

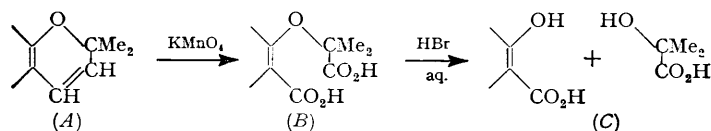
804. *The Chemistry of Extractives from Hardwoods. Part XIV.**
The Constitution of Jacareubin, a Pyranoxanthone from Calophyllum brasiliense.

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A yellow colouring-matter, jacareubin, $C_{18}H_{14}O_6$, has been extracted from the wood of *Calophyllum brasiliense*. The compound contains a reactive double bond, and its trimethyl ether can be oxidised to a dicarboxylic acid, $C_{21}H_{20}O_{10}$, which when hydrolysed with boiling hydrobromic acid yields α -hydroxyisobutyric acid. Simultaneously, the nucleus is demethylated and decarboxylated to give a tetrahydric phenol, $C_{13}H_8O_6$, also obtained directly from jacareubin by alkali fusion and identified by synthesis as 1 : 3 : 5 : 6-tetrahydroxyxanthone. A pyranoxanthone structure is thus attributable to the natural product, which from its formation of a methylene ether and from the chelate character of the remaining hydroxyl group is regarded as 1 : 5 : 6-trihydroxy-2' : 2'-dimethylpyrano(5' : 6'-2 : 3 or -4 : 3)xanthone.

THE tropical American tree *Calophyllum brasiliense* Camb., family *Guttiferae*, produces a strong and durable timber which is available commercially and known as Santa Maria or jacareuba. The heartwood varies from pink to light mahogany in colour, but on close examination of a typical commercial specimen it was observed that the minute deposits within the cavities were occasionally bright yellow. The crude colouring matter can be obtained from the powdered wood by ether-extraction with or without previous treatment with boiling light petroleum. From it a deep yellow crystalline constituent, $C_{18}H_{14}O_6$, has been isolated which we have called jacareubin.

Jacareubin yields a triacetate and, from its formation with diazomethane of a dimethyl ether having a pronounced ferric reaction, it was evident that all three hydroxyl groups were phenolic. More vigorous treatment, with methyl sulphate-potassium carbonate, was required in order to prepare a trimethyl ether. A Zeisel estimation showed that the parent compound is devoid of simple alkyloxy-groups, and it does not possess carbonyl reactions. Reduction to a dihydro-derivative by catalytic hydrogenation therefore implied the presence of an olefinic bond, and the oxidation of trimethyljacareubin with potassium permanganate in acetone to a dicarboxylic acid of identical carbon content, trimethyljacareubic acid, $C_{21}H_{20}O_{10}$, proved the double bond to be part of a cyclic structure. The action of boiling hydrobromic acid on trimethyljacareubic acid liberated α -hydroxyisobutyric acid, identified by comparison of its crystalline *p*-bromophenacyl ester with an authentic specimen. These results are consistent with the degradation of a 2 : 2-dimethylpyran nucleus, the reactions following the course shown by the partial formulæ (A) to (C).



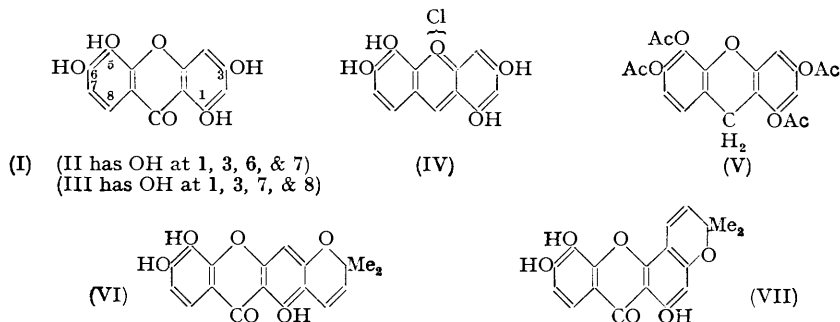
The principal hydrolysis product of trimethyljacareubic acid was, however, no longer a carboxylic acid but consisted of a tetrahydric phenol, $C_{13}H_8O_6$, both decarboxylation and demethylation having occurred during the treatment with hydrobromic acid. With diazomethane the new phenol yielded a trimethyl ether of which an acetyl derivative was prepared. The trimethyl ether exhibited a marked ferric reaction, and a tetramethyl derivative resulted only from the use of more vigorous methylation conditions.

