Populus candicans and the Balm of Gilead

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Dedicated to Professor Achim Trebst on the occasion of his 60th birthday

Populus candicans, Populus balsamifera, Balm of Gilead, *Populi gemma,* GC-MS

Bud exudates of some poplars are compared using GC-MS. *P. candicans* resembles *P. balsamifera*. A sample of "Balm of Gilead" purchased in Oxford proved not to resemble its supposed source, *P. candicans*. Instead it was similar to *P. nigra,* from which it was presumably collected in Europe.

Introduction

Balm of Gilead is referred to in the Bible as having healing properties [1]. This balm was supposedly a resin derived from *Commiphora opobalsamum,* Engl., a plant related to myrrh and containing essential oils. More recently early setlers in New England used the name Balm of Gilead for an alcoholic extract (tincture) of poplar buds collected from *Populus candicans* Ait. This tincture has bactericidal fungicidal and generally soothing properties. Later *P. candicans* was widely planted for windbreaks in north eastern North America and across the Canadian prairies and the buds were thus freely available – they still have a following in folk medicine in spite of the fact that occasional cases of dermatitis are brought on by some components of the tincture [2].

Gerard in his Herbal [3] mentions *Unguentum Populeon* as a profitable ointment prepared from the dormant buds of black poplar (*P. nigra* L.), and the medicinal properties of poplar buds were early recognized in Europe. The buds, under the name *"Populi gemma"*, are still available from apothecaries, particularly in central and eastern Europe, and alcoholic extracts are recognized as useful for surface infections.

The constituents in alcoholic extracts of *Populi gemma* and propolis have been compared and shown to be similar in many respects [4]. Honey bees collect the exudate from poplar buds and incorporate it into propolis, a material they use to seal their hives. Propolis is also a source of some folk medicines and alcoholic extracts of it are used in eastern Europe as a mild natural antibiotic. Analyses of the chemical components of poplar buds and propolis confirm that all of the phenolics in the propolis from Buckland we examined had been collected by bees from buds of *P.* × *euramericana* (Dode) Guinier, hybrids of the Mediterranean *P. nigra* with the North American *P. deltoides* Marsh occurring widely in Britain [5]. The use of propolis extracts as a folk medicine is, like Balm of Gilead, again accompanied occasionally by the onset of dermatitis and one of the compounds responsible, prenyl caffeate, has been identified [6].

P. candicans, popularly called in England the Balm of Gilead, (the name *P. gileadensis* Rouleau has also been proposed for it) is of unknown ancestry. Some authorities say it is merely a female clone of *P. balsamifera* L., the balsam poplar, though its habit of growth and leaf form are distinctive; others suggest that it is a hybrid between *P. deltoides* and *P. balsamifera* [7]. Since the bud exudate of *P. balsamifera* has recently been analysed by us and found to be distinctive [8], a comparison with the bud exudate of *P. candicans* may throw light on this question.

In Oxford we purchased a sample of "Balm of Gilead" from a local herbalist, supposing from its name that it had been imported from North America. Analysis of the buds indicated that this was not so.

Materials and Methods

Reagents and materials

Bis(trimethylsilyl)trifluoroacetamide (BSTFA) including 1% trimethylchlorosilane (TMCS) was obtained from Sigma (Poole, U.K.). Ethyl acetate was Mallinckrodt (St. Louis, U.S.A.) Nanograde. Flavonoid standards were either purchased from Apin Chemicals Ltd. (Abingdon, U.K.) or from Plantech, U.K. (Reading, U.K.) or provided as a gift

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by Professor E. Wollenweber (Darmstadt, F.R.G.). The sample of Balm of Gilead was purchased from a local herbalist in Oxford.

Poplar bud exudate

Bud exudate was obtained from specimens of *P. candicans* of known origin.
#89 was from a mature specimen growing in the Plant Sciences Department, Oxford and originally obtained as *cv.* Aurora from Hillier's Nursery, Winchester, U.K.
#C/E-13, Q/10 and M/11 were from the Alice Holt Arboretum, Farnham, U.K.
#C/E-13 originated in 1950 from Forest and Orchard Nurseries Ltd., Falfield, Glos., U.K.
#Q/10 was a variegated form growing semi-wild in Yardley Forest, Northants., U.K.
#M/11 originated in 1986 as *cv.* Aurora from Hillier's Nursery, Winchester, U.K.

