CXXXV.—*The Constitution of Irigenin and Iridin. Part I.*

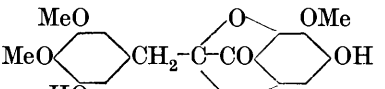
By WILSON BAKER.

THE glucoside iridin * contained in the dried rhizomes of the *Iris florentina* has been carefully examined by de Laire and Tiemann (*Ber.*, 1893, **26**, 2010), who found that on hydrolysis with dilute acid it gave one molecule of glucose and one molecule of irigenin, a phenolic substance of empirical formula $C_{18}H_{16}O_8$. This compound gave an impure dibenzoyl derivative by the Schotten–Baumann reaction and a so-called diacetyl derivative which readily underwent partial hydrolysis with production of a "monoacetylirigenin." Decomposition with aqueous potassium hydroxide in an atmosphere of hydrogen gave one molecule of iridic acid (3-hydroxy-4 : 5-dimethoxyphenylacetic acid), one molecule of iretol (methoxyphloroglucinol), and one molecule of formic acid. These authors assigned to it the formula (I).

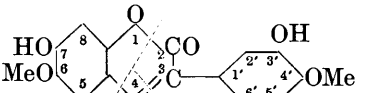
The formulation of irigenin by (I) is, however, not justified by the experimental evidence, no satisfactory proof being offered that

* This compound must not be confused with the "iridin" of the Pharmacopœia ("The Extra Pharmacopœia," Martindale and Westcott, 17th ed., 1920, p. 802), which is a dark brown, powdered resin, obtained by extraction of the root of the North American "blue flag" (*Iris versicolor*) with 60% alcohol. An examination of its constituents by Power and Salway (*Amer. J. Pharm.*, 1911, **83**, 1) showed that it was entirely lacking in the glucoside iridin.

the two aromatic nuclei are united through a straight chain of three carbon atoms. The essential correctness of the work has been borne out by the syntheses of iridic acid by Mauthner (*Annalen*, 1926, **449**, 102) and of iretol by Kohner (*Monatsh.*, 1899, **20**, 928).



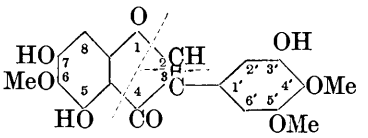
(I.)



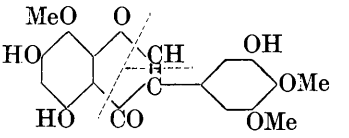
(II.)

Bargellini has recently expressed the view (*Gazzetta*, 1925, **55**, 945) that irigenin should be regarded as a coumarin derivative (II). Although such a structure would account for most of its properties, including its decomposition by alkali (see Bargellini, *loc. cit.*; Baker, J., 1925, **127**, 2351), yet the production of de Laire and Tiemann's dibenzoyl derivative cannot readily be interpreted by this formula (de Laire and Tiemann's diacetyl- and monoacetyl-irigenin are referred to later); for (II) should give a tribenzoyl derivative, since the hydroxyl group occupying position 5 in coumarins of this type (unlike chromones, see below) possesses normal phenolic properties (see 5 : 7 : 4′-trihydroxy-4-phenylcoumarin, Bargellini, *Atti R. Accad. Lincei*, 1925, **2**, 32; 5 : 7-dihydroxy-3-phenylcoumarin, Bargellini, *Gazzetta*, 1927, **57**, 461; 5 : 7 : 4′-trihydroxy-3-phenylcoumarin, Bargellini and Monti, *ibid.*, p. 464).

It seemed much more probable that irigenin should be represented by one of the formulæ (III) and (IV) as belonging to the *iso*flavone



(III.)



(IV.)

(3-phenylchromone) group, two members of which, genistein and prunetin, are now known to occur in nature (Baker and Robinson, J., 1925, **127**, 1981; 1926, 2713). These formulæ represent irigenin as possessing *three* phenolic hydroxyl groups, one of which, occupying position 5 ortho to the carbonyl group, would have very weak phenolic properties, not forming an alkali salt in aqueous solution and being difficult to methylate with methyl iodide, but which would yet give a positive ferric chloride reaction and an easily hydrolysable acetyl derivative. Thus the formation of the dibenzoyl derivative is satisfactorily accounted for owing to the weakly phenolic nature of the hydroxyl group in the 5-position.

