NOTES.

The Colouring Matter on the Stems of the Tomato. By B. K. Blount.

The staining of the fingers due to handling tomato (*Lycopersicum esculentum*) plants is caused by an exudation of minute liquid droplets, which occurs on the stalks, giving them their peculiar sheen, but not on the leaves.

The colouring matter was readily isolated, and preliminary investigation indicated that it was probably a flavonol glycoside. It was therefore hydrolysed with dilute acid, yielding a sugar-free compound identified as quercitin by its properties and those of its acetyl derivative. The original colouring matter was consequently a glycoside of quercitin, and its properties suggested that it might be rutin, a quercitin-3-rhamnoglucoside. Analysis, and direct comparison with a specimen obtained from common buckwheat (*Polygonum fagopyrum*), proved this to be the case.

Isolation of the Colouring Matter.—The stems of tomato plants were rubbed with pieces of linen (about 10 cm. square), care being taken to avoid breaking the skin. When saturated they were dried, and the process was repeated. The colouring matter was extracted from the cloth with alcohol (Soxhlet), and the extract concentrated and mixed with ether. The amorphous yellow precipitate crystallised from dilute alcohol, and after four recrystallisations, with filtration each time from traces of resinous material, pure rutin was obtained as small, pale greenish-yellow needles. The substance changed at 185—190° into a thick resin; the same behaviour was noticed with authentic rutin and with a mixture of the two (Found in material dried on the water-bath and then exposed to the air for some hours : C, 49·1; H, 5·5; loss at 160° in a high vac., 8·3. Calc. for $C_{27}H_{30}O_{16},3H_2O$: C, 48·8; H, 5·4; loss, 8·1%. Found in material dried at 160° : C, 53·2; H, 5·1. Calc. for $C_{27}H_{30}O_{16}$: C, 53·1; H, 4·9%). The yield of pure rutin was about 10 mg. per tomato plant.

Hydrolysis to Quercitin.—The above glycoside (50 mg.), when boiled with 2% sulphuric acid (40 c.c.), went into solution, and after about 1 hour crystals began to separate. After 2 hours the mixture was cooled, and the solid collected. The filtrate was practically colourless. The flavonol, crystallised twice from dilute alcohol, formed yellow needles, m. p. 313—314° (decomp.) with previous blackening, alone or mixed with quercitin (Found in air-dried material : C, 53·4; H, 4·2; loss at 130° in a high vac., 10·8. Calc. for $C_{15}H_{10}O_7,2H_2O$: C, 53·4; H, 4·1; loss, 10·7%. Found in material dried at 130° : C, 59·9; H, 3·4. Calc. for $C_{15}H_{10}O_7$: C, 59·6; H, 3·3%).

The acetyl derivative, prepared by heating the flavonol with acetic anhydride and a trace of camphorsulphonic acid, melted, alone or mixed with penta-acetyl quercitin, at 195° (Found : C, 58·5; H, 3·9. Calc. for $C_{25}H_{20}O_{12}$: C, 58·6; H, 3·9%).

The author is grateful to Professor Robinson for specimens of rutin and quercitin, and to the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship.—The Dyson Perrins Laboratory, Oxford. [*Received, October 9th,* 1933.]

7-Phenylthio-derivatives of Deoxybenzoin. By William A. Mitchell and Samuel Smiles.

Posner (*Ber.*, 1902, **35**, 506) has shown that the condensation of benzoin with thiols yields the 7 : 7′-bisaryl(alkyl)thio-derivatives of stilbene (IV). If, however, the process is carried out in concentrated solution in alcohol with the less soluble thiols, the 7-arylthio-derivatives of deoxybenzoin (III) may be isolated. These substances are also formed by acetylative reduction of the monomercaptols of benzil (I), followed by alkaline hydrolysis of the 7′-acetoxy-7-arylthiostilbene (II) produced.

$$\underset{\text{(I.)}}{(\mathrm{ArS})_2\mathrm{CPh{\cdot}COPh}} \longrightarrow \underset{\text{(II.)}}{\mathrm{ArS{\cdot}CPh{:}CPh{\cdot}OAc}} \longrightarrow \underset{\text{(III.)}}{\mathrm{ArS{\cdot}CHPh{\cdot}COPh}} \longrightarrow \underset{\text{(IV.)}}{\mathrm{ArS{\cdot}CPh{:}CPh{\cdot}SAr}}$$

$$\text{(V.)}\quad (\mathrm{ArS})_2\mathrm{CPh{\cdot}CH_2{\cdot}SAr} \qquad (\mathrm{ArS})_2\mathrm{CPh{\cdot}CHPh{\cdot}SAr}\quad \text{(VI.)}$$

