treated with alcoholic 2,4-dinitrophenylhydrazine in the presence of concd. hydrochloric acid as described above.

2-(α-Bromobenzyl)-1,3-dioxolane.[3]—A solution containing 5 g. (0.023 mole) of bromomethoxystyrene, 10 g. (0.11 mole) of trimethylene glycol, 10 ml. of purified dioxane and 3 drops of concd. sulfuric acid was left at room temperature for 10 days. An excess of dilute sodium bicarbonate solution was added, water and dioxane removed under reduced pressure on the steam-bath and the residue taken up in ether, dried and distilled, b.p. 120–125° (1 mm.). The distillate solidified on standing, yield 2.8 g. (47%), m.p. 47–48° after one recrystallization from 50% ethanol.

LOS ANGELES 4, CALIFORNIA

[CONTRIBUTION FROM THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

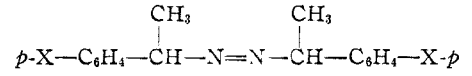
The Effects of Structure on the Kinetics of Decomposition of Substituted Phenyl-azo-triphenylmethanes

BY SAUL G. COHEN AND CHI HUA WANG

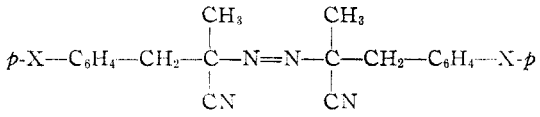
RECEIVED MAY 23, 1953

In a study of the effects of substituents on the formation of substituted phenyl radicals, a series of *p*-substituted-phenyl-azo-triphenylmethanes was prepared and decomposed, *p*-X-C_6H_4—N=N—$C(C_6H_5)_3$, X = H, CH_3, Br, NO_2, HO, CH_3O, CH_3CONH. The decompositions showed first-order kinetics. The rates were determined for each compound at two temperatures (at about 43 and 53° or 53 and 64°) in toluene and for two of the compounds, X = H, HO, in acetic acid and in pyridine. Energies of activation were in the range of 27–30 kcal. mole^{-1}, except for one compound, X = CH_3, E_A 24 kcal.; entropies of activation were not constant. All substituents (except methyl) decreased the rates of decomposition as compared with the unsubstituted compound, which decomposed about four times as fast as the slowest (X = *p*-NO_2). The results were compared with those of the decomposition of similarly substituted peroxy compounds and of other azo compounds, and discussed in terms of the conjugation of the phenyl and azo groups and the effects of the substituents on the phenyl radicals.

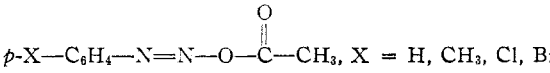
Examination of the effects of substituents in the benzene ring on the rates of decomposition of certain azo compounds has been of interest to us as an aspect of the relation of structure and reactivity in the chemistry of free radicals. In the decomposition of 1-azo-bis-1-phenylethanes[1]



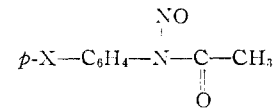
the substituents methyl and methoxyl led to small (about 8 and 30%) increases in rate, while the substituents chlorine and nitro led to small decreases (about 24 and 14%) in the rates of decomposition of azo compounds of structure[2]



Still smaller effects (a total range of ±10% in the rate constants) were observed in the decomposition of the benzene diazoacetates[3]

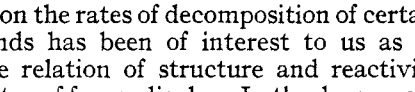


but it is not clear whether the decompositions of the diazoacetates or the rearrangements of the nitroso-acetanilides



were actually being measured.[4]

We are reporting a study of the effects of substituents on the rates of decomposition of phenyl-azo-triphenylmethanes



