	1·95 g	0·09 g

Phloroglucinol, resorcinol and orcinol were identified in the phenolic fraction from ABHA which also contained two unidentified substances giving coloured spots with tetrazotized benzidine. Resorcinol and orcinol were detected in the phenolic fraction from the furfural "polymer", but the phenol fractions from the benzoquinone "polymers" were not examined fully.

The acidic fractions from the KOH fusion of ABHA, and a mixed quinone "polymer" were analysed qualitatively by paper chromatography, and the numerous constituents include in Table 2 show that 3,4- and 3,5-dihydroxybenzoic acids† and at least eleven additional components are obtained in both cases. The products from the furfural "polymer" are also included in Table 2.

The acids from ABHA and the benzoquinone "polymers" were separated into six fractions A–F by counter-current distribution between ether and water using 45 tubes. Some of the fractions were separated into sub-fractions, e.g. D_1, D_2, etc., by preparative paper chromatography, and examined by mass spectrometry.

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† 3,4-Dihydroxybenzoic acid was recovered in about 70% yield after recrystallization of the product isolated from a KOH fusion at 280–290° for 4 hr.

TABLE 2

Fractions		Fluorescence			Tetrazotized benzidine			Assignment
R_f(a)	R_f(b)	ABHA	Furfural	Mixed "polymer" of *o*- and *p*-benzoquinone	ABHA	Furfural	Mixed "polymer" of *o*- and *p*-benzoquinone	
0·06–0·14	0·02–0·07	+	+	+	—	—	—	
0·1–0·18	0·18–0·24	+	+	+	—	—	—	
0·1–0·18	0·31–0·36	+	+	+	violet	violet	—	
0·22–0·28	0·03–0·07	+	+	+	—	—	—	
0·24–0·3	0·18–0·22	+	+	−	—	—	—	
0·2–0·28	0·66–0·72	+	+	+	violet	violet	—	
0·42–0·5	0·27–0·32	+	−	+	—	—	—	
0·46–0·54	0·19–0·24	+	+	+	yellow	yellow	yellow	3,4-dihydroxybenzoic acid
0·45–0·54	0·08–0·15	−	−	−	red-brown	red-brown	red-brown	3,5-dihydroxybenzoic acid
0·42–0·54	0·45–0·52	+	+	+	—	—	—	
0·44–0·54	0·57–0·61	+	+	+	—	—	—	
0·48–0·56	0·63–0·69	+	+	+	—	—	—	
0·58–0·64	0·02–0·07	+	+	−	—	—	—	
0·59–0·62	0·09–0·11	+	+	−	—	—	—	
0·59–0·64	0·2–0·25	+	+	−	—	—	—	
0·6–0·68	0·32–0·38	−	−	+	—	—	yellow	2,5-dihydroxybenzoic acid
0·64–0·70	0·45–0·52	+	+	−	—	—	—	
0·7–0·78	0·0–0·05	+	−	+	—	—	—	
0·7–0·78	0·07–0·12	−	−	+	—	—	—	
0·68–0·71	0·18–0·23	−	−	+	—	—	—	
0·66–0·72	0·27–0·32	+	+	−	—	—	—	
0·76–0·78	0·27–0·32	−	−	+	—	—	—	
0·76–0·88	0·82–0·87	−	+	−	—	—	—	2-furoic acid
0·56–0·60	0·5–0·54	−	−	−	yellow	yellow	yellow	
0·58–0·62	0·63–0·67	−	−	−	—	pink	pink	
0·58–0·62	0·70–0·74	−	−	−	yellow	yellow	—	
0·6–0·66	0·13–0·19	−	−	−	—	yellow	yellow	
0·66–0·72	0·27–0·32	−	−	−	yellow	—	—	
0·72–0·76	0·5–0·57	−	−	−	—	—	yellow	

The R_f(a) and R_f(b) values and colour tests of authentic samples of the dihydroxybenzoic and furoic acids are identical with those given in Table 2.

(a) *Acidic product from* ABHA. The acids (4·5 g) were methylated with diazomethane in ether and the ester distilled under reduced press; dimethyl oxalate (0·2 g), m.p. 54° was obtained from a fraction boiling below 80°/1 mm.

Fractions A, C and F gave diffuse paper chromatograms, no assignments could be made concerning fraction B and the products obtained from some sub-fractions of D are described in Table 3.

Fraction E, which resembled fraction D on paper chromatography was esterified with diazomethane and partially separated by TLC into four fractions; the mass spectrum of sub-fraction E_1 is described in Table 3.

