

ラン科植物のフラボノイド — その花色への貢献と分布 —

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IWASHINA, Tsukasa*: The Flavonoids in the Family Orchidaceae: Contribution to Flower Colours and Distribution

ラン科は約1万7千(里見1982)とも2万(Stewart and Griffiths 1995)とも、あるいはそれ以上ともいわれている種を有する大きな科である。ほぼ全世界に分布し、その外部形態や受粉様式などで砂漠のような極端な乾燥地や南極のような極寒地を除く様々な環境に適応しており、植物界の中でも最も進化している種群の一つである。特に受粉のための昆虫など花粉媒介動物との相互進化の結果としての花の形態の多様性に関しては見るべきものがある。一方でその花色についてもかなりの変異がある。ラン科に限らず、多くの植物の花色に関わる色素は主としてアントシアニンである(Timberlake and Bridle 1975, 吉玉・石倉1988)。しかしながら今日、ラン科植物は鑑賞用として極めて重要な位置にありながら、花に含まれるアントシアニンも加えたフラボノイド化合物の研究はほとんどなされていなかった。近年、特に鑑賞用として栽培される種群を中心にフラボノイドのうち、アントシアニンについては分離・同定が行われるようになった(立澤1996, Strack *et al.* 1989など)。これは高速液体クロマトグラフィー(HPLC)や核磁気共鳴スペクトル(NMR)、質量スペクトル(MS)などの分析機器の発達によって、少量の化合物の分析や、より複雑な構造の化合物の同定が可能になった事が大きい。しかし、それでも少なく見積もっても1万7千以上といわれる種の数に比べて含有されるフラボノイドが今日までに明らかになった植物はまだ少ない。

本論文では、今までにラン科植物から報告されたフラボノイドを列挙し、これらの化合物と花色との関連を述べるばかりでなく、フラボノイドを指標としたラン科植物の化学分類学的知見も併せて総説する。

ラン科植物に含まれるフラボノイドの種類

Table 1には今までにラン科でフラボノイドが報告された種、同定されたフラボノイドの構造、分離された植物部位、および記載された文献を示した。現在までにラン科でフラボノイドが完全に、あるいは部分的に定性された植物は著者の知る限り、82属290種類である。フラボノイドのクラスとしてはアントシアニンが圧倒的に多くの種から報告されている。これらの多くは、ラン科植物に美しい花を咲かせる種が多いために花の色との関連で調査されたものである。その他に、フラボノール、フラボン、C-グリコシルフラボンに加えて、少数の植物からフラバノン、ジヒドロフラボノール、プロアントシアニン、それに自然界では極めてまれなアントシアニン-フラボノール複合体も見出されている(Fig. 1.)。しかし、イソフラボン、フラバン3,4-ジオール、ビフラボン、黄色花の発現に重要であるカルコンやオーロンは今のところラン科植物からは報告されていない。なお、キサントンもいくつかの植物から報告されているが、フラボノイドがC₆-C₃-C₆を基本骨格としているのに対して、キサントンはC₆-C₁-C₆が基本骨格であり、フラボノイ

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ドではないが、生合成経路がフラボノイドと密接に関連している化合物群であるので、Table 1に加えた。フラボノイドが分離された植物部位は圧倒的に花が多く、その他では、Williams (1979) が多くの種の葉から分離同定した報告があるばかりで、果実や根からは今までフラボノイドは報告されていない。これもやはり花の色との関連でのみ従来フラボノイドが分析されてきたからであろうと思われる。

フラボノイドは今まで例外的に藻類の *Nitella* 属で発見されている (Markham and Porter 1969) 以外には一般に蘚苔類以上の高等植物から広く報告されている (Markham 1988, Niemann 1988, Giannasi 1988, Williams and Harborne 1988)。特にシダ類、裸子植物および被子植物では花や葉にはむしろ含有されていると考える方が常識である。したがって、ラン科植物でもムヨウラン属 (*Lecanorchis*) の仲間のような無葉緑腐生植物では合成されない可能性もあるが、ほとんどの植物の花や葉には存在すると考えられる。にもかかわらず、わずか300弱の種でしか報告がないのは、フラボノイドが存在しないというよりもむしろ、ラン科であまり調査分析がなされていないためであると考えられる。

