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PHENOLIC COMPOUNDS OF THE SUBFAMILY POMOIDEAE: A CHEMOTAXONOMIC SURVEY*

JAMES S. CHALLICE
Long Ashton Research Station, University of Bristol, Bristol BS18 9AF

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Abstract—The subfamily Pomoideae has been surveyed for leaf phenolics and it has been shown that flavone glycosides are present in the genera *Sorbus*, *Aronia*, *Chaenomeles* and *Hesperomeles* in addition to the previously reported occurrences in *Crataegus*, *Malus* and *Pyrus*. The dihydrochalcone phloridzin, a typical constituent of *Malus*, has also been found in *Docynia*. Arbutin and phenolic acid-calleryanin esters are apparently restricted to *Pyrus*. Naringenin and eriodictyol glucosides have been detected in *Pyracantha*, *Sorbus*, *Photinia*, *Chaenomeles* and *Hesperomeles*. A number of Pomoideae phenolics have been found in two Spiraeoideae genera; luteolin 7-glucoside, luteolin 7-diglucoside, luteolin 7-rhamnosylglucoside and apigenin 7-glucoside in *Exochorda* and the dihydrochalcone trilobatin in *Sorbaria*. The chemotaxonomic evidence is consistent with the hypothesis that the Pomoideae evolved through a process of allopolyploidy from primitive members of the Spiraeoideae and Prunoideae.

INTRODUCTION

THE SUBFAMILY Pomoideae of the family Rosaceae is listed by Rehder[1] as containing eighteen genera: *Cotoneaster* B. Ehrh., *Pyracantha* Roem., *Mespilus* L., *Crataegus* L., *Osteomeles* Lindl., *Sorbus* L., *Aronia* Med., *Photinia* Lindl., *Stranvaesia* Lindl., *Eriobotrya* Lindl., *Raphiolepis* Lindl., *Amelanchier*. Med., *Peraphyllum* Nutt., *Malus* Mill., *Docynia* Dcne., *Chaenomeles* Lindl., *Cydonia* Mill. and *Pyrus* L. In addition to the above, Bailey[2] lists the monotypic genus *Heteromeles* M. Roem. (previously included within *Photinia*). Weber[3] also mentions *Chamaemeles* Lindl. and *Hesperomeles* Lindl. and proposes the removal of one species from the genus *Chaenomeles* to form a new monotypic genus *Pseudocydonia* Schneid.

Geographically the Pomoideae are nearly restricted to the northern temperate hemisphere; the subfamily probably originated in Eastern Asia before migration eastwards towards the Americas (one genus *Osteomeles* in Hawaii) with only *Hesperomeles* reaching S. America, following the Andes as far as Chile.[4] Migration must also have taken place from E. Asia in a westward direction reaching as far as Spain, Portugal and the extreme north of Africa. *Crataegus*, *Sorbus*, *Aronia*, *Heteromeles*, *Amelanchier*, *Peraphyllum* and *Malus* are the only Pomoideae found in N. America, reached apparently by the Pacific route. Sax[5] considers that the genera of the Pomoideae (many of which are very closely related) had a common origin and developed by differentiation within the basic set of $x = 17$ chromosomes. Genetically the Pomoideae genera are quite distinct from the

* Part of a Ph.D. Thesis, submitted by the author to the University of Bristol.

[1] REHDER, A. (1940) *Manual of Cultivated Trees and Shrubs*, 2nd Edn, Macmillan, New York.
[2] BAILEY, L. H. (1949) *Manual of Cultivated Plants*, 2nd Edn, Macmillan, New York.
[3] WEBER, C. (1964) *J. Arnold Arb.* **45**, 162, 302.
[4] SAX, K. (1931) *J. Arnold Arb.* **12**, 3.
[5] SAX, K. (1933) *Proc. Am. Soc. Hort. Sci.* **30**, 147.

remainder of the Rosaceae which have basic chromosome numbers of $x = 7$, 8 and 9. There is good evidence, both botanical[4–8] and chemical[8] that Pomoideae is of allopolyploid origin, produced by ancient hybridisation between primitive forms of the Rosaceae having $x = 8$ and 9; these were possibly primitive forms of the Prunoideae and Spiraeoideae respectively.