The 7-arylthio-derivatives of deoxybenzoin (III) are converted into the stilbene derivatives (IV) by further reaction with phenylthiols and into the monomercaptols of benzil (I) by reaction with disulphoxides in alkaline solution (Brooker and Smiles, J., 1926, 1724). Benzoylcarbinol or its acetate yields with phenylthiols derivatives of type (V). This fact and the conversion of (I) into (II) appear to support Posner's assumption that the production of (IV) from a thiol and benzoin is preceded by formation of (VI), which subsequently loses a molecule of the thiol. Attempts to remove a molecule of the thiol from (V) were, however, unsuccessful.

Types (II) and (III) are illustrated by the derivatives of phenylthiol and 5-chloro-2-methoxyphenylthiol.

7′-*Acetoxy*-7-*phenylthiostilbene*, obtained by reducing the phenylmercaptol of benzil with zinc and acetyl chloride in ether, formed needles, m. p. 141°, from alcohol (Found : C, 76·3; H, 5·3; S, 9·4. $C_{22}H_{18}O_2S$ requires C, 76·3; H, 5·2; S, 9·2%). When hydrolysed, it gave 7-*phenylthiodeoxybenzoin*, m.p. 81° (Found : C, 78·4; H, 5·2; S, 10·5. $C_{20}H_{16}OS$ requires C, 78·9; H, 5·3; S, 10·5%).

7-(5-*Chloro*-2-*methoxyphenylthio*)-7′-*acetoxystilbene*, obtained by reduction of the corresponding mercaptol of benzil (m. p. 178°), had m. p. 114° (Found : C, 66·9; H, 4·3. $C_{23}H_{19}O_3ClS$ requires C, 67·2; H, 4·6%). It was hydrolysed in alcohol by the calculated amount of sodium ethoxide, yielding 7-(5-*chloro*-2-*methoxyphenylthio*)*deoxybenzoin*, m. p. 102° (Found : C, 68·6; H, 4·7. $C_{21}H_{17}O_2ClS$ requires C, 68·4; H, 4·6%). This was also obtained by the condensation of 5-chloro-2-methoxyphenylthiol with benzoin in alcohol with dry hydrogen chloride. By using excess of the phenylthiol in this condensation, 7 : 7′-*bis*-(5-*chloro*-2-*methoxyphenylthio*)*stilbene*, m. p. 208°, was isolated (Found : C, 63·4; H, 4·1. $C_{28}H_{22}O_2Cl_2S_2$ requires C, 64·0; H, 4·2%).

The *phenylmercaptol* of ω-phenylthioacetophenone (V) was obtained by the interaction of dry hydrogen chloride, benzoylcarbinyl acetate (1 mol.), and phenylthiol (3 mols.) in alcohol (5—10°). It had m. p. 82° (Found : C, 72·4; H, 4·9; S, 22·4. $C_{26}H_{12}S_3$ requires C, 72·5; H, 5·1; S, 22·3%).—King's College, London. [*Received, September 13th,* 1933.]

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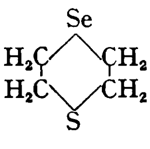
1 : 4-*Selenothian.* By Charles S. Gibson and John D. A. Johnson.

The preparation of 1 : 4-selenoxan by the interaction of ββ′-dichlorodiethyl ether and sodium selenide (J., 1931, 266) suggested the possibility of preparing the analogous 1 : 4-selenothian by the action of (i) sodium sulphide on ββ′-dichlorodiethyl selenide (Bell and Gibson, J., 1925, **127**, 1877) or (ii) sodium selenide on ββ′-dichlorodiethyl sulphide.



(i) When treated with an aqueous solution of sodium sulphide, ββ′-dichlorodiethyl selenide decomposed readily with evolution of an inflammable gas (? ethylene), selenium being precipitated.

(ii) ββ′-Dichlorodiethyl sulphide (25·4 g.) was boiled for 4 hours under reflux with aqueous sodium selenide prepared from aluminium selenide (60 g.) (Johnson and Gibson, *loc. cit.*). Distillation in steam removed a crystalline material which, on recrystallisation from ethyl alcohol, gave 1 : 4-*selenothian*, colourless thin plates, m. p. 107° (Found : C, 28·9; H, 4·9: Se, 47·9. C_4H_8SSe requires C, 28·7; H, 4·8; Se, 47·3%), in small yield.

