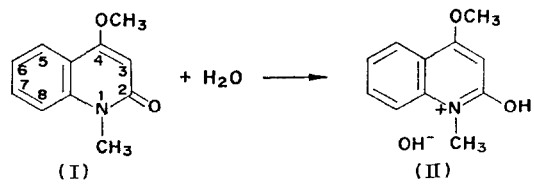

(I) (II)

on the basis that the alkaloid in solution reacts with the water of hydration to exist as a 2-hydroxyquinoline(II), rather than as the 2-quinolone(I). The signal at $\delta 2{\cdot}2$ is assigned to the hydroxyl group at position 2 of the hydroxyquinoline. The hydroxyl ion was not located in the NMR spectrum.

More detailed investigations are being undertaken to study the structural changes of the molecule in solution as well as in the solid state. To the best of our knowledge the compound does not appear to have isolated from a natural source before and constitutes an example of previously synthesized compound being isolated from a natural source.

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SALICACEAE

PHENOLIC EXTRACTIVES OF THE LEAVES OF *POPULUS BALSAMIFERA* AND OF *P. TRICHOCARPA**

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Abstract—Fresh June leaves of *Populus balsamifera* and *P. trichocarpa* were extracted with ethanol, and the hot water-soluble portions were fractionated by ethyl acetate extraction and polyamide chromatography and step gradient elution with water and dilutions of ethanol. Although generally similar, several important differences were noted in the components of the leaves of the two related species.

IN AN earlier study on the leaves of *Populus balsamifera*[1] the similarity of the components isolated from the leaves of *P. balsamifera* and those obtained in the past from the bark of *P. trichocarpa*[2,3] and the bark of *P. balsamifera*[4] was noted, and it was suggested that the

* Part XVI in the series "Studies on the Leaves of the Family Salicaceae".

[1] I. A. PEARL and S. F. DARLING, *Phytochem.* **7**, 1845 (1968).
[2] I. A. PEARL and S. F. DARLING, *Tappi* **51**, No. 11, 537 (1968).
[3] I. A. PEARL and S. F. DARLING, *Phytochem.* **7**, 825 (1968).
[4] I. A. PEARL and C. R. POTTENGER, *Tappi* **49**, No. 4, 152 (1966).

leaves of *P. trichocarpa* might yield the same crystalline products as did the leaves of *P. balsamifera*. Accordingly, fresh leaves of the two *Populus* species were processed by the Waring Blendor ethanol extraction and step-gradient water and ethanol elution polyamide chromatography procedures evolved in our laboratory since the earlier studies.[5,6]

RESULTS

Fresh June leaves of *P. trichocarpa* and *P. balsamifera* were processed exactly as described for *Salix purpurea* bark[6] including Waring Blendor extraction with ethanol, hot water extraction of the evaporated ethanol extracts, fractional ethyl acetate extraction of the concentrated water extractives, and step gradient elution of the individual ethyl acetate extracts on polyamide columns with water, 20% ethanol, and 50% ethanol. All eluate fractions were monitored by means of TLC, concentrated to small volumes, allowed to stand, filtered if crystals separated, and finally freeze-dried. Weights of all fractions and of separated crystals were noted, and elution curves were obtained. The results obtained for the several ethyl acetate extracts for the two species have been combined and are presented in Table 1.

DISCUSSION

The recovery of crystalline products as noted in Table 1 represented a relatively small proportion of the total products recovered from the chromatograms. TLC of filtrates from the crystals noted in Table 1 in all instances indicated more of the specific compound

TABLE 1. CRYSTALLINE COMPONENTS FROM CHROMATOGRAPHY OF ETHYL ACETATE-SOLUBLE PORTIONS OF HOT WATER EXTRACTIVES OF LEAVES OF *Populus balsamifera* AND *P. trichocarpa*