なお、Table 1 で記載した種以外に、いくつかの園芸品種や雑種の花などに含まれるフラボノイド (主にアントシアニン) の分離同定の報告 (Tatsuzawa *et al.* 1994, 1996b など) もあるが、繁雑さを避けるために今回は原種に含まれるフラボノイドのみに記載をとどめた。

フラボノイドの構成と花色

植物の花の色は青紫～紫、赤、橙、黄、白、さらには褐色や緑色など多彩である。これらのうち、青紫～紫や赤色の花はベタレイン系の色素を合成するヒユ科、オンシロバナ科、スベリヒユ科、アカザ科、サボテン科などの中心子目に属する植物を除けば (Piattelli and Minale 1964, 岩科ら1985)、一般にアントシアニンによって発現され、橙色はアントシアニンかカロチノイド、あるいはその共存によって、また黄色は上記の中心子目の植物 (ベタキサンチンを含有) を除いて、カロチノイドが一般的であるが、黄色系のフラボノイドであるカルコンやオーロン、時にはフラボノールによっても発現される (斎藤1988)。さらに白色花でもほとんどの植物で、非常に淡い黄色のフラボン、フラボノール、フラバノンなどのフラボノイドが存在する。

ラン科植物の場合でも、青紫～紫や赤色花は主にアントシアニンによって発現されていることは古くから報告されていた (Robinson and Robinson 1932, Lawrence *et al.* 1939)。しかし、今までの多くの報告はアントシアニンの存在は認めているながらも、その同定はまったくといっていいほどなされていなかった (Sanford *et al.* 1964, 1965, Harper 1972)。あるいはアグリコンレベルの同定にすぎなかった (Gascoigne *et al.* 1949, Forsyth and Simmonds 1954)。

近年になって HPLC や NMR などの機器の発達によりラン科植物の花に含まれるアントシアニンの分離同定が急速に進んだ。これは Strack *et al.* (1986, 1989) と斎藤、立澤 (Saito *et al.* 1994, 1995, Tatsuzawa *et al.* 1994, 1996a, 1996b, 1997, 立澤1996) の功績によるところが大きい。

Table 2 にみられるように、ラン科植物の花に含まれるアントシアニンは自然界に普遍的に存在する 6 種類のアントシアニジン、すなわち pelargonidin, cyanidin, peonidin, delphinidin, petunidin および malvidin がすべて報告されている。これらのアントシアニジンは緋色の pelargonidin から紫色の delphinidin までの大きな色の変化がある。ひとつの科の中に 6 種類のアントシアニジンがすべて分布することは植物界では比較的まれで、これがランの花色が多彩である原因の一つとも考えられる。しかしながら、今までに報告されたアントシアニンのほとんどは cyanidin の配糖体であり、その他のアントシアニジンの配糖体はごく僅かであるので (Table 2)、その外にもランが多彩である原因が考えられた。