RESULTS AND DISCUSSION

Table 1 lists the Pomoideae species which have been surveyed, together with the phenolics which have been detected. Many specimens examined were obtained as dried herbarium leaf and even in specimens of considerable age the range of phenolic glycosides and depsides appears to have survived intact. The genus *Malus* is currently being surveyed for phenolics by Williams[9–19] but a representative selection of species has been included in the present Pomoideae survey in order to facilitate the detection of *Malus* phenolics outside this genus. In *Crataegus*, apigenin and luteolin 7-glucosides, apigenin 7-rhamnosylglucoside,[20] vitexin 4′-rhamnoside, vitexin 4′-rutinoside, vitexin 7,4-′diglucoside[21] and apigenin 8-*C*-rhamnosylglucoside[20] have already been reported; *C*-glycosides in general (e.g. vitexin, apigenin 8-*C*-glucoside) have not yet been detected in any other genus of the Rosaceae.[8] Apigenin 7-glucoside has been reported in *Sorbus hybrida* leaf[22] but examination of the species in this laboratory suggests a mistaken identification of quercetin 4′-glucoside. Eriodictyol 7-glucoside has been found in *Pyracantha coccinea*[23] and naringenin and eriodictyol glycosides have been found in *Crataegus phenophyrum* leaf.[24] *Docynia* has previously been reported as containing arbutin[13,25,26] but it is now known that the specimen then examined was wrongly identified and is actually a *Pyrus* species. The occurrence of phloridzin in authentic specimens of *Docynia* leaf is of systematic interest since botanists have considered this genus to be closely related to *Cydonia*; it is now evident that there is a particularly close relationship with *Malus*. Vidal[27] in a recent revision of the genus *Docynia* recognises only two species, *D. delavayi* and *D. indica*. Attempts to locate living specimens of authentic *Docynia* have so far proved unsuccessful. In the Pomoideae, arbutin could be detected only in *Pyrus* but within the Rosaceae as a whole it has also been reported in *Sorbaria*,[28] *Exochorda*[8] (Spiraeoideae) and in *Adenostoma* (Rosoideae).[29] The genus *Adenostoma* is reported[30] to have a basic chromosome number of $x = 9$, a fact which would favour the placing of this genus within the Spiraeoideae. The single report of arbutin in *Rubus* (Rosoideae, $x = 7$)[31] could not be substantiated. Within the Rosaceae, dihydrochalcones are restricted

[6] STEBBINS, G. L. (1950) *Variation and Evolution in Plants*, p. 359, Oxford University Press, Oxford.
[7] STEBBINS, G. L. (1958) *Evolution* **12**, 267.
[8] CHALLICE, J. S. (1972) Ph.D. thesis, University of Bristol.
[9] WILLIAMS, A. H. (1969) *Rep. Long Ashton Res. Stn.* for 1969, 61.
[10] WILLIAMS, A. H. (1969) *Rep. Long Ashton Res. Stn.* for 1968, 44.
[11] WILLIAMS, A. H. (1966) *Rep. Long Ashton Res. Stn.* for 1966, 37.
[12] WILLIAMS, A. H. (1967) *Chem. Ind. (London)* 1526.
[13] CHALLICE, J. S. and WILLIAMS, A. H. (1968) *Phytochemistry* **7**, 1781.
[14] CHALLICE, J. S. and WILLIAMS, A. H. (1970) *Phytochemistry* **9**, 1271.
[15] WILLIAMS, A. H. (1966) in *Comparative Phytochemistry* (SWAIN, T., ed.), p. 297, Academic Press, London.
[16] WILLIAMS, A. H. (1967) *Rep. Long Ashton Res. Stn.* for 1967, 39.
[17] WILLIAMS, A. H. (1962) *Rep. Long Ashton Res. Stn.* for 1962, 30.
[18] WILLIAMS, A. H. (1970) *Rep. Long Ashton Res. Stn.* for 1970, 66.
[19] WILLIAMS, A. H. (1964) *Rep. Long Ashton Res. Stn.* for 1964, 36.
[20] BATYUK, V. S. (1966) *Chem. Abstr.* **66**, 38200.
[21] LEWAK, S. (1966) *Roczn. Chem.* **40**, 443.
[22] PAVLII, O. I. and MAKAROVA, G. V. (1970) *Chem. Abstr.* **74**, 84008.

to *Malus* and *Docynia*[8] (Pomoideae), *Adenostoma*[29] (Rosoideae) and *Sorbaria*[8] (Spiraeoideae).