Component	*P. balsamifera* yield (%)*	*P. trichocarpa* yield (%)
Crude extract	10·73	9·1
Salicin	P†	0·74
Salicortin	P	P
Salicyl alcohol	P	P
Pyrocatechol	P	P
1-*O*-*p*-Coumaroylglucose	0·02	
Tremuloidin		0·42
Mixed tremuloidin and trichocarpin		0·08
Trichocarpin	0·20	0·05
Mixed trichocarpin and tremulacin		0·04
Mixed trichocarpin, tremulacin and salireposide		0·02
Salireposide		0·11
ω-Salicyloylsalicin	0·01	P
(+)-Catechin	0·23	
Isoquercitrin		0·01
Mixed flavonoid glycosides	0·66	0·01
Total solids recovered from eluate	8·12	7·92

* On basis of ovendry leaf solids.
† P = present in quantity by TLC, but not isolated and weighed as crystals.

[5] I. A. PEARL and S. F. DARLING, *Phytochem.* **8**, 2393 (1969).
[6] I. A. PEARL and S. F. DARLING, *Phytochem.* **9**, 1277 (1970).

together with one or more components, some in substantial amounts. However, complete fractionation of individual components was not attempted in the present study.

In the polyamide chromatograms of Table 1, as in those of earlier studies employing Waring Blendor processing of *Populus* species barks and leaves, a substantial portion of the total eluate solids was collected in the first ten eluate fractions. TLC of these fractions indicated that they comprised essentially salicin and salicortin with only traces of other components. In the *P. balsamifera* experiment these combined components amounted to 35% of the total ethyl acetate extractives, and in the *P. trichocarpa* experiment, to 38%. If desired, the individual crystalline components could be obtained by rechromatography on silica gel as described previously.[6]

The data of Table 1 demonstrate that, although there are similarities in the components of the leaves of these two species, there are some obvious differences. Tremuloidin and its precursor, tremulacin, are present in quantity in *P. trichocarpa*, but are absent in *P. balsamifera*. Similarly, salireposide is present in *P. trichocarpa* and absent in *P. balsamifera*. On the other hand, 1-*O*-*p*-coumaroylglucose is present in *P. balsamifera* and not in *P. trichocarpa*. Thus, the earlier prognostication concerning the similarity of components in the leaves of the two species[1] proved far from correct.

In almost all polyamide chromatograms of individual ethyl acetate extracts, shortly after elution with 50% ethanol was initiated, relatively large amounts of crystalline material were obtained. The chromatogram of the first ethyl acetate extract of *P. balsamifera* leaves yielded almost pure (+)-catechin, but that of the second extract of the same leaves yielded a mixture of flavonoid glycosides. This mixture was separated by means of preparative paper chromatography into myricetin-3-galactoside and another mixture of quercetin-3-galactoside and quercetin-3-glucoside (isoquercitrin). The myricetin-3-galactoside was identified by melting point, UV spectral analysis,[7] and quantitative hydrolysis to myricetin and galactose and found to be identical with arbusculin isolated from *Salix arbuscula* leaves by Rabate.[8] The quercetin glycoside mixture was identified by quantitative hydrolysis to quercetin and one mole of mixed glucose and galactose. UV spectral analysis indicated 3-position glycosides. The quercetin glycoside mixture was identical with one isolated previously from the leaves of *P. tremuloides*.[9]

In the case of the chromatograms of *P. trichocarpa* leaf extracts, the only crystalline component obtained in quantity in the flavonoid glycoside eluate was isoquercitrin.

Cinnamic, *p*-coumaric, and (−)-3-hydroxy-5-phenylvaleric acids were obtained as crystalline products in the eluate fractions from polyamide chromatograms in the earlier study on *P. balsamifera* leaves in which fresh leaves were processed immediately with a large excess of boiling water.[1] None of these acids was obtained in the present investigation. Inasmuch as the leaves of the present study were obtained at approximately the same time of the year from approximately the same location as those of the earlier study, it appears that the differences in the preliminary processing of the leaves in the two studies were responsible for the differences in the two results. In addition, our supposition that the products obtained in the earlier study were all present *per se* in the leaves also appears to be incorrect.

