Gibberellic Acid. Part II. The Structure and Synthesis of Gibberene.*

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Gibberene, one of the dehydrogenation products of gibberic acid, is shown to be 1 : 7-dimethylfluorene. This hydrocarbon, 1 : 7-dimethylfluorenone (gibberenone), and methyl fluorenone-1 : 7-dicarboxylate have been synthesised.

IT has been reported that dehydrogenation of gibberellin A and B and gibberic acid with selenium yields a mixture of a hydrocarbon, gibberene, and a ketone, gibberone (Yabuta, Sumiki, Azabu, Tamura, Igarashi, and Tamari, *J. Agric. Chem. Soc. Japan*, 1940, **16**, 975; *Chem. Abs.*, 1950, **44**, 10816). Gibberene was identified as a substituted fluorene and the formula $C_{16}H_{16}$ was proposed. Oxidation gave the corresponding fluorenone (gibberenone).

The formation of gibberene by dehydrogenation of gibberic acid with selenium has been confirmed. Gibberene was also obtained by dehydrogenation of the gums recovered from the crystallisation mother-liquors of gibberellic acid. Gibberene and gibberenone are now shown to be 1 : 7-dimethylfluorene ($C_{15}H_{14}$) and 1 : 7-dimethylfluorenone respectively, by degradation and synthesis.

Oxidation of gibberene with potassium permanganate in acetone gave gibberenone, $C_{15}H_{12}O$. Oxidation with sodium dichromate in acetic acid also gave the fluorenone together with a yellow fluorenone monocarboxylic acid, $C_{15}H_{10}O_3$. This acid was shown to be 1-methylfluorenone-7-carboxylic acid; first, by oxidation to fluorenone-1 : 7-dicarboxylic acid, identified by direct comparison of the dimethyl and diethyl esters with authentic specimens prepared from retene (Bamberger and Hooker, *Annalen*, 1885, **229**, 102); and, secondly, by decarboxylation to 1-methylfluorenone which was synthesised by Lothrop and Goodwin's method (*J. Amer. Chem. Soc.*, 1943, **65**, 363). 1-Methylfluorenone was also obtained by the reduction of fluorene-1-carboxylic acid to fluorene-1-aldehyde by McFadyen and Stevens's method (*J.*, 1936, 584) followed by catalytic reduction to 1-methylfluorene and subsequent oxidation. It follows that gibberenone is 1 : 7-dimethylfluorenone.

Gibberenone is somewhat resistant to oxidation and was not readily attacked by permanganate in sodium hydroxide. Oxidation with sodium dichromate gave 1-methylfluorenone-7-carboxylic acid, but with more difficulty than gibberene did. Oxidation with permanganate in pyridine gave a mixture of 1-methylfluorenone-7-carboxylic acid, fluorenone-1 : 7-dicarboxylic acid, and traces of a red acid. The last acid is considered to

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* Part I, preceding paper.

be 7-methylfluorenone-1-carboxylic acid; in colour and m. p. it resembles fluorenone-1-carboxylic acid, the other three fluorenonemonocarboxylic acids being yellow. Further oxidation of the mixed acids with permanganate gave fluorenone-1 : 7-dicarboxylic acid. The " gibberenone monocarboxylic acid " prepared by Yabuta *et al.* (*loc. cit.*) may be identical with 1-methylfluorenone-7-carboxylic acid, but the latter melts 20° higher.

Finally 1 : 7-dimethylfluorene, 1 : 7-dimethylfluorenone, and methyl fluorenone-1 : 7-dicarboxylate were prepared by unambiguous synthesis, being identical with the corresponding compounds obtained by degradation of gibberic acid.

2-Amino-5-methylbenzoic acid was converted by acetic anhydride into 2 : 6-dimethyl-4-oxo-3 : 1-benzoxazine (Ring Index numbering, No. 947), which with *o*-tolylmagnesium bromide (cf. Lothrop and Goodwin, *loc. cit.*) gave 2-acetamido-5 : 2′-dimethylbenzophenone. A small amount of 2-acetamido-5-methylbenzoic acid was also formed but none of the expected ditolyl-alcohol (cf. Lothrop and Goodwin) was isolated. Hydrolysis of the benzophenone with sulphuric acid gave the corresponding amine, from which 1 : 7-dimethylfluorenone was obtained by diazotisation and ring closure. Wolff–Kishner reduction of the fluorenone gave 1 : 7-dimethylfluorene and oxidation of the dimethylfluorenone gave fluorenone-1 : 7-dicarboxylic acid which hitherto has only been obtained from retene and by oxidation of fluoranthene-12-carboxylic acid (von Braun and Manz, *Annalen*, 1932, **496**, 170).