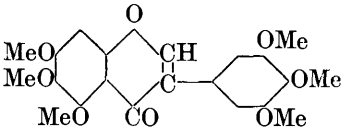
The starting material used in the present investigation was the

" Florentine Orris Root " of commerce, a supply of the finely powdered rhizomes being obtained through Messrs. James Woolley, Sons and Co., Ltd., Manchester. According to Parry (" The Chemistry of Essential Oils and Artificial Perfumes," 3rd ed., Vol. I, p. 92) and other authorities, commercial florentine orris root is a mixture of the rhizomes of three species of iris, *Iris germanica*, *Iris pallida*, and to a lesser extent *Iris florentina*. It seems doubtful whether de Laire and Tiemann's material consisted solely of the rhizomes of the last species, as the florentine orris root has often been erroneously assumed to be synonymous with the *Iris florentina*.

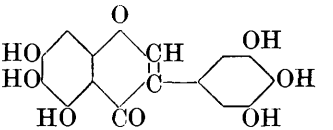
de Laire and Tiemann give very scanty details for the isolation of the glucoside iridin, and the yield is not stated, but it was probably poor, as it was necessary to have the preliminary operations carried out on the works scale. Attempts to follow their method gave only hopelessly bad results, so the problem had to be reinvestigated. A satisfactory process for the extraction of iridin has now been worked out, and in a large number of consecutive experiments the yields averaged just over 0·9% on the weight of the root. It is safe to say that iridin *occurs* to the extent of 1% in florentine orris root. Irigenin is easily prepared by hydrolysis of iridin with dilute sulphuric acid, and is now shown to be dimorphous. The formula $C_{15}H_7O_5(OMe)_3$ was confirmed, and the experiments now described prove conclusively that irigenin possesses the structure (III).

Irigenin very closely resembles the known naturally occurring and synthetical members of the *iso*flavone group. This is evident from its reactions with ferric chloride, dilute alkalis and sulphuric acid (experimental section), and from its dyeing properties (below). The dibenzoyl derivative possesses the properties previously described, except that it melts at 155—160° (de Laire and Tiemann give m. p. 123—126°, probably an error for 153—156°). The substance is impure, but undoubtedly consists essentially of dibenzoylirigenin, since it is insoluble in alkali and gives a positive ferric chloride reaction. The " diacetylirigenin " prepared as described by heating with acetic anhydride and sodium acetate in a sealed tube, or more readily by boiling with acetic anhydride under reflux, melts, when pure, at 127—128° (recorded m. p. 122°). It gives no colour reaction with ferric chloride, and an acetyl determination showed it to be *triacetylirigenin* (disproof of formula I), with which the previous carbon and hydrogen determinations agree. The " monoacetylirigenin " of m. p. 169° is hence *diacetylirigenin*, with which their analysis agrees, its formation being obviously due to the known ready hydrolysis of the 5-acetoxy-group in chromones (see 5 : 7 : 4′-triacetoxy-2-methyl*iso*flavone, Baker and Robinson, J., 1926, 2716), and it is therefore 7 : 3′-*diacetylirigenin*.

Vigorous methylation of irigenin with methyl sulphate readily gives a characteristic *irigenin trimethyl ether* (V) (disproof of formula I). The position of the methoxy-groups in the tetrahydroxybenzene nucleus is proved by decomposition of the ether with alkali, whereby 3 : 4 : 5-trimethoxyphenylacetic acid and antiarol (3 : 4 : 5-trimethoxyphenol) are formed.



(V.)

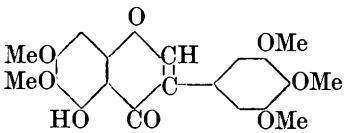


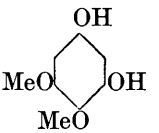
(VI.)

Demethylation of irigenin produces the hexahydric phenol (VI), which may be termed *irigenol*. This substance is oxidised with extreme readiness in alkaline solution, gives a *hexa-acetyl* derivative, a *hexamethyl ether* identical with (V), and a crystalline, orange *oxonium sulphate*, $C_{15}H_{10}O_8,H_2SO_4$. The formation of the last compound proves that irigenin cannot be represented as a coumarin (II).

