thrins. The low pyrethrin content of the outer parts of the flower is important because it affords a means for detecting certain types of adulteration.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MCLAUGHLIN GORMLEY KING COMPANY]

STUDIES ON PYRETHRUM FLOWERS. III. THE PYRETHRIN CONTENT OF DIFFERENT COMMERCIAL VARIETIES

BY C. B. GNADINGER AND C. S. CORL

RECEIVED JULY 23, 1929 PUBLISHED FEBRUARY 6, 1930

The three species of *Pyrethrum* flowers that have insecticidal value are *Pyrethrum cinerariaefolium*, *Pyrethrum roseum* and *Pyrethrum carneum;* of these *Pyrethrum cinerariaefolium* is by far the most important. In 1928 more than eleven million pounds of *Pyrethrum cinerariaefolium* were imported into the United States from Europe and Japan, the latter country supplying about five times as much as all other sources combined. The amount of *Pyrethrum roseum* imported is negligible, but it is widely grown in this country for its ornamental flowers. *Pyrethrum carneum* is of no commercial importance.

The two principal commercial varieties of flowers, Dalmatian and Japanese, belong to the species *Pyrethrum cinerariaefolium*. There are several commercial grades of these flowers and it has been shown[1] that the trade preference for certain grades is unwarranted. The purpose of this paper is to show the comparative value of the different commercial varieties of *Pyrethrum* flowers.

Experimental

Twenty-eight commercial samples of whole flowers were collected from dealers in the United States and also from agents in Japan and Europe. Twenty samples of powdered commercial flowers were kindly supplied by Dr. C. C. McDonnell, Chief, Insecticide Control, United States Department of Agriculture. These powders had been kept in air-tight containers for two or three years. Two samples of *Pyrethrum cinerariaefolium* grown in Virginia were obtained through the courtesy of Dr. A. F. Sievers, Senior Biochemist, Bureau of Plant Industry, United States Department of Agriculture. Five samples of Minnesota and Iowa grown *Pyrethrum roseum* were collected and ten samples of ground or powdered commercial lots were obtained from large manufacturers of *Pyrethrum* sprays. Samples of *Pyrethrum carneum* could not be obtained.

The flowers were examined to determine the proportion of closed, half-closed, and open flowers and stems. Some of the Japanese flowers were com-

[1] Gnadinger and Corl, THIS JOURNAL, **52**, 680 (1930).

Table I

The Pyrethrin Content of Pyrethrum Flowers

No.	Description *Pyrethrum cinerariaefolium*	Crop, year	Composition of sample, %: Closed	Half-closed	Open	Stems	Misc.[a]	Achenes	Receptacles	Disk florets	Ray florets	Moisture, %	Pyrethrins, %
46	Closed Dalmatian, powdered	1926	..	..	..	...	1.3	6.5	28.0	43.2	21.0	...	0.38
35	Closed Dalmatian, powdered	1925	..	..	..	...	4.2	13.0	24.0	34.0	24.8	...	.39
42	Closed Dalmatian, powdered	1926	..	..	..	...	0.8	6.8	28.9	37.0	26.5	4.0	.39
7	Closed Dalmatian, whole	1928	74.1	14.0	8.9	0.8	1.6	..	..	..	..	6.2	.40
27	Closed Dalmatian, whole	1928	44.0	22.0	18.0	0.8	15.2	..	..	..	..	7.0	.40
45	Closed Dalmatian, powdered	1926	..	..	..	...	0.8	6.9	28.0	44.4	19.9	4.2	.41
33	Closed Dalmatian, powdered	1926	..	..	..	...	1.9	9.9	26.5	38.5	23.2	...	.42
13	Closed Dalmatian, whole	1925	..	..	..	...	..	..	..	..	..	5.9	.44
21	Closed Dalmatian, whole	1925	..	..	..	1.1	..	..	..	..	..	...	.45
48	Closed Dalmatian, powdered	1926	..	..	..	...	1.4	8.4	27.0	42.1	21.1	...	.45
24	Closed Dalmatian, whole	1928	53.2	24.4	16.6	2.1	3.7	..	..	..	..	4.3	.52
14	Closed Dalmatian, whole	1925	..	..	..	...	..	..	..	..	..	...	.53
23	Closed Dalmatian, whole	1928	68.4	16.0	12.1	0.7	2.8	..	..	..	..	6.0	.53
11	Closed Dalmatian, whole	1925	..	..	..	...	..	..	..	..	..	...	.57
37	Half-closed Dalmatian, powdered	1925	..	..	..	...	0.3	34.7	22.0	23.1	19.9	4.0	.38
38	Half-closed Dalmatian, powdered	1926	..	..	..	...	0.8	38.5	20.4	22.4	17.9	...	.38
47	Half-closed Dalmatian, powdered	1926	..	..	..	...	1.9	28.0	20.0	30.6	19.5	4.5	.38
29	Half-closed Dalmatian, whole	1928	15.4	21.5	46.2	1.5	15.4	..	..	..	..	...	.53
4	Half-closed Dalmatian, whole	1927	..	..	..	...	..	..	..	..	..	...	.57
40	Open Dalmatian, powdered	1925	..	..	..	...	0.9	47.9	16.4	18.8	16.0	...	.39
31	Open Dalmatian, powdered	1925	..	..	..	...	..	52.0	..	16.6	..	...	.40
50	Open Dalmatian, powdered	1926	..	..	..	...	1.5	51.4	18.3	14.0	14.8	5.0	.40
6	Open Dalmatian, whole	1927	..	..	..	...	..	..	..	..	..	...	.43
43	Open Dalmatian, powdered	1926	..	..	..	...	1.1	47.4	18.3	13.4	19.8	...	.43
16	Open Dalmatian, whole	1925	..	..	..	...	..	..	..	..	..	...	.47
28	Open Dalmatian, whole	1928	5.5	11.0	66.7	0.7	16.1	..	..	..	..	...	.51
36	Open Dalmatian, powdered	1926	..	..	..	...	6.4	57.1	18.0	5.5	13.0	...	.58
22	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.58
32	Japanese, powdered, compressed	1925	..	..	..	...	..	..	..	..	..	...	.62
44	Japanese, powdered, compressed	1926	..	..	..	...	..	..	..	..	..	...	.62
39	Japanese, powdered, compressed	1926	..	..	..	...	..	..	..	..	..	...	.64
41	Japanese, powdered, compressed	1926	..	..	..	...	..	..	..	..	..	...	.68
34	Japanese, powdered, compressed	1926	..	..	..	...	..	..	..	..	..	4.6	.71
49	Japanese, powdered, compressed	1926	..	..	..	...	..	..	..	..	..	3.9	.74
60	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.74