1 : 4-Selenothian resembles dithian in its ready volatility in steam and in ethyl alcohol vapour and in odour and crystalline appearance. Since dithian (m .p. 112°) does not depress the m. p. (107°) of selenothian, the two substances are not readily distinguished from each other : they appear to form solid solutions. Selenothian reacts very readily with bromine, but the product has not been investigated in detail.

The interaction of aluminium selenide (17 g.) and ββ'-dichlorodiethyl sulphide (14·3 g.) for 1½ hours at 150—170° was also investigated. The product was cautiously treated with water and then submitted to steam distillation, but the only compound obtained from the distillate was dithian. Hydrogen selenide was evolved in considerable quantity. On a larger scale the evolution became difficult to control and owing to the distressing physiological action of the gas one of us (J. D. A. J.) was seriously incapacitated. Chiefly for this reason the more complete investigation of 1 : 4-selenothian, which will involve the preparation of larger quantities, has had to be postponed.—GUY'S HOSPITAL MEDICAL SCHOOL, UNIVERSITY OF LONDON, LONDON, S.E. 1. [*Received, September 25th,* 1933.]

Some Physical Constants of Thioxan, Selenoxan, and Dithian. By JOHN D. A. JOHNSON.

THE following physical constants of the pure materials are recorded :

Boiling points (corr.)/mm.

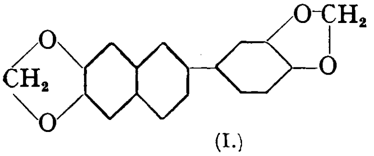
Thioxan : 69·9°/47, 86·5°/97, 100·0°/165, 109·8°/233, 129·7°/441, 137·7°/549.
Selenoxan : 79·5°/37, 100·8°/95, 119·7°/183, 138·7°/330, 148·9°/440, 156·6°/548.
Dithian : 115·6°/60, 133·2°/119, 144·3°/170, 154·7°/232, 158·0°/252, 163·7°/306.

Refractive indices ($n_D^{20°}$).

Thioxan, 1·5081 (m. p. − 17°); selenoxan, 1·5480 (m. p. − 21·5°) (Gibson and Johnson, J., 1931, 266); dioxan, 1·4217.—GUY'S HOSPITAL MEDICAL SCHOOL, UNIVERSITY OF LONDON, LONDON, S.E. 1. [*Received, September 25th,* 1933.]

Preparation of Homopiperonal. By HOLGER ERDTMAN and ROBERT ROBINSON.

HOMOPIPERONAL, hitherto a not readily accessible substance (compare Semmler and Bartelt, *Ber.*, 1908, **41**, 2751; Harries and Adam, *Ber.*, 1916, **49**, 1030; Rosenmund and Dornsaft, *Ber.*, 1919, **52**, 1742), has now been obtained from the so-called safrole glycol, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, by Criegee's method (*Ber.*, 1931, **64**, 260; compare Dimroth and Schweizer, *Ber.*, 1923, **56**, 1375), the only difficulty being the formation of the glycol from safrole in good yield.



(I.)

Homopiperonal is very readily changed to the naphthalene *derivative* (I) under the influence of acid catalysts and therefore could not be converted into an *iso*flavylium salt by condensation with *O*-benzoylphloroglucinaldehyde in the presence of hydrogen chloride (compare the condensation of *O*-acetylphloroglucinaldehyde dimethyl ether and homoveratraldehyde; Freudenberg, Carrara, and Cohn, *Annalen*, 1925, **446**, 93).

Safrole Glycol.—The smooth oxidation of safrole by sodium chlorate and osmium tetroxide could not be effected, nor could safrole oxide be hydrolysed to the glycol. The oxidation of safrole by means of potassium permanganate failed under the conditions (rather vaguely specified) of Tiemann (*Ber.*, 1891, **24**, 2881); the claims of Wagner (*ibid.*, p. 3489) were confirmed but not in respect of the yield. The best results were obtained as follows.

Safrole (20 g.) was suspended in water (400 c.c.) containing ice, and a solution of potassium permanganate (30 g.) in water (1500 c.c.) was rapidly introduced into the *very vigorously* stirred mixture, ice being added when necessary to maintain the temperature at 0° throughout the oxidation, the final volume reaching 4000—4500 c.c. Sulphur dioxide was passed to dissolve the manganese sludge and the solution was then concentrated to 250 c.c., cooled, acidified with sulphuric acid, and extracted several times with ethyl acetate (in which the glycol is freely soluble; it is sparingly soluble in ether). The extract was shaken with 2*N*-sodium hydroxide to remove acids, dried (magnesium sulphate), and evaporated, leaving nearly pure glycol (9 g.), which was recrystallised from benzene and then distilled, b. p. 233—236°/20 mm. The crude mixture of piperonylic acid and preponderating homopiperonylic acid obtained from the alkaline extract weighed 4 g.