reactions which lead to a substituted phenyl radical, a nitrogen molecule and a triphenylmethyl radical by the dissociation of two carbon–nitrogen bonds.[7] While the decomposition of symmetrical azo compounds like azomethane[8] or azo-bis-isobutyronitrile[9] and the unsymmetrical methyl-azo-2-propane[8a] may proceed by simultaneous symmetrical dissociation of the two carbon–nitrogen bonds, the decomposition of the phenyl-azo-triphenylmethanes need not. The triphenylmethyl–nitrogen bond is probably much weaker than the phenyl–nitrogen bond and might be almost completely broken when the phenyl–nitrogen bond is only in small part dissociated. In an extreme case, the weaker bond might break first in a rate-determining process, leading to an unstable intermediate radical of type R—N=N·, and the nature of the group R and the R–N bond would have no effect on the observed rate. However, the apparent differences in the ease of decomposition of aryl-azo-triphenylmethanes, acyl-azo-triphenylmethanes[6] and azo-bis-triphenylmethanes[10] indicate that such decompositions are affected by the strength of both carbon–nitrogen bonds or by the ease of formation of both radicals, and that substituents in the phenyl group of the phenyl-azo-triphenylmethanes would influence the kinetics of the decompositions, the effects possibly being damped by the dominant ease of formation of the triphenylmethyl radicals.

(1) S. G. Cohen, S. J. Groszos and D. B. Sparrow, THIS JOURNAL, **72**, 3947 (1950).

(2) C. Overberger and H. Biletch, *ibid.*, **73**, 4880 (1951).

(3) S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 689 (1935).

(4) D. F. DeTar, THIS JOURNAL, **73**, 1446 (1951).

(5) M. Gomberg and A. Campbell, *ibid.*, **20**, 780 (1898).

(6) H. Wieland, A. Hintermaier and J. Dennstedt, *Ann.*, **452**, 1 (1927).

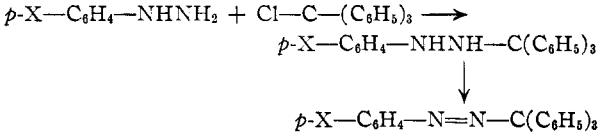
(7) *Cf.* W. A. Waters, "The Chemistry of Free Radicals," 2nd Ed., Oxford University Press, New York, N. Y., 1948, p. 147–148.

(8) (a) H. C. Ramsperger, THIS JOURNAL, **49**, 912 (1917); (b) **50**, 714 (1928); (c) **51**, 2134 (1929).

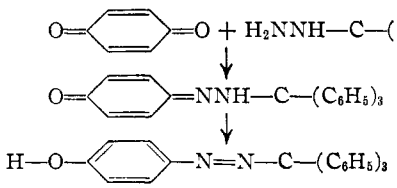
(9) F. M. Lewis and M. Matheson, *ibid.*, **71**, 747 (1949).

(10) H. Wieland, H. vom Hove and K. Borner, *Ann.*, **456**, 31 (1926). Azo-bis-triphenylmethane was too unstable to be isolated, and attempts to prepare it by oxidation of the hydrazine led to the decomposition products.

In the present series, all the compounds except the *p*-hydroxy derivative were prepared by the general method of Gomberg,[11] condensation of the phenylhydrazine with trityl chloride and oxidation of the disubstituted hydrazine, which need not be purified, with hydrogen peroxide.[1] The easily oxi-



dized phenylhydrazines, X = CH_3O, CH_3CONH, were used as the hydrochlorides and condensed with one molar equivalent of trityl chloride in pyridine. In the other cases the free phenylhydrazines were condensed with one-half equivalent of trityl chloride in ether. It was anticipated that it would be difficult to prepare the *p*-hydroxy compound by this sequence of reactions and an alternative procedure was devised, condensation of 1,4-benzoquinone with triphenylmethylhydrazine, which was present as the hydrochloride



The rates of decomposition of the azo compounds in approximately 0.01 *M* solution in toluene were determined at two temperatures by measurement of the volume of evolved nitrogen as a function of time (V_t), essentially as described previously.[1] Linear plots of ln $V_\infty/(V_\infty - V_t)$ *vs.* time were obtained in satisfactorily duplicated runs and indicated that the decompositions were first order. The unsubstituted compound (X = H) was also decomposed at higher initial concentration, 0.07 *M*, the sevenfold increase in concentration leading to a small (5%) and presumably insignificant decrease in rate, giving additional but not conclusive[12] evidence that higher order reactions may be absent. Rate constants were determined from the slopes of the plots and are probably accurate to within ±3%. Two compounds, X = H and HO, were also decomposed in acetic acid and in pyridine. Fewer runs were made in these solvents and the accuracy of the rate constants was less. Activation energies were calculated from the rate constants at the two temperatures by application of the Arrhenius equation, and entropies of activation were calculated according to the equation derived from transition state theory.[13] Typical plots of rate data are given in Fig. 1, and the results are summarized in Table I.