TABLE I (*Concluded*)

No.	Description	Crop, year	Composition of sample, %: Closed	Half-closed	Open	Stems	Misc.[a]	Achenes	Receptacles	Disk florets	Ray florets	Moisture, %	Pyrethrins, %
	Pyrethrum cinerariaefolium												
3	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	0.80
61	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.81
25	Japanese, whole, not compressed	1928	36.0	40.0	16.0	1.2	1.8	34.2	22.8	25.8	17.2	...	.84
30	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.86
2	Japanese, whole, compressed	1926	..	..	..	...	..	..	..	..	..	5.7	.87
62	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.87
56	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.92
20	Japanese, whole, not compressed	1928	9.8	20.0	64.0	0.4	5.8	..	..	..	..	...	.96
51	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	6.5	.99
19	Japanese, whole, not compressed	1928	..	..	..	...	..	..	..	..	..	...	1.10
17	Japanese, whole, not compressed	1928	..	..	..	...	..	..	..	..	..	...	1.17
18	Japanese, whole, not compressed	1928	..	..	..	...	..	..	..	..	..	...	1.20
1	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	1.21
26	Half-open American, whole (Virginia)	1928	27.2	18.0	54.0	3.0	0.8	..	..	..	..	...	0.85
58	Half-open American, whole (Virginia)	1929	..	..	..	...	..	..	..	..	..	7.3	1.11
	Pyrethrum roseum												
52	American whole, Minnesota	1929	74.2	25.8	0.0	0.0	0.0	..	..	..	..	...	0.25
59	American whole, Minnesota	1929	0.0	0.0	100	.0	.0	..	..	..	..	...	.56
54	American whole, Minnesota	1929	.0	.0	100	.0	.0	..	..	..	..	6.0	.73
55	American whole, Iowa	1929	.0	.0	100	.0	.0	..	..	..	..	6.6	.79
53	American whole, Minnesota	1929	.0	10.1	89.9	.0	.0	..	..	..	..	8.9	.82
	Commercial lots, unknown origin												
70	Powdered	..	..	..	..	...	..	..	..	..	..	...	.41
67	Ground	..	..	..	..	...	..	..	..	..	..	...	.54
68	Powdered	..	..	..	..	...	..	..	..	..	..	...	.57
65	Ground	..	..	..	..	...	..	..	..	..	..	...	.58
5	Ground	..	..	..	..	...	..	..	..	..	..	...	.59
66	Ground	..	..	..	..	...	..	..	..	..	..	...	.66
57	Ground	..	..	..	..	...	..	..	..	..	..	...	.68
63	Ground	..	..	..	..	...	..	..	..	..	..	...	.72
69	Powdered	..	..	..	..	...	..	..	..	..	..	...	.72
64	Ground	..	..	..	..	...	..	..	..	..	..	...	.79

[a] Parts of flowers, principally.