Within *Pyrus* it is now clear that the occurrence of flavone glycosides is restricted to those species which are of East Asian or North African origin; species from Europe or Western Asia completely lack flavones.[8,13,14] In *Sorbus* the converse seems to hold; flavone glycosides are restricted to two species of Rehder's Section III Aria, one of Mediterranean and the other of North European origin. All *Sorbus* species of East Asian origin (six were examined) lacked flavones. Although the two N. American *Sorbus* species examined were found to lack flavones, the very closely related genus *Aronia* (restricted to N. America) was found to contain flavones. It is of considerable systematic interest that *Hesperomeles* (the only Pomoideae genus in S. America) contains flavones. The finding by Williams of chrysin 5- and 7-glucosides in *Malus* indicates some affinity here with *Prunus*, where chrysin 7-glucoside has also been found;[32] these are the only reported occurrences of flavones lacking B-ring hydroxylation in the Rosaceae. Also of systematic interest is the finding that *p*-hydroxybenzoyl, protocatechuoyl and vanilloylcalleryanin and protocatechuic acid 3-glucoside are restricted to *Pyrus calleryana* and *Pyrus koehnei* (Pomoideae) and to *Prunus lusitanica* (Prunoideae).

Flavanones are generally considered to be more characteristic of woody tissues rather than leaf; hence it is difficult to assess the systematic significance of their distribution within the Pomoideae on the basis of leaf material only.

A review of the occurrence of all phenolics within the Rosaceae[8] has shown that flavone glycosides are present in all four subfamilies, Pomoideae, Prunoideae, Spiraeoideae and Rosoideae. However, within the Rosoideae, flavones appear to be restricted to the genera *Kerria*,[33] *Rhodotypos*[34] and *Neviusia*[35] all of which have a basic chromosome number of $x = 9$ rather than $x = 7$ as possessed by most other genera of the Rosoideae.[36] Bate-Smith[34,37] has found that within the Rosaceae, ellagic acid is restricted to the Rosoideae where it occurs in all tribes except the tribe Kerrieae (*Kerria*, *Rhodotypos*, *Neviusia* and *Coleogyne*). Whilst sorbitol has been found throughout the Pomoideae, Prunoideae and Spiraeoideae, in the Rosoideae this polyhydric alcohol is apparently restricted to the genera *Kerria*, *Rhodotypos* and *Neviusia*.[38] Thus it would appear that on chemical grounds there is a case for transferring the tribe Kerrieae from the Rosoideae to the Spiraeoideae, as already suggested by some botanists. This fits in quite well with Gajewski's hypothesis that the Prunoideae and Spiraeoideae represent distinct and primitive developmental lines of the Rosaceae and that the Rosoideae probably developed later from the Spiraeoideae.[39,40] It is considered that for numerous tribes of the Rosoideae the original forms were trees or

[23] PARIS, R. R. and ETCHEPARE, S. (1965) *Ann. Pharm. Fr.* **23**, 627.
[24] KOWALEWSKI, Z. and MRUGASIEWICZ, K. (1971) *Planta Med.* **19**, 311.
[25] WILLIAMS, A. H. (1960) in *Phenolics in Plants in Health and Disease* (PRIDHAM, J. B., ed.), p. 3, Pergamon Press, Oxford.
[26] WILLIAMS, A. H. (1964) *Nature, Lond.* **202**, 824.
[27] VIDAL, J. E. (1967) *Adansonia* (2) **6**, 563.
[28] PLOUVIER, V. (1971) *Compt. Rend.* **272**, 1443.
[29] MCPHERSON, J. K., CHOU, C.-H. and MULLER, C. H. (1971) *Phytochemistry* **10**, 2925.
[30] ORNDUFF, R. (1967) *Index to plant chromosome numbers for 1965* (*Regnum Vegetabile* **50**) p. 65, Utrecht.
[31] KARRER, W. (1958) *Konstitution und Vorkommen der Organischen Pflanzenstoffe*, Birkhauser, Basel.
[32] HASEGAWA, M. (1958) *J. Jap. For. Soc.* **40**, 111.
[33] HARBORNE, J. B. and WILLIAMS, C. A. (1971) *Phytochemistry* **10**, 367.
[34] BATE-SMITH, E. C. (1961) *J. Linn. Soc. Bot.* **58**, 39.
[35] PLOUVIER, V. (1966) *Compt. Rend.* **263**, 1529.