Further indications of the 2 : 2-dimethylpyran nucleus were obtained from the fusion of jacareubin with alkalis: acetone distilled from the mixture, this being a well-known feature of the 2 : 2-dimethylpyran series. The alkali-soluble residue consisted of the same

tetrahydric phenol, $C_{13}H_8O_6$, as was derived from the hydrolysis of trimethyljacareubic acid.

When trimethyljacareubic acid was heated in quinoline with a copper catalyst, which by analogy with the behaviour of similar compounds, *e.g.*, the isomeric tephrosincarboxylic acids (Clark, *J. Amer. Chem. Soc.*, 1932, **54**, 3000), was expected to eliminate the α -hydroxyisobutyryl residue, decarboxylation accompanied by demethylation of a methoxyl group also took place. The product, $C_{15}H_{12}O_6$, was thus a hydroxy-dimethoxy-compound and its relation to the phenol $C_{13}H_8O_6$ was shown by their formation of identical fully methylated derivatives. The pyrolytic decomposition of trimethyljacareubic acid is therefore similar to that of acronycinic acid [an oxidation product of acronycine, 4-methoxy-2':2':*N*-trimethylpyrano(5':6'-1:2 or -2:3)acridone], which by the loss of α -hydroxyisobutyryl, carboxyl and an *O*-methyl group yields 2:4-dihydroxy-*N*-methylacridone (Brown, Drummond, Lahey, and Thomas, *Austral. J. Sci. Res.*, 1949, *A*, **2**, 622).

From its molecular formula and the inert character of its remaining oxygen atoms there was little difficulty in recognising the tetrahydric phenol, $C_{13}H_8O_6$, as a derivative of xanthone. The diminished reactivity of one of the hydroxyl groups was accordingly explicable on grounds of chelation, thus enabling it to be located at the 1-position. Moreover, both jacareubin and dihydrojacareubin gave, with boracetic anhydride-acetic anhydride, complexes which when treated with water yielded diacetyl derivatives exhibiting strong ferric reactions. An examination of the infra-red absorption of both dimethyl- and trimethyl-jacareubin in chloroform solutions, kindly carried out by Dr. M. St. C. Flett by arrangement with Dr. M. A. T. Rogers, Imperial Chemical Industries Ltd., showed no bands characteristic of unbonded hydroxyl groups.



Further evidence concerning the disposition of the remaining hydroxyl groups was obtained by the preparation from jacareubin of a methylene ether, thus proving two of them to be *ortho* to each other. Moreover, it was apparent from the yellow colour of the product and from its marked ferric reaction that the chelated hydroxyl was not one of those concerned in methylene ether formation. The fourth hydroxyl group, *i.e.*, that formed with the destruction of the dimethylpyran ring, was tentatively considered to be part of a phloroglucinol nucleus, the lability of the aromatic carboxyl group in trimethyljacareubic acid evident in its various reactions being characteristic of a 2:4- or 2:6-dihydroxybenzoic acid and especially of phloroglucinolcarboxylic acid. If a phloroglucinol nucleus is in fact present in jacareubin, then the possible structures of the tetrahydroxyxanthone are thereby restricted to (I) and to two others, (II) and (III) in which the vicinal hydroxyl groups are respectively at the 6:7- and the 7:8-positions. An account of the synthesis of several tetrahydroxyxanthenes, including (I) and (II), has been published by Tanase (*J. Pharm. Soc. Japan*, 1941, **61**, 341), but the article, written in Japanese, was not available in *Gt. Britain*, nor does it appear to have been abstracted. We are greatly indebted to Professor S. Hattori, Tokyo University, for a translation of the experimental section of the memoir, in which the general method is illustrated by several examples. Few details are recorded for the relevant xanthenes (I) and (II), but the melting point of 1-hydroxy-3:5:6-trimethoxyxanthone was observed to correspond with that of the trimethyl ether of the xanthone $C_{13}H_8O_3$. 1:3:5:6-Tetrahydroxyxanthone was there-