EXPERIMENTAL

Some microanalyses are by Messrs. W. Brown and A. G. Olney. In chromatography, unless otherwise stated, Spence alumina was rendered alkali-free (Prins and Shoppee, *J.*, 1946, 498) and then activated for 3 hr. at 250°/17 mm. Infra-red absorption spectra were determined with a Grubb-Parsons S 3A Spectrometer through which dry air was continuously circulated. Ultra-violet absorption spectra were measured with a Unicam S.P. 500 Spectrophotometer.

Dehydrogenation of Gibberic Acid.—The yield of gibberene depended on the apparatus used. The best yield was obtained when the reaction was carried out in a small distillation flask (capacity *ca.* 2 ml.) with a narrow neck (7 × 0·6 cm.) to ensure that the refluxing material returned to the flask. A mixture of gibberic acid (1·00 g.) and selenium powder (1·00 g.) was heated in a slow stream of nitrogen to 320° in 20 min. (evolution of carbon dioxide), then raised to and kept at 360° ± 5° for 2¼ hr. No volatile carbonyl compounds were detected (2 : 4-dinitrophenylhydrazine trap). The mixture was distilled at *ca.* 15 mm. An ethereal solution of the solid distillate from four experiments on the same scale was washed with 3N-sodium hydroxide, and the recovered neutral fraction (2·12 g.) in light petroleum (b. p. 40—60°) (60 ml.) and ether (6 ml.) was chromatographed on alumina (26 × 2 cm.). Elution in ultra-violet light with light petroleum followed by light petroleum (b. p. 40—60°)–ether (70 : 1) removed first a violet-fluorescing band. Further elution removed gibberone and other products which are under investigation.

The crude product (1·29 g.) recovered from the violet band was fractionally crystallised from methanol, giving 1 : 7-*dimethylfluorene* (gibberene) as needles and plates, m. p. 107—107·5° (715 mg.) (Found : C, 92·0, 92·2; H, 7·2, 7·4. $C_{15}H_{14}$ requires C, 92·7; H, 7·3%), and impure material, m. p. 88—94° (306 mg.). 1 : 7-Dimethylfluorene obtained in this way was identical (mixed m. p. and infra-red absorption spectrum) with a synthetic specimen. The m. p. of gibberene is given as 106—108° (Yabuta *et al., loc. cit.*). After crystallisation the fluorene did not fluoresce on alumina in ultra-violet light. It gave a blue colour with concentrated sulphuric acid. The unstable picrate, prepared by fusion, formed orange-red needles, m. p. 85—86°, not depressed by a synthetic specimen, but could not be recrystallised. The 1 : 3 : 5-trinitrobenzene adduct crystallised from ethanol in yellow needles, m. p. 98°, not depressed by a synthetic specimen. Yabuta *et al.* record m. p. 84—85° and 98° respectively for these derivatives of gibberene.

Dehydrogenation of the gums (*ca.* 6·0 g.) from the crystallisation mother-liquors of gibberellic acid also gave 1 : 7-dimethylfluorene (560 mg., m. p. 102—104°).

Oxidation of 1 : 7-*Dimethylfluorene.*—(i) Potassium permanganate (172 mg.) was added in portions (2 hr.) to a shaken solution of the fluorene (80 mg.) in acetone (4 ml.) at room temperature. When oxidation was complete the mixture was filtered. The product obtained by evaporation of the filtrate and acetone washings was chromatographed in light petroleum (5 ml., b. p. 40—60°) on alumina (17 × 0·8 cm.). A band fluorescing violet in ultra-violet light was eluted with light petroleum–ether (20 : 1) and on recovery gave unchanged starting material (20 mg.). Further elution removed a yellow band from which 1 : 7-*dimethylfluorenone* (62 mg.; m. p. 71—73°) was recovered. It crystallised from methanol in yellow plates and flat needles, m. p. 76·5—77°, identical (mixed m. p. and ultra-violet absorption spectrum) with a synthetic specimen (Found: C, 86·5, 86·4; H, 5·9, 5·95. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%). The m. p. of gibberenone is 77° (Yabuta *et al., loc. cit.*). Infra-red absorption (Nujol mull): CO, 1700 cm.$^{-1}$. 1 : 7-Dimethylfluorenone gave a purple colour with concentrated sulphuric acid.

