mit Ⅳa zeigte keine Schmp.-erniedrigung. Deshalb wurde geschlossen, daß die Verseifungsreaktion bei der Chromatographie stattfand und dabei das freie Phenol entstand.

Zusammenfassung

Es wird die Aromatisierungsreaktion von Cholesta-2,4-dien-1-on mittels Zinkstaub beschrieben. Dabei wird bewiesen, daß die Reaktion auf analoge Weise wie die Dienon-Phenol-Umlagerung durch Angriff des Zink-Ions verläuft und schließlich 19-Nor-4-methylcholesta-1,3,5(10)-trien-3-ol ergibt.

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118. **Hiroaki Matsuda**: Studies on the Constituents of the Leaves of *Rhus* and of Some Species of Related Genera in Japan.[*1]

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Many *Rhus* species have been examined exclusively for tannin materials,[1] and some of them have been known to contain gallotannin, such as Chinese gallotannin in the galls of *Rhus chinensis* Mill. (syn. *R. semialata*) and sumactannin in the dried leaves of various *Rhus* species. From the leaves of Japanese *Rhus*, Ueda and Ukida[2] obtained an amorphous tannin, and ellagic acid from *R. trichocarpa* Miq.

Now a crystalline tannin was isolated from the leaves of *R. succedanea* L. (m.p. 202～204°, decomp.). After hydrolysis, it gave each one mol. of glucose, gallic acid and ellagic acid. When methylated, the tannin gave a nonamethyl ether and on hydrolysis it gave trimethyl gallic acid, hexamethoxydiphenic acid and glucose. This tannin was ellagitannin, while lactone rings of ellagic acid were opened and an acid, hexahydroxydiphenyldicarboxylic acid was formed. The carboxyl groups of gallic and diphenyldicarboxylic acid combined with hydroxyl groups of glucose.

Schmidt, *et al.* isolated corilagin (I), a crystalline ellagitannin, m.p. 202～204° (decomp.) from divi-divi[3] (dried fruit of *Caesalpinia coriaria*), and myrobalan[4] (dried fruit of *Therminalia chebula*), and its constitution was determined as 1-galloyl-3,6-hexahydroxydiphenoyl-D-glucose.[5]

The tannin obtained from the leaves of *Rhus succedanea* was quite alike to corilagin. When this tannin was compared directly with corilagin, which was kindly given me by late Dr. O. Th. Schmidt, Heidelberg and isolated from divi-divi, there

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[*1] A brief outline of this paper was presented by Dr. Shizuo Hattori in 1961 before the symposium on Phytochemistry, Golden Jubilee Congress, Univ. Hong Kong.

[*2] Hongo, Bunkyo-ku, Tokyo (松田弘明).

1) H. Gnamm: "Die Gerbstoffe u. Gerbmittel," Wissenschaftlicher Verlag, Stuttgart (1949); F. N. Howes: "Vegetable Tanning Materials," Butterworths Scientific, London (1953).

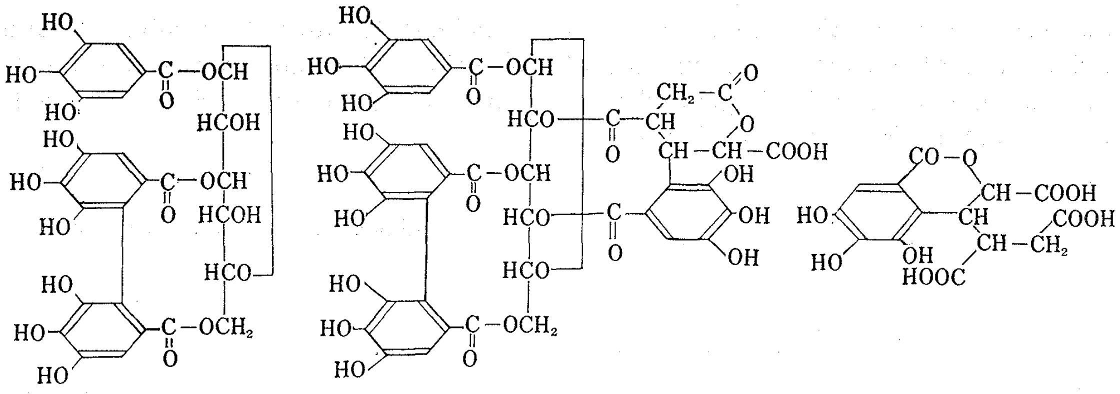
2) K. Ueda, I. Ukida: Kogyo Kagaku Zasshi, **28**, 156 (1925); **29**, 557 (1926).