fore synthesised by the method employed by Tanase (*loc. cit.*) from phloroglucinol and pyrogallol- α -aldehyde in acetic acid containing aqueous hydrochloric acid. The resulting xanthylum chloride (IV) was then converted into its anhydro-base which was reduced in acetic anhydride with zinc dust to the corresponding tetra-acetoxyxanthen (V), the xanthone (I) being obtained by oxidation with chromic acid and hydrolysis. Comparison of the appropriate derivatives thereupon confirmed the identity of the compound $C_{13}H_8O_6$. Since two of the hydroxyl groups in jacareubin are *ortho* to each other and the third is chelated with the carbonyl group, it follows that the natural product is 1 : 5 : 6-trihydroxy-2' : 2'-dimethylpyrano(5' : 6'-2 : 3 or -4 : 3)xanthone, (VI or VII). As with the very similar pyranoacridine alkaloid acronycine already mentioned, it has not been possible to decide between these alternative structures (cf., however, Brown, *Austral. J. Sci. Res.*, 1950, A, 3, 607, footnote).

The discovery of jacareubin introduces yet another example of a naturally occurring heterocyclic system (pyranoxanthone) incorporating the 2 : 2-dimethylpyran nucleus. Others include the simple dimethylbenzopyrans, *e.g.*, evodione (Wright, *J.*, 1948, 2005), the dimethylpyrano-coumarins, *e.g.*, xanthyletin (Bell, Bridge, and Robertson, *J.*, 1937, 1542) and xanthoxyletin (Robertson and Subramaniam, *J.*, 1937, 286), -acridone, acronycine (Brown *et al.*, 1949, *loc. cit.*), -isoflavones, osagin and pomiferin (Wolfrom, Harris, Johnson, Mahan, Moffett, and Wildi *J. Amer. Chem. Soc.*, 1946, 68, 406), and -chromanochromanones, deguelin, tephrosin, and toxicarol.

EXPERIMENTAL

Isolation of Jacareubin.—The wood, obtained commercially, was examined by Mr. B. J. Rendle, D.S.I.R. Forest Products Research Laboratory, to whom we are grateful for the following report. " *Calophyllum* is a large genus of many species difficult to distinguish anatomically. In this case I can only say that it is a species of *Calophyllum*. Jacareuba from Brazil is the only species of *Calophyllum* currently imported in quantity so there is a strong presumption that your material is correctly named."

The coarsely powdered heartwood (3.5 kg.) was extracted by continuous percolation with boiling ether for 24 hr. The solvent was then evaporated and, by treating the residue with boiling light petroleum, a friable red-brown solid (24—25 g.) was obtained. When a solution of the solid (5 g.) in acetone was concentrated to 20 c.c. crystalline *jacareubin* was deposited during 1—2 weeks but the compound was more conveniently obtained by dissolving the crude extract (18 g.) in a mixture of acetone (300 c.c.) and acetic acid (50 c.c.); evaporation under reduced pressure to 60 c.c. gave within 3 hr. a precipitate which when crystallised from methanol yielded *jacareubin* (8 g.) of m. p. 250° (decomp.). Repeated crystallisation from methanol gave the pure product as bright yellow prisms, m. p. 256—257° (decomp.) [Found : C, 65.9, 66.0; H, 4.3, 4.6%; *M*, (Rast) 294, (*X*-ray diffraction) 1287/*n*. $C_{18}H_{14}O_6$ requires C, 66.25; H, 4.3%; *M*, 326]. For the *X*-ray molecular-weight estimation the authors are indebted to Dr. S. C. Wallwork. Light absorption in ethanol : max. at 2400 ($\epsilon = 12,200$), 2790 ($\epsilon = 40,200$) and 3340 Å ($\epsilon = 18,200$). *Jacareubin* dissolved readily in hot acetone, ethyl acetate, and simple alcohols, and sparingly in ether, chloroform, and benzene. Its ferric reaction in ethanol is green; with sodium amalgam-ethanol it gives a purple-violet colour changed by acid to cherry-red, the latter similar to that produced by magnesium-hydrochloric acid. With zinc-acetic acid a red-brown colour results. Solutions of *jacareubin* in strong acids are yellow to yellow-orange and in alkalis red-brown and darkening in air. *Triacetyljacareubin* (prepared with acetic anhydride-pyridine) separated from methanol in feathery needles, m. p. 212—213° (Found : C, 63.7; H, 4.6. $C_{24}H_{20}O_9$ requires C, 63.7; H, 4.5%).