The 2 : 4-*dinitrophenylhydrazone* crystallised from nitrobenzene–light petroleum (b. p. 80—100°) in orange-red needles, or from benzene in orange-red plates, m. p. 269—270° (Found: C, 65·0; H, 4·0; N, 14·3. $C_{21}H_{16}O_4N_4$ requires C, 64·9; H, 4·15; N, 14·4%). The *oxime*, prepared in pyridine (Neish, *Rec. Trav. chim.*, 1950, **69**, 207), crystallised from light petroleum (b. p. 80—100°) in pale yellow needles, m. p. 188·5—189·5° (Found: C, 80·1; H, 5·9; N, 6·0. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·9; N, 6·3%). Preparation of the oxime in alcohol–sodium acetate as described by Yabuta *et al.* gave a poor yield of impure material, m. p. 184°. Yabuta *et al.* give the m. p. of gibberenone oxime at 184°. The m. p.s of the derivatives were not depressed on admixture with synthetic specimens.

(ii) A solution of sodium dichromate dihydrate (0·45 g.) in 90% acetic acid (2·54 ml.) was added in 1 hr. to a boiling solution of 1 : 7-dimethylfluorene (104 mg.) in acetic acid (1·10 ml.). The mixture was heated under reflux for 1 hr., kept overnight at room temperature, and heated for 4 hr. more. On cooling, yellow needles separated [38 mg.; m. p. 328—332° (decomp.)] and were filtered off. The precipitate obtained by dilution of the filtrate was collected and washed with a little ether, giving a mixed acid fraction (4 mg., m. p. 180—294°); recovery from the ether washings gave starting material (32 mg.). The yellow needles were purified by precipitation from sodium carbonate solution with hydrochloric acid, followed by crystallisation from acetic acid, giving 1-*methylfluorenone*-7-*carboxylic acid* as light yellow needles, m. p. 330—331° (decomp.) (partial sublimation from *ca.* 250°) [Found: C, 75·4; H, 4·5%; equiv. (potentiometric), 236. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2%; equiv. (monobasic), 238]. Light absorption in EtOH: max. at 259, 268—269, ~290, 303, and ~325 mμ (log ε, 4·65, 4·78, 3·68, 3·68, and 3·45 respectively).

The *methyl ester*, prepared with diazomethane, crystallised from methanol in yellow needles m. p. 173—175° (Found: C, 75·8; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%). Light absorption (in EtOH): max. at 262·5, 272, 292, 303, and ~317 mμ (log ε, 4·74, 4·84, 3·79, 3·86, and 3·28 respectively). Infra-red absorption (carbonyl): 1706, 1715 cm.$^{-1}$ (Nujol mull); 1716, 1728 cm.$^{-1}$ (solution in carbon tetrachloride).

Decarboxylation of 1-*Methylfluorenone*-7-*carboxylic Acid.*—A mixture of the acid (30 mg.), copper chromite (33 mg.), and redistilled quinoline (0·6 ml.) was heated at 250—260° for 1 hr. in a stream of nitrogen, then cooled. Concentrated hydrochloric acid (2 ml.) and water (2 ml.) were added and the mixture was extracted with ether. The extract was washed with hydrochloric acid, aqueous sodium hydroxide, and water and then evaporated. The residue in light petroleum (b. p. 40—60°)–ether (5 : 1) was chromatographed on alumina (9 × 0·4 cm.). Elution in ultra-violet light with light petroleum gave first a violet-fluorescing eluate. Further elution with light petroleum–ether (10 : 1) removed a yellow band, the main part of which gave a solid (18 mg.; m. p. 96—98°) on recovery. This crystallised from methanol in yellow needles, m. p. 97—98°, identical (mixed m. p. and infra-red spectrum) with synthetic specimens of 1-methylfluorenone (Found: C, 86·35; H, 5·6. Calc. for $C_{14}H_{10}O$: C, 86·6; H, 5·2%). The m. p. (189°) of the crude oxime was not depressed on admixture with a synthetic specimen.