Assignments. Fractions D_4 and D_5 both show M^+ at *m/e* 154 corresponding with dihydroxybenzoic acids and the fragmentation pattern showing 154 → 137 → 109 (with corresponding m^* at *m/e* 121·8 and 86·7 respectively) but no M-18 ion excludes salicylic acid derivatives. Paper chromatographic and mass spectroscopic comparison with authentic specimens, however showed the presence of 3,4- and 3,5-dihydroxybenzoic acids respectively. Authentic specimens of these two acids each show a strong M^+ at *m/e* 154 and the fragmentation pattern 154 → 137 → 109 (with corresponding m^* at *m/e* 121·8 and 86·7 respectively). The presence in the ester fraction E_1, of the M^+ at *m/e* 196 and the fragmentation pattern (196 → 165 → 137 → 122, with corresponding m^* at *m/e* 139, 113·7 and 108·7 respectively) support this assignment.

Table 3

Source	Fraction number	Colours with		Mass spectra	
		Tetrazotized benzidine	Gibbs reagent	Low eV	70 eV
(a) Ringinglow ABHA	D_1	pink	blue grey	s: 182[b]	s: 57[b] m: 60, 69, 71, 73, 97, 111, 123
	D_4	yellow	blue mauve	s: 154[b]	s: 137, 154[b] w: 109
	D_5	crimson	purple	s: 154[b]	s: 154[b] m: 137 w: 60, 69, 109, 126
	E_1	—	—		s: 165, 193, 196[b] m: 224
(b) *p*-Benzoquinone "polymer"	B_2	yellow	grey	s: 182[b]	s: 73, 74, 100, 122[b] m: 101, 123, 150 w: 94, 182
	D_2	chestnut	—	s: 154[b]	s: 154[b] m: 137 w: 109
	E_2	yellow	purple	s: 154[b]	s: 69, 136[b] m: 71 w: 80, 95, 97, 108, 154
(c) *o*-Benzoquinone "polymer"	C_1	yellow	violet	s: 168[b] w: 182	s: 123[b] w: 77, 120, 122, 168
	$(D + E)_2$	yellow	purple	s: 154[b] w: 168	s: 69[b], 137, 154 m: 71, 73, 97 w: 109, 111, 129
	$(D + E)_3$	chestnut	purple	s: 154[b]	s: 69[b], 154 m: 137 w: 71, 73, 97, 109

Fraction D_1, shows M^+ at *m/e* 182 which is possibly a hydroxybenzene dicarboxylic acid and the ester fraction E_1 mentioned above also shows M^+ at *m/e* 224 and fragment ions at *m/e* 193, 165 (with corresponding m^* at 166·5 and 141 respectively) corresponding with a fully methylated hydroxybenzene dicarboxylic acid.

(b) *Acidic product from* p-*benzoquinone "polymer"*. Fractions A, C and F gave diffuse chromatograms and the last two were not investigated further. Fraction A was esterified with diazomethane and the product distilled to give dimethyl oxalate (0·32 g); the residue did not distil below 200°/10 mm. Fractions B, D and E were separated by paper chromatography into sub-fractions, some of which were examined by mass spectroscopy (Table 3).

Assignments. Fraction B_2 showed a strong M^+ at *m/e* 182 for which the formula $C_9H_{10}O_4$ was obtained by high resolution methods (Found: 182·058. Calc. for $C_9H_{10}O_4$, 182·0579). The fragmentation pattern 182 → 150 → 122 → 94 (with corresponding m^* at 123·6, 99·3, 72·4 respectively) suggests the presence of a methyl *o*-hydroxybenzoate structure which would lose MeOH followed by two CO units but it is difficult to imagine how such a structure can arise.

Fraction D_2 was identified as 3,5-dihydroxybenzoic acid as discussed for fraction D_5 from the ABHA fusion. Fraction E_2 showed M^+ at *m/e* 154 and a strong fragment at *m/e* 136 corresponding to a loss of water; this suggested an *o*-hydroxybenzoic acid and the product was identified as 2,5-dihydroxybenzoic acid by paper chromatographic and mass spectroscopic comparison. Fraction E_2 and authentic 2,5-dihydroxybenzoic acid gave the same fragmentation pattern 154 → 136 → 108 → 80 (with corresponding m^* at 120·0, 85·9 and 59·3 respectively).

(c) *Acidic product from* o-*benzoquinone "polymer"*. Fractions A, B and F gave very diffuse paper chromatograms but fraction A was shown to contain oxalic acid as described for fraction A from *p*-benzoquinone "polymer". Fractions C, D and E were separated and identical materials from fractions D and E were combined. Some of the results are in Table 3.