3) O. Th. Schmidt, R. Lademann: Lieb. Ann., **571**, 232 (1951).

4) O. Th. Schmidt, D. M. Schmidt: *Ibid.*, **576**, 31 (1952).

5) O. Th. Schmidt, F. Blinn, R. Lademann: *Ibid.*, **576**, 75 (1952); O. Th. Schmidt, D. M. Schmidt: *Ibid.*, **578**, 25 (1952); O. Th. Schmidt, D. M. Schmidt, J. Herok: *Ibid.*, **587**, 67 (1954).

was neither difference of the properties nor mixed melting point depression between both substances. Corilagin was obtained from myrobalan or divi-divi in a free state or partly degradation product of chebulagic acid (II), this acid decomposed with ease to corilagin and chebulic acid (III) by heating.



I : corilagin. II : chebulagic acid III : chebulic acid

Chart 1.

The extract or the pressed sap of the fresh leaves, however, gave almost the same results on the paper chromatograms. If corilagin were solely derived from chebulagic acid, there should exsist a corresponding chebulic acid and at least a small amount of chebulagic acid itself should be left in the extract, but no definite result was obtained nor remarkable substance was detected on a chromatogram.

In the leaves of *Rhus succedanea* it was considered that corilagin was contained in a free state, or it was partly derived from another source. If it was the latter case, it might be considered probable that the tannin consisted mainly of corilagin and some substance such as gallic or ellagic acid (hexahydroxydiphenic acid form). Indeed, these acids were isolated from the extract, but corilagin was partly hydrolyzed by heating and gallic and ellagic acid were obtained. Any distinct proof, however, could not be obtained whether or not gallic and ellagic acid were both derived from corilagin.

Corilagin was also isolated from the leaves of *Rhus trichocarpa* Miq., *R. sylvestris* Sieb. et Zucc., *R. ambigua* Lavallée ex Dippel and *Poupartia Fordii* Hemsl. (*Anacardiaceae*). But in the leaves or galls of *Rhus chinensis* Mill. no corilagin was recognized. The tannin substance in the leaves of *R. chinensis* resemble to gallotannin in the galls. In Japan, galls are obtained only from *Rhus chinensis* and neither from other *Rhus* species nor other genera. This fact may probably suggested that there are some differences in the constituents of the leaves, and gallotannin in the galls has been considered probably to have accumulated abnormally from the leaves.

Euphorbiaceae are separated from *Anacardiaceae* in the plant taxonomy. Constituents of the leaves resemble each other, and corilagin, gallic and ellagic acid were recognized in some euphorbiaceous genera (*Sapium japonicum* Pax et Hoffmann, *S. sebiferum* Roxb., *Ricinus communis* L., *Aleurites cordata* Stend.).

Many flavonoid compounds have been isolated from the leaves of various *Rhus* species,[6] but all of them being found in non-glycosidic state. The flavonoid compounds isolated from the fresh leaves of *Rhus* or some genera of *Euphorbiaceae*, from which corilagin was isolated, consisted of glycoside form and a small amount of their aglycones.

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6) A.G. Perkin : J. Chem. Soc., **71**, 1131 (1897); C. **1897**, II, 1047. A.G. Perkin, P.J. Wood : Proc. Chem. Soc. (1897/98), **193**, 104. C. **1898**, I, 1300. A.G. Perkin : *Ibid.*, **198**, 183 (1898/99); C. **1899**, I, 127; **16**, 45, 22/2; C. **1900**, I, 669. S.F. Acree, W.A. Syme : J. Am. Chem. Soc., **36**, 301 (1906).

The flavonoid glycoside in the leaves of *Rhus chinensis* was described previously as merely quercitrin,7) but by further examination, myricitrin and myricetin were also isolated. In the galls, any flavonoid compound could not be detected.