Oxidation of 1 : 7-*Dimethylfluorenone.*—(i) Sodium dichromate (0·23 g.) in 90% acetic acid (1·29 ml.) was added to a boiling solution of the fluorenone (124 mg.) in acetic acid (0·90 ml.) in 1¼ hr. The mixture was kept at room temperature for 70 hr., heated under reflux for 4 hr., then cooled, and the solid A (14 mg.) was collected. The filtrate was heated under reflux for ½ hr. with more oxidising solution (1·4 ml.) and, after cooling, solid B (4 mg.) was collected. The filtrate was diluted. Sublimation at 70° *in vacuo* of the precipitate and material recovered by ethereal extraction of the aqueous mother-liquor gave starting material (54 mg.).

Solids A and B crystallised from acetic acid in yellow needles, m. p. 328—330° (with sublimation and decomp.), not depressed on admixture with 1-methylfluorenone-7-carboxylic acid.

(ii) Potassium permanganate (1·00 g.) was added in portions (15 min.) to a solution of 1 : 7-dimethylfluorenone (208 mg.) in pyridine (1·6 ml.) and water (0·8 ml.) at 100°, small amounts of pyridine and water being added at intervals. The diluted mixture was filtered, the precipitate being washed with water and acetone. The filtrate and washings were concentrated to remove the acetone, and then acidified with hydrochloric acid. The precipitate was filtered off, washed with water, and extracted with cold 0·7N-potassium hydroxide. Starting material (13 mg.) remained.

Acidification of the alkaline extract gave a gelatinous precipitate which, after being washed and dried at 100°, formed an orange-yellow powder (155 mg.), m. p. *ca.* 300—320° (with sublimation). It was heated under reflux with toluene (10—15 ml.) for a few minutes and the hot toluene was decanted through a filter. The undissolved material and fluffy needles retained by the filter were re-oxidised (below). The cooled toluene extract gave yellow needles of 1-methylfluorenone-7-carboxylic acid (5 mg.), m. p. 328—330° (decomp.).

An acetone solution of the residue obtained by removal of the toluene mother-liquor was allowed to evaporate slowly. Part of the product formed yellow needles mixed with a number of deep red needles. The latter were separated by hand and had m. p. 206—208° (Kofler block), depressed on admixture with fluorenone-1-carboxylic acid, m. p. 197°. They probably consisted of 7-methylfluorenone-1-carboxylic acid.

The toluene-insoluble fractions were crystallised from acetic acid, and the first two fractions (121 mg.; m. p. 305—330°) were re-oxidised in dilute sodium carbonate (6 ml.) by dropwise addition of 5% aqueous potassium permanganate (3·7 ml.) in 1 hr. at 100°. After cooling, the mixture was filtered; the filtrate and water washings were acidified with hydrochloric acid and the gelatinous precipitate was separated, washed with water, and dried at 100°. Fractional crystallisation of the product (101 mg.) from acetic acid gave (i) 10 mg., m. p. 348—352° (decomp.), (ii) 80 mg., m. p. 335—340° (decomp.), and (iii) 7 mg., m. p. 305—335° (all with sublimation).

Fractions (i) and (ii) consisted mainly of fluorenone-1 : 7-dicarboxylic acid (Found : Equiv., 130. Calc. for $C_{15}H_8O_5$: Equiv., 134), but the infra-red spectrum suggested that both fractions contained a little 1-methylfluorenone-7-carboxylic acid. The m. p. of fraction (i) was not depressed on admixture with fluorenone-1 : 7-dicarboxylic acid prepared from retene.

Fractions (i) and (ii) with methanolic hydrogen chloride gave methyl fluorenone-1 : 7-dicarboxylate which crystallised from methanol in yellow plates and needles, m. p. 188—190°, identical (mixed m. p. and infra-red spectrum) with specimens prepared from retene and by oxidation of synthetic 1 : 7-dimethylfluorenone (Found : C, 68·8; H, 4·2; OMe, 21·15. Calc. for $C_{17}H_{12}O_5$: C, 68·9; H, 4·1; 2OMe, 21·0%).

The diethyl ester, prepared in an analogous manner, formed yellow plates and needles (from ethanol), m. p. 117—118°, identical (mixed m. p. and infra-red spectrum) with an authentic specimen prepared from retene (Found : C, 70·2; H, 5·1. Calc. for $C_{19}H_{16}O_5$: C, 70·4; H, 5·0%).