Homopiperonal.—Lead tetra-acetate (34 g.) was introduced in portions of 1—2 g. during 3—4 minutes into a solution of safrole glycol (15 g.) in dry boiling benzene (300 c.c.) with vigorous shaking. After cooling, the lead acetate was collected and washed with benzene, and the filtrate shaken twice with water (300 c.c.). The benzene was then evaporated in a vacuum, and the residual crude homopiperonal distilled, b. p. 123—125°/1 mm. (yield, 9 g.). The oxime, m. p. 121°, crystallised from aqueous alcohol in long glistening needles (slow crystallisation) or in pearly leaflets (rapid crystallisation). Semmler and Bartelt give 124—125°, Harries and Adam give 115°, and Rosenmund and Dornsaft give 119—120° as the m. p. of this derivative (*locc. cit.*).

The 2 : 4-*dinitrophenylhydrazone* was prepared in acetic acid solution and separated as orange-yellow leaflets; recrystallised from acetic acid, it had m. p. 140—141° (Found : N, 16·4. $C_{15}H_{12}O_6N_4$ requires N, 16·3%).

6 : 7 : 3′ : 4′-*Bismethylenedioxy-2-phenylnaphthalene* (I).—When hydrochloric acid (1 c.c., *d* 1·16) was added to a mixture of homopiperonal (5 g.) and acetic acid (10 c.c.), a faint brownish colour appeared and after some minutes a colourless substance was precipitated; the solution, which tended to become hot, was cooled in running water. After 5 minutes the pale violet reaction mixture was semi-solid; methyl alcohol (10 c.c.) was added, and the solid collected (4—4·5 g.). This product was a mixture; it was dissolved in boiling acetic acid (100 c.c.) and, on cooling, about 2 g. of a substance separated which was obtained pure after several recrystallisations in leaflets, m. p. 200—201° (Found : C, 73·8; H, 4·3. $C_{18}H_{12}O_4$ requires C, 74·0; H, 4·1%), soluble in sulphuric acid to a brown solution giving a greyish-green precipitate on addition of water.

The mother-liquor from the first crystallisation had a marked violet fluorescence and contained, in addition to the above *phenylnaphthalene* derivative, m. p. 200—201°, and amorphous matter, at least one additional crystalline compound, faintly greenish-yellow needles, m. p. 206—208°, but this substance has not yet been further investigated.

Tribromopiperonylmethylenedioxynaphthalene.—The pure condensation product, m. p. 200—201°, was spread in a thin layer on a clock-glass and bromine, diluted with ten times its weight of chloroform, gradually added until no more was decolorised; hydrogen bromide was evolved. The *product* crystallised from much acetic anhydride in colourless needles, m. p. 165—167° (Found : Br, 45·1. $C_{18}H_9O_4Br_3$ requires Br, 45·4%).

Nitropiperonylmethylenedioxynaphthalene.—When the substance, m. p. 200—201°, suspended in acetic acid was treated with an excess of nitric acid diluted with acetic acid, it gradually passed into solution and was replaced by a precipitate of yellow needles, which after crystallisation from acetic acid melted at 225—228° (decomp.) (Found: N, 4·5. $C_{18}H_{11}O_6N$ requires N, 4·2%). This compound, probably a 6′-*nitropiperonyl* derivative, became brown under the action of light.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, September 28th,* 1933.]

αε-*Dibromopentane*. By JOHN D. A. JOHNSON.

αε-DIBROMOPENTANE prepared from benzopiperidide and phosphorus pentabromide and purified as described by von Braun (*Ber.*, 1904, **37**, 3211; 1905, **38**, 2338; Ger. Pat. 164365; "Organic Syntheses," Adams, vol. IX, p. 70) contains so much benzonitrile as to be almost unacted upon by magnesium in dry ether (compare von Braun, *Ber.*, 1905, *loc. cit.*).

Benzopiperidide (338 g.) was used in each of four preparations and after removal of the phosphorus oxybromide (ice and water) a mixture of dibromopentane and benzonitrile was obtained. Three-quarters of this was worked up as described by von Braun, except that the hydrolysis with 40% hydrobromic acid was prolonged to 16 hours. The material isolated had $d_{4°}^{20°}$ 1·604 (approx.), $n_D^{20°}$ 1·5160, b. p. 93—95°/10 mm.—constants which indicated that it contained 15—16% of benzonitrile. Experiments on the remaining quarter showed that the ligroin–sulphuric acid process of purification suggested by Dix and Yoder (*J. Amer. Chem. Soc.*, 1921, **43**, 1366) and by Clarke (J., 1913, **103**, 1703) could be made practicable, the loss of dibromide by decomposition by the concentrated sulphuric acid being quite small.