Previously we isolated rhoifolin from the leaves of *R. succedanea*8). In other *Rhus* species, rhoifolin was present in the leaves of *R. trichocarpa*, *R. sylvestris*, *R. ambigua*. Myricitrin was also present in *R. ambigua*. In *Poupartia Fordii*, quercitrin and myricitrin were present. Some species of *Euphorbiaceae*, from which corilagin was recognized, some flavonoid compounds were known in previous works.9) Now astragalin and isoquercitrin were isolated from the leaves of *Sapium japonicum*.

Shikimic acid was isolated in a high yield from the mother liquor of corilagin or gallotannin of the leaves of *Rhus* and *Sapium*, and galls of *R. chinensis*, but could not be found in the *Poupartia Fordii*. Shikimic acid has been isolated from Sicilian sumac (*R. coriaria*10)) and considered to be widely distributed in the plant kingdom11) and to be precursor of aromatic compounds. It is an interesting fact that from the leaves of *Rhus* and *Sapium* species, shikimic acid obtained in a high yield, almost the same yield as that of corilagin or gallotannin, and, however, absent in *Poupartia*.

Experimental[*3]

1. Leaves of *Rhus succedanea* L.

Extraction——Fresh leaves (8 kg.) were extracted with hot water (2×30 L.), the aqueous extract was treated with $(AcO)_2Pb$ until no more precipitate occurred. The yellowish white precipitate was obtained and from the supernatant liquor a white fibrous precipitate was formed (2.85 g., 0.03%). It was crude rhoifolin.

$(AcO)_2Pb$ precipitate was treated with H_2S. The yellow aqueous solution was filtered and evaporated and the residue was dissolved in water, then shaken with ether and exhausted with AcOEt. The residue of AcOEt was dissolved in a small amount of water. A brown precipitate (chiefly ellagic acid, 3.6 g.) was filtered off. The filtrate was concentrated and allowed to stand. A yellow globose crystalline mass was collected and dried in the air (58 g.). From the mother liquor the same compound was further obtained (8 g.). The combined crystalline mass was recrystallized from water and almost colorless corilagin was obtained (55 g., 0.68%).

From the above ethereal solution were obtained insoluble brown precipitate (1.8 g., almost ellagic acid) and hot water soluble colorless needles (almost gallic acid, 14.5 g.). The aqueous filtrate, separated from rhoifolin, was treated with H_2S, concentrated and passed through a column of Amberlite IR-120, then of IR-4B, until it gave a negative test for periodate-aniline reaction of shikimic acid.12) Acidic fraction, eluted with AcOH, was concentrated to complete dryness and the residue crystallized from 95% EtOH, white sandy crystals separated, recrystallized from EtOH (54 g., 0.56%).

Corilagin——Corilagin crystallized from water in white needles or long prisms, m.p. 202~204°(decomp.). The mixed melting point with corilagin isolated from divi-divi, showed no depression. It was slightly soluble in cold water and AcOEt, considerably in hot water, readily soluble in EtOH, MeOH or acetone and insoluble in benzene, $CHCl_3$ and ether. Corilagin recrystallized from water and dried in the air, had 3 mol. of water, and this was lost at 116°, 0.1 mm. on P_2O_5 in 5 hr. $[\alpha]_D^{25}$ $-229.6°$(MeOH, c=1.16), $[\alpha]_D^{23}$ $-248°$(H_2O, c=0.28). The rotatory power did not change after standing for 24 hr. Molecular weight by ebullioscopy in acetone :

[*3] All melting points were uncorrected; M. p. (B) was observed in Al-block.
Paper chromatography (PC) was carried out on Watmann No. 1 filter paper using following solvents :
(a) BuOH-AcOH-H_2O (4:1:5) upper phase (b) BuOH-AcOH-H_2O (4:1:2)
(c) Phenol saturated with water (d) 6% AcOH

7) M. Aritomi, K. Miyazaki, T. Mazaki : Yakugaku Zasshi, **84**, 894 (1964).

8) S. Hattori, H. Matsuda : Arch. Biochem. Biophys., **37**, 85 (1952).

9) M. Shimokoriyama : Nippon Kagaku Zasshi, **68**, 1 (1949); Acta Phytochimica (Tokyo), **15**, 63 (1949). T. Nakaoki, N. Morita, S. Nishino : Yakugaku Zasshi, **77**, 110 (1957). N. Kutani, A. Kawase : Scient. Pap. Kumamoto Women's College, **11**, 111 (1959); Nippon Kagaku Sôran, **34**, 1633 (1960).