(iii) 1 : 7-Dimethylfluorenone was recovered (60%) when oxidised with potassium permanganate (equiv. to 7·6 O) in aqueous sodium hydroxide at 100°. Oxidation with dilute nitric acid (cf. Lothrop and Coffman, *J. Amer. Chem. Soc.*, 1941, **63**, 2564) gave a neutral nitrogenous product which was not investigated.

Synthetic Compounds.

1-*Methylfluorenone*.—(i) Prepared by Lothrop and Goodwin's method (*loc. cit.*), 1-methylfluorenone crystallised from methanol in yellow needles, m. p. 97·5—98·5°. The *oxime* crystallised from ethanol in pale yellow needles, m. p. 195—196° (Found : C, 80·4; H, 5·4. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3%).

(ii) (*a*) Benzenesulphonyl chloride (3·8 ml.) was added slowly to a cooled, stirred solution of the hydrazide of fluorene-1-carboxylic acid (6·5 g.) (Bergmann and Orchin, *J. Amer. Chem. Soc.*, 1949, **71**, 1111) in pyridine (250 ml.). Then the mixture was kept at room temperature for 3 hr. and poured on ice–hydrochloric acid. The precipitated *benzenesulphonhydrazide* crystallised from dilute ethanol (charcoal) in needles (7·95 g.), m. p. 222—223° (Found : C, 66·1; H, 4·6; N, 8·0. $C_{20}H_{16}O_3N_2S$ requires C, 65·9; H, 4·4; N, 7·7%).

Powdered anhydrous sodium carbonate (350 mg.) was added to this hydrazide (500 mg.) in ethylene glycol (5 ml.) at 160°. The mixture was kept at 160° for 1 min., diluted with hot water (25 ml.), cooled, and extracted with ether. The recovered material was sublimed *in vacuo* at 70—80°, giving *fluorene*-1-*aldehyde* (140 mg.), m. p. 79—81°, which crystallised from ethanol in needles, m. p. 90° (Found : C, 86·1; H, 5·4. $C_{14}H_{10}O$ requires C, 86·6; H, 5·3%). The 2 : 4-*dinitrophenylhydrazone* formed orange crystals (from nitrobenzene), m. p. 284—286° (Found : C, 64·4; H, 3·8. $C_{20}H_{14}O_4N_4$ requires C, 64·2; H, 3·8%). The *oxime* crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 138·5—139° (Found : C, 80·4; H, 5·8. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3%).

(*b*) The above aldehyde (200 mg.) in acetic acid (5 ml.) was hydrogenated at room temperature and pressure over a catalyst prepared *in situ* from palladium chloride (40 mg.), charcoal (200 mg.), and water (1 ml.). After 18 hr. the product was recovered and chromatographed in benzene (5 ml.) on alumina (5 × 0·8 cm.). Elution with benzene containing 0·5% of ether removed a band fluorescing very pale blue in ultra-violet light. Recovery gave 1-methylfluorene (160 mg.), m. p. 81—83°, which crystallised from methanol in needles, m. p. 84—86°. Lothrop and Goodwin (*loc. cit.*) record m. p. 87°. The 1 : 3 : 5-*trinitrobenzene* adduct crystallised from ethanol in yellow needles, m. p. 96° (Found: C, 61·3; H, 3·8; N, 10·7. $C_{14}H_{12},C_6H_3O_6N_3$ requires C, 61·1; H, 3·8; N, 10·7%).

(*c*) Oxidation of 1-methylfluorene (40 mg.) with potassium permanganate (40 mg.) in acetone and chromatography of the product, as described for 1 : 7-dimethylfluorenone, gave starting material (20 mg.) and 1-methylfluorenone (12 mg.; m. p. 94—95°) which crystallised from methanol in yellow needles, m. p. 98° not depressed on admixture with the material prepared as in (i).

Fluorenone-1 : 7-*dicarboxylic Acid.*—Prepared from retene by Bamberger and Hooker's method (*loc. cit.*) the acid formed, from acetic acid, yellow crystals which partly sublimed at *ca.* 300° and melted at 350—354° (decomp.) (Found: C, 67·0; H, 3·3. Calc. for $C_{15}H_8O_5$: C, 67·2; H, 3·0%). Bamberger and Hooker record that the acid is stable to 270°.

