

variable, the red flowers being slightly more acid than the blue; varieties which do not blue have unusually low  $pH$ . If the petals of a blue variety are allowed to develop in a weak light more anthocyanin is produced and a red color partly masks the blue.

***Ipomea Learii***.—Young red buds ( $pH$  6.4) become blue flowers ( $pH$  6.2–6.3) and the pigment concentration diminishes slightly. This process does not occur in cut flowers kept in hard tap water, but always when distilled water is used. Here again the change of color is associated with a flower of unusually high  $pH$ . The range in the majority of flower petals is from 4.0 to 5.0.

***Malcomia maritima***.—The buds and young flowers are red and change to dullish violet. The  $pH$  in both cases is about 6.4. The anthocyanin concentrations, red to violet, are about in the ratio 3:2. Flavone is present in approximately the same concentration in both cases. It is very interesting that the variety "Crimson King," which does not blue, has  $pH$  5.17. All varieties of the virginian stock are colored by cyanidin diglucoside.

***Meconopsis Baileyi***.—The purple flowers contain more anthocyanin than the blue.

***Rosa***.—The "Veilchen" rambler rose has red buds ( $pH$  6.3) changing to dullish violet flowers ( $pH$  6.3). The anthocyanin ratio, red to violet, is 29.6:22.9. In a dry season the flowers become violet almost as soon as they open but in a wet season the change occurs just before fading. In the latter case the anthocyanin concentration is higher than in the former.

The rose, Madame Ed. Herriot, has salmon-pink young flowers changing to bluish-pink. The  $pH$  in both cases is 5.9. The anthocyanin ratio of young to older flower petals is 44:26. Flavones are present but show little change.

The rambler "Excelsior," like "Veilchen," is colored by cyanin but the  $pH$  is 5.6 and the color change does not occur.

**Chlorogenic Acid**.—The method of Gorter<sup>2</sup> has been employed and it appears that this plant constituent may have some significance in relation to flower color. Blue hydrangea flowers do not contain any chlorogenic acid but the red flowers have a substantial amount.

Blue flowers of *Ipomea Laurii* are free from the acid but fading, accompanied by reddening, causes the development of this substance. Red buds and purple flowers of *Centaurea* contain chlorogenic acid but there is none in blue cornflowers.

***Arnebia cornuta***.—This plant, known as Mahomet's Fingers, produces yellow flowers and shortly after opening (incipiently also in the bud) dark purplish-brown areas appear on each petal; the colored spots later disappear. The anthocyanin is malvidin diglucoside. The colored areas are opposite the anthers and in the bud follow their shape. If tissue paper is interposed at an early stage between anther and petal, the spot does not develop. Also, if the petal is tied away the same result is achieved in a large majority of cases. The petals on which this operation is performed grow, but do not reach full normal size. It would appear that the anther contains a stimulant (? volatile) to anthocyanin formation although this view is necessarily tentative because the normal physiology of the plant may have been modified by the mechanical operation.

(2) Gorter, *Rec. trav. chim.*, **31**, 281 (1912).

In one case the anthers were successfully excised and a good flower developed. It was always pure yellow.

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## The Identity of Pyrethrosin with Chrysanthin and Non-identity with Geigerin

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A crystalline compound isolated from pyrethrum flowers (*Chrysanthemum cinerariaefolium*) has been described recently by Rose and Haller.<sup>1</sup> The compound was named "chrysanthin" because its physical properties appeared to be identical with those of a compound obtained by Chou and Chu<sup>2</sup> from benzene extracts of pyrethrum flowers, and named by them "chrysanthine."<sup>3</sup> The compound described by Rose and Haller melted at 201° when crystallized from ethyl acetate and at 177–178° when crystallized from ethanol. Its optical rotation in chloroform was  $[\alpha]^{20}_D -30.5^\circ$ . Analyses and molecular weight determinations showed it to have the molecular formula  $C_{17}H_{22}O_5$ .

Chou and Chu stated that the compound isolated by them had a melting point of 200° and a rotation of  $[\alpha]^{20}_D -30^\circ$  in chloroform. The empirical formula,  $C_{10}H_{13}O_3$ , assigned by them was based on combustion analyses only, no molecular weight determinations having been made.

Thoms<sup>4</sup> in 1891, during a study on the insecticidal principle of pyrethrum flowers, isolated an insecticidally inert product which he termed "pyrethrosin," and which he regarded as being identical with one obtained by Marino-Zuco<sup>5</sup> in a similar study. Thoms found that pyrethrosin had a melting point of 189° and suggested the provisional formula  $C_{34}H_{44}O_{10}$  on the basis of four combustions but no molecular weight determination. This formula is exactly twice that proposed for chrysanthin by Rose and Haller.

In the course of a chemical study of *Geigeria aspera*, a plant that causes "vermeersickte" or vomiting disease of sheep, Rimington and Roets<sup>6</sup> isolated a bitter principle which they called

(1) Rose and Haller, *J. Org. Chem.*, **2**, 484 (1937).