10) G. N. Catravas, K. S. Kirby : J. Soc. Leather Trades' Chemists, **32**, 155 (1948).

11) M. Hasegawa, T. Nakazima, S. Yoshida : Nippon Ringaku Zasshi, **39**, 159 (1957). D. E. Hathway : Biochem. J., **63**, 380 (1956); **67**, 445 (1957). S. Hattori, S. Yoshida, M. Hasegawa : Physiol. Plant., **7**, 283 (1954).

12) S. Yoshida, M. Hasegawa : Arch. Biochem. Biophys., **70**, 377 (1957).

650. λ_{max}^{EtOH} mμ: 219, 271; λ_{min}^{EtOH} 252. Rf 0.30 (a), 0.38 (d). *Anal.* Calcd. for $C_{27}H_{22}O_{18}\cdot 3H_2O$ (688.5): C, 47.10; H, 4.10; H_2O, 7.85. Found: C, 47.28; H, 4.36; H_2O, 7.28.

Corilagin gave a blue coloration with $FeCl_3$, which turned to red with aqueous Na_2CO_3, a brown color with KCN reagent, it formed a greenish blue amorphous precipitate with lime-water, and a white precipitate with gelatin solution and Molisch reaction was positive. Griessmayer-Reichel reagent[13] gave at first wine red and then a brown precipitate. An aqueous solution of corilagin, heated on a boiling water-bath for a long time, gradually decomposed and gave ellagic acid.

Hydrolysis of Corilagin——Corilagin (5.7849 g.) was dissolved in water (200 ml.), added with H_2SO_4 (10 g.) with stirring and refluxed for 6 hr. The colorless solution gradually changed to yellow brown and formed a brown precipitate which was collected (ellagic acid, 2.7165 g.). The aqueous filtrate was extracted with ether. From the brown residue of the ethereal extract more insoluble brown precipitate was obtained (0.1825 g., ellagic acid). From the filtrate gallic acid was obtained (1.565 g.). The acidic hydrolyzate was neutralized by Amberlite IR-4B and concentrated. On PC it showed a single spot of glucose. Estimation of glucose by rotatory power, corresponding to 1.285 g. Corilagin, $C_{27}H_{22}O_{18}\cdot 3H_2O$ (688.5): ellagic acid $C_{14}H_6O_8\cdot 2H_2O$ (338.23), Found 50.1, theoretical 49.1; gallic acid $C_7H_6O_5\cdot H_2O$ (180.06), Found 27.0, theoretical 27.3; glucose $C_6H_{12}O_6$ (180.1), Found 22.4, theoretical 26.5. Ellagic acid was recrystallized from pyridine-water, giving white grey needles, m.p. (B) >360°, wine red with Griessmayer-Reichel reagent, blue-black with $FeCl_3$. *Anal.* Calcd. for $C_{14}H_6O_8\cdot 2H_2O$: C, 49.69; H, 2.98. Found: C, 50.12; H, 3.31. $\lambda_{max}^{diox.}$ mμ: 260, 367; $\lambda_{min}^{diox.}$ 325. Tetraacetyl ellagic acid, prepared with Ac_2O and pyridine, crystallized from Ac_2O in colorless needles, m.p. (B) 340~343° (decomp.), undepressed on admixture with the authentic specimen.[14] *Anal.* Calcd. for $C_{14}H_2O_4(O\cdot COCH_3)_4$: C, 56.17; H, 3.00. Found: C, 56.29; H, 3.18.

Gallic acid crystallized from water in white needles, m.p. 240° (decomp.) undepressed on admixture with the authentic compound. Rf 0.62 (a). It gave a blue coloration with $FeCl_3$ and pink one with KCN solution. Trimethyl gallic acid was prepared with diazomethane, followed by saponification, crystallized from aqueous MeOH, in colorless long needles, m.p. 166~167°, the mixed melting point showed no depression. *Anal.* Calcd. for $C_7H_3O_2(OCH_3)_3$: OCH_3, 42.9. Found: OCH_3, 40.3.

The aqueous sugar solution was concentrated and the phenylosazone made in the usual manner. Glucosazone was obtained in deep yellow needles (0.6 g.), m.p. 204~205° (decomp.), undepressed on admixture with the authentic specimen.