Methylation of irigenin with three molecules of methyl iodide and alkali in a sealed tube gives *irigenin* 7 : 3′-*dimethyl ether* (VII), though with an excess of the reagents the product is a mixture of (VII) and the trimethyl ether (V), and under certain conditions a third compound, m. p. 154·5°, is produced. This dimethyl ether

(VII.)



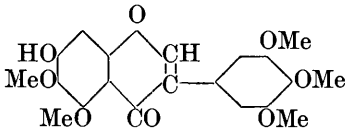


(VIII.)

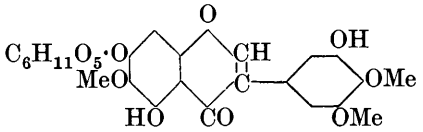
has very weak phenolic properties, being insoluble in sodium hydroxide solution even on warming, a behaviour which is inexplicable on the basis of formula (II), and establishes the position of the free hydroxyl group. It gives a positive reaction with ferric chloride, an *acetyl* derivative, and by methylation with methyl sulphate in methyl-alcoholic solution, irigenin trimethyl ether (V). Decomposition with aqueous alkali at 100° in hydrogen gives 3 : 4 : 5-trimethoxyphenylacetic acid and 4 : 5-dimethoxyresorcinol (VIII). These results prove that irigenin possesses the formula (III), and is consequently 5 : 7 : 3′-*trihydroxy*-6 : 4′ : 5′-*trimethoxy*isoflavone.

The position of the glucose nucleus in iridin was established in the following way. Methylation of iridin in methyl alcohol with an excess of diazomethane gave a resinous, methylated glucoside; this on hydrolysis yielded an irigenin dimethyl ether, possessing normal phenolic properties, which reacted readily with methyl sulphate

to give irigenin trimethyl ether (V). Decomposition with alkali gave the same products as were given by its isomeride (VII), namely, 3 : 4 : 5-trimethoxyphenylacetic acid and 4 : 5-dimethoxyresorcinol (VIII). This substance must therefore be *irigenin* 5 : 3′-*dimethyl ether* (IX), and the glucoside iridin hence has the constitution (X) with the glucose nucleus in the 7-position.



(IX.)



(X.)

The 5 : 6 : 7-structure of the tetrahydroxybenzene nucleus in irigenin is similar to that occurring in a few other natural products, the flavones scutellarein (see Bargellini, *Gazzetta*, 1919, **49**, ii, 47) and baicalein (Shibata, Iwata, and Nakamura, *Acta Phytochim.*, 1923, **1**, 105), the salts of the anhydrobenzopyranol base carajuretin, and probably the flavonol quercetagetin (Chapman, Perkin, and Robinson, J., 1927, 3015). The position of the glucose nucleus in iridin is the same as is probably occupied by the sugar nucleus in the flavone glucosides (Tasaki, *Acta Phytochim.*, 1925, **2**, 129), and lends support to the view, first suggested to the author by Professor R. Robinson some years ago, that in the *iso*flavone prunetin the methoxy-group occupies position 4′, and not position 7 as originally proposed by Finnemore (*Pharm. J.*, 1910, **31**, 604).

The dyeing properties of irigenin are very similar to those of the naturally occurring flavones, and of the *iso*flavone genistein (prunetol) in particular. Irigenin gives on woollen cloth mordanted with aluminium, tin, chromium, and iron, very pale yellow, exceedingly pale yellow, light yellowish-olive, and chocolate-brown colours, respectively. Iridin, with aluminium and tin mordants, gives almost the same colours as irigenin, but iron-mordanted wool is dyed a much paler brown, and with chromium mordant a paler, greyish-olive is produced. Addition of powdered chalk to the dye-bath gives brighter shades. Irigenol is a much more powerful dye than either iridin or irigenin, as might be expected from the fact that it contains two pyrogallol groupings. With the above-mentioned mordants it gives light yellow, bright yellow, yellow-brown, and olive-black colours, respectively.

Synthetical experiments in connexion with irigenin are in progress.

EXPERIMENTAL.