O⁵O⁶-Dimethyljacareubin.—*Jacareubin* (1.5 g.), dissolved in methanol (20 c.c.), was treated at 0° with ethereal diazomethane and after 8 hr. the excess of reagent was destroyed with acetic acid. When concentrated to 20 c.c. the solution deposited *O⁵O⁶-dimethyljacareubin* which crystallised from methanol in bright yellow iridescent long rectangular plates (1.2 g.), m. p. 191—192°, having a green ferric reaction in ethanol (Found, in a sample dried at 120° *in vacuo* : C, 67.8; H, 5.3; OMe, 17.8. $C_{20}H_{18}O_6$ requires C, 67.8; H, 5.1; OMe, 17.5%).

OOO-Trimethyljacareubin.—With methyl sulphate and potassium carbonate in boiling acetone (6 hr.) *jacareubin* (5 g.) yielded the *trimethyl ether* which crystallised from methanol (300 c.c.; charcoal) in needles (4.5 g.), m. p. 182—183° (Found : C, 68.5; H, 5.5; OMe, 24.5. $C_{21}H_{20}O_6$

requires C, 68.5; H, 5.5; 3OMe, 25.3%). The product gave no ferric reaction and did not react with acetylating agents.

Dihydrojacareubin.—A solution of jacareubin in ethanol containing palladised charcoal absorbed hydrogen at room temperature and pressure equivalent to 1 mol. The liquid was heated to boiling and filtered, and the *dihydrojacareubin* which later separated was recrystallised from methanol; it formed dull yellow prisms, m. p. 245° (decomp.) (Found: C, 65.7; H, 4.9. C₁₈H₁₆O₆ requires C, 65.85; H, 4.9%). A solution in methanol treated with ethereal diazomethane gave *dihydro-OO-dimethyljacareubin*, bright yellow lath-shaped crystals (from methanol), m. p. 138—139°, having in ethanol solution a dark green ferric reaction (Found, in a specimen dried at 120° *in vacuo*: C, 67.8; H, 5.7; OMe, 16.2. C₂₀H₂₀O₆ requires C, 67.4; H, 5.7; 2OMe, 17.4%).

O¹O⁵O⁶-*Trimethyljacareubic Acid*.—A solution of trimethyljacareubin (5 g.) in boiling acetone (300 c.c.) was treated during 8 hr. with powdered potassium permanganate (12 g.). The mixture was cooled and the solid collected and stirred with water (200 c.c.). Treatment of the aqueous solution with sulphur dioxide precipitated O¹O⁵O⁶-*trimethyljacareubic acid* which crystallised from aqueous methanol in rosettes of needles (4.9 g.), m. p. 249° (decomp.; rapid heating) (Found, in a sample dried *in vacuo* at 120°: C, 58.2; H, 4.6; OMe, 21.4%; equiv., 219. C₂₁H₂₀O₁₀ requires C, 58.3; H, 4.7; 3OMe, 21.5%; equiv., 216). The *dimethyl* ester, prepared with diazomethane, crystallised from methanol in needles, m. p. 186—187° (Found, in a sample dried *in vacuo* at 120°: C, 60.0; H, 5.1; OMe, 33.0. C₂₃H₂₄O₁₀ requires C, 60.0; H, 5.25; 5OMe, 33.6%).