Methyl fluorenone-1 : 7-dicarboxylate, prepared with methanolic hydrogen chloride, crystallised from methanol–benzene in yellow needles and plates, m. p. 190—192° (Found: C, 69·0; H, 4·1; OMe, 20·7. Calc. for $C_{17}H_{12}O_5$: C, 68·9; H, 4·1; 2OMe, 21·0%). Recorded m. p., are: Bamberger and Hooker, 184°; Lux (*Monatsh.*, 1908, **29**, 763), 188—189° (corr.). Ethyl fluorenone-1 : 7-dicarboxylate crystallised from ethanol in yellow needles and plates, m. p. 118—118·5° (Found: C, 70·5; H, 5·0. Calc. for $C_{19}H_{16}O_5$: C, 70·4; H, 5·0%). Bamberger and Hooker record m. p. 114·5°.

2-*Amino*-5-*methylbenzoic Acid.*—5-Methyl-2-nitrobenzoic acid (m. p. 135—138°, from benzene: Giacolone, *Gazzetta*, 1935, **65**, 840) was catalytically hydrogenated in ethanol over Raney nickel at room temperature and pressure. 2-Amino-5-methylbenzoic acid crystallised from ethanol in needles, m. p. 176—178° (decomp.) (92%). Ehrlich (*Ber.*, 1901, **34**, 3366) gives m. p. 172·5°; Findeklee (*Ber.*, 1905, **38**, 3553) gives m. p. 175°.

2 : 6-*Dimethyl*-4-*oxo*-3 : 1-*benzoxazine.*—The above amino-acid (24·9 g.) was added in portions in 10 min. to acetic anhydride (60 ml.) at 140°. The mixture was then distilled until *ca.* 50 ml. of distillate were collected. The product obtained by cooling of the residue was crushed, filtered, washed with acetic anhydride, and crystallised once from the same solvent, giving the *benzoxazine* (21·95 g.), m. p. 121—122°; a recrystallised specimen (charcoal) formed needles, m. p. 125—126° (Found: C, 68·4; H, 5·2; N, 7·7. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·2; N, 8·0%).

2-*Acetamido*-2′ : 5-*dimethylbenzophenone.*—A Grignard reagent prepared from *o*-bromotoluene (10·6 g.) and magnesium (1·5 g.) in ether (40 ml.) was added dropwise during 1 hr. to a stirred solution of the oxazine (10·75 g.) in benzene (155 ml.) cooled in ice–salt. The gummy mixture was heated at 30° for 1 hr. and decomposed with dilute sulphuric acid. The material recovered from the organic layer by evaporation was steam-distilled. The cooled non-volatile fraction was filtered and the solid product was extracted with light petroleum (b. p. 40—60°; 150 ml.) containing 1% of methanol. A solid (2·3 g.) remained undissolved.

The extract was chromatographed on alumina (70 × 3·0 cm.) and eluted with the same solvent in ultra-violet light. A dark band (which preceded a blue band) was eluted and on recovery gave the *acetamido-compound* (8·6 g.) which crystallised from light petroleum (b. p. 60—80°) in very pale yellow needles, m. p. 88—89° (Found: C, 76·6; H, 6·3; N, 5·2. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%).

The petroleum-insoluble by-product was purified by dissolution in dilute aqueous sodium hydroxide, precipitation from the filtered solution with hydrochloric acid, and sublimation at 170°/10^{-4} mm. The sublimate formed needles of 2-acetamido-5-methylbenzoic acid, m. p. 191—193°, after crystallisation from acetone–light petroleum (b. p. 40—60°) and from ethyl methyl ketone (Found: C, 62·5; H, 6·0; N, 7·2. Calc. for $C_{10}H_{11}O_3N$: C, 62·2; H, 5·7; N, 7·25%). The m. p. of the acetate has been recorded as 193—194° (von Miller and Ohler, *Ber.*, 1891, **24**, 1910). Hydrolysis of the by-product with boiling 70% sulphuric acid for 30 min. gave the free acid, m. p. and mixed m. p. 170—173°.