The following process has therefore been devised. After removal of the phosphorus oxybromide (above) the crude mixture is washed and distilled (this operation prevents the dangerous evolution of hydrogen bromide which would occur during the subsequent extraction with concentrated sulphuric acid). The fraction boiling up to 105°/10 mm. is dissolved in about twice its volume of ligroin (b. p. 40°) and extracted seven times with concentrated sulphuric acid (3 c.c. for each 10 c.c. of the dibromide fraction). The ligroin solution is washed with dilute aqueous sodium hydroxide and with water (any emulsions formed on shaking at these stages are easily dispersed by filtration), dried with calcium chloride, and evaporated, and the residue distilled under diminished pressure. With ordinary care, 200 c.c. of a mixture of dibromopentane and benzonitrile may be safely dealt with in a 1½ l.-separating funnel. The αε-dibromopentane obtained is pure and reacts so readily with magnesium in dry ether that cooling may be necessary.

Pure αε-dibromopentane has m. p. — 29·5° (Hochstetter, *Monatsh.*, 1902, **23**, 1071, gives — 34° to — 35°), b. p. 95·5°/10 mm., $d_{4°}^{20°(\text{vac.})}$ 1·6995, $d_{4°}^{50°(\text{vac.})}$ 1·6583, $n_{\text{D}}^{20°}$ 1·5136, $\gamma^{20·0°}$ 40·3 dynes/cm., $\gamma^{50·0°}$ 36·8 dynes/cm.; $[P]^{20°}$ 340·9, $[P]^{50°}$ 341·6 (calc., $[P]$ 331·0). The parachor anomaly will be discussed in another communication.

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Preparation of Halogeno- and Other 2-Phenylbenzopyrylium Salts.

By CATHERINE G. LE FÈVRE and RAYMOND J. W. LE FÈVRE.

THE preparations of 2-phenylbenzopyrylium salts by the three-stage processes already described (J., 1929, 2771; 1932, 1988) gave unsatisfactory results, especially with halogenated compounds, when carried out with quantities of the intermediate chalkones much greater than *ca.* 0·2 g. The following procedure, first described by Löwenbein and Katz (*Ber.*, 1926, **59**, 1377) for the condensation of *o*-hydroxy-aldehydes with β-ketonic esters, has now been found to yield the perchlorates in one step and to be amenable to large-scale operation: To the appropriately substituted acetophenone (0·01 g.-mol.) and salicylaldehyde (0·01 g.-mol.), dissolved in anhydrous ether (40 c.c.), is added perchloric acid (70%; 3 c.c.), and the mixture saturated with hydrogen chloride (temperature not above 0°). After 24 hours the crystalline deposit of perchlorate is collected and washed with ether. Crystallisation from the solvents specified in the above references does not usually effect further purification. The results are tabulated below.

Kation.	Initial substances taken.	Product.	M. p. (crude).	M. p. previously given.	Found, %.		Calc., %.	
					C.	H.	C.	H.
2-Phenylbenzopyrylium	Acetophenone, salicylaldehyde	Green pearly plates	180°	178—179°*	58·5	3·7	58·7	3·6
3′-Nitropyrylium	*m*-Nitroacetophenone, salicylaldehyde	Yellow-green powder	241—243	240—243 *	50·5	2·9	51·2	2·8
6-Chloropyrylium	5-Chlorosalicylaldehyde, acetophenone	Yellow powder	240	240 †	52·3	3·0	52·8	2·9
6-Bromopyrylium	5-Bromosalicylaldehyde, acetophenone	Yellow plates	250—251	248—250 †	46·4	2·8	46·7	2·6
6 : 8-Dichloropyrylium	3 : 5-Dichlorosalicylaldehyde, acetophenone	,,	270—271	249—250 †	48·1	2·7	47·9	2·4
6 : 8-Dibromopyrylium	3 : 5-Dibromosalicylaldehyde, acetophenone	,,	273—275	257—259 †	38·3	1·9	38·8	1·9
4′-Chloropyrylium	Salicylaldehyde, *p*-chloroacetophenone	,,	192—193	193 †	52·1	3·1	52·8	2·9
4′-Bromopyrylium	Salicylaldehyde, *p*-bromoacetophenone	,,	243—244	243—245 †	46·6	3·1	46·7	2·6

* Le Fèvre, J., 1929, 2771. † Le Fèvre and Le Fèvre, J., 1932, 1988.

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