TABLE 1. LEAF PHENOLICS OF POMOIDEAE SPECIES

Plant species†	Compounds*								
	Flavones**		DHC††	Flavanones‡	Flavonols§		Isochlorogenic acid‖	Catechins	
	FT	F2	Ph	FN	F7	FSP		U1	U2
Cotoneaster									
C. horizontalis						t	++	++	t
C. francheti					t	+	+	++(+)	+
C. melanocarpa var. *laxipolius*							t	++	
C. racemiflora H							t	+(+)	
Pyracantha									
P. coccinea				(+)	(t)			+++	
P. atalantioides					++			++	+
Mespilus									
M. germanica							++	++	+
Crataegus									
C. carrierei		+(+)			++			+++	+
C. orientalis var. *sanguinea*		+(+)						++(+)	t
Osteomeles									
O. schwerinae H									
O. anthyllidifolia H									
Sorbus									
(Section I Aucuparia)									
S. americana							++	+	t
S. commixta H				++	t		+		
S. decora							+	+	+
S. tianshanica				++			++	++	+(+)
S. aucuparia							++	++	+
S. pohuashanensis							+(+)	++	+
S. vilmorini				+(+)		++	++	+	
S. koehneana H				t					
(Section II Cormus)									
S. domestica H (2 sources)									
(Section III Aria)									
S. tormunalis H									
S. intermedia	+(+)								
S. aria	+(+)					+	+	++	+(+)
							+	++	+
(Section IV Micromeles)									
S. japonica								t	t
(Section I × III)									
S. hybrida									
(*S. aucuparai* × *S. intermedia*)							+(+)	++	+
S. thuringiaca									
(*S. aucuparia* × *S. aria*)							++	++	+
Aronia									
A. arbutifolia									
A. prunifolia H	++(+)	+			+	+(+)	++	++	t
A. melanocarpa	+(+)	(+)			+(+)		+(+)		
					++			++	+
Photinia									
P. villosa								?	+++
P. serrulata H							+		
P. davidsoniae H				+ ?			t		
P. flava								?	+++
Heteromeles									
H. arbutifolia M. Roem (14 sources)							++		++(+)
Stranvaesia									
S. davidiana H							++(+)		
S. davidiana var. *undulata*							++(+)		
S. nussia H					++		(t)		
Eriobotrya									
E. japonica H									
E. bengalensis H									
Raphiolepis									
R. japonica H									
R. indica H									
Amelanchier									
A. asiatica							t	++	+
A. ovalis							+		
A. canadensis							+	++	+
A. laevis							+	++	+
Peraphyllum									
P. ramosissimum H					t		+		
Malus									
(Section I Emumalus)									
M. 'prunifolia Rinkii'			+++			+		t	+
M. hupehensis			+++			t		t	+

TABLE 1—*continued*

Plant species†	Compounds*								
	Flavones**		DHC††	Flavanones‡	Flavonols§		Isochlorogenic acid‖	Catechins	
	FT	F2	Ph	FN	F7	FSP		U1	U2
(Section II Sorbomalus)									
M. fusca			+++			t			+
M. toringoides			+++			t			+
(Section III Chloromeles)									
M. glaucescens			+++			+			+
(Section IV Eriolobus)									
M. trilobata					t	+			+(+)
(Section V Docyniopsis)									
M. tschonoskii			+++			+(+)			+(+)
(Section ?)									
M. Sp. 'H'									++
Docynia									
D. delavayi H (3 sources)			+++						
D. indica H (3 sources)			+(+)						
Chaenomeles									
(Section I Euchaenomeles)							++		++?
C. cathayensis									
C. japonica cv. 'Maulei'				(t)	+		t?	++(+)	
C. speciosa cv. 'Moerloosei'				++	+		+		
(Section II Pseudocydonia)									
C. sinensis	++(+)							++(+)	
Cydonia									
C. oblonga							+	++	+
C. vulgaris var. *vranja*							+(+)	++	+
Pyrus¶									
see Refs. 8, 13, 14		pres.			pres.	pres.	pres.	pres.	
Hesperomeles									
H. oblonga Lindl. H									
H. heterophylla (R & P) Hook. H	++								
H. cuneata Lindl. H	+(+)	+				(+)			
H. glabrata H.B.K. H						++			
H. intermedia Pittier H	++					(+)			
H. ferruginea (Pers.) *Beveh.* H									

* Blank space indicates that the phenolic could not be detected. Scoring code: t trace; + small amount; ++ moderate amount; +++ large amount; () reservations regarding enclosed symbol, score on low side. FT luteolin 7-rhamnosylglucoside; F2 luteolin 7-glucoside; DHC, dihydrochalkone; Ph phloridzin (phloretin 2'-glucoside); FN incompletely identified glucoside of naringenin (Williams, unpublished); F7 quercetin or kaempferol 3-triglycosides ?; F5P quercetin or kaempferol 3-monopentosides ?; U1 epicatechin; U2 catechin.