(2) Chou and Chu, *Chinese J. Physiol.*, **8**, 187 (1934).

(3) The final *e* was dropped by Rose and Haller in accordance with present standards of nomenclature.

(4) Thoms, *Ber. deut. pharm. Ges.*, **1**, 241 (1891).

(5) Marino-Zuco, *Atti accad. Lincei*, 1 Sem., 571 (1890); abstr. in *Ber.*, **24**, 201 (1891).

(6) Rimington and Roets, *Onderstepoort J. Vet. Sci. Animal Ind.*, **7**, 485 (1936).

TABLE I  
 SOME PROPERTIES AND REACTIONS OF CHRYSANTHIN, PYRETHROSIN AND GEIGERIN

Property or reaction	Chrysanthin <sup>1</sup>	Pyrethrosin <sup>4</sup>	Geigerin <sup>5</sup>
Melting point, °C.	{ 201 from EtOAc 177-178 from EtOH	188-189 from EtOH	α-Form 78 and 189 β-Form 68 and 169
Taste	Bitter	Bitter	Bitter
Crystalline form	Orthorhombic octahedra	Rhombic octahedra	Rhombic
Optical rotation {	(α) <sup>20</sup> D in CHCl <sub>3</sub> (-30.5) c = 5.16	...	(-42.58) c = 0.335
(α) <sup>20</sup> D in abs. EtOH	(-38.1) c = 0.315	...	(-60.23) c = 0.349
Carbon, % (av.)	66.73	66.49	68.20
Hydrogen, % (av.)	7.25	7.27	7.75
Molecular weight (av.)	311	Not detd.	303 on monohydrate
Formula	C <sub>17</sub> H <sub>22</sub> O <sub>5</sub>	C <sub>34</sub> H <sub>44</sub> O <sub>10</sub>	C <sub>15</sub> H <sub>20</sub> O <sub>4</sub>
Color tests	Warm 25% HCl	Violet soln., amorphous yellow ppt. on dilution	Cherry-red soln.
	Warm 20% HCl	Pink-violet soln., yellow amorphous ppt. on diln.	Cherry-red soln., unchanged geigerin on diln.
	Concd. H <sub>2</sub> SO <sub>4</sub>	Yellow-brown solution	Yellow-brown solution
Tetranitromethane	No color	...	No color
Bromine in CHCl <sub>3</sub>	No decol., excess reacts	...	No decol.
Cold aq. KMnO <sub>4</sub>	Reduction	Rapid redn. warm	None; reduc. warm
Fehling's solution	Sl. redn. prolonged boiling	...	Sl. redn. prolonged boiling
2,4-Dinitrophenylhydrazone	None	...	Formed
Lactone group	Present	...	Present

geigerin. It has the empirical formula C<sub>15</sub>H<sub>20</sub>O<sub>4</sub> and exists in two isomeric forms, an alpha form which shows a double melting point, the final one being 189°, and a beta form which also exhibits two melting points, melting finally at 169°. Both forms have the same composition and the same optical rotation, [α]<sup>20</sup>D -42.71°, in chloroform or ethyl acetate.

Largely on the basis of a comparison of melting point of the alpha form of geigerin with that of pyrethrosin, both 189°, and a color test of each with hydrochloric acid, Rimington and Roets have concluded that geigerin and pyrethrosin are identical, a conclusion with which we are not in accord.

Some of the properties and reactions of each compound are recorded in Table I.

All three substances are bitter in taste.

The melting point reported by Thoms for pyrethrosin is 189°; that for chrysanthin, as already indicated, is 178 or 201°. However, it has been shown that the melting point behavior of chrysanthin varies with the solvent from which it is crystallized and also with the rate of heating.

The carbon and hydrogen combustion values for pyrethrosin and chrysanthin are almost identical, both sets of values being satisfactory for the empirical formula C<sub>17</sub>H<sub>22</sub>O<sub>5</sub>. Both carbon and hydrogen combustion values of geigerin are higher than those of pyrethrosin and with consideration of molecular weight data indicate an empirical formula of C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>.

Neither chrysanthin nor geigerin decolorizes bromine in chloroform solution; however, chrysanthin reacts with a concentrated solution of bromine in chloroform with the liberation of hydrogen bromide and the separation of an oil.

Chrysanthin reacts readily with 2 moles of alkali with the formation of acetic acid and an acid, C<sub>15</sub>H<sub>26</sub>O<sub>7</sub>, which is very soluble in water, only slightly soluble in ether, and difficult to crystallize. Geigerin reacts with 1 mole of alkali with the formation of an acid, C<sub>15</sub>H<sub>22</sub>O<sub>5</sub>, which is not very soluble in water, dissolves readily in ether, and is crystalline.

The color test given by chrysanthin with hydrochloric acid is the same as that recorded for pyrethrosin; the color test given by geigerin with this reagent is similar but not the same.