Assignments. Fraction C_1 gave M^+ at *m/e* 168 and a fragment at *m/e* 123. The formation of M-17 and M-17-28 ions is not observed but the direct formation of the M-45 ion suggests that this product may be a dihydroxyphenylacetic acid; the mass spectrum of an authentic specimen of phenylacetic acid showed a weak M^+ at *m/e* 136 and a strong M-45 fragment ion at *m/e* 91. Paper chromatography showed that fractions $(D + E)_2$ and $(D + E)_3$ contained 3,4- and 3,5-dihydroxybenzoic acids respectively and mass spectrometry (*m/e* 154) supported the assignment.

(d) *Acidic product from furfural "polymer"*. Paper chromatography showed the presence of 15 fluorescent spots (one of which is 2-furoic acid), and nine spots with tetrazotized benzidine (Table 2), two of which were 3,4- and 3,5-dihydroxybenzoic acids. When the total acidic fraction was esterified with diazomethane and then distilled, no dimethyl oxalate was obtained.

Pyrolysis of ABHA. ABHA (2·76 g dried at 75°/20 mm) was heated in a stream of H_2 for 30 min at 550° and the effluent gas was passed through a cold trap and then through a sofnolite absorber for CO_2 (0·35 g). The distillate consisted of water (0·83 g) and a dark brown oil (0·08 g) which was isolated by ether extraction; the infusible black residue (1·5 g) (Found: C, 82·7; H, 3·1; N, 0·6; O, 8·0; Ash 4·0%) which was insoluble in NaOH aq and all organic solvents, gave a non-crystalline X-ray diagram.

The combined ether soluble distillate (0·25 g) from three such experiments was washed successively with dilute HCl and dilute NaOH and the neutral fraction (0·09 g) was separated giving the fractions described in Table 4.

TABLE 4

Fraction	λ_{max} (n-Hexane)	Assignment
1	221, 246*, 252, 270, 273, 281, 288, 317* 335, 352, 356, 370, 376	anthracene
2	220, 243–250*, 254, 272, 287, 293, 320, 336	pyrene
3	218, 254, 260*, 263, 276, 289, 304, 316	benzofluorene

Zinc dust distillation of model compounds. The distillation and isolation of the neutral products were carried out as described in Part II[1] using 0·5 g of each compound. In all cases the yield of acidic product was small (2 %); the neutral products usually obtained in about 5 % yield, were separated and the fractions are described in Table 5.

TABLE 5

Compound	Fraction	λ_{max} (n-Hexane)	Mass spectrum		Assignment
			Low eV	70 eV	
3,4-Dihydroxy-benzoic acid	1	215, 247*, 252, 290, 302, 324, 339, 356, 370*, 375			anthracene
	3	220, 235, 259, 270*, 292*, 304	s: 242, 244, 258^{b}	s: 242^{b}, 258 m: $^{\oplus}$241, 244 w: $^{\oplus}$165	9-phenylfluorene (see Note 1)
3,5-Dihydroxy-benzoic acid	1	215, 247, 253, 290, 301, 324, 339, 356, 370, 375			anthracene
	2	216, 223–226*, 258, 264, 304, 320*, 347, 364, 383		s: 242^{b} m: $^{\oplus}$151, $^{\oplus}$165, $^{\oplus}$241, 256	9-phenylfluorene (see Note 1)
Phloroglucinol	1	220, 245*, 253, 274, 293, 320, 335	s: 192^{b}, 206, 218 m: 216, 232, 252 w: 202, 178, 246	s: 192, 218^{b} m: 178, 202, 206, $^{\oplus}$215, 216, 232	phenanthrene pyrene
	2	215, 250, 258 287	s: 230, 244^{b} w: 216, 228	w: 216, $^{\oplus}$215	*m/e* 228; possibly triphenylene
p-Benzoquinone "polymer"	1	222, 253, 273, 288, 301, 321, 334, 339, 352*, 355, 370*, 375	s: 178^{b} m: 192 w: 164, 206		anthracene
	2	217, 254, 273, 293, 300, 319 335	s: 192^{b} w: 178, 206	s: 192^{b} m: 178 w: 202, 206	*m/e* 202; probably pyrene
	3	255*, 260, 264, 277, 289, 303, 316	s: 216^{b}, 230 m: 242, 244	s: 216, $^{\oplus}$215 M^{++} at 107·5	benzofluorene
	4	251, 259, 268*, 287	s: 228^{b}, 242 m: 230, 256 w: 216		*m/e* 228; possibly triphenylene
	5	260, 270, 282*, 290, 322, 332, 363*, 385, 402, 430		s: 252^{b}, 258 m: 254, 256, 266, 268 w: 228	*m/e* 252; possibly benzopyrene