そのような点で従来、ランから分離されたアントシアニンで特に注目すべきなのはシラン

Table 1. The reports of flavonoids in the family Orchidaceae

Species	Classes of flavonoids
Flavonoids	
<i>Aceras anthropophora</i>	Flavonol Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)
<i>Acianthus fornicatus</i>	Anthocyanin Cyanidin bioside. (Fl) (Gascoigne <i>et al.</i> 1949)
<i>Aerides fieldingii</i>	Flavonol Quercetin 3- <i>O</i> -glucoside, Kaempferol 3- <i>O</i> -glucoside. (Lv) (Williams 1979) Dihydroflavonol Dihydroquercetin 3- <i>O</i> -glucoside. (Lv) (Williams 1979)
<i>Aerides japonicum</i> (ナゴラン)	Anthocyanin Cyanidin glycoside. (Fl) (Arditti 1992)
<i>Aerides odorata</i>	Flavonol Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979) Dihydroflavonol Dihydroquercetin glycoside. (Lv) (Williams 1979)
<i>Anacantpis pyramidalis</i>	Anthocyanin Cyanidin 3, 5-di- <i>O</i> -glucoside. (Fl) (Harborne 1963, Strack <i>et al.</i> 1986) Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3, 7-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 7-di- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989) Cyanidin 3- <i>O</i> -[6- <i>O</i> -(oxalyl)-glucoside]. (Fl) (Strack <i>et al.</i> 1986) Anthocyanin-flavonol complex Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside-kaempferol 7- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
<i>Anacheillium alagoense</i> , <i>A. allemanii</i> , <i>A. allemanoides</i> , <i>A. calamarium</i> , <i>A. caetense</i> , <i>A. cochleatum</i> , <i>A. campos-portoi</i> , <i>A. faresianum</i> , <i>A. faustum</i> , <i>A. fragrans</i> , <i>A. glumaceum</i> , <i>A. grammatoglossum</i> , <i>A. hartwegii</i> , <i>A. inversum</i> , <i>A. kaustkyi</i> , <i>A. lividum</i> , <i>A. moogenii</i> , <i>A. papilio</i> , <i>A. radiatum</i> , <i>A. suzanense</i> , <i>A. vespa</i> and <i>A. widgrenii</i>	Dihydroflavonol 3, 5, 7, 3'-tetrahydroxy-4'-methoxydihydroflavonol 3- <i>O</i> -rutinoside. (Fl) (Ferreira <i>et al.</i> 1986)
<i>Anguloa brevilabris</i>	C-glycosylflavone Vitexin. (Lv) (Williams 1979)
<i>Ansellia africana</i>	

Table 1.

-(continued)-

Anthocyanin

Cyanidin glycoside, Peonidin glycoside. (Fl) (Arditti 1992)

*Appendicula undulata***Anthocyanin**

Cyanidin glycoside. (Lv) (Lowry and Keong 1973)

Cyanidin 3-*O*-(*p*-coumaryl, ferulyl)-arabinosylglucoside. (Lv) (Arditti 1992)*Arundina bambusaefolia***Anthocyanin**

Acylated cyanidin glycoside. (Fl) (Lowry and Keong 1973)

Cyanidin 3-*O*-(*p*-coumaryl, ferulyl)-arabinosylglucoside. (Lv) (Arditti 1992)*Ascocentrum carvifolium***Anthocyanin**

Cyanidin glycoside. (Fl) (Arditti 1992)

*Barlia metlesicsiana***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Barlia robertiana***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979, Strack *et al.* 1989)Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Bletilla striata* (シラン)**Anthocyanin**Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-glucoside-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-glucoside-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeyl)-glucosyl)-caffeyl)-glycoside], Cyanidin 3-*O*-glucoside-7,3'-*O*-hydroxycinnamylglucoside, Cyanidin 3-*O*-malonylglucoside-7, 3'-*O*-hydroxycinnamylglucoside. (Fl) (Saito *et al.* 1995)Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside].

-(continued)-

Table 1.

-(continued)-

(Fl) (立澤 1996)

*Brassavola nodosa***Anthocyanin**Cyanidin 3-*O*-sophoroside, Cyanidin 5-*O*-*P*-coumarylglucoside. (Fl) (Arditti 1969a)*Bromheadia finlaysoniana***Anthocyanin**

Cyanidin glycoside. (Lv) (Lowry and Keong 1973)

FlavonolQuercetin 3-*O*-rutinoside. (Fl) (Lowry and Keong 1973)*Broughtonia domingensis***Anthocyanin**Pelargonidin 3-*O*-rutinoside, Pelargonidin 5-*O*-*P*-coumarylglucoside. (Fl) (Arditti 1969a)*Broughtonia negrilensis***Anthocyanin**Pelargonidin 3-*O*-glucoside, Pelargonidin 3-*O*-rutinoside, Pelargonidin 3, 5-di-*O*-glucoside, Pelargonidin 5-*O*-*P*-coumarylglucoside. (Fl) (Arditti 1969a, Arditti and Ernst 1969b)*Broughtonia sanguinea***Anthocyanin**Cyanidin 3-*O*-sophoroside, Cyanidin 5-*O*-ferulylglucoside, Petunidin 3-*O*-glucoside, Pelargonidin 3-*O*-sophoroside, Pelargonidin 5-*O*-ferulylglucoside. (Fl) (Arditti 1969a)*Bulbophyllum bequaertii* var. *brachyanthum***Flavonol**