Enzymatic Hydrolysis of Corilagin——Corilagin (3.126 g.) was dissolved in water (300 ml.), added with tannase (2.2 g.) prepared from *Aspergillus niger*,[15] and toluene (2 ml.), and incubated at 28° for 10 days. The separated ellagic acid was collected (1.482 g.). The filtrate was extracted with ether, ellagic acid (0.042 g.) and gallic acid (0.725 g.) were obtained. The concentration of glucose in the resulting hydrolysate was estimated by the usual manner. Found: ellagic acid 48.8; gallic acid 23.2; glucose 15.2.

Nonamethyl Corilagin——Air-dried corilagin (1.5 g.) was methylated with ethereal diazomethane. The resulting methyl ether, giving no $FeCl_3$ reaction, was recrystallized from MeOH. Nonamethyl corilagin was obtained in white long needles, m.p. 224°, readily soluble in acetone and AcOEt, moderately soluble in warm MeOH and EtOH. $[\alpha]_D^{16}$ −140° (acetone, c=0.856). Molecular weight by Rast: 800, 780. *Anal.* Calcd. for $C_{36}H_{40}O_{18}$ (760.7): C, 56.84; H, 5.30; OCH_3, 36.71. Found: C, 57.12, 56.70; H, 5.42, 5.43; OCH_3, 36.2, 35.71.

Nonamethyl corilagin (4.126 g.) was dissolved in 1.5% KOH-EtOH (100 ml.) and added with a few drops of water. The solution was refluxed in a H_2 atmosphere for 5 hr. The solution gradually discolored into brown and an oily precipitate was formed. After cooling, the brown EtOH solution was acidified with H_2SO_4 and K_2SO_4 separated and was filtered off. The filtrate was concentrated and an oily brown mass, which partly crystallized, collected and washed with water, then boiled with water and filtered while hot. When the filtrate was allowed to stand, a white crystalline mass separated (1.0 g.). It was recrystallized from dilute EtOH, giving colorless long needles, m.p. 166~167°, undepressed on admixture with trimethyl gallic acid. *Anal.* Calcd. for $C_7H_3O_2(OCH_3)_3$: OCH_3, 42.9. Found: OCH_3, 39.6.

The aqueous hydrolysate from which trimethyl gallic acid was obtained, was shaken with AcOEt, the AcOEt extract was dried on anhyd. Na_2SO_4 and evaporated, the residue was collected (0.7 g.), dried and dissolved in ether and was precipitated with hexane. The precipitate was recrystallized from a small amount of EtOH, giving colorless needles (0.1 g.). *Anal.* Calcd. for $C_{12}H_2(OCH_3)_6(COOH)_2$: OCH_3, 44.07. Found: OCH_3, 43.5, 43.1. It melted at 157~159° and gradually solidified, then melted again at 238~240°. The synthetical hexamethoxydiphenic acid, prepared from ellagic acid,[14] gave colorless sandy prisms and melted at 240°. The mixed melting point of both acids was 237~240°.

Gallic Acid—— Gallic acid obtained from the ethereal extract, recrystallized from water, gave white long needles, m.p. 240° (decomp.), undepressed on admixture with authentic gallic acid. It gave trimethyl gallic acid methyl ester, colorless prisms, m.p. 82°, the ester was saponified, giving trimethyl gallic acid, m.p. 166~167°.

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13) L. Reichel, A. Schwab: Lieb. Ann., **550**, 152 (1942).
14) J. Herzig, J. Pollak: Monatsh. Chem., **29**, 263 (1908).
15) K. Freudenberg, E. Vollbrecht: Hoppe-Seyler's Zeits. Physiol. Chem., **116**, 277 (1921).

Gallic Acid Methyl Ester——Fresh leaves were extracted with MeOH, the extract was concentrated and a resinous green precipitate was filtered off. The aqueous extract was shaken with ether. From the ethereal extract, a brown crystalline mass was obtained. It was recrystallized from water, giving white plates, m.p. 194~195°. Blue with $FeCl_3$. The mixture of this compound and gallic acid methyl ester (m.p. 195°), showed no depression on melting point. Both ester gave the same Rf 0.80 (a), 0.61 (c), gallic acid, Rf 0.65 (a), 0.13 (c).