Iridin (X).—Powdered orris root (1 kg.) is boiled under reflux for ½ hour with alcohol (2 l.), and the extract filtered while hot

from the residue of starch, which is well pressed down and drained. The pale brown extracts from two experiments are distilled until the residue boils frothily (volume about 300 c.c.); it is then poured into a stirring jar. On standing, or preferably on seeding and stirring from time to time, the glucoside slowly separates, giving a thick, crystalline paste. After at least 48 hours alcohol (200 c.c.) is added and the mixture stirred for about 10 minutes; then, after standing, the glucoside settles to the bottom of the vessel and the dark brown, supernatant, alcoholic solution is poured off. The glucoside is again stirred with alcohol (200 c.c.) and the process repeated with a further quantity of alcohol (100 c.c.), and then with ether (100 c.c.). The mixture consisting of iridin and a large amount of glucose usually clots together after the first washing with alcohol and the mass may then have to be worked by hand. The very thick, pale yellowish, viscous material is stirred with water (250 c.c.) until the glucose dissolves, leaving a milky white suspension of the iridin, which is filtered, washed thoroughly with cold water, and dried on the steam-bath, whereby it acquires a very slight yellow colour. The yield of this almost pure glucoside from 2 kg. of the powdered rhizomes is about 18 g. The iridin may be recrystallised from a large volume of alcohol, or, better, from 50% methyl alcohol.

An alcoholic solution of iridin develops with a trace of ferric chloride a somewhat intense, dull reddish-violet colour, changing to dull olive-green with excess. It dissolves in concentrated sulphuric acid to a yellow solution which, on heating to 100°, rapidly darkens and chars, and iridin is thus easily distinguished from irigenin, whose pale yellow solution is unaltered under these conditions.

Irigenin (III).—Iridin (30 g., not recrystallised), water (35 c.c.), alcohol (45 c.c.), and concentrated sulphuric acid (3 c.c.) are heated in a pressure flask at 100° for 5 hours with occasional shaking. The product is poured into a mixture of alcohol (200 c.c.) and water (100 c.c.), boiled with charcoal, filtered, and treated again with charcoal after addition of water (100 c.c.) (compare de Laire and Tiemann). The filtrate slowly deposits yellowish crystals (about 17 g.), and a further small quantity separates on dilution of the mother-liquor. By recrystallisation from hot, dilute alcohol irigenin is first deposited in very pale yellow, almost rectangular plates, m. p. 185° (Found*: C, 59·9; H, 4·5. Calc. for $C_{18}H_{16}O_8$: C, 60·0; H, 4·4; 3MeO, 25·8%), and later in tiny bunches of pointed needles having the same melting point (Found*: C, 59·9; H, 4·6; MeO, 24·3%). The plate form crystallises unchanged from alcohol, but gives the needle form on recrystallisation from either dilute alcohol or dilute acetic acid. Irigenin gives a ferric chloride reaction

similar to that of iridin. Its non-fluorescent solutions in dilute aqueous sodium hydroxide and concentrated sulphuric acid are very pale yellow, and on dilution of the latter the colour is discharged and irigenin separates unchanged.

Benzoylation of Irigenin.—An alkaline solution of irigenin was shaken with excess of benzoyl chloride below 15°, and the oily product fractionally precipitated from warm benzene by the addition of ligroin. The first dark portion was rejected and then a colourless oil and a flocculent material separated, which were dissolved in much hot alcohol. On cooling, flocks separated and on the first appearance of crystals the solution was rapidly filtered; it then deposited colourless, compact, stellar bunches of tiny needles, m. p. 155—160° with previous softening [Found : C, 66·0; H, 4·2. Calc. for $C_{18}H_{14}O_8(COPh)_2$: C, 67·6; H, 4·2%]. This product is insoluble in caustic alkalis and gives an olive-green colour with ferric chloride in alcoholic solution, and is doubtless a mixture consisting essentially of 7 : 3′-*dibenzoylirigenin*. Attempts to prepare an acetyl derivative gave a white, non-homogeneous, crystalline powder, m. p. 155—165°, which gave no reaction with ferric chloride.

Triacetylirigenin.—Irigenin (5 g.) was boiled under reflux with acetic anhydride (20 c.c.) for 5 hours. The product, isolated after the addition of water and shaking, was recrystallised from dilute acetic acid and obtained in tiny, colourless prisms, m. p. 127—128° [Found (C and H by de Laire and Tiemann) : C, 59·3; H, 4·7; Ac, 26·6. $C_{18}H_{13}O_5(OAc)_3$ requires C, 59·3; H, 4·5; Ac, 26·5%]. The acetyl estimation was carried out by Wenzel's method (*Monatsh.*, 1897, **18**, 659) by decomposition with dilute sulphuric acid and estimation of the acetic acid. de Laire and Tiemann estimated the acetyl groups (Found : Ac, 21·4%) by hydrolysis with dilute alkali, and made an approximate correction for the formic acid produced by decomposition of the irigenin; this correction, however, was certainly too great, as irigenin only slowly decomposes even on treatment with concentrated alkali solution. The double compound with chloroform prepared by precipitating its solution in chloroform with ligroin has an indeterminate composition, since it rapidly loses chloroform (Found in freshly prepared substance : Cl, 7·2. After exposure to the air for 3 days : Cl, 3·5%). It melts at 82° to a frothy, viscous melt with partial loss of chloroform.