The data at 53.35 and 54.0° indicate that the unsubstituted and the *p*-methyl compounds decomposed at about the same rate and more rapidly than the others at this temperature. The rates of decomposition of the *p*-methoxy, *p*-hydroxy, *p*-acetamino, *p*-bromo and *p*-nitro compounds decreased in this order, and there was a fourfold diminution in rate between the unsubstituted and the *p*-nitro compounds, a factor somewhat greater than those observed in the free radical decompositions of the correspondingly substituted *t*-butyl perbenzoates[14] and benzoyl peroxides.[15] However, this range of rates and the limited accuracy of the data are inadequate for a significant analysis of the effects of substituents on the energies and entropies of activation beyond noting that the energy of

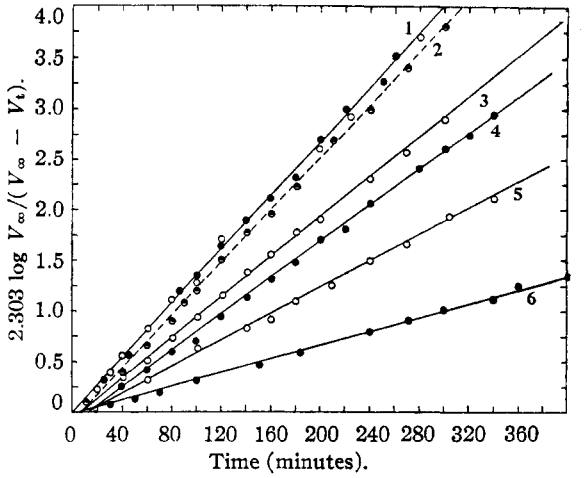


Fig. 1.—Decomposition of *p*-X—C_6H_4—N=N—$C(C_6H_5)_3$ in toluene: curve 1, —O—O—, X = H, T = 53.35°; curve 1, —●—●—, X = CH_3, T = 53.35°; curve 2, X = CH_3O, T = 54.0°; curve 3, X = HO, T = 54.0°; curve 4, X = CH_3CONH, T = 54.0°; curve 5, X = Br, T = 53.35°; curve 6, X = NO_2, T = 53.35°.

TABLE I

DECOMPOSITION OF SUBSTITUTED PHENYL-AZO-TRIPHENYLMETHANES, *p*-X—C_6H_4—N=N—$C(C_6H_5)_3$

X	T, °C. ±0.05°	$k_1 \times 10^4$, sec.$^{-1}$	E_A, kcal. mole^{-1}	$\Delta S^\pm$, cal. mole^{-1} degree^{-1}
CH_3[a]	53.35	2.25 ± 0.05	24 ± 1	−3 ± 3
CH_3[a]	43.30	0.69 ± .01		
H[a]	53.35	2.25	27	5
H[a]	43.30	0.60		
CH_3O[a]	54.00	2.13	28	8
CH_3O[a]	64.00	7.6		
HO[a]	54.00	1.70	29	11
HO[a]	64.00	6.4		
CH_3CONH[a]	54.00	1.46	30	15
CH_3CONH[a]	64.00	5.9		
Br[a]	53.35	1.05	28	7
Br[a]	64.30	4.28		
NO_2[a]	53.35	0.57	27	4
NO_2[a]	64.30	2.25		
H[b]	43.30	0.57	28	7
H[b]	64.00	8.4		
HO[b]	54.00	1.42	32	20
HO[b]	64.00	6.2		
H[c]	53.35	1.74	31	18
H[c]	64.00	8.0		
HO[c]	54.00	1.52	32 ± 2	21 ± 5
HO[c]	64.00	6.7		

[a] In toluene. [b] In acetic acid. [c] In pyridine.

(11) M. Gomberg, *Ber.*, **30**, 2044 (1897).

(12) J. E. Leffler, THIS JOURNAL, **72**, 67 (1950).

(13) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 199.

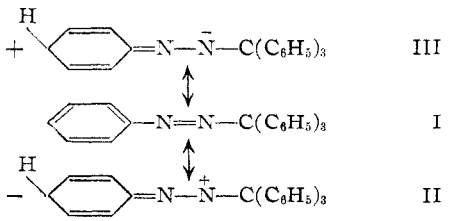
(14) A. T. Blomquist and J. A. Berstein, THIS JOURNAL, **73**, 5546 (1951).