Rhoifolin——Rhoifolin was recrystallized from MeOH in white yellow minute needles, softened at 200~203° and decomposed at 240~245°, $[\alpha]_D^{22}$ −23.5° (MeOH, c=0.2), Rf 0.65 (a), 0.75 (c), λ_{max}^{EtOH} mμ: 214, 269, 337; λ_{min}^{EtOH} 248, 282.

Shikimic Acid——Shikimic acid crystallized from 95% EtOH in white sandy prisms or needles, m.p. 184°, undepressed on admixture with authentic shikimic acid (m.p. 184°) isolated from *Illicium anisatum*,[16] $[\alpha]_D^{22}$ −182°(H_2O, c=3.821), Rf 0.51 (b). Shikimic acid methyl ester was prepared with diazomethane and recrystallized from anhyd. AcOEt, gave white needles, m.p. 116~117°, undepressed on admixture with an authentic specimen.

2. Leaves of *Rhus trichocarpa* Miq. and *R. sylvestris* Sieb. et Zucc.

Fresh leaves were extracted almost in the same way described with *R. succedanea*. A white crystalline tannin was obtained and recrystallized from water, melting point alone or mixed with corilagin, 200~201° (decomp.). From the former plant 0.23% corilagin, and from the latter plant 0.15% corilagin. Ellagic acid and gallic, rhoifolin and shikimic acid were also obtained and identified in the same way.

3. Leaves of *Rhus chinensis* Mill.

Extraction——Fresh leaves (7.5 kg.) were extracted with boiling water. The extract treated with MeOH for the separation of mucilage, was concentrated and separated into the ether soluble part (A) and the AcOEt soluble part (B). From (A) a small amount of water insoluble precipitate was collected (0.2 g.), Griessmayer-Reichel reaction was positive, by Rf values and UV spectrum, it was considered to be ellagic acid. The aqueous extract was treated with ion-exchange resin and acidic fraction (C) was collected.

Gallic and Shikimic Acid——From the fraction (A), gallic acid was obtained, and from the fraction (C) shikimic acid (m.p. 184°, 34.5 g.) was obtained. They were identified by the same method.

Flavonoid Glycosides——From the yellow crystalline mass (22.5 g.) separated from (B), were isolated two flavonoid glycosides, (1) light yellow plates or needles, m.p. 182~184°(indistinctly), Rf 0.82 (a), 0.48 (c), identical with quercitrin, and (2) slightly yellow needles, m.p. 194~197°, and gave a dark green color with $FeCl_3$ and a red with Mg-HCl, Molisch and orcinol test were positive, Rf 0.68 (a), 0.38 (c), λ_{max}^{EtOH} mμ: 215, 256, 356; λ_{min}^{EtOH} 242, 285. *Anal.* Calcd. for $C_{21}H_{20}O_{12} \cdot H_2O$: H_2O, 3.74. Found: H_2O, 3.61. *Anal.* Calcd. for $C_{21}H_{20}O_{12}$: C, 54.31; H, 4.34. Found: C, 55.10; H, 4.46. When admixed with myricitrin, prepared from the bark of *Myrica rubra* Sieb. et Zucc.,[17] no depression of the melting point was observed.

Tannin Fraction——The fraction (B) was extracted with BuOH after separation of the flavonoid crystals; the aqueous phase contained chiefly tannin. On PC, it gave a distinct spot, Rf 0.65 (a), 0.08 (c). The tannin fraction was dissolved in MeOH and precipitated with $(AcO)_2Pb$ into 3 fractions, then each fraction was treated with H_2S and concentrated. The second fraction gave an almost single spot on PC, detectable with $FeCl_3$. This fraction was hydrolyzed with H_2SO_4 and gave no precipitate. The aqueous brown solution was extracted with ether and then with AcOEt. From the ethereal extract, only gallic acid was obtained. The resulting aqueous solution was treated with the usual manner, glucose alone was detected. Corilagin could not be recognized in all fractions.

4. Leaves of *Rhus ambigua* Lavallée ex Dippel.

Fresh leaves (350 g.) were extracted with EtOH. From the extract following materials were isolated, ellagic acid (0.2 g.); gallic acid (0.3 g.); ethyl gallate, m.p. 158°, Rf 0.86 (a), 0.78 (c); rhoifolin (0.4 g.); myricitrin (0.25 g.); shikimic acid (1.25 g.); they were identified by the same method. Corilagin could not be isolated in a crystalline state but PC showed clearly its presence.