Sample preparation and GC-MS

These were carried out as previously described [5].

Results

Analysis by GC-MS allowed the separation and identification of the compounds in bud exudate of *P. candicans* and in the Balm of Gilead sample. The compounds were identified by comparison of the mass spectral characteristics and the chromatographic retention times with those of known reference standards. Table I lists the principal compounds observed in bud extract of *P. candicans* M/11, together with an indication of the contribution each made to the total ion current in the mass spectrometer. The total ion current generated by a compound depends on the chromatographic and mass spectrometric properties of that compound and therefore does not represent a true quantitation [5], only an approximate one.

Table II provides a summary of the major groups of compounds found in bud extracts of four samples of *P. candicans* (columns 1–4) and in extracts of the herbalist's Balm of Gilead sample (column 5). For comparison, we also list the summary data for two samples of bud extract of *P. balsamifera* (columns 8 and 9) taken from Greenaway *et al.* [8] and for bud

Table I. Compounds identified in bud extracts of *P. candicans*. The compounds are listed in the order they eluted from the GC, the compounds shown in the left column preceding those shown in the right column. The retention times of most of these compounds are given elsewhere [5, 8].

Compound	% Total ion current	Compound	% Total ion current
benzyl alcohol	0.1	2′,6′-dihydroxy-4′-methoxy-dihydrochalcone	8.5
2-phenylethanol	0.1	2′,4′,6′-trihydroxy-dihydrochalcone	31.6
3-phenyl-2-propenal	<0.1	2′,6′-dihydroxy-4′-methoxychalcone	0.6
benzoic acid	0.2	benzyl-*trans*-4-coumarate	0.1
α-terpineol	0.1	5,7-dihydroxyflavanone	1.0
4-hydroxybenzaldehyde	<0.1	2′,4′,6′-trihydroxychalcone	0.3
α-copaene	<0.1	C_{25} hydrocarbon	0.1
3-phenylpropanoic	0.2	phenylethyl-*trans*-4-coumarate	0.7
cis-3-phenylpropenoic	0.1	3,5,7-trihydroxyflavanone	0.5
3-phenyl-1-propanol	<0.1	2′,6′-dihydroxy-4′,4-dimethoxy-dihydrochalcone	1.4
α-bergamotene	<0.1	3-O-acetyl-5,7-dihydroxyflavanone	0.2
β-farnesene	<0.1	2′,4′,6′,4-methoxydihydrochalcone	13.6
trans-3-phenylpropenoic	3.1	5,7-dihydroxyflavone	1.0
cadinene	0.4	2,′,6′,4-trihydroxy-4′-methoxy-dihydrochalcone	4.0
1,3,5-trihydroxybenzene	<0.1	3,5,7-trihydroxyflavone	6.0
trans-nerolidol	1.1	5,7-dihydroxy-4′-methoxyflavanone	0.2
bisabolol	16.1	*trans*-4-coumaryl-*trans*-cinnamate	0.4
guaiol*	0.3	*trans*-cinnamyl-*trans*-4-coumarate	0.7
cis-4-coumaric acid	<0.1	C_{29} hydrocarbon	0.1
coumaryl alcohol	<0.1	1-hexacosanol	<0.1
terpenoid alcohol*	0.3	3,5,7-trihydroxy-4′-methoxyflavone	0.1
trans-4-coumaric acid	1.1	*trans*-4-coumaryl-*trans*-4-coumarate	0.1
trans-cinnamyl-*trans*-cinnamate	0.1		

* Not positively identified.

Table II. Summary of the major constituents of bud exudates of *Populus candicans* and other poplars compared with Balm of Gilead. The data for *P.* × *euramericana* are derived from the Buckland sample in Ref. [5].