Kaempferol glycoside. (Lv) (Williams 1979)

*Caladenia carnea***Anthocyanin**Cyanidin bioside, Malvidin bioside. (Fl) (Gascoigne *et al.* 1949)*Caladenia patersoni***Anthocyanin**Malvidin bioside. (Fl) (Gascoigne *et al.* 1949)*Caleana major***Anthocyanin**Acylated cyanidin glycoside. (Fl) (Gascoigne *et al.* 1949)*Calypso borealis*Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979)*Catasetum saccatum*

-(continued)-

Table 1.

-(continued)-

Anthocyanin

Cyanidin glycoside, Peonidin glycoside, Pelargonidin glycoside. (Fl) (Arditti 1992)

Cattleya aclandiae, *C. bowringiana* var. *coerulea*, *C. dowiana* var. *aurea*, *C. harisoniana*, *C. intermedia* var. *aquinii*, *C. labiata*, *C. loddigesii*, *C. maxima*, *C. nobillior*, *C. nobillior* var. *coerulea*, *C. percivaliana*, *C. skinneri*, *C. trianae* var. *anelata*, *C. velutina* and *C. walkeriana* var. *tipo*

Anthocyanin

Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(caffeoyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(4-O-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(4-O-(glucosyl)-p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(caffeoyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside]. (Fl) (立澤 1996)

Cattleya amethystoglossa, *C. guatemalensis*, *C. intermedia* var. *flamea* and *C. mossiae* var. *coerulea*

Anthocyanin

Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(caffeoyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(4-O-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(4-O-(glucosyl)-p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(caffeoyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside]. (Fl) (立澤 1996)

Cattleya bicolor

Anthocyanin

Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(caffeoyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(4-O-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside]. (Fl) (立澤 1996)

Cattleya bowringiana

Anthocyanin

Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(caffeoyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(4-O-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(4-O-(glucosyl)-p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(caffeoyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(p-coumaroyl)-glucoside]-3'-O-[6-O-(4-O-(6-O-(p-coumaroyl)-glucosyl)-p-coumaroyl)-glucoside]. (Fl) (立澤 1996)

-(continued)-

Table 1.

-(continued)-

C-Glycosylflavone

Apigenin di-C-glycoside. (Lv) (Williams 1979)

Cattleya chocoensis, *C. dorosa*, *C. dormaniana*, *C. loddigesii* var. *tipo* and *C. trianae***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside].

(Fl) (立澤 1996)

*Cattleya forbesii***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(6-*O*-(caffeoyl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside]. (Fl) (立澤 1996)

Cattleya intermedia var. *moculata* and *C. schilleriana***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside].

(Fl) (立澤 1996)

*Cattleya rex***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-*p*-coumaryl)-glucoside].

(Fl) (立澤 1996)

*Cattleya walkeriana***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-

-(continued)-

Table 1.

-(continued)-

(glucosyl)-caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-(glucosyl)-caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside]. (Fl) (Tatsuzawa *et al.* 1996b, 立澤 1996)

*Cattleyopsis lindenii***Anthocyanin**

Pelargonidin 3-*O*-sophoroside, Pelargonidin 5-*O*-*p*-coumarylglucoside. (Fl) (Arditti 1969a)

*Cephalanthera damasonium***Flavonol**

Quercetin glycoside. (Lv) (Williams 1979)

*Cephalanthera kurdica***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Cephalanthera longifolia***Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

*Cephalanthera rubra***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Flavonol

Quercetin glycoside. (Lv) (Williams 1979)

*Chamaeangis odoratissima***C-Glycosylflavone**

Chrysoeriol C-glycoside -7-*O*-glucoside. (Lv) (Williams 1979)

*Coeloglossum viride***Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

-(continued)-

Table 1.