5. Galls of *Rhus chinensis*

1) Fresh galls (900 g.), removed from the insects inside, were extracted with boiling acetone. The extract was concentrated, and then shaken with benzene. From the resulting viscous emulsion, a white grey amorphous substance gradually separated. After several days, a greater part of the emulsion turned to an amorphous mass and washed with benzene. The white grey amorphous mass was dried *in vacuo*, ground and extracted with anhyd. ether. The ethereal extract consisted of mainly gallic acid and other substances, which showed some resemblance to gallic acid, being low molecular compound. The ether insoluble powder, giving a single spot on PC, consisted of the main gallotannin fraction of the galls. This tannin fraction, on hydrolysis with acid or tannase, gave gallic acid and glucose, and neither ellagic acid nor flavonoid compound could be recognized. The aqueous filtrate, from which an amorphous mass separated, contained shikimic acid and glucose beside an unknown tannin substance. In every fraction of the galls, the presence of a flavonoid compound and corilagin or another ellagitannin could not be detected. A trace of ellagic acid was detected.

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16) J. F. Eykmann: Chem. Ber., **24**, 1278 (1891).

17) M. Shimizu, G. Ohta, T. Yoshikawa, A. Kasahara: Yakugaku Zasshi, **72**, 338 (1952).

2) Fresh galls (56.6 g.), removed from the insect (7.4 g.), were dried at 110° for 10 hr. (28.95 g.). The dried galls were extracted with MeOH and the residue was dried at 110° (12.95 g.). The MeOH extract was diluted with water and treated with $(AcO)_2Pb$. The $(AcO)_2Pb$ precipitate was hydrolyzed with H_2SO_4, and extracted with ether, gallic acid (10.9 g., 19.25%) was obtained. Non-precipitated fraction was concentrated and dried (2.48 g.), dissolved in water, treated with ion-exchange resin, the concentration of shikimic acid was estimated, and 428 mg. shikimic acid (0.756%) was obtained. The neutral fraction by PC was recognized as glucose and sucrose.

6. Leaves of *Poupartia Fordii* Hemsl.

Fresh leaves (1.1 kg.) were extracted. Quercitrin and myricitrin were isolated and identified by the same method. Gallic and ellagic acid were also isolated, but corilagin itself could not be isolated from the extract, but a small amount of the compound was recognized on PC. In acidic fraction, shikimic acid was absent and quinic acid, Rf 0.36 (c), was present (reagent used for the detection were periodate-aniline, diazotized benzidine and B. C. G.).

7. Leaves of *Sapium japonicum* Pax et K. Hoffmann.

Fresh leaves (12 kg.) were extracted with hot water, and following substances were isolated: From ether soluble fraction and precipitate, gallic and ellagic acid, kaempferol (m.p. 274~276°), and quercetin (m.p. 312~315°). From AcOEt soluble fraction were obtained two flavonoid glycosides, which were precipitated with $(AcO)_2Pb$ in MeOH. From the filtrate, pale yellow needles (3.1 g.), m.p. 225~227° were obtained, Rf 0.78 (a), 0.68 (c), $\lambda_{\max}^{\mathrm{EtOH}}$ mμ: 267, 355; $\lambda_{\min}^{\mathrm{EtOH}}$ 241, 282, greenish brown with $FeCl_3$, red with Mg-HCl. *Anal.* Calcd. for $C_{21}H_{20}O_{11}\cdot 3H_2O$: H_2O, 11.2. Found: H_2O, 10.8. *Anal.* Calcd. for $C_{21}H_{20}O_{11}$: C, 56.25; H, 4.47. Found: C, 56.30; H, 4.51. On acidic hydrolysis, it gave each one mol. of kaempferol and glucose, and methylation followed by hydrolysis gave 3-hydroxy-5,7,4′-trimethoxy-flavone in pale yellow needles, m.p. 149~150°. The glucoside was identical with kaempferol-3-monoglucoside (astragalin).[18] From the $(AcO)_2Pb$ precipitate, obtained yellow needles (0.4 g.), m.p. 206~207°, decomposed at 225°, Rf 0.68 (a), 0.58 (c), $\lambda_{\max}^{\mathrm{EtOH}}$ mμ: 256, 360; $\lambda_{\min}^{\mathrm{EtOH}}$ 239, 283, brownish green with $FeCl_3$, red with Mg-HCl. *Anal.* Calcd. for $C_{21}H_{20}O_{12}\cdot 2H_2O$: H_2O, 7.2. Found: H_2O, 6.86. *Anal.* Calcd. for $C_{21}H_{20}O_{12}$: C, 54.31; H, 4.32. Found: C, 53.88; H, 4.29. On hydrolysis it gave each one mol. of quercetin and glucose, and on hydrolysis of the methylated glycoside, 3-hydroxy-5,7,3′,4′-tetramethoxy-flavone was obtained in pale yellow needles, m.p. 191~192°. The glucoside was identical with quercetin-3-monoglucoside (isoquercitrin).