† Where the authority is not given after a given specific name, this authority will be found in Rehder,[1] where geographical origins are also listed. The origin of *Heteromeles* is given by Bailey[2] and the origins of *Chaenomeles* and *Hesperomeles* species are given by Weber[3] and Sax.[4,5] All specimens designated 'H' were obtained only as dried herbarium leaf samples from Kew, the remainder of the specimens were obtained as fresh leaf from various sources. Full details of sources and identifications of both fresh and herbarium specimens are given elsewhere.[8]

** Besides FT, a second luteolin 7-rhamnosylglucoside (F1) is present in *Pyrus* species, in *Crategus carrieri*, and in *Aronia arbutifolia*: a luteolin 7-diglucoside (FV) is present in all species containing the monoside (F2) except *Crategus orientalis*, *Pyrus* species, and *Hesperomeles cuneata*, FV is present without F2 in *Sorbus torminalis*. Apigenin 7-glucoside (F3) and chrysoeriol 7-glucoside (F2) are found in *Pyrus* species; F3 is also in *Crategus ᵃarrierei* and F2 in *Hesperomeles glabrata*. Flavone 4'-*O*-glucosides and a suspected luteolin 5-methyl ether (FS) are apparently restricted to *Pyrus*.[13,14] Williams has found chrysin 5-glucoside and its corresponding β-hydroxychalcone[9,10] in *Malus* bark (but not in leaf) and chrysin 7-glucoside and its corresponding β-hydroxychalcone[11,12] in *Malus* leaf and bark; these compounds could not be detected elsewhere in the Pomoideae.

†† Dihydrochalkones: phloridzin (Ph) is replaced in *Malus trilobata* and *M.* sp. 'H' by trilobatin (Tri) the corresponding 4'-glucoside of phloretin; Sieboldin (Sie, 3-hydroxytrilobatin) is found in *M. prunifolia Rinkii* and *M.* sp. 'H'., Williams[15,16,18,19] has also detected the following minor dihydrochalcones in *Malus*: phloretin 2'-xylosylglucoside, 4-desoxyphloretin 4'-glucoside and *p*-coumaroylphloridzin.

‡ Besides the naringenin derivatives (FN) unknown eriodictyol glucosides (FE) are present in all species containing FN except *Sorbus vilmorini*, *S. koehneana*, *Chaenomeles japonica* and *Photinia davidsoniae*. In addition FE is present alone in *Pyracantha atalantioides*, *Hesperomeles cuneata* and *glabrata*. Williams has reported naringenin and eriodictyol 7-glucoside as present in leaf and bark of some *Malus* species[18,16] and eriodictoyl 7-glucoside as present in the bark only of *Cydonia*.[1]

§ Quercetin 4'-glucoside was detected in trace amounts in the leaf of 3 species of *Sorbus* (*S. aucuparia*, *S. decora* and *S. commixta*); Williams[9] reported this flavonoid in the bark of some *Malus* species but could not detect it in the leaf. Williams[10] has found quercetin 5-glucoside in substantial amount as a bark constituent of a few *Malus* species. In the corresponding leaf specimens this flavonoid was detected in trace amounts only. Traces of quercetin 5-glucoside have been detected in the leaf of *Cotoneaster racemiflora* and *Pyracamtha atalantioides* only. Azaleatin 3-glucoside has been found in the bark lof a few *Malus* species,[18] it could not be found in the correspondiing leaf, nor in the leaf of any other Pomoideae species. Quercetin or kaempferol 3-mono- and di-glycosides occur in all genera listed in Table 1.

‖ Chlorogenic acid occurs in all genera listed in Table 1.

