cool. The precipitated aglycone was rendered easier to filter by warming, and then was collected and dried; yield 34.3 mg.

After repeated recrystallization from methanol, the aglycone melted at 283°; it gave a purplish brown color with ferric chloride and an orange color with magnesium and concentrated hydrochloric acid. The aglycone was identical with the genkwanin obtained from *Prunus yedoensis* as shown by mixed melting point determination.

Glucogenkwanin (0.25 g.) was hydrolyzed by the same procedure. The filtrate was neutralized with barium carbonate and the osazone prepared by the usual method. The melting point 208° did not change when it was mixed with an authentic specimen of glucosazone.

Water (30 ml.) and 8 ml. of concentrated HCl were added to 50 mg. of glucogenkwanin in 50 ml. of methanol, and the mixture heated for 8 hours on a water-bath. After evaporation of the methanol, the aglycone was filtered. The filtrate was concentrated in a vacuum desiccator over KOH granules and examined chromatographically. Glucose was the only sugar found.

Genkwanin Diacetate.—A mixture of 0.2 g. of genkwanin, 4 ml. of acetic anhydride and 4 drops concentrated sulfuric acid in a small test-tube was set aside for an hour. Cold water was then added and the precipitate of acetylgenkwanin filtered, washed and recrystallized from methanol. The melting point 200° was not depressed by admixture with an authentic specimen of genkwanin diacetate, m.p. 204°.

Acknowledgment.—We wish to thank Mr. K. Sato of the Akanuma Experimental Nursery and Mr. S. Shirai of Ohshima Island for the samples of wood; Dr. Masatake Ohmasa, Director of the Government Forest Experiment Station and Dr. Shizuo Hattori of the University of Tokyo for their advice, and Dr. T. Ohta of the Tokyo Pharmaceutical College, who made the mixed melting test with glucogenkwanin. Cordial thanks are also due to Dr. Simon H. Wender, of the University of Oklahoma, who has very kindly arranged for the revision of this manuscript.

GOVERNMENT FOREST EXPT. STATION OF JAPAN
MEGURO, TOKYO, JAPAN

Flavonoids of Various *Prunus* Species. III. The Flavonoids in the Wood of *Prunus campanulata*

BY MASAO HASEGAWA AND TERUO SHIRATO

RECEIVED MARCH 3, 1954

This paper deals with the flavonoids of the wood of *Prunus campanulata* Maxim[1] which is cultivated in the Arboretum of the Government Forest Experiment Station in Tokyo. The method of extraction has been described previously.[2] Three flavanones were isolated from the ether-soluble fraction of the methanol extract as follows: the first product which separated from hot benzene proved to be naringenin,[2] the second which separated from hot water to be taxifolin[3] (distylin),[4] and the third which separated from a hot methanol–benzene mixture to be eriodictyol.[5] These products were identified by mixed melting point determinations of the compounds and their derivatives. The chromatographic data are given in Table I.

No glucosides of these flavanones were detected; only one phlobaphane-like substance was found in the ethyl acetate fraction.

TABLE I[a]

CHROMATOGRAPHIC DATA OF FLAVONOIDS OBTAINED FROM VARIOUS PRUNUS WOODS

Substance	R_f Developing agent[b] A	B	C	D	Detecting agent[c]
Eriodictyol		0.72	0.34		E, F, UV
Taxifolin	0.89	.55	.49		E, F, UV
Naringenin		.88	.37	0.05	E, F, UV
Sakuranetin		.95	.26	.71	E, F, UV
Prunin	.70	.75	.63		E, F, UV
Sakuranin	.68		.06		UV
Genkwanin		.98	.00		E, F,
Glucogenkwanin		.91	.20		UV

[a] The chromatograms were run at room temperature, 20–26°. [b] A = butanol:acetic acid:water, 4:1:5; B = *m*-cresol:acetic acid:water, 25:1:24; C = isopropyl alcohol:water, 22:78; D = water-saturated mixture of benzene and ligroin (30:1) containing methanol. [c] E = diazotized benzidine solution; F = 2% methanolic ferric chloride; UV = ultraviolet light. Results with filter paper made in Japan. Fluorescence in ultraviolet light did not occur except in the case of taxifolin, genkwanin and glucogenkwanin, when Whatman No. 1 filter paper was used.

Experimental

Extraction.—Wood chips (500 g.) of *Prunus campanulata* prepared from a dried stem[6] of 15-cm. diameter were twice extracted with 3-l. portions of methanol for 3 hours. The methanol filtrates were concentrated to 500 ml. on a water-bath. The solution was extracted repeatedly with ether, and the combined ether extract evaporated to dryness. The residue was extracted with boiling benzene (about 1500 ml.) and then with hot water (1500 ml.) and finally dissolved in 6 ml. of methanol to which 700 ml. of benzene was added.

Naringenin.—After filtration of the hot benzene extract, naringenin gradually deposited; an additional amount was obtained from the mother liquor. After five recrystallizations from methanol, the compound melted at 248°.

