Analysis of Phenolics of Bud Exudate of *Populus laurifolia* by GC-MS

W. Greenaway, J. May, and F. R. Whatley

Department of Plant Sciences, University of Oxford, South Parks Road, Oxford, OX1 3RB, U.K.

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Analysis by GC-MS identified 30 phenolic components of the bud exudate of *P. laurifolia*. The majority of the exudate was composed of flavanones, flavanonols and chalcones, with pinobanksin-3-acetate being the major component. The bud exudate resembled that of the Asian Section *Tacamahaca* poplars *P. cathayana* and *P. szechuanica* but was unlike that of the North American Section *Tacamahaca* poplars, *P. balsamifera* and *P. trichocarpa*.

Introduction

Populus laurifolia Ledeb. is an Asiatic balsam poplar native to Siberia, particularly the Altai Mountains, but with a range extending into Mongolia and Central Asia [1]. The plant is little known in the 'West' [2] and we are aware of only a few descriptions of the tree in the Western literature [3–6]. Greater consideration is usually given to the several hybrids of *P. laurifolia* [3], especially *P.* × *berolinensis* Dippel, which is widely cultivated [3, 4].

Materials and Methods

Plant material

Bud exudate was collected from plants grown from cuttings originating from Urumqui, Xinjiang Province, P.R.C. and sent to us by Professor Changyou Yang; from plant ref. BEI 101 originating from Beitun, Xinjiang Province, P.R.C. and grown at the Poplar Research Bureau of Shanxi Province, P.R.C. and from plants ref. 60-0972 and 60-0973 of unknown origin and grown at the Morden Arboretum, Canada.

Sample preparation

Sample preparation was done as described previously [7], using 10 buds from each of the sampled trees.

Reprint requests to W. Greenaway.

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Gas chromatography – mass spectrometry

This was carried out as described previously [7].

Identification of compounds

Compounds in bud exudate were identified by comparison of the GC R_ts and MS with those of reference compounds [8].

Results and Discussion

Analysis by GC-MS of the bud exudate of *P. laurifolia* from Urumqui identified 32 phenolic components representing 30 compounds (Fig. 1, Table I), which comprised 75% of the total ion current (TIC) recorded. Terpenoid compounds represented a further 20% of TIC (Fig. 1). The majority of the exudate consisted of flavanones together with their chalcones (27% TIC) and flavanonols (24% TIC), the principal components being pinostrobin chalcone[21]* (13% TIC), pinocembrin chalcone[23] (11% TIC) and pinobanksin-3-acetate[26,27] (17% TIC). The flavones chrysin[31] (4% TIC) and galangin[29,34] (11% TIC) were present, as also were several methyl butenyl esters of caffeic acid[13,14,17–19] (6% TIC).

Both the specimens from Morden Arboretum, ref. 60-0972 and 60-0973 produced bud exudate which was closely similar both qualitatively and quantitatively to that described above. Bud exudate of specimen of BEI 101 from Beitun was qualitatively similar to the other three specimens but showed marked quantitative differences in composition. The terpenoids comprised a much higher percentage of the TIC (49%), whereas the flavones (2% TIC), flavanonols (5% TIC) and flavanones and their chalcones (23% TIC) were present in relatively lower amounts.

The bud exudate of *P. laurifolia* is similar in composition to those of two other Asiatic poplars, *P. cathayana* Rehd, and *P. szechuanica* Schneid that we have analyzed [9]. These poplars, together with other Asiatic poplars currently classified in section *Tacamahaca,* such as *P. simonii* Carr. and the closely related *P. yunnanensis* Dode [10], appear to form a chemotaxonomic grouping which is clearly distinct from the North American Section

* Superscripts refer throughout to peak numbers in Fig. 1 and Table I.

Table I. Phenolic compounds identified in bud exudate of *Populus laurifolia*.

Peak No.	Compound	No. of TMS groups	Mu[1] R_ts	Percentage[2] total ion current
1	benzoic acid	1	12.32	<0.1
2	1,2-benzenediol	2	13.02	0.1
3	2-hydroxybenzyl alcohol	2	14.89	0.1
4	4-hydroxybenzyl alcohol	2	15.72	<0.1
10	*trans*-3(4-hydroxyphenyl)-2-propenoic acid (*p*-coumaric acid)	2	19.29	<0.1
12	*trans*-3(4-dihydroxyphenyl)-2-propenoic acid (caffeic acid)	3	21.46	2.2
13	3-methyl-3-butenyl *cis* – caffeate[3]	2	21.74	<0.1
14	3-methyl-2-butenyl *cis* – caffeate[3]	2	22.08	0.2
15	butyl *trans* – caffeate	2	22.71	<0.1
16	3-methylbutyl *trans* – caffeate	2	23.42	0.2
17	3-methyl-3-butenyl *trans* – caffeate[3]	2	23.47	2.3
18	2-methyl-2-butenyl *trans* – caffeate	2	23.79	0.1
19	3-methyl-2-butenyl *trans* – caffeate	2	23.93	3.4
20	5-hydroxy-7-methoxyflavanone (pinostrobin)	1	24.52	0.2
21	2′,6′-dihydroxy-4′-methoxychalcone (pinostrobin chalcone)	2	24.53	13.0
22	5,7-dihydroxyflavanone (pinocembrin)	2	24.97	1.3
23	2′,4′,6′-trihydroxychalcone (pinocembrin chalcone)	3	24.99	11.2
25	3,5,7-trihydroxyflavanone (pinobanksin)	3	25.78	0.9
26	5,7-dihydroxy-3-acetyloxyflavanone[4] (pinobanksin-3-acetate)	1	25.81	0.4
27	5,7-dihydroxy-3-acetyloxyflavanone[4]	2	26.45	16.6
28	benzyl *trans*-caffeate	2	26.98	0.5
29	3,5,7-trihydroxyflavone (galangin)[4]	2	26.99	1.0
31	5,7-dihydroxyflavone (chrysin)	2	27.11	3.8
32	5,7-dihydroxy-3-methoxyflavone	2	27.16	1.0
33	5,7-dihydroxy-3-propanyloxyflavanone[5]	2	27.16	0.6
34	3,5,7-trihydroxyflavone[4]	3	27.52	10.3
35	5,7-dihydroxy-4′-methoxyflavanone (isosakuranetin)	2	27.59	0.2
36	2′,4′,6′-trihydroxy-4′-methoxychalcone (isosakuranetin chalcone)	3	27.70	0.1
38	5,7-dihydroxy-3-butanyloxyflavanone[5]	2	28.01	0.7
39	5,7-dihydroxy-3-pentanyloxyflavanone[5]	2	28.30	4.8
41	5,7-dihydroxy-3-hexanyloxyflavanone[5]	2	29.68	0.7
42	cinnamyl *trans*-caffeate	2	29.94	<0.1