The " monoacetylirigenin," m. p. 169°, is really 7 : 3′-*diacetylirigenin* (Found by de Laire and Tiemann : C, 59·8; H, 4·7. Diacetylirigenin, $C_{22}H_{20}O_{10}$, requires C, 59·5; H, 4·5%).

Irigenin Trimethyl Ether (V).—Irigenin (10 g.) was shaken alternately with 10% potassium hydroxide solution (200 c.c.) and methyl sulphate in small portions at about 60°. The solid which finally

separated from the alkaline solution was collected, washed, and crystallised from alcohol (charcoal), in which it was easily soluble when hot, but very sparingly soluble when cold. After a further crystallisation from alcohol, it was obtained in colourless, highly refracting prisms, m. p. 163° (Found* : C, 62·8; H, 5·7; MeO, 44·6. $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5; 6MeO, 46·3%). (The methylated derivatives of irigenin gave variable and low values for carbon by ordinary analytical methods, probably owing to the formation of methane—compare Bradley and Robinson, J., 1926, 2361; Oxford and Raper, J., 1927, 421—but good results were obtained by micro-analytical methods—marked*—carried out at especially high temperatures.) As prepared above, and even after many recrystallisations from ethyl or methyl alcohol, this apparently pure irigenin trimethyl ether gives an exceedingly faint ferric chloride reaction. By treating its slightly warm solution in absolute methyl alcohol with diazomethane it is obtained of the same melting point, but now gives no ferric chloride reaction. Thus treated, it shows the curious property of turning very faintly brown on exposure to light.

Decomposition of Irigenin Trimethyl Ether with Alkali.—Irigenin trimethyl ether (6 g.), methyl-alcoholic potash (24 c.c. of 20%), and water (2 c.c.) were heated during 2 hours until the temperature slowly rose to 180° and the methyl alcohol distilled off. The product was dissolved in water (150 c.c.), almost neutralised, saturated with carbon dioxide, and filtered, and the filtrate was repeatedly extracted with ether. The extracts yielded a colourless substance (1·5 g.), which crystallised from a small amount of hot water, containing a little sulphur dioxide, in almost rectangular, irregular plates, m. p. 147°; these were identified as antiarol (Found : MeO, 47·8. Calc. : MeO, 50·5%). The *O*-acetyl derivative (Chapman, Perkin, and Robinson, *loc. cit.*) crystallised very readily from ligroin in flat, lustrous needles, m. p. 74° (Found : C, 58·4; H, 6·2. Calc. : C, 58·4; H, 6·2%), and the *O*-benzoyl derivative from alcohol in lustrous, flat needles, m. p. 117° (Kiliani, *Arch. Pharm.*, 1896, **234**, 443). (The remarkable ease of oxidation of antiarol to 2 : 6-dimethoxybenzoquinone does not seem to have been recorded. When a drop of ferric chloride is added to its aqueous solution a transient green colour is produced, which reappears with each drop of the reagent till finally bright yellow needles of the quinone separate, m. p. 256°. This is reduced by sulphur dioxide to 2 : 6-dimethoxyquinol, m. p. 158°.) The liquor remaining after the ether extractions was acidified, and further extractions yielded a carboxylic acid (2·5 g.) which crystallised from hot water in colourless, flat prisms, m. p. 120°, and possessed all the properties of 3 : 4 : 5-trimethoxyphenylacetic acid.