Hydrolysis of Trimethyljacareubic Acid.—Trimethyljacareubic acid (5 g.) was refluxed with hydrobromic acid (150 c.c.; *d* 1.42) until dissolved (1½ hr.). After further heating (¼ hr.) the solution was cooled and diluted with water, and the crystalline precipitate collected. Recrystallised from methanol it gave 1 : 3 : 5 : 6-*tetrahydroxyxanthone* (2.85 g.) in pale yellow needles, m. p. ca. 310° (decomp.) (Found: C, 60.2; H, 2.6. C₁₃H₈O₆ requires C, 60.0; H, 3.1%). The ferric reaction of the xanthone in ethanol was green. With acetic anhydride-pyridine 1 : 3 : 5 : 6-*tetra-acetoxxyxanthone* was obtained, and it crystallised from acetone-methanol in colourless fibrous needles, m. p. 246° (decomp.) (Found: C, 58.8; H, 4.0. C₂₁H₁₆O₁₀ requires C, 58.9; H, 3.8%). Methylation of the tetrahydroxyxanthone with diazomethane in ether-methanol gave the 3 : 5 : 6-*trimethyl ether*, yellow lath-shaped prisms (from methanol), m. p. 181—182° (Found: C, 63.4; H, 4.3; OMe, 29.3. C₁₆H₁₄O₆ requires C, 63.6; H, 4.7; 3OMe, 30.8%). The *trimethyl ether acetate* crystallised from methanol in colourless prisms, m. p. 147—148° (Found: C, 62.9; H, 4.8; OMe, 27.4. C₁₈H₁₆O₇ requires C, 62.8; H, 4.7; 3OMe, 27.0%).

The diluted acid solution from which the xanthone had been precipitated was saturated with ammonium sulphate and exhaustively extracted with ether. The ethereal solution was washed with a little saturated aqueous ammonium sulphate and mixed with water (100 c.c.), and the ether was evaporated. The residual aqueous solution was neutralised with 0.1N-sodium hydroxide (phenolphthalein), and treatment with *p*-bromophenacyl bromide (0.8 g., 75% theory) and sufficient ethanol to form a clear solution at the b. p. gave after 1 hr.' refluxing *p*-*bromophenacyl α*-hydroxyisobutyrate. The ester could be crystallised from aqueous methanol or light petroleum (b. p. 80—100°) and formed needles, m. p. 155—157° alone or mixed with a specimen prepared from synthetic *α*-hydroxyisobutyric acid (Bargellini, *Gazzetta*, 1906, 36, II, 337) (Found: C, 47.6; H, 4.1; Br, 25.0. C₁₂H₁₃O₄Br requires C, 47.9; H, 4.35; Br, 26.5%).

Alkali Hydrolysis of Jacareubin.—(a) A solution of jacareubin (0.2 g.) in 33% aqueous potassium hydroxide (10 c.c.) was heated on a steam-bath for 8 hr. After the addition of water (200 c.c.) the mixture was concentrated, a distillate of 100 c.c. being collected. The 2 : 4-dinitrophenylhydrazone (0.015 g.), precipitated by a 2% solution of the reagent (50 c.c.), had m. p. 118°. Paper chromatography with heptane-methanol (Meigh, *Nature*, 1952, 170, 579), and use of formaldehyde and acetone 2 : 4-dinitrophenylhydrazones for comparison, enabled the product to be identified as the acetone derivative, no formaldehyde 2 : 4-dinitrophenylhydrazone being detected.

The residual alkaline solution was acidified and extracted with ether (3 × 25 c.c.), and the product removed from the ethereal solution with sodium hydrogen carbonate was crystallised from methanol. The yellow solid thus isolated, m. p. ca. 300° (decomp.), was methylated with excess of diazomethane in ether, and the product crystallised from methanol. It then had m. p. 181—182° and was identical (mixed m. p.) with 1-hydroxy-3 : 5 : 6-trimethoxyxanthone (see above).