-(continued)-

*Cyclopogon congestus***Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

Cymbidium ensifolium (スルガラン)**Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3-*O*-diglucoside. (Fl) (杉山ら 1977)*Cymbidium finlaysonianum***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3-*O*-rutinoside. (Fl) (Lowry and Keong 1973)**C-Glycosylflavone**Vitexin 7-*O*-glucoside, Isovitexin 7-*O*-glucoside, Apigenin di-*C*-glycoside. (Lv) (Williams 1979)*Cymbidium insigne* and *C. tracyanum***Anthocyanin**Cyanidin 3-*O*-rutinoside, Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside], Peonidin 3-*O*-rutinoside, Peonidin 3-*O*-malonylglycoside, Cyanidin 3-*O*-glucoside, Peonidin 3-*O*-glucoside. (Fl) (立澤 1996, Tatsuzawa *et al.* 1996a)*Cymbidium lowianum***Anthocyanin**

Cyanidin glycoside. (Fl) (Arditti 1992)

*Cymbidium madidum***C-Glycosylflavone**Vitexin, Vitexin 7-*O*-glucoside, Isovitexin 7-*O*-glucoside, Apigenin di-*C*-glycoside. (Lv) (Williams 1979)*Cymbidium pumilium* (キンリョウヘン)**Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3-*O*-diglucoside. (Fl) (杉山ら 1977)*Cypripedium calceolus* (カラフトアツモリソウ)**Anthocyanin**Cyanidin 3-*O*-glucoside. (Uphoff 1979)*Cypripedium cordigerum***Anthocyanin**Cyanidin 3-*O*-glucoside. (Uphoff 1979)*Cypripedium reginae***Anthocyanin**Cyanidin 3-*O*-glucoside. (Uphoff 1979)*Dactylorhiza baumanniana*, *D. coccinea*, *D. foliosa*, *D. incarnata*, *D. kalopissii*, *D. osmanica*, *D. romana* and *D. saccifera*

-(continued)-

Table 1.

-(continued)-

Anthocyanin

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Dactylorhiza fuchsii***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)
Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Flavonol

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

Dactylorhiza iberica and *D. umbrosa***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Dactylorhiza maclata***Anthocyanin**

Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979, Strack *et al.* 1989)

*Dactylorhiza majalis***Anthocyanin**

Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979, Strack *et al.* 1989)
Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)
Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Dactylorhiza purpurella and *D. sphagnicola***Anthocyanin**

Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Dactylorhiza sambucina***Anthocyanin**

-(continued)-

Table 1.

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Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979, Strack *et al.* 1989)
 Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex
 Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Dactylorhiza traunsteineri
Anthocyanin
 Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)
 Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)

Anthocyanin-flavonol complex
 Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Dendrobium chrysanthum, *D. fimbriatum* var. *oculatum* and *D. gracilicaule* var. *howeanum*
Flavonol
 Kaempferol glycoside. (Lv) (Williams 1979)

Dendrobium cornutum
Anthocyanin
 Cyanidin glycoside. (Fl) (Lowry and Keong 1973)

Dendrobium crocatum
Anthocyanin
 Cyanidin 3-*O*-glucoside. (Fl) (Lowry and Keong 1973)

Dendrobium crumenatum
Flavonol
 Quercetin 3-*O*-rutinoside. (Fl) (Lowry and Keong 1973)

Dendrobium densiflorum, *D. farmeri* and *D. kingianum*
Flavonol
 Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

Dipodium punctatum
Anthocyanin
 Acylated cyanidin glycoside. (Fl) (Gascoigne *et al.* 1949)

Diuris aurea
Anthocyanin
 Cyanidin di-monoside. (Fl) (Gascoigne *et al.* 1949)

Diuris elongata
Anthocyanin
 Malvidin bioside. (Fl) (Gascoigne *et al.* 1949)

-(continued)-

Table 1.