TABLE 5—*continued*

Compound	Fraction	λ_{max} (n-Hexane)	Mass spectrum		Assignment
			Low eV	70 eV	
o-Benzoquinone "polymer"	1	221, 248*, 253, 273, 320, 335, 338*, 356, 370*, 375			anthracene
	2	217, 245*, 254, 272, 320, 335			pyrene
	3	215, 259, 266*, 289, 299*, 331, 363, 379*, 386		s: 252^b m: 256, 266 w: 254, 268, 276, 280	1,2- and 3,4-benzopyrene (see Note 2)

Note 1. High resolution on the *m/e* 242 peak established the formula $C_{19}H_{14}$ (Found: 242·107. Calc. for $C_{19}H_{14}$ 242·110) which together with the observed metastable ion at *m/e* 112·5 (Calculated for $242^+ \rightarrow 165^+$ is 112·5) suggested 9-phenylfluorene. The UV and mass spectra of authentic 9-phenylfluorene[5] confirm this assignment.

Note 2. High resolution on the peak at *m/e* 252 in fraction 3 established the formula $C_{20}H_{12}$ (Found: 252·089. Calc. for $C_{20}H_{12}$, 252·094) for which both 1,2- and 3,4-benzopyrene are suggested by the UV spectrum.

Reduction of ABHA *with hydriodic acid and red phosphorus.* A mixture of ABHA (1 g) red P (1 g) and HI (30 ml; d. 1·74) was heated in a sealed tube at 250° for 24 hr. The contents of 8 such tubes were filtered and the resinous product was extracted several times with boiling ether; the residue, after washing with benzene, was a yellow-green solid (2 g). (Found: C, 34·8; H, 3·5; Ash 47·7%). The diluted filtrate was extracted with ether (3 × 200 ml) and the extract combined with the ether and benzene extracts of the solid residue, washed successively with water, $Na_2S_2O_3$aq, dil NaOH and water, dried ($MgSO_4$), the solvent removed and the residual oil distilled in steam. The steam distillate was extracted with ether, dried, the solvent removed and the residual oil was separated by TLC into iodoform (0·2 g) and oil X (0·25 g) b.p. 135–145°/25 mm (Found: C, 86·6; H, 12·6%).

Ether extraction of the non-steam volatile residue gave the reduction product G (1·4 g) as a viscous pale brown oil; ν_{max} (film) 2950, 2850, 1460 and 1380 cm^{-1}. VPC showed the presence of 21 components with retention times in the range 1·5–27·7 min.

Dehydrogenation of oil X. Dehydrogenation of oil X (0·2 g) gave a neutral product (0·043 g) which was separated by TLC into several fractions, some of which are described below in Table 6.

TABLE 6

Fraction	λ_{max} (n-Hexane)	Mass spectrum		Assignment
		Low eV	70 eV	
X	220, 250, 270, 275, 280	s: 232^b m: 218, 220, 234, 246 w: 202, 206, 216, 248	no M^{++}	aliphatic
X_1	216	s: 192^b, 206 m: 218, 220 w: 178, 232	no M^{++}	aliphatic

TABLE 6—*continued*

Fraction	λ_{max} (n-Hexane)	Mass spectrum		Assignment
		Low eV	70 eV	
X_2	228, 278, 287*, 325	s: 210, 224^b m: 196, 226, 238, 240 w: 168, 170, 182, 184, 212, 252	M^{++} at 82·5	possibly naphthalenic
X_3	232, 254, 273, 293, 320, 335, 357, 376	s: 192^b, 206 w: 178	s: 192^b m: 178, $^{\oplus}$191 M^{++} at 94·5, 95·5	anthracene, methylanthracene
H_1	216, 270, 273, 279	—	—	aliphatic
H_2	215*, 233, 260*, 280, 330, 338, 382, 411, 440	—	—	
H_3	248, 263, 279*, 306*, 338*, 344, 381, 408, 437	s: 216, 230^b m: 242, 244, 256, 270 w: 202, 228, 232, 258, 272	s: $^{\oplus}$215 many M^{++}	—
H_4	232, 267, 306, 330*, 385, 438	s: 230, 232, 244, 246^b m: 216, 218, 258, 260, 272, 286	m: $^{\oplus}$215, $^{\oplus}$229 many M^{++}	—
H_{3_1}	238*, 245, 265, 276, 310*, 323, 338	s: 216, 230^b m: 202, 244	m: $^{\oplus}$215 w: $^{\oplus}$229	pyrene, methylpyrene