¶ Arbutin (hydroquinone monoglucoside) is restricted to *Pyrus* where it is present in all species. Caffeoylcalleryanin is present in the leaf of some species only, but it ubiquitous as a bark constituent; *p*-Hydroxybenzoyl, protocatechuoyl and vanilloylcalleryanin and protocatechuic acid 3-glucoside are present only in *Pyrus calleryana* and *P. koehnei*.

shrubs with a basic chromosome number of $x = 9$. Present-day Rosoideae genera having $x = 9$ could be regarded as relicts of the transitional forms between the Spiraeoideae and Rosoideae. The evidence reviewed here certainly does not favour Darlington's hypothesis[41] that the Pomoideae evolved through unequal reduplication of a basic set of 7 chromosomes ($7 + 7 + 3 = 17$) in a primitive member of the Rosoideae.

TABLE 2. R_f DATA FOR *Exochorda* PHENOLICS AND SOME REFERENCE COMPOUNDS

Phenolic	OR 2% HOAc*	2% HOAc	SBA	PWA	50% HOAc
FV	4·5	0·03	0·10	0·21	0·50
FT	9·6	0·08	0·37	0·61	0·69
F2 auth. luteolin 7-glucoside	2·3	0·03	0·37	0·60	0·50
F3 auth. apigenin 7-glucoside	7·2	0·06	0·58	0·80	0·66
FV, FT and F2 aglycone† auth. luteolin	0·8	0·00	0·81	0·62	0·44
F3 aglycone auth. apigenin	0·8	0·00	0·85	0·80	0·55
A1 auth. arbutin	—	0·80	0·45	—	—

* Numbers refer to distance in cm of spot from origin (sheet 37·5 cm long with the end serrated) and solvent over-run for 24 hr. SBA and PWA solvents (see Experimental).

† In Forestal solvent it was subsequently shown that these aglycones could be clearly distinguished from 6-OH luteolin and 6-OH apigenin (scutellarein): FV, FT, F2 aglycones and auth. luteolin (R_f 0·60); F3 aglycone and auth. apigenin (R_f 0·72); scutellarein (R_f 0·57); 6-OH luteolin (R_f 0·43).

Stebbins[42] has suggested that the genus of Spiraeoideae which resembles most closely the Pomoideae is *Vauquelinia* which in all characteristics except its gynaecia and fruits bears a strong resemblance to *Photinia* and *Heteromeles* of the Pomoideae. Unfortunately, the two latter genera were found to lack phenolics of any real systematic significance. Bate-Smith has found the rare flavonol quercetagetin (6-hydroxyquercetin) in *Vauquelinia* but not elsewhere in the Rosaceae.[43] However, 6-methoxykaempferol has recently been found in *Prunus avium*.[44] Although 6-hydroxylation or methoxylation of flavonols is restricted to the Spiraeoideae and Prunoideae, 6-hydroxylation or methoxylation of flavones (scutellarein derivs.) is restricted to the Spiraeoideae (*Sorbaria*)[45,46] and Rosoideae (*Kerria*).[33] Stebbins

[36] DARLINGTON, C. D. and WYLIE, A. P. (1955) *Chromosome Atlas of Flowering Plants*, George Allen & Unwin, London.
[37] BATE-SMITH, E. C. (1962) *J. Linn. Soc. Bot.* **58**, 95.
[38] PLOUVIER, V. (1963) in *Chemical Plant Taxonomy* (SWAIN, T., ed.), Chap. 11, Academic Press, London.
[39] GAJEWSKI, W. (1957) *Monographiae Botanicae* (*Warszawa*) **4**, 1–416.
[40] GAJEWSKI, W. (1959) *Evolution* **13**, 378.
[41] DARLINGTON, C. D. (1963) *Chromosome Botany and the Origins of Cultivated Plants*, 2nd Edn, George Allen & Unwin, London.
[42] STEBBINS, G. L. (1958) *Evolution* **12**, 267.
[43] BATE-SMITH, E. C. (1965) *Phytochemistry* **4**, 535.
[44] LEBRETON, P., WOLLENWEBER, E., SOUTHWICK, I., and MABRY T. J. (1971) *Compt. Rend.* **272**, 1529.
[45] ARISAWA, M. and NAKAOKI, T. (1970) *Biol. Abstr.* **51**, 34381.
[46] ARISAWA, M., TAKAKUWA, T. and NAKAOKI, T. (1970) *Chem. Pharm. Bull.* (*Tokyo*) **18**, 916.

has also mentioned the Spiraeoideae genera *Kageneckia* and *Quillaja* but no chemical link could be found between these genera and the Pomoideae.[8] Within the Spiraeoideae, isochlorogenic acid could be detected only in *Lindleya*.[8] Of the Pomoideae flavones listed in Table 1, all except F1 and FZ have also been detected in the leaf of *Exochorda*.