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*Diuris sulphurea***Anthocyanin**Malvidin di-monoside. (Fl) (Gascoigne *et al.* 1949)*Doritis pulcherrima***Anthocyanin**Delphinidin 3, 5-di-*O*-glucoside. (Fl) (Harper 1974)**Flavonol**Quercetin 3, 4'-di-*O*-glucoside, Quercetin 7, 4'-di-*O*-glucoside. (Fl) (Harper 1974)**Flavanone**Naringenin 7-*O*-glucoside. (Fl) (Harper 1974)*Elythranthera brunonis***Anthocyanin**Cyanidin 3, 5-di-*O*-glucoside, Delphinidin 3, 5-di-*O*-glucoside. (Fl) (Strauss *et al.* 1974)*Elythranthera emarginata***Anthocyanin**Cyanidin 3, 5-di-*O*-glucoside, Delphinidin 3, 5-di-*O*-glucoside. (Fl) (Strauss *et al.* 1974)*Epidendrum cochleatum***Anthocyanin**

Cyanidin glycoside, Peonidin glycoside. (Fl) (Arditti 1992)

*Epidendrum huebneri***Proanthocyanin**

Procyanidin. (Lv) (Williams 1979)

*Epidendrum radicans***Anthocyanin**

Cyanidin glycoside. (Fl) (Arditti 1992)

*Epidendrum pirismatocarpum***Anthocyanin**

Cyanidin glycoside, Peonidin glycoside. (Fl) (Arditti 1992)

*Epigeneium triflorum***Proanthocyanin**

Procyanidin. (Lv) (Williams 1979)

*Epipactis atrorubens***Anthocyanin**Cyanidin 3-*O*-diglucoside. (Fl) (Uphoff 1979)Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979, Strack *et al.* 1989)Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

-(continued)-

Table 1.

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Cyanidin 3- <i>O</i> -[6- <i>O</i> -(oxaly)-glucoside]. (Fl) (Strack <i>et al.</i> 1986)
Anthocyanin-flavonol complex
Cyanidin oxaly-1,3, 5-di- <i>O</i> -glucoside-kaempferol 7- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
Flavonol
Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)
<i>Epipactis helleborine</i>
Anthocyanin
Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3, 5-di- <i>O</i> -glucoside, Cyanidin 3- <i>O</i> -diglucoside. (Fl) (Uphoff 1979)
Flavonol
Quercetin glycoside. (Lv) (Williams 1979)
<i>Epipactis leptochila</i> and <i>E. veratifolia</i>
Flavonol
Quercetin glycoside. (Lv) (Williams 1979)
<i>Epipactis palustris</i>
Anthocyanin
Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3- <i>O</i> -diglucoside. (Fl) (Uphoff 1979)
<i>Eria javanica</i>
Flavone
Pectolinarigenin, Pectolinarigenin 7- <i>O</i> -glucoside. (Lv) (Williams 1979)
<i>Glossodia major</i>
Anthocyanin
Delphinidin di-monoside. (Fl) (Gascoigne <i>et al.</i> 1949)
<i>Glossodia minor</i>
Anthocyanin
Petunidin di-monoside. (Fl) (Gascoigne <i>et al.</i> 1949)
<i>Grammatophyllum speciosum</i>
Anthocyanin
Cyanidin 3- <i>O</i> -glucoside. (Fl) (Lowry and Keong 1973)
<i>Gymnadenia conopea</i>
Anthocyanin
Cyanidin 3, 5-di- <i>O</i> -glucoside. (Fl) (Uphoff 1979)
Flavonol
Kaempferol 3- <i>O</i> -glucoside, Kaempferol 3, 7-di- <i>O</i> -glucoside, Quercetin 3- <i>O</i> -glucoside, Quercetin 3, 7-di- <i>O</i> -glucoside. (Fl) (Schönsiegel und Egger 1969)
<i>Gymnadenia conopsea</i> (テガタチドリ)
Anthocyanin
Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3, 5-di- <i>O</i> -glucoside, Cyanidin 3, 7-di- <i>O</i> -glucoside, Cyanidin oxaly-1,3, 5-di-

-(continued)-

Table 1.