Anal. Calcd. for $C_{15}H_{12}O_5$: C, 66.17; H, 4.41. Found: C, 66.00; H, 4.26.

Naringenin triacetate, colorless needles, m.p. 126°.

The dimethyl ether was prepared by the reaction of naringenin with dimethyl sulfate and potassium carbonate in acetone; colorless long needles, m.p. 121°.

Anal. Calcd. for $C_{15}H_{10}O_3(OCH_3)_2$: OCH_3, 20.66. Found: OCH_3, 20.19.

Taxifolin (distylin).—The fraction soluble in hot water was extracted with ether. After evaporation of the ether, the residue was recrystallized from dilute methanol to give taxifolin as colorless prisms, m.p. 233°.

Anal. Calcd. for $C_{15}H_{12}O_7 \cdot H_2O$[7]: C, 55.90; H, 4.34. Found: C, 55.86; H, 4.46.

Taxifolin pentaacetate was obtained by treating taxifolin with pyridine and acetic anhydride without heating; colorless prisms, m.p. 155°.

Taxifolin.—5,7,3′,4′-Tetramethyl ether was prepared by heating an acetone solution of taxifolin with dimethyl sulfate and potassium carbonate, colorless prisms, m.p. 171°. The acetate of this methyl ether was obtained as colorless prisms, m.p. 169°. The melting points of taxifolin and its derivatives were not altered by admixture with the corresponding compounds prepared from an authentic specimen of taxifolin obtained from the wood of *Larix leptolepis*.

Eriodictyol.—As the methanol–benzene extract was slowly evaporated on a water-bath, eriodictyol deposited; after three recrystallizations from methanol, it was obtained as colorless needles, m.p. 263°.

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(1) See M. Hasegawa and T. Shirato, THIS JOURNAL, in press for flavonoids of *Prunus donarium*.

(2) M. Hasegawa and T. Shirato, *ibid.*, **74**, 6114 (1952).

(3) J. C. Pew, *ibid.*, **70**, 3031 (1948); J. Gripenberg, *Acta Chem. Scand.*, **6**, 1152 (1952).

(4) T. Kondo, *J. Fac. Agr. Kyushu Univ.*, **10**, 79 (1951).

(5) J. Shinoda and S. Sato, *J. Pharm. Soc. Japan*, **49**, 7 (1929).

(6) Almost identical results were obtained with chips from a living stem of 4-cm. diameter.

(7) M. Hasegawa and T. Shirato, *J. Chem. Soc. Japan*, **72**, 279 (1951).

Anal. Calcd. for $C_{15}H_{12}O_6$: C, 62.50; H, 4.16. Found: C, 62.57; H, 4.04.

Eriodictyol acetate was prepared from acetic anhydride and pyridine without heating; colorless needles, m.p. 138°.

Eriodictyol trimethyl ether was obtained as colorless needles, m.p. 136°.

Anal. Calcd. for $C_{15}H_9O_3(OCH_3)_3$: OCH_3, 27.19. Found: OCH_3, 27.90.

The yield from 3 kg. of wood chips was 23 g. of naringenin, 6.5 g. of taxifolin and 7.4 g. of eriodictyol.

Oxidation of Eriodictyol.—Eriodictyol (0.1 g.) was fused for 10 minutes at 230° with 1.5 g. of potassium hydroxide in 3 drops of water, and the reaction product dissolved in water, after acidification with 25% sulfuric acid; the solution was exhaustively extracted with ether; the ether extract was washed with 1% sodium bicarbonate solution and then evaporated to dryness.

These two fractions were paper chromatographed. The bicarbonate-soluble fraction gave one spot (R_f 0.35) which corresponds to that of protocatechuic acid; the ether soluble fraction gave one spot (R_f 0.16) which corresponds to that of phloroglucinol.[8]

Acknowledgment.—We wish to thank Dr. Masataka Ohmasa, Director of the Government Forest Experiment Station and Prof. Shizuo Hattori of the University of Tokyo for their advice. We are grateful to Mrs. Hrauko Nakamura for her help with the chromatograms. We are grateful to Dr. Simon H. Wender, of the University of Oklahoma, for his kindness in arranging for revision of the manuscript.

[8] Developing solvent, *m*-cresol:water:glacial acetic acid = 25:24:1; detecting agent, 2% methanolic ferric chloride.