TABLE 7

Fraction	λ_{max} (n-Hexane)	Mass spectrum		Assignment
		Low eV	70 eV	
I	220, 250, 255, 270–275, 280	s: 192^b, 206 m: 178, 218, 220, 232 w: 174, 194, 234, 246	no M^{++}	aliphatic
J	242, 250, 261, 274, 285, 310, 340*, 350	s: 272^b m: 260, 274, 286 w: 258, 288, 300	no M^{++}	aliphatic see Note 1
I_1	215	s: 246^b, 230 m: 260, 272 w: 234, 248, 258, 262, 274	no M^{++}	aliphatic
I_3	215, 245, 256, 276, 303, 322, 337	s: 216^b m: 218, 220, 230, 232, 236	s: 202^b M^{++} at 94·5, 106·5, 107·5	pyrene methylpyrene
J_1	221, 265	s: 260, 272^b m: 246, 258, 274, 286 w: 232, 262, 288	no M^{++}	aliphatic: 2 homologous series (?)

TABLE 7—*continued*

Fraction	λ_{max} (n-Hexane)	Mass spectrum		Assignment
		Low eV	70 eV	
J_3	247*, 256, 273*, 275, 322, 337	s: 206, 216^b, 218, 220 m: 202, 230, 232, 234 w: 192, 246	s: 202^b, 192, 206 m: $^{\oplus}189$, $^{\oplus}191$, $^{\oplus}215$, 216 M^{++} at 107·5	pyrene methylpyrene
J_4	216, 235, 244, 257, 266, 277, 313, 326, 343	s: 216^b	s: 216^b m: $^{\oplus}215$ M^{++} at 107·5	methylpyrene
J_5	228, 253, 265*, 290, 332, 368, 386, 410, 430*, 436	s: 252^b m: 266	M^{++} at 126	perylene
J_6	230, 247, 259, 279, 330, 345, 388, 410, 435	s: 256, 270^b m: 258, 272, 284, 286, 298, 300, 312, 314, 328	many M^{++}	complex pyrene type

Note 1. High resolution on the peak at *m/e* 272 in fraction J established formula $C_{20}H_{32}$ (Found: 272·251. Calc. for $C_{20}H_{32}$, 272·250).

Dehydrogenation of oil G. Oil G (1·0 g) gave on dehydrogenation a neutral product H (0·85 g); some of the fractions of this product are included in Table 6. VPC showed that fraction H_1 contains 26 components with retention times in the range 1·75–60·2 min. Fraction H_2 showed 8 peaks with retention times varying from 1·75–5·1 min.

Fraction H_3 (0·05 g) was heated with S (1·0 g) at 220° for 2 hr; the product, isolated with ether, gave a main fraction H_{3_1} described in Table 6.

TABLE 8

Fraction	λ_{max} (n-Hexane)	Mass spectrum		Assignment
		Low eV	70 eV	
G_1	230	s: 192, 206, 232^b m: 178, 218, 220, 234, 246, 260 w: 248, 262, 272, 274	no M^{++}	aliphatic
G_2	240, 265, 275*, 282	s: 244^b m: 204, 218, 232 w: 230, 246, 258	no M^{++}	aliphatic
G_{1_1}	232, 250*	s: 246^b m: 190, 204, 248, 260 w: 216, 218, 232, 234, 262, 274	no M^{++}	largely aliphatic
G_{1_2}	243, 258*, 274, 276, 295*, 303, 321, 336, 342*	s: 202, 216^b, 218 m: 192, 206, 222, 232	m: $^{\oplus}191$, $^{\oplus}215$	pyrene methylpyrene
G_{1_3}	235, 266, 285, 332, 352, 387, 409, 431*, 436	s: 252^b w: 266	M^{++} at 126	perylene

Distillation of oil G and dehydrogenation of the fractions. Distillation of oil G (1·04 g) gave fraction I (0·22 g) as a colourless mobile liquid, b.p. 110–120°/0·15 mm and fraction J (0·60 g) which was a viscous dark brown oil, b.p. 180–250°/0·2 mm. (Found: C, 86·75; H, 12·2%). The small charred residue was discarded. The UV and mass spectra of fractions I and J are included in Table 7.

Fractions I (0·22 g) and J (0·29 g) were dehydrogenated and the products (0·20 and 0·17 g respectively) separated; the properties of some of the fractions are given in Table 7.

Chromatographic fractionation of oil G and dehydrogenation of the fractions. Oil G (0·86 g) was separated on a silica gel column (30 × 1·5 cm) into 5 fractions two of which are shown in Table 8. The main fraction G_1(0·54 g) was dehydrogenated and the product (0·36 g) was separated by TLC into the fractions G_{1_1}, G_{1_2} and G_{1_3} included in Table 8.

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