(b) Jacareubin (1 g.) was heated under nitrogen at 180° for 15 min. with a mixture of sodium and potassium hydroxides (1 : 1; 10 g.) containing a little water. The whole was then dissolved

in water and acidified (hydrochloric acid). Isolation as in (a) and distillation of the product ($200^{\circ}/5 \times 10^{-4}$ mm.) yielded a pale yellow solid (0.05 g.) identified as 1 : 3 : 5 : 6-tetrahydroxy-xanthone by its formation with diazomethane of the 3 : 5 : 6-trimethyl ether, m. p. and mixed m. p. 181—182°.

Pyrolysis of OOO-Trimethyljacareubic Acid.—A solution of trimethyljacareubic acid (1.7 g.) in quinoline (80 c.c.) containing freshly precipitated copper (5 g.) was heated under reflux in a stream of nitrogen for 5 hr. The course of the reaction was followed by passing the issuing gas into aqueous barium hydroxide. The cooled mixture was poured into a large volume of ether, and the filtered liquid was washed with 5% aqueous sodium hydrogen carbonate and then with excess of dilute hydrochloric acid. The washed and dried ethereal solution was evaporated, to leave an orange-red solid which by recrystallisation from methanol gave supposedly 1 : 3-dihydroxy-5 : 6-dimethoxyxanthone as pale orange needles (0.5 g.), m. p. 288—290° (decomp.) (Found : C, 62.6; H, 4.5; OMe, 20.9. $C_{15}H_{12}O_6$ requires C, 62.5; H, 4.2; 2OMe, 21.5%). The diacetate crystallised from methanol in colourless needles, m. p. 162—163° (Found : C, 61.7; H, 4.7; OMe, 17.9. $C_{19}H_{16}O_8$ requires C, 61.3; H, 4.3; 2OMe, 16.8%). When the dihydroxy-dimethoxyxanthone was refluxed in acetone with methyl sulphate-potassium carbonate for 24 hr., 1 : 3 : 5 : 6-tetramethoxyxanthone was obtained as a monohydrate crystallising from benzene in needles, m. p. 136—137° (Found : C, 61.7; H, 5.9; OMe, 35.5. $C_{17}H_{16}O_6 \cdot H_2O$ requires C, 61.8; H, 5.4; 4OMe, 37.1%). Drying at 120° *in vacuo* gave the anhydrous compound, m. p. 151—152° (Found : C, 64.8; H, 5.2; OMe, 36.8. $C_{17}H_{16}O_6$ requires C, 64.55; H, 5.1; 4OMe, 39.3%).

O⁵O⁶-Diacetyljacareubin.—A solution of jacareubin (1 g.) and boroacetic anhydride (1 g.) in acetic anhydride (7.5 c.c.) was heated under reflux for 3 min. The cherry-red liquid remained clear when cooled and was then treated with dry ether (20 c.c.). The crystalline solid which separated during 2 hr. at 0° was collected, washed with ether, and shaken with water (50 c.c.). When recrystallised from methanol the yellow-orange solid gave the diacetyljacareubin as bright yellow needles, m. p. 173—174°, having a dark green ferric reaction (Found : C, 64.4; H, 4.4. $C_{22}H_{18}O_8$ requires C, 64.4; H, 4.4%).

O⁵O⁶-Diacetyldihydrojacareubin.—A suspension of dihydrojacareubin (2 g.) in acetic anhydride (10 c.c.) with boroacetic anhydride (2.5 g.) was heated under reflux until a clear solution was obtained which was shortly afterwards cooled and diluted with ether (25 c.c.). The solid deposited at 0° was collected after 2 hr. and treated with water, and finally crystallised from methanol. The resulting diacetate (1.7 g.) formed yellow needles, m. p. 172—173°, exhibiting a green ferric reaction (Found : C, 64.1; H, 5.0. $C_{22}H_{20}O_8$ requires C, 64.1; H, 4.9%).

Methylation of Diacetyldihydrojacareubin.—The diacetate (2.25 g.) was heated under reflux with methyl sulphate-potassium carbonate in acetone for 6 hr. The then almost colourless mixture was evaporated and shaken with ether and 2N-sodium hydroxide for $\frac{1}{2}$ hr. The ethereal layer yielded dihydro-O¹O⁵O⁶-trimethyljacareubin which crystallised from methanol (charcoal) in colourless needles (1.3 g.), m. p. 156—156.5° (Found : C, 67.9; H, 6.0; OMe, 23.4. $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.0; 3OMe, 24.6%). It did not depress the m. p. of a sample prepared by the hydrogenation of trimethyljacareubin in presence of palladised charcoal.