-(continued)-

O-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Flavonol

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

*Gymnadenia odorata***Anthocyanin**

Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979)

*Gymnadenia odoratissima***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Himantoglossum adriaticum***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Laelia acuminata, *L. alauri*, *L. crispa*, *L. crispata*, *L. crispilabia*, *L. dayana*, *L. perinii*, *L. perinii* var. *tipo*, *L. perinii* var. *semi-alba*, *L. pumila* var. *oculata*, *L. pumila* var. *coerulea*, *L. praestans*, *L. purpurata* var. *sanguinea* and *L. sincorata*

Anthocyanin

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside]. (Fl) (立澤 1996)

*Laelia anceps***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-glucoside-7-*O*-[6-*O*-(sinapyl)-glucoside]-3'-*O*-[6-*O*-(sinapyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(sinapyl)-glucoside]-3'-*O*-[6-*O*-(sinapyl)-glucoside]. (Fl) (立澤 1996)

-(continued)-

Table 1.

-(continued)-

*Laelia cinnabarina***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-glucoside-7-*O*-[6-*O*-(sinapyl)-glucoside]-3'-*O*-[6-*O*-(sinapyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(sinapyl)-glucoside]-3'-*O*-[6-*O*-(sinapyl)-glucoside]. (Fl) (立澤 1996)

*Laelia gouldiana***Anthocyanin**

Cyanidin glycoside. (Fl) (Arditti 1992)

*Laelia lundii***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(4-*O*-(glucosyl)-caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-glucoside-7-*O*-[6-*O*-(sinapyl)-glucoside]-3'-*O*-[6-*O*-(sinapyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(sinapyl)-glucoside]-3'-*O*-[6-*O*-(sinapyl)-glucoside]. (Fl) (立澤 1996)

*Laelia pumila***Anthocyanin**

Cyanidin 3-*O*-malonylglucoside-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-*p*-coumaryl)-glucoside], Cyanidin 3-*O*-malonylglucoside-7-*O*-caffeoylglucoside-3'-*O*-glucosyl-caffeoylglucosylcaffeoylglucoside, Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(*p*-coumaryl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeoyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeoyl)-glucosyl)-caffeoyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(hydroxycinnamyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(hydroxycinnamyl)-glucosyl)-hydroxycinnamyl)-glucoside], Cyanidin 3-*O*-malonylglucoside-7, 3'-*O*-acylated glucoside. (Fl) (立澤 1996, Tatsuzawa *et al.* 1996b)

*Laeliopsis domingensis***Anthocyanin**

Pelargonidin 3-*O*-rutinoside, Pelargonidin 5-*O*-*p*-coumarylglucoside. (Fl) (Arditti 1992)

*Leucorchis albida***Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

*Limodorum abortivum***Anthocyanin**

-(continued)-

Table 1.

-(continued)-

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Liparis taiwaniana***Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

*Listera ovata***Anthocyanin**

Cyanidin 3-*O*-glucoside. (Fl) (Uphoff 1979)

Flavone

Luteolin 3', 4'-di-*O*-glucoside. (Lv) (Williams 1979)

*Lockhartia acuta***Flavonol**

Quercetin glycoside. (Lv) (Williams 1979)

*Lycaste skinneri***Anthocyanin**

Cyanidin glycoside, Peonidin glycoside. (Fl) (Arditti 1992)

*Masdevallia harr yana***Anthocyanin**

Cyanidin diglycoside. (Fl) (Lawrence *et al.* 1939)

*Maxillaria aff. ruteo-alba***Xanthone***

Mangiferin, Isomangiferin. (Lv) (Williams 1979)

*Meiracyllium trinasutum***Proanthocyanin**

Procyanidin. (Lv) (Williams 1979)

*Miltonia warszewiczii***Anthocyanin**

Cyanidin glycoside, Peonidin glycoside. (Fl) (Arditti 1992)

*Mormolyca ringens***Xanthone***

Mangiferin, Isomangiferin. (Lv) (Richardson 1983, Williams 1979)

*Neobenthamia gracilis***Flavonol**

 -(continued)-

Table 1.

-(continued)-

Quercetin 3-*O*-glucoside, Quercetin 3-*O*-[6-*O*-(acetyl)-glucoside], Isorhamnetin 3-*O