(15) A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

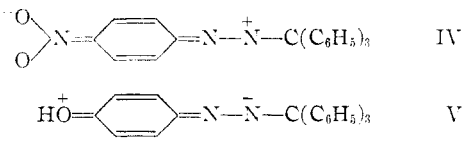
activation of decomposition of the *p*-methyl compound is somewhat lower than those of the other compounds, and that the entropies of activation are not constant and parallel in compensatory fashion the variations in activation energy to which they are very sensitive.

The effects of the substituents on the rates are significant and novel since, except for the methyl group, all substituents, both electron-attracting and electron-repelling, decrease the rates of decomposition of these azo compounds. This result is in clear contrast with the effects of substituents on the decomposition of *t*-butyl perbenzoates[14] and benzoyl peroxides[15,16] in which substituents which activate the benzene ring toward electrophilic substitution generally increase the rates and deactivating substituents decrease the rates of decomposition; those data[14] were correlated by the Hammett relationship, $\log k/k_0 = p\sigma$, despite the variations in entropy of activation. Those results were interpreted in terms of the effects of substituents on (a) the ionic character and strength of the peroxide bond[14] and (b) the electron density at the peroxide linkage and the electrostatic repulsion between the two benzoate groups.[16] On the other hand, the available information about the effects of structure on the decomposition of the aliphatic azo compounds, R—N=N—R, indicates that these compounds decompose at faster rates and with lower activation energies as the group R corresponds to apparently more stable free radicals. The azo compound is most stable when R = CH_3 and the ease of thermal decomposition increases progressively in the order: CH_3[8] < *i*-C_3H_7[8] < $C_6H_5CH_2$[17] < $C_6H_5CHCH_3$[1] < $(CH_3)_2C$-CN[9] ~ $(CH_3)_2CCOOCH_3$[9] < $(C_6H_5)_2CH$[18] < $(C_6H_5)_3C$.[10] The factors which may contribute to stabilization of the radical products presumably contribute similarly to stabilization of the transition states and weaken the carbon–nitrogen bonds which are broken in the decompositions.

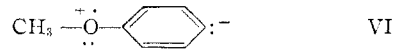
A general structural feature present in the phenylazo-triphenylmethanes and absent in the other compounds discussed above is the conjugation between the benzene ring and the azo group which leads to resonance stabilization of these compounds. The azo group



may either send in II or withdraw III a pair of electrons[19] and both the electron-attracting IV and the electron-repelling V substituents may contribute to and enhance this conjugation, adding to the double bond character of the phenyl–nitrogen bond, decreasing the double bond character of the azo group and generally stabilizing the molecule toward homolytic cleavage and formation of a nitrogen molecule and a phenyl radical.



However, consideration of the effects of the individual substituents on the rates indicates that this conjugation may not be the only important factor. The substituents which deactivate the benzene ring toward electrophilic substitution, bromine and nitro, have the most marked effects in stabilizing these azo compounds, while the activating groups, and notably the methoxyl which would be expected to be strongly conjugated with the azo group as in formula V, decrease the rates of decomposition to a lesser extent. It may be that stabilization of the phenyl radicals (and the transition states) by accession of electrons from the substituent to the radical carbon, possibly by contributions from a structure of type VI, is a compensatory activating factor which contributes



to the observed order of reactivity. The effect of the methyl substituent may be analyzed in similar terms involving hyperconjugation or it may be that stabilization of the phenyl radical by a positive inductive effect is important in decreasing the activation energy in this case. Indeed the entire observed order of reactivity would be consistent with an explanation in terms of the inductive effects of the substituents, the phenyl radicals being stabilized by a +I effect and made less stable by a −I substituent. However it seems unlikely that this is the sole cause of the observed order of reactivity.

Because the *p*-hydroxy compound, from its method of preparation and structure, may exist as a tautomeric mixture of the azo compound and the quinone-hydrazone, its rate of decomposition was examined in acetic acid and in pyridine, in addition to toluene, and the unsubstituted parent compound was examined similarly for comparison. The more polar solvents caused similar effects in both cases, small changes in the rates and some increases in the activation energies, and it seems that the azo structure which we assign to the hydroxy compound is probably correct.