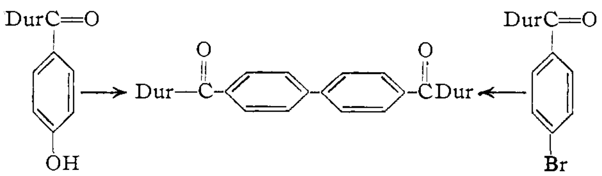
GOVERNMENT FOREST EXPT. STATION OF JAPAN
MEGURO, TOKYO, JAPAN

Bimolecular Reduction of *p*-Duroylphenoxide by Grignard Reagents

BY REYNOLD C. FUSON AND GEORGE W. PARSHALL[1]

RECEIVED JUNE 25, 1954

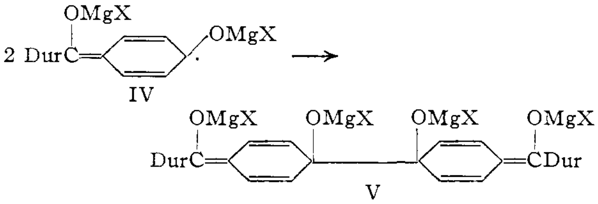
In the preceding paper,[2] it was reported that *p*-duroylphenol (I) reacts with tertiary alkyl Grignard reagents to give addition products in good yields. An attempt to employ primary and secondary Grignard reagents has disclosed a remarkable new reaction. When *p*-duroylphenol was treated with isopropylmagnesium bromide, none of the expected addition product could be isolated. Instead *p,p'*-diduroylbiphenyl (II) was obtained in a 19% yield. The same product was also formed by the action of benzylmagnesium chloride on *p*-duroylphenol. With methylmagnesium iodide and *p*-duroylphenol neither addition nor coupling occurred; however addition of cobaltous chloride to the reaction mixture brought about the formation of the biphenyl derivative.



I II III

The structure of *p,p'*-diduroylbiphenyl was proved by an independent synthesis. *p*-Bromophenyl duryl ketone (III) was coupled by treatment with the binary mixture, magnesium–magnesium iodide,[3] according to the method previously described for the synthesis of *p,p'*-dimesitoylbiphenyl.[4] The reaction of *p*-bromophenyl duryl ketone with methylmagnesium iodide in the presence of cobaltous chloride also gave *p,p'*-diduroylbiphenyl.

The favorable effect of cobaltous chloride on the reaction of *p*-duroylphenol with methylmagnesium iodide suggests that a free radical mechanism is involved.[5] In this respect the reaction resembles the formation of acyloins by the reaction of carboxylate ions with the binary mixture, magnesium–magnesium iodide.[6] The *p*-duroylphenoxide ion formed by the reaction with one mole of Grignard reagent is attacked probably by the magnesious halide to give a free radical IV. Dimerization of the radical IV would give a complex V which might be expected to decompose directly to the diketone II or to yield a hydrolysis product which could form the diketone by loss of two molecules of water.



IV

V

Experimental[7]

Action of Grignard Reagents on *p*-Duroylphenol. (a) **Isopropylmagnesium Bromide.**—The Grignard reagent prepared from 1.5 g. of magnesium and 4.8 ml. of isopropyl bromide in 50 ml. of ether was filtered and added rapidly to a solution of 2.54 g. of *p*-duroylphenol in 50 ml. of hot benzene. The mixture, which became purple immediately, was boiled under reflux for 45 minutes and poured into dilute hydrochloric acid. The organic layer became cherry-red, but the color faded to yellow after a few minutes. The organic layer was washed with water, dried over magnesium sulfate and freed of solvent by evaporation. A yellow solid was deposited when the gummy residue was extracted with methanol. Recrystallization from benzene converted the solid to light yellow flakes which melted at 322–326°, yield 0.45 g. (19%). A mixed melting point with an authentic sample of *p,p'*-diduroylbiphenyl was not depressed.

Anal.[8] Calcd. for $C_{34}H_{34}O_2$: C, 86.04; H, 7.22. Found: C, 85.90; H, 7.42.

The infrared spectrum[9] contains bands assignable to a hindered conjugated carbonyl group (1667 cm.$^{-1}$), to an aromatic system (1558, 1606 cm.$^{-1}$) and to a *para*-substituted phenyl radical (822 cm.$^{-1}$).

(b) **Benzylmagnesium Chloride.**—A solution of 2.56 g. of *p*-duroylphenol in 30 ml. of hot benzene was added to the Grignard reagent prepared from 1.2 g. of magnesium and 5.5 ml. of benzyl chloride in 30 ml. of ether. After being heated under reflux overnight, the reaction mixture was poured into cold dilute hydrochloric acid and the product was isolated as in the preceding experiment. Recrystallization from petroleum ether gave yellow flakes of *p,p'*-diduroylbiphenyl, m.p. 320–322°. The infrared spectrum

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[1] National Science Foundation Fellow, 1952–1953; Allied Chemical and Dye Fellow, 1953–1954.

[2] R. C. Fuson, W. D. Emmons and G. W. Parshall, THIS JOURNAL, **76**, 5466 (1954).

[3] M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 236 (1927).

[4] R. C. Fuson and M. D. Armstrong, *ibid.*, **63**, 2650 (1941).

[5] M. S. Kharasch and E. K. Fields, *ibid.*, **63**, 2316 (1941).

[6] M. Gomberg and W. E. Bachmann, *ibid.*, **50**, 2762 (1928).

[7] All melting points are corrected.

[8] The microanalyses were performed by Mrs. Esther Fett, Mrs. Katherine Pih and Mrs. Lucy Chang.

[9] The infrared spectra were determined and interpreted by Miss Helen Miklas.