The finding of trichocarpin and its isomer, salireposide, in the same *P. trichocarpa*

[7] L. JURD, Spectral Properties of Flavonoid Compounds. *The Chemistry of Flavonoid Compounds* (edited by GEISSMAN) p. 107. Macmillan, New York (1962).
[8] J. RABATÉ, *J. Pharm. Chem.* **28**, 443 (1938).
[9] H. KINSLEY and I. A. PEARL, *Tappi* **50**, No. 8, 419 (1967).

leaves suggests the possible disproportionation of one to the other noted earlier[10] for *P. balsamifera* bark. It is interesting to note that *P. balsamifera* leaves contained no salireposide whatsoever.

EXPERIMENTAL

Materials. Fresh leaves from a *P. balsamifera* tree cut in Langlade County, Wisconsin on June 17, 1968 were processed within a few hours with EtOH by the Waring Blendor procedure. *P. trichocarpa* leaves were stripped from trees in Pierce County, Washington on June 13, 1969, placed immediately into 95% EtOH, and processed a few days later by the Waring Blendor procedure.

Isolation and identification of components. The following crystalline components were isolated from the eluate fractions and identified by mixed m.p. and identity of IR spectra with authentic material indicated by reference: salicin[11], 1-*O*-*p*-coumaroyl-glucose,[12] tremuloidin,[11] trichocarpin,[13] tremulacin,[14] salireposide,[15] ω-salicyloylsalicin,[16] *d*-catechin,[6] and isoquercitrin.[6]

Chromatography of flavonoid components. Flavonoid components of eluate fractions were monitored by means of TLC on Polygram Cell developed with 30% AcOH and sprayed with ethanolic KOH. Plates were examined under visible and UV light before and after spraying.

The flavonoid glucosides were separated preparatively on Whatman 3M paper developed with the upper layer of 4:1:5 *n*-BuOH–AcOH–H_2O at 25°.

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[10] I. A. PEARL, *Tappi* **52**, No. 3, 428 (1969).
[11] I. A. PEARL and S. F. DARLING, *J. Org. Chem.* **24**, 731 (1959).
[12] I. A. PEARL and S. F. DARLING, *Tappi* **50**, No. 7, 324 (1967).
[13] I. A. PEARL and S. F. DARLING, *Phytochem.* **7**, 1951 (1968).
[14] I. A. PEARL and S. F. DARLING, *Phytochem.* **10**, 483 (1971).
[15] I. A. PEARL and S. F. DARLING, *J. Org. Chem.* **24**, 1616 (1959).
[16] I. A. PEARL and S. F. DARLING, *Arch. Biochem. Biophys.* **102**, 33 (1963).

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SAPINDACAE

CHEMICAL INVESTIGATION ON THE LEAVES OF *EUPHORIA LONGANA*

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Plant. Euphoria longana Lam. (Syn. *Nephelium longana* Cambess., Longan). Sapindaceae.

Uses. Medicinal.[1]

Previous work. On seeds,[2] stem and leaves.[3]

Leaves. Extracted with light petroleum, chloroform and ethanol.

Petroleum ether extract. This was chromatographed on alumina. Petroleum fraction on further purification by chromatography and crystallization afforded friedelin,[4] $C_{30}H_{50}O$

[1] *The Wealth of India, Volume III*, p. 230, C.S.I.R., New Delhi (1952).
[2] J. GEDEON and F. A. KINCL, *Arch. Pharm.* **289**, 162 (1956).
[3] T. TSUKAMOTO, T. TOMINAGA and J. TAKAHASHI, *J. Pharm. Soc.* **69**, 40 (1949).
[4] E. J. COREY and J. J. URSPRUNG, *J. Am. Chem. Soc.* **78**, 5041 (1956).