The presence of a carbonyl group can be demonstrated in geigerin by the formation of a 2,4-dinitrophenylhydrazone, but it has not been possible to prepare such a derivative from chrysanthin.

All the foregoing evidence, together with the fact that chrysanthin or pyrethrosin has been obtained by several investigators from only one species of plant, *Chrysanthemum cinerariaefolium*, seems to establish their identity.

It is clear from the recorded data that chrysanthin and geigerin are not identical, and therefore it follows that geigerin and pyrethrosin are not the same.

It is suggested that the name "pyrethrosin" be retained for this crystalline product obtained from *Chrysanthemum cinerariaefolium* and that all others be discarded.

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### Tetraphenyllead and Diphenyllead Dihalides

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The Pfeiffer<sup>1</sup> procedure for the preparation of  $R_4Pb$  compounds by interaction of the Grignard reagent and lead chloride is admirably suited for laboratory purposes. However, the yields of tetraphenyllead by this method are about 50% in moderate sized runs.<sup>2</sup>

Incidental to a study on the mechanism of formation of some organometallic compounds, it has been found possible to increase the yield of tetraphenyllead to 83%. An occasional by-product is triphenyllead bromide, isolated in yields up to 6%. This compound does not owe its formation to a secondary reaction between tetraphenyllead and magnesium bromide or the binary system ( $Mg + MgBr_2$ ), inasmuch as tetraphenyllead is unaffected by these substances under the conditions of the Pfeiffer reaction. A recent<sup>3</sup> study showed that  $R_3Pb$  compounds react with magnesium iodide to give  $R_3PbI$  compounds. A corresponding reaction of triphenyllead and magnesium bromide suggests itself for the formation of triphenyllead bromide. Actually, we have found that triphenyllead and magnesium bromide give triphenyllead bromide. Triphenyllead is undoubtedly an intermediate in the preparation of tetraphenyllead; and when the time of reaction (in the directions which follow) is decreased, the tetraphenyllead is contaminated with some triphenyllead.

To a vigorously stirred solution of phenylmagnesium bromide (prepared from 1.5 moles of bromobenzene) in 500 cc. of ether, is added 500 cc. of dry toluene and 181 g. (0.65 mole) of dry, finely ground lead chloride. The lead chloride is added in three portions at five-minute intervals. The mixture is stirred with gentle refluxing for five hours, and thins out appreciably after the initial fifteen to thirty minutes of heating.

(1) Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904).

(2) Gilman and Robinson, *THIS JOURNAL*, **49**, 2315 (1927).

(3) Gilman and Bailie, *ibid.*, **61**, 731 (1939).

Hydrolysis is effected by pouring upon crushed ice mixed with ammonium chloride or hydrochloric acid. Vigorous stirring should be maintained during hydrolysis.

The toluene-ether layer is decanted and the water layer filtered. Distillation of the organic solvent layer leaves a residue consisting of a few grams of tetraphenyllead and triphenyllead bromide together with about 10 g. of biphenyl which probably came largely incidental to the formation of the Grignard reagent. The filtered solid from the aqueous layer is air dried, and extracted with 400 cc. of chloroform in a Soxhlet extractor to give an 82-83% yield of crystalline, pure tetraphenyllead (m. p. 225-226°). In the directions just noted, which do not necessarily give maximum yields, no inert atmosphere was used and the Grignard reagent was not filtered free of magnesium.

Diphenyllead dibromide and diphenyllead diiodide are prepared conveniently and in excellent yields in essential accordance with the procedure of Polis.<sup>4</sup> To 50 cc. of *boiling* concentrated nitric acid is added slowly 10 g. (0.019 mole) of tetraphenyllead. The mixture is cooled, filtered through glass wool, and washed with a little water. The diphenyllead dinitrate is dissolved in boiling water acidulated with a little nitric acid, and to the hot solution is added a solution of sodium bromide (4.1 g., 0.04 mole). The diphenyllead dibromide precipitates immediately, and the yield is 96%. In a corresponding manner, diphenyllead diiodide is obtained in a 98% yield when sodium iodide is used. Diphenyllead dichloride is most conveniently prepared, in a 98% yield, from tetraphenyllead and hydrogen chloride.<sup>5</sup> It can be prepared in a 93% yield by the addition of concd. hydrochloric acid to an aqueous solution of diphenyllead dinitrate.

Diphenyllead difluoride is obtainable in a 92% yield by the addition of an aqueous solution of potassium fluoride to an alcoholic solution of diphenyllead diiodide. Diphenyllead difluoride is insoluble in the usual organic solvents and does not melt up to 300°.

*Anal.* Calcd. for  $C_{12}H_{10}PbF_2$ : Pb, 51.88. Found: Pb, 52.07, 51.65.

Diphenyllead difluoride and phenylmagnesium bromide give tetraphenyllead.

(4) Polis, *Ber.*, **20**, 720 (1887).

(5) Gilman and Robinson, *THIS JOURNAL*, **51**, 3112 (1929).