Experimental[20]

N-Phenyl-N′-tritylhydrazine[21] was prepared by interaction of 11 g. (0.1 mole) of phenylhydrazine and 14 g. (0.05 mole) of trityl chloride in anhydrous ether under reflux for one hour. The mixture was filtered and concentrated, and the product was crystallized from benzene, 50% yield, m.p. 134–135° (reported m.p. 136–137°).

Phenyl-azo-triphenylmethane[5] was prepared by treatment of a solution of 8.4 g. of N-phenyl-N′-tritylhydrazine in 100 ml. of ether with 50 ml. of saturated aqueous sodium bicarbonate and 50% excess of 30% hydrogen peroxide with

(16) C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950).

(17) J. Thiele, *Ann.*, **376**, 265 (1910), qualitative results.

(18) S. G. Cohen and C. H. Wang, unreported results.

(19) W. T. Campbell, W. A. McAllister and M. T. Rogers, THIS JOURNAL, **75**, 864 (1953).

(20) Melting points are uncorrected. On decomposition points the rate of heating was two degrees per minute. Analyses are by S. M. Nagy, Massachusetts Institute of Technology.

(21) M. Gomberg and H. W. Berger, *Ber.*, **36**, 1089 (1903).

stirring at room temperature for five hours. The ether was evaporated and the azo compound was crystallized from ethanol, 5.8 g., 70% yield, m.p. 110–112° dec. (reported m.p. 110–112°).

p-**Nitrophenyl-azo-triphenylmethane**.[5]—*p*-Nitrophenylhydrazine, 15.3 g. (0.1 mole) was treated with 14 g. (0.05 mole) of trityl chloride as described above. The mixture was filtered and concentrated, diluted with chloroform and treated directly with saturated bicarbonate solution and excess 30% hydrogen peroxide as described above. The azo compound was crystallized from methanol and obtained in over-all yield of 47%, 9.2 g., m.p. 118–119° dec. (reported m.p. 118.5°).

p-**Tolyl-azo-triphenylmethane**.[5]—*p*-Toluidine (18 g.) was diazotized by treatment with hydrochloric acid and sodium nitrite, and the diazonium compound was reduced with stannous chloride, leading to *p*-tolylhydrazine hydrochloride. This was isolated and converted to *p*-tolylhydrazine, 7.5 g., 37% yield, m.p. 61–65°. Treatment with 8.6 g. of trityl chloride and oxidation with hydrogen peroxide as described for the unsubstituted compound led to N-*p*-tolyl-N′-tritylhydrazine, 7.5 g., 66% yield, m.p. 155° (from ethanol), and then to the azo compound, 62% yield, m.p. 103° dec. (reported m.p. 103.5°).

p-**Bromophenyl-azo-triphenylmethane**.—*p*-Bromophenylhydrazine hydrochloride, 22.3 g. (0.1 mole) was treated with sodium hydroxide and extracted with ether. The ether solution was dried over potassium hydroxide, treated with 0.05 mole of trityl chloride in the usual way, filtered and oxidized directly with hydrogen peroxide, leading to the azo compound in over-all yield of 30%, m.p. 114–115° dec.

Anal. Calcd. for $C_{25}H_{16}N_2Br$: C, 70.3; H, 4.48. Found: C, 70.3; H, 4.55.

p-**Acetaminophenyl-azo-triphenylmethane**.—*p*-Aminoacetanilide, 25 g. (Matheson Co.) was converted to *p*-acetaminophenylhydrazine hydrochloride, 18.5 g. Attempts to use the free base, or the hydrochloride, neutralized by alkali, in ethanol in the next stage were unsuccessful. The hydrazine hydrochloride, 5 g., and 7 g. of trityl chloride were dissolved in 80 ml. of pyridine, which had been dried over potassium hydroxide, and allowed to react at room temperature for two hours. The mixture was filtered and the filtrate was diluted with water until it became turbid. A product slowly solidified; it was crystallized from ethanol, 8 g., 80% yield, m.p. 122 dec., presumably the N-*p*-acetaminophenyl-N′-tritylhydrazine. The hydrazine, 4 g., was dissolved in 1:1 acetone–alcohol and oxidized in the usual way. The azo compound was crystallized from ethanol, 3 g., 73% yield, m.p. 112–113° dec.