Irigenol (VI).—Irigenin (10 g.) was demethylated with hydriodic acid (100 c.c.; *d* 1·7) at 130° for 1 hour. Crystals separated during the latter part of the reaction and were isolated by the addition of water and filtration. The substance crystallises slowly from 50% acetic acid in pale yellow, microscopic needles, m. p. 331° (decomp.; rapid heating) (Found : C, 53·3; H, 3·9. $C_{15}H_{10}O_8,H_2O$ requires C, 53·6; H, 3·6%). The water of crystallisation is not lost at 140°. *Irigenol* is very sparingly soluble in acetic acid, water, ethyl alcohol, benzene, and ethyl acetate, but dissolves more readily in a mixture of the first two solvents and also in acetone. In the complete absence of air it dissolves in aqueous sodium hydroxide to a yellow, stable solution which deposits unchanged irigenol on acidification, but in the presence of air the solution rapidly assumes an intense crimson colour, and acids now throw down a dark, flocculent precipitate, and the crimson colour only weakly returns when the solution is again made alkaline. Irigenol dissolves in aqueous sodium carbonate to a yellow solution, which slowly turns red in presence of air. Its alcoholic solution develops with a little ferric chloride an intense olive-green colour, changed by excess to a deep reddish-brown, and when treated with a trace of sodium amalgam gives green flocks, a reaction which is shown by scutellarein and baicalein (Bargellini, *Gazzetta*, 1919, **49**, ii, 47). Methylation with methyl sulphate and alkali in an atmosphere of hydrogen readily gave irigenin trimethyl ether (V), m. p. 162°. The *hexa-acetyl* derivative separates after irigenol has been boiled with an excess of acetic anhydride and a few drops of pyridine for 4 hours. Recrystallisation from acetic anhydride gives colourless, microscopic prisms, m. p. 237—238° [Found : C, 57·1; H, 4·1; Ac, 43·9. $C_{15}H_4O_2(OAc)_6$ requires C, 56·8; H, 3·9; Ac, 44·2%].

Irigenol Sulphate.—Irigenol, in common with all irigenin derivatives and other *iso*flavones, dissolves in concentrated sulphuric acid to a yellow solution, which on dilution becomes colourless and deposits the unchanged substance. This general reaction is doubtless due to the formation of coloured oxonium sulphates. Owing to the very sparing solubility of irigenol in acetic acid, the sulphate cannot be prepared by addition of sulphuric acid to this solution. It is best prepared by dissolving irigenol (1 g.) in cold, concentrated sulphuric acid (5 c.c.) and adding glacial acetic acid (20 c.c.); the solution shortly becomes turbid, and after 12 hours is thick with microscopic, orange crystals, which are collected, washed with acetic acid, and dried in a vacuum over soda-lime (Found as hydrate by decomposition with water : $C_{15}H_{10}O_8$, 76·6. $C_{15}H_{10}O_8,H_2SO_4$ requires $C_{15}H_{10}O_8$, 76·4%). *Irigenol sulphate* reacts instantaneously with cold water, the bright orange colour

changing to the yellow of irigenol, and it also decomposes when heated under acetic acid. When dry, it is stable at 135°.

Irigenin 7 : 3′-*Dimethyl Ether* (VII).—Methylation of irigenin by boiling under reflux with an excess of methyl iodide and alkali led to very poor yields of (VII), the product being largely the trimethyl ether (V), though under certain conditions it consisted wholly or chiefly of a third substance, m. p. 154·5° (see below). With three molecules of alkali, the product was almost entirely alkali-soluble, but in a sealed tube satisfactory results were obtained.

Irigenin (5 g.), methyl iodide (3 mols.), and a solution of sodium methoxide (3 mols.) in methyl alcohol (30 c.c.) were heated in a sealed tube at 100° for 16 hours. After cooling, the product was crushed, treated with dilute alkali solution for 24 hours, washed well, and dried. It was then dissolved in hot methyl alcohol (240 c.c.) and the pale yellow needles which separated were filtered off after an hour (yield 1·5 g.). After several recrystallisations from methyl alcohol, it was obtained in tiny, lustrous, pale yellow needles, m. p. 166—167° (Found* : C, 61·7; H, 5·4; MeO, 38·4. $C_{20}H_{20}O_8$ requires C, 61·8; H, 5·2; 5MeO, 39·9%).