EXPERIMENTAL

Plant material. Fresh or dried herbarium leaf (see Table 1) was extracted with EtOH in the normal manner. Herbarium leaf was previously moistened with an equal wt H_2O.

PC. 0·25 ml EtOH extract (representing 50 mg fresh leaf) was spotted on Whatman No. 1 paper and run with the following solvent-pairs (solvents run *ca.* 35 cm in each direction, first named solvent run first): SBA/2% HOAc (4 hr run), SBA/2% HOAc (over-run 1–2 days), SBA/50% HOAc. Where flavone glycosides are absent, only chromatography in the first solvent-pair is necessary. Solvents: SBA (*sec*-BuOH–HOAc–H_2O, 35:1:14), 50% HOAc (HOAc–H_2O, 1:1), 2% HOAc (HOAc–H_2O, 1:49). When phenolics were isolated from leaf extracts, this was done on Whatman 3MM thick paper using SBA and 2% HOAc for the initial fractionations followed by purity checks using the following additional solvent: PWA (molten phenol–HOAc–H_2O, 39:1:10).

Colour reagents. Diazo and Gibbs reagents (general phenolics reagents) and $NaBH_4$–HCl reagent (flavanones and dihydrochalcones), preceded by UV inspection of sheets before and after NH_3-fuming. An additional reagent for flavonoids was sometimes used: 1% $AlCl_3$–EtOH dip followed by drying and UV inspection. Full details of all these reagents are given elsewhere.[13,47]

Hydrolyses of phenolic glycosides. As described in an earlier paper.[47]

Identification of phloridzin in Docynia delavayi *and* D. indica. Since only small samples of herbarium leaf were available, identification was by R_f and colour reactions only. However, since phloridzin (phloretin 2′-glucoside) is such a well known constituent of *Malus* leaf[15] and Weber, on botanical grounds,[48] considers that *Malus* and *Docynia* are quite closely related, the identification is reasonably certain.

Identification of trilobatin in Sorbaria arborea *var.* glabrata. A small amount of a phenolic, identical in R_f and colour reactions to authentic trilobatin (phloretin 4′-glucoside),[49] was isolated from the fresh leaf of this species (obtained from the Royal Botanic Gardens, Kew). Acid hydrolysis gave phloretin + glucose. UV spectra and shifts of both glucoside and aglycone agreed reasonably well with authentic trilobatin and phloretin respectively.[8]

Identification of flavone glycosides and arbutin in Exochorda racemosa. Table 2 gives the R_f data for the phenolics FV, FT, F2, F3 and A1 which were isolated from the fresh leaf of the above species (growing at Long Ashton Research Station). The UV spectra and shifts of FV, FT and F2 agreed with authentic luteolin 7-glucoside and the UV spectra and shifts of F3 agreed with authentic apigenin 7-glucoside.[8,13] Acid hydrolysis of F2 and FV each gave luteolin and glucose, FT gave luteolin, glucose and rhamnose and F3 gave apigenin and glucose. F2 and F3 are luteolin and apigenin 7-glucosides and on the basis of its paper chromatographic behaviour FV is almost certainly luteolin 7-diglucoside. FT would appear to be a luteolin 7-rhamnosyl-glucoside but it differed in R_f from a flavonoid of apparently identical structure (F1) previously isolated from *Pyrus*.[13] Whilst F1 and FT have much the same R_f in 2% HOAc, F1 has a noticeably lower R_f than FT in SBA solvent. When *Exochorda* FT was added to a *Pyrus* leaf extract and chromatographed (SBA/2% HOAc over-run 24 hr), FT and F1 could clearly be differentiated. *Exochorda* A1 was identified as arbutin on the basis of R_f and colour reactions alone; in view of the fact that arbutin has already been found in another Spiraeoideae genus (*Sorbaria*)[28] the identification would seem reasonably certain.

Location of Pomoideae phenolics on 2-dimensional paper chromatograms. 2-D PC maps are given elsewhere.[8,13]

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[47] Challice, J. S. and Williams, A. H. (1968) *Phytochemistry* **7**, 119.
[48] Weber, C. (1964) *J. Arnold Arb.* **45**, 161, 302.
[49] Williams, A. H. (1961) *J. Chem. Soc.* 4133.