[1] GC rentention times in methylene units (MU; defined by Dalgliesh *et al.* [13]) are given to two decimal places to indicate the elution sequence of peaks which chromatograph closely. Factors such as concentration of the compound concerned and/or characteristics of a particular GC column are liable to affect the chromatography, and for general purposes the MU figures are probably reliable to a single decimal place only [14].

[2] The ion current generated depends on the characteristics of the compound concerned and is not a true quantitation (see [8]). The higher molecular weight flavones and flavanones will be underestimated compared to lower molecular weight compounds.

[3] Both *cis* and *trans* isomers of this compound are present.

[4] This compound is present as two TMS derivatives.

[5] We do not know whether the substituent at the 3 position is linear or branched.

Tacamahaca poplars *P. balsamifera* L. and *P. trichocarpa* Torr. and Gray.

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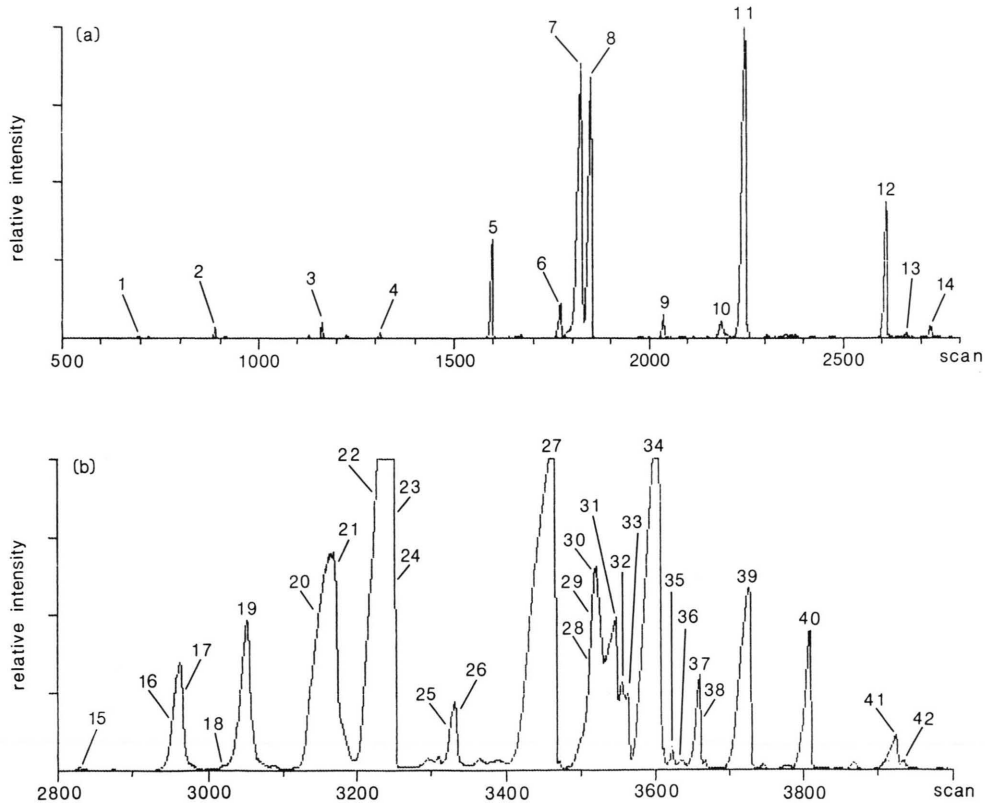

Fig. 1. Total ion current (TIC) chromatogram of bud exudate from *Populus laurifolia*. (a) Scans 500–2800 (MU 11.5–22.5); (b) scans 2800–4000 (MU 22.5–31.0). Phenolic components are identified in Table I. Other components were: 5–9, 11 = terpenoids; 24, 30, 37, 40 = C_{25}, C_{27}, C_{28}, C_{29} st. chain hydrocarbons respectively.

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