Irigenin 7 : 3′-*dimethyl ether* in alcoholic solution gives with a trace of ferric chloride an intense violet colour, changing to olive-green with excess. It is insoluble in warm, aqueous sodium hydroxide, but if to its suspension in methyl alcohol a drop of methyl-alcoholic potash is added it at once dissolves with a bright yellow colour, which fades when the solution is diluted with water and at the same time the dimethyl ether separates unchanged. By vigorous treatment with methyl sulphate in methyl-alcoholic potash, it was partly converted into the characteristic, colourless prisms of (V), m. p. 163°. The *acetyl* derivative crystallised after concentration of the acetic anhydride solution in which it was prepared, and formed colourless rhomboids, m. p. 191° (Found : C, 61·2; H, 5·4. $C_{22}H_{22}O_9$ requires C, 61·4; H, 5·1%). It is hydrolysed to (VII) by a few moments' treatment with alcoholic potash.

The *compound* of m. p. 154·5° is obtained when the methylation of irigenin is continued for 24 hours or more, with frequent addition of relatively large amounts of alkali and methyl iodide. The excess of methyl iodide and alcohol are distilled off and the substance is precipitated by water, washed with dilute alkali, and crystallised from ethyl alcohol (charcoal), then from benzene, and again from alcohol, being finally obtained in colourless, glistening leaflets, m. p. 154·5°. This substance is devoid of phenolic properties, and is being subjected to further examination.

Alkaline Decomposition of Irigenin 7 : 3′-*Dimethyl Ether*.—Hydrolysis was effected as in the case of irigenin 5 : 3′-dimethyl

ether (below), but twice the quantity of alkali was used and the solution was allowed slowly to become concentrated by distillation. The phenolic and acidic products were isolated as described, and identified as 4 : 5-dimethoxyresorcinol (VIII) and 3 : 4 : 5-trimethoxyphenylacetic acid.

Methylation of Iridin : Irigenin 5 : 3′-Dimethyl Ether (IX).—A freshly prepared, filtered solution of iridin (4 g.) in absolute methyl alcohol (60 c.c.) was treated with diazomethane, prepared from nitrosomethylurethane (16 c.c.) in ether (160 c.c.) and 25% methyl-alcoholic potash (25 c.c.). After 12 hours, the ether was distilled off and the remaining solution treated as before with diazomethane, which still remained in excess after a further 12 hours. After complete evaporation the residue was dissolved in a little water, and the solution was filtered from a slight flocculent precipitate and evaporated to dryness in a vacuum, leaving a yellowish-brown, uncrystallisable resin. This was hydrolysed on the steam-bath with 1% sulphuric acid for 6 hours; crystals were then obtained which separated from methyl alcohol (charcoal) in colourless, silky needles, m. p. 218° (Found* : C, 62·1; H, 5·5; MeO, 36·1. $C_{20}H_{20}O_8$ requires C, 61·8; H, 5·2; 5MeO, 39·9%). *Irigenin 5 : 3′-dimethyl ether* dissolves readily in dilute aqueous sodium hydroxide with a pale yellow colour, and its alcoholic solution gives a very faint brownish colour with ferric chloride. Methylation with methyl sulphate and alkali readily gave irigenin trimethyl ether (V).

Decomposition of Irigenin 5 : 3′-Dimethyl Ether with Alkali.—The dimethyl ether (0·75 g.) was boiled with water (75 c.c.) in a slow current of hydrogen, and a solution of potassium hydroxide (2·5 g. KOH) added. The colour, at first yellow, rapidly became red and finally faded to a very pale yellow. Decomposition was then probably complete, but boiling was continued for 2 hours, after which the solution was acidified, boiled with charcoal, and filtered. Excess of sodium bicarbonate was now added, and the solution extracted 12 times with ether. The extracts left on evaporation an oil which crystallised completely in a few hours on being kept at about 30°. By recrystallisation from a small amount of benzene, well-formed rhomboids separated (0·17 g.), m. p. 76°, which gave a reddish-brown colour with ferric chloride and had the properties of the 4 : 5-dimethoxyresorcinol recently prepared by Chapman, Perkin, and Robinson (*loc. cit.*). When heated with aqueous sodium hydroxide and chloroform, it develops a bright orange-red colour. Fusion with phthalic anhydride and zinc chloride, followed by treatment with alkali, gives a red solution devoid of fluorescence. The alkaline solution remaining after the

extraction of the 4 : 5-dimethoxyresorcinol was acidified, and the product then obtained by repeated extractions with ether crystallised from a small amount of water (charcoal) in colourless, flat needles, m. p. 120°, and had all the properties of 3 : 4 : 5-trimethoxyphenylacetic acid.

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THE DYSON PERRINS LABORATORY,
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