Table II

Summary of Analyses of Pyrethrum Flowers

Samples analyzed	Species	Description	Pyrethrin content, % Minimum	Maximum	Average
14	*Cinerariaefolium*	Dalmatian closed	0.38	0.57	0.448
5	*Cinerariaefolium*	Dalmatian half-closed	.38	.57	.448
8	*Cinerariaefolium*	Dalmatian open	.39	.58	.451
27	*Cinerariaefolium*	Dalmatian, all grades	.38	.58	.449
21	*Cinerariaefolium*	Japanese	.58	1.21	.853
2	*Cinerariaefolium*	American	.85	1.11	.980
50	*Cinerariaefolium*	All sources	.38	1.21	.640
5	*Roseum*	American, all grades	.25	0.82	.630
10	Unknown, probably *Cinerariaefolium*	Commercial lots	.41	.79	.626

pressed so that such a separation could not be made. The Department of Agriculture samples (numbers 31 to 50 inclusive) had been examined, before powdering, by Mr. George L. Keenan, Microanalyst, Food, Drug and Insecticide Administration. The results showing the percentage of achenes, disk florets, ray florets and receptacles in the twenty powdered samples are Mr. Keenan's and are published by permission. The whole flowers were ground to about 40-mesh, taking care to avoid heating during the grinding.

The pyrethrins, or active principles, were determined by the method previously described;[2] the analyses are reported in Table I and are summarized in Table II.

There was little or no difference in the pyrethrin content of the different grades of Dalmatian flowers. In general, the closed flowers yielded more color and extractive than the open flowers. Some of the samples that had been powdered for several years yielded almost colorless extracts but the pyrethrin content was as high as that of freshly ground new flowers. The pyrethrin content of the Dalmatian flowers ranged from 0.38 to 0.58%. Staudinger and Harder[3] found 0.4 to 0.6% of pyrethrins in the Dalmatian samples they analyzed.

The Japanese flowers contained from 0.58 to 1.21% of pyrethrins and averaged twice the pyrethrin content of the Dalmatian flowers.

It is interesting to note that American grown *Pyrethrum cinerariaefolium* is richer in active principle than Dalmatian and equal to Japanese. American grown *Pyrethrum roseum* averaged higher than Dalmatian *P. cinerariaefolium* and lower than Japanese. Ten commercial samples averaged 0.63%. No connection could be found between the appearance of the flowers and the pyrethrin content.

Summary

Japanese *Pyrethrum cinerariaefolium* has about twice the insecticidal value of Dalmatian flowers. Flowers equal to the Japanese can be grown

[2] Gnadinger and Corl, This Journal, **51**, 3054 (1929).

[3] Staudinger and Harder, *Ann. Acad. Sci. Fennicae*, **29A**, 1–14 (1927).

in America. The pyrethrin content of *P. roseum* is about the same as that of *P. cinerariaefolium*.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 226]

ALKALI METAL DERIVATIVES OF PHENYLATED METHANES AND ETHANES

BY CHARLES BUSHNELL WOOSTER[1] AND NEWELL WILSON MITCHELL[2]

RECEIVED JULY 29, 1929 PUBLISHED FEBRUARY 6, 1930

The fact that many of the colored organo-alkali compounds conduct the electric current in ether and in liquid ammonia solution,[3] and behave in other ways as salts, implies that the corresponding hydrides should exhibit an acidic character, albeit an exceedingly weak one. In fact, it has been shown that they may react with the ammono-base, potassium amide, in liquid ammonia solution to form the potassium salts. Thus triphenylmethane forms potassium triphenylmethide[4]

$$(C_6H_5)_3CH + KNH_2 \longrightarrow NH_3 + (C_6H_5)_3CK \quad (1)$$

and potassium benzhydrolate yields dipotassium benzophenone[5]

$$(C_6H_5)_2CHOK + KNH_2 \longrightarrow (C_6H_5)_2CKOK + NH_3 \quad (2)$$

This behavior indicates that these hydrides are ionized to a greater degree than the solvent ammonia, for otherwise reaction would be expected to proceed in the opposite direction corresponding to an ammonolysis of the salts. In the case of the alkali alkyls and alkali phenyls[6] such an ammonolysis does occur, demonstrating that the corresponding hydrocarbons are ionized to a less degree than ammonia.[7] Accordingly it is impossible to obtain organo-alkali compounds by the action of potassium amide upon these hydrocarbons.

[1] National Research Fellow.

[2] A portion of this material was submitted by N. W. Mitchell in a thesis for the degree of Bachelor of Science at the Massachusetts Institute of Technology.

[3] (a) Schlenk and Marcus, *Ber.*, **47**, 1664–1678 (1914); (b) Kraus and Rosen, THIS JOURNAL, **47**, 2739–2740 (1925); (c) Wooster, "Dissertation," Brown University, **1927**.

[4] Kraus and Rosen, Ref. 3b, p. 2741.

[5] Wooster, THIS JOURNAL, **50**, 1389 (1928).

[6] (a) Kraus and White, *ibid.*, **45**, 777 (1923); (b) White, *ibid.*, **45**, 779 (1923).

[7] Strictly speaking the ionization of ammonia does not constitute a sharp line of demarcation between hydrocarbons whose salts are completely stable and those whose salts are completely ammonolyzed. Hydrocarbons whose ionization lies either closely above or below that of ammonia would be expected to yield salts whose ammonolysis would reach an equilibrium when appreciable amounts of both the salt and hydrocarbon were present. In all cases considered in this paper, however, the salt was either formed in very large proportions or else in amounts so minute as to escape detection. Thus it is permissible to conclude that the ionization of these hydrocarbons was either considerably above or considerably below that of the solvent.