Corilagin was purified by charcoal column chromatography and obtained in white needles (26.2 g., 0.22%), m.p. 202~204° (decomp.).

Shikimic acid was obtained from the aqueous extract of the leaves (2.3 kg.), yield 8.2 g. (0.356%).

8. Leaves of *Sapium sebiferum* Roxb.

The aqueous extract of the leaves (1.5 kg.) was worked by the same method. Corilagin was obtained from the tannin fraction in white needles, m.p. 204° (decomp.) (3.13 g., 0.21%). From the flavonoid fraction, yellow crystals were obtained, m.p. 225° (decomp.). It was the same substance which was isolated by Shimokoriyama[9] and identified with isoquercitrin. Ellagic, gallic and shikimic acid were also isolated.

9. Leaves of *Ricinus communis* L.

Fresh leaves (7 kg.) were extracted with water and following substances isolated from the extract. Rutin, m.p. 192~194° (9.2 g., 0.13%); corilagin, m.p. 202~204° (decomp.) (1.4 g., 0.02%); gallic and ellagic acid.

10. Leaves of *Aleurites cordata* Steudel.

Fresh leaves were extracted with water and the extract showed corilagin, gallic and ellagic acid on PC.

11. Shikimic Acid Concentration in Leaves and Galls

Following materials were extracted.

(1) Galls of *Rhus chinensis* (56.6 g.) with MeOH.
(2) Commercial tannin (5 g.) dissolved in water.
(3) Leaves of *R. chinensis* (a), separated from galls (100 g.) with water.
(4) Leaves of *R. chinensis* (b) normal leaves (100 g.) with water.
(5) Leaves of *Sapium japonicum* (100 g.) with water.
(6) Leaves of *S. sebiferum* (150 g.) with water.
(7) Leaves of *Rhus succedanea* (100 g.) with water.

The extracts were treated with $(AcO)_2Pb$ and the precipitates were removed by centrifuging and washed well with water. The combined supernatant solution and washings were treated with H_2S and acidic fractions collected by ion-exchange resin. Every eluate was concentrated, dissolved in water, treated with periodate-aniline reagent[12] and resulting colored solution was estimated by spectrophotometer at 510 mμ.

The following results were obtained (Table I).

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[18] T. Nakabayashi: Nôgeikagaku Zasshi, **26**, 539 (1952); Bull. Agri. Chem. Soc. Jap., **19**, 104 (1955). Y. Kishimoto: Yakugaku Zasshi, **76**, 250 (1956).

Table I.

Material	Shikimic acid (%) by estimation	Shikimic acid (%) yield by extraction
(1) *Rhus chinensis* (galls)	0.766	
(2) Commercial tannin	0.36	
(3) *Rhus chinensis* (a)	0.08	
(4) *Rhus chinensis* (b)	0.21	0.26
(5) *Sapium japonicum*	0.52	0.36
(6) *Sapium sebiferum*	0.41	0.17
(7) *Rhus succedanea*	0.65	0.56
(8) *Rhus trichocarpa*	—	0.23
(9) *Rhus sylvestris*	—	0.48
(10) *Rhus ambigua*	—	0.38
(11) *Poupartia Fordii*	—	absent

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Summary

A study of polyphenolic compounds and shikimic acid in the leaves of *Rhus* and *Poupartia* (*Anacardiaceae*), *Sapium*, *Ricinus* and *Aleurites* (*Euphorbiaceae*) have been undertaken. From the results obtained on the constituents of these plants, corilagin, an ellagitannin, proved to be common except in *Rhus chinensis*. Shikimic acid is also common except in *Poupartia*. Flavonoid compounds consisted of glycosides of flavonols and apigenin.

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