2-*Amino*-2′ : 5-*diethylbenzophenone.*—The crude acetamido-compound (8·6 g.) was hydrolysed by 70% sulphuric acid (81 ml.) on the steam-bath for 3 hr. The mixture was cooled, diluted, made alkaline with sodium hydroxide, and extracted with ether. The product recovered from the extract was dissolved in hot hydrochloric acid. After filtration from an insoluble gum, the cooled solution was made alkaline and the product was recovered in ether. The concentrated ethereal extract was passed through a short column of alkaline alumina (B.D.H. activated for 3 hr. at 250°/17 mm.) and then evaporated, giving the amine as a yellow oil (6·1 g.). A specimen acetylated with 1 : 1 acetic anhydride–acetic acid gave the monoacetate, m. p. and mixed m. p. 88—89°.

1 : 7-*Dimethylfluorenone*.—The above amine (6·1 g.) was dissolved in dilute sulphuric acid (15 ml. of concentrated acid and 30 ml. of water) by heat and then diazotised at 0° with sodium nitrite (1·90 g.) in water (40 ml.). The diazonium solution was heated at 80° for ½ hr., then at 100° for ½ hr., and cooled. An ethereal extract of the mixture was washed several times with 1% aqueous sodium hydroxide and then evaporated. A solution of the residue in light petroleum (b. p. 40—60°) containing 10% of ether was chromatographed on alumina (22 × 4 cm.). Elution with light petroleum (b. p. 40—60°)–ether (20 : 1) in ultra-violet light removed a yellow-brown band which gave 1 : 7-dimethylfluorenone, m. p. 74—76° (3·23 g.), on evaporation. It crystallised from methanol in yellow plates and needles, m. p. 77° (Found : C, 86·7; H, 5·6. Calc. for $C_{15}H_{12}O$: C, 86·5; H, 5·8%). Light absorption (in EtOH) : max. at 254, 262, 276, 289, 300, 316, ~322, and 331 mμ (log ε, 4·76, 4·96, 3·34, 3·43, 3·48, 3·30, 3·23, and 3·22 respectively).

The oxime crystallised from light petroleum (b. p. 80—100°) in pale yellow needles, m.p. 188·5—189·5° (Found : C, 80·8; H, 6·0; N, 6·4. Calc. for $C_{15}H_{13}ON$: C, 80·7; H, 5·9; N, 6·3%). The 2 : 4-dinitrophenylhydrazone crystallised from benzene in orange-red leaflets, m. p. 269—270° (Found : C, 64·7; H, 4·3; N, 14·45. Calc. for $C_{21}H_{16}O_4N_4$: C, 64·9; H, 4·15; N, 14·4%).

Methyl Fluorenone-1 : 7-*dicarboxylate*.—Oxidation of 1 : 7-dimethylfluorenone with potassium permanganate in pyridine followed by further oxidation of the crude product in sodium carbonate as described previously gave fluorenone-1 : 7-dicarboxylic acid. After one crystallisation from acetic acid, the acid, m. p. 345—350° (decomp.), was esterified with methanolic hydrogen chloride, giving the methyl ester which crystallised from methanol–benzene in yellow needles and plates, m. p. 189—191° (Found : C, 69·0; H, 4·25. Calc. for $C_{17}H_{12}O_5$: C, 68·9; H, 4·1%).

1 : 7-*Dimethylfluorene*.—Reduction of 1 : 7-dimethylfluorenone (1·004 g.) with hydrazine hydrate as described for the 3 : 6-isomer by Chardonnens and Würmli (*Helv. Chim. Acta*, 1946, **29**, 922) gave a crude product, m. p. 103—107°. This, in light petroleum (b. p. 40—60°) (40 ml.), was chromatographed on alumina (30 × 1·2 cm.), and eluted with the same solvent. Impurities fluorescing blue in ultra-violet light remained at the top of the column. Recovery gave pure 1 : 7-dimethylfluorene, m. p. 108—108·5° (877 mg.). It crystallised from methanol in plates, needles, and curled hair-like needles (Found : C, 92·7; H, 7·2. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%). Light absorption (in EtOH) : max. at 269, ~275, ~293, ~297, and 304 mμ (log ε, 4·44, 4·33, 3·95, 3·90, and 3·95 respectively).

The unstable picrate formed orange-red needles, m. p. 85—86°, and could not be recrystallised. The 1 : 3 : 5-*trinitrobenzene* adduct crystallised from ethanol in yellow needles, m. p. 98—98·5° (Found : C, 61·8; H, 4·2; N, 10·5. $C_{15}H_{14},C_6H_3O_6N_3$ requires C, 61·9; H, 4·2; N, 10·3%).

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