Anal. Calcd. for $C_{27}H_{23}N_3O$: N, 10.36. Found: N, 10.35.

p-**Methoxyphenyl-azo-triphenylmethane**.[6]—*p*-Anisidine (25 g.) was diazotized and reduced to *p*-methoxyphenylhydrazine hydrochloride; this was isolated and converted to the free base, m.p. 65°. The hydrazine, 5 g., was dissolved in 20 ml. of dried pyridine and treated with a solution of 10 g. of trityl chloride in 40 ml. of dried pyridine under nitrogen, first at 0°, then at 25° for one hour. The mixture was diluted with ether, washed with water, hydrochloric acid and water, dried, concentrated, triturated with 95% ethanol and cooled. A yellow solid was isolated, m.p. 80–90° dec., which was dissolved in chloroform and oxidized with hydrogen peroxide at 0° for one hour. The chloroform was evaporated and the residue, 9 g., was crystallized rapidly from ethanol, leading to the azo compound, 5.3 g., 41% yield, m.p. 113–114° dec. (reported m.p. 114°).

Triphenylmethylhydrazine.[22]—Trityl chloride, 0.075 mole, was treated with 68% hydrazine hydrate, 0.16 mole, in ether. The mixture was warmed gently and filtered, and the filtrate treated with hydrogen chloride gas, leading to crude tritylhydrazine hydrochloride, 87% yield, melting variously in different runs from 105–115° to 130–140° (reported m.p. 108–113°).

p-**Hydroxyphenyl-azo-triphenylmethane**.—Triphenylmethylhydrazine hydrochloride, 12 g., m.p. 130–140°, was dissolved in 50 cc. of 95% ethanol and added at 0° to a solution of quinone (freshly crystallized from benzene, m.p. 113–115°) in 100 cc. of 95% ethanol. The solution was diluted with 10 volume per cent. of water and kept at 4° for 24 hours. The mixture was filtered, the filtrate concentrated in vacuum, the residue taken up in ether, washed repeatedly with water, dried over magnesium sulfate, concentrated in vacuum, dissolved in 95% ethanol, treated with a little water and cooled. A yellow solid, 4.5 g., m.p. 70–80°, was collected and crystallized several times from 3:1 alcohol–water, leading to the azo compound, m.p. 115–116° dec., 3.2 g., 23% yield.

Anal. Calcd. for $C_{25}H_{20}N_2O$: C, 82.4; H, 5.53. Found: C, 82.5; H, 5.45.

Acknowledgment.—We are pleased to acknowledge generous support of this work by Frederick Gardner Cottrell Grants of Research Corporation and by an allocation from the Committee on Research Grants of Brandeis University.

(22) J. Stieglitz, THIS JOURNAL, **38**, 2720 (1916).

WALTHAM, MASSACHUSETTS

[CONTRIBUTION FROM THE GOVERNMENT FOREST EXPERIMENT STATION OF JAPAN]

Two New Flavonoid Glycosides from the Leaves of *Phellodendron amurense* Ruprecht

BY MASAO HASEGAWA AND TERUO SHIRATO

RECEIVED JUNE 26, 1953

From the fresh leaves of *Phellodendron amurense*, a tree of *Rutaceae*, two new flavonoid glycosides have been isolated. One of them, phellamurin, is shown to be 5,7,4′-tetrahydroxy-8-(γ-hydroxyisovaleryl)-flavanonol-7-glucoside, and the other, amurensin, to be the corresponding flavonol glucoside. The conversion of phellamurin into amurensin has been successfully achieved.

Introduction

Phellodendron amurense Ruprecht is a tree widely distributed in mountainous regions of the central and northern part of Japan, and when adult usually attains a height of 20 m. From the water soluble portion of the methanolic extract of the leaves of this tree, a colorless flavanonol glycoside has been obtained, and from the water-insoluble portion, a yellow flavonol glycoside. These two substances are new to the literature, and the name phellamurin for the former glycoside and the name amurensin for the latter have been proposed.

The structures of phellamurin and amurensin (Fig. 1) have been established, utilizing in part the study of the relationship of these new compounds with the compounds icariin, nor-icariin and β-anhydroicaritin (Fig. 2), whose structures had previously been established by Akai and coworkers.[1] These established interrelationships are shown in Fig. 3.

Details of the isolation, properties and proof of structure of the compounds phellamurin and amur-

(1) S. Akai and K. Nakagawa, *J. Pharm. Soc. Japan*, **55**, 155 (1935); S. Akai, M. Imaida and T. Matsukawa, *ibid.*, **55**, 214 (1935).