Acidification of the sodium hydroxide solution gave dihydro-O¹O⁵(or O¹O⁶)-dimethyljacareubin (1 g.), colourless needles (from methanol), m. p. 217—218° (Found, in a specimen dried at 120° *in vacuo* : C, 67.0; H, 5.8; OMe, 17.0. $C_{20}H_{20}O_6$ requires C, 67.4; H, 5.7; 2OMe, 17.4%). The dimethyl ether gave in ethanol a yellow colour with ferric chloride.

Jacareubin 5 : 6-Methylene Ether.—A solution of jacareubin (0.5 g.) in acetone was heated with aqueous sodium hydroxide (0.5 g. in 10 c.c.) at 45° in an atmosphere of coal gas. Methylene sulphate (Baker and Field, *J.*, 1931, 1765) (0.7 g.) was gradually added with stirring and after $\frac{1}{2}$ hr. the mixture was poured into dilute hydrochloric acid. The orange-red precipitate was dried and crystallised from methanol-ethyl acetate, yielding the 5 : 6-methylene ether (0.2 g.) as bright yellow iridescent lath-shaped crystals, m. p. 220°, having in alcohol a green ferric reaction (Found : C, 67.7; H, 3.9. $C_{19}H_{14}O_6$ requires C, 67.45; H, 4.2%).

Synthesis of 1 : 3 : 5 : 6-Tetrahydroxyxanthone (cf. Tanase, *loc. cit.*).—A solution of phloroglucinol (4.5 g.) and 2 : 3 : 4-trihydroxybenzaldehyde (5 g.) in acetic acid (40 c.c.) and concentrated hydrochloric acid (15 c.c.) was heated under reflux for 15 min. The bright red 1 : 3 : 5 : 6-tetrahydroxyxanthylum chloride (7.55 g.) was collected 8 hr. later, washed with acetic acid-hydrochloric acid and dissolved in acetic anhydride (40 c.c.). Zinc dust (12 g.) was added in portions to the boiling solution which finally became pale yellow, whereupon it was filtered and the filtrate poured into water (500 c.c.). The friable biscuit-coloured solid (1 : 3 : 5 : 6-tetra-acetoxanthone) was collected, dissolved in acetic anhydride (50 c.c.) and acetic acid (20 c.c.),

and treated with 5% chromium trioxide in acetic acid (diphenylamine indicator) in 50% excess. The 1:3:5:6-tetra-acetoxyanthone which had separated after 3 hr. at room temperature when recrystallised from 25% aqueous acetic acid formed needles (1.2 g.), m. p. 246° (decomp.; rapid heating) (Found: C, 58.9; H, 4.1%).

A solution of the tetra-acetate (1 g.) prepared by vigorous stirring with cold concentrated sulphuric acid (10 c.c.) was poured into water after 10 min., and the precipitate collected and crystallised from benzene. The 1:3:5:6-tetrahydroxyxanthone (0.4 g.) thus prepared had m. p. *ca.* 310° (decomp.) (Found: C, 59.8; H, 3.3%). Methylation with diazomethane gave 1-hydroxy-3:5:6-trimethoxyxanthone, m. p. and mixed m. p. 182—183° (Found: C, 63.8; H, 4.7; OMe, 29.3%), from which was obtained the acetyl derivative, m. p. 147—148° (Found: C, 62.6; H, 4.7; OMe, 26.5; OAc, 13.1%). Prolonged methylation ($\text{Me}_2\text{SO}_4\text{-K}_2\text{CO}_3$ in acetone) gave 1:3:5:6-tetramethoxyxanthone monohydrate, m. p. 136—137°, which after drying at 120° *in vacuo* had m. p. and mixed m. p. 151—152° (Found: C, 64.3; H, 5.1%).

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[Received, July 28th, 1953.]