	P. candicans				Balm of	*P.* × *eur-*	*P. nigra*	*P. balsamifera*	
	89	C/E13	Q/10	M/11	Gilead	*americana*		347	349
Substituted benzoic acids	<0.1	<0.1	<0.1	<0.1	0.2	9.9	0.1	<0.1	<0.1
Substituted phenyl propenoic acids and esters	13.2*	7.1*	6.4*	6.0*	23.2**	34.4**	44.5**	8.9*	15.9*
Flavones	1.0	1.0	0.9	0.6	27.9	12.8	1.0	4.5	5.4
Flavonones	3.1	2.2	1.1	1.7	26.8	7.6	2.2	2.4	2.0
Chalcones	2.4	2.6	2.5	1.0	0.5	17.4	10.9	3.7	3.3
Dihydrochalcones	41.5	55.8	56.8	59.0	<0.1	<0.1	2.1	63.3	49.3
Terpenoids	12.0	13.4	14.3	19.1	1.8	0.3	0.5	12.7	11.2

* These are cinnamic acid together with coumaric acid and their esters; caffeic and ferulic acids are virtually absent.
** These are principally caffeic and ferulic acids and their esters; cinnamic and coumaric acids are low.

extracts from samples of *P. nigra* (column 7) and the cross *P.* × *euramericana* (column 6) respectively. The entry in line 2 obscures the fact that for *P. candicans* and *P. balsamifera* the principal constituents are cinnamic acid together with coumaric acid and their esters; caffeic and ferulic acids are almost absent. On the other hand, for *P. nigra*, *P.* × *euramericana* and Balm of Gilead the entry in line 2 represents principally caffeic and ferulic acids and their esters; cinnamic and coumaric acids though present are very low.

Discussion

Bud extracts of *P. balsamifera* and *P. candicans*, which belong to the Section Tacamahaca [7] are very high in dihydrochalcones and are rich in cinnamic and coumaric acids plus their esters (Table II). Volatiles from *P. candicans* buds were trapped on Tenax and injected by flash volatilization into a GC-MS. This revealed only terpenoid compounds in the volatile fraction. We therefore suggest that the characteristic smell of *P. candicans* may well be due to these terpenoid compounds, though others have suggested the importance of phenolic compounds such as cinnamyl cinnamate, salicyl benzoate and vanillin [9]. Bud extracts of *P. balsamifera* and *P. candicans* resemble each other quite closely in all respects except that the *P. balsamifera* examples appear to be higher in flavones. These data may suggest that *P. candicans* is only a *P. balsamifera* clone and not a cross with *P. deltoides*. Although we have not had the opportunity to analyse the bud exudate from *P. deltoides* in detail, this species is placed in the Section Aigeiros [7] and it is characteristic of *P. nigra* (also from this Section) and *P.* × *euramericana* (a *P. nigra* × *P. deltoides* cross) that their bud exudates are low in terpenoids (they are not balsam poplars), very low in dihydrochalcones and low in cinnamic and coumaric acids plus their esters. If it is a cross *P. candicans* must have inherited all its bud exudate characteristics from the *P. balsamifera* parent and none from the *P. deltoides* and this is perhaps unlikely.

We consider now the Oxford herbalist's sample of "Balm of Gilead". It is low in terpenoids, very low in dihydrochalcones and rich in caffeic and ferulic acids plus their esters. In this it does not resemble at all the buds of *P. candicans*, its supposed origin. Rather it resembles in these characters the bud exudate samples of *P. nigra* and *P.* × *euramericana* that we report in Table II. We therefore conclude that the sample is wrongly labelled "Balm of Gilead" since it clearly does not have the general characteristics of *P. candicans*. It much more closely resembles *P. nigra* and its crosses. Subsequent discussion with the herbalist elicited the information that his supplies of "Balm of Gilead" originated in Albania. Since supposedly pure populations of *P. nigra* occur in Albania, we assume the buds were collected from these. We believe the herbalist actually supplied us with *Populi gemma*, which is, in effect, the European equivalent

of the American "Balm of Gilead". We observe that the Albanian race of *P. nigra* is not exactly comparable with the "specimen" which we obtained previously from Ghoy, Belgium, since the herbalist's "Balm of Gilead" *(Populi gemma)* is richer in flavones and flavanones and poorer in chalcones than either *P. nigra* or *P.* × *euramericana*. We note, however, that chalcones are converted by the enzyme chalcone isomerase to the corresponding flavanones and the differences may reside simply in the relative amounts of this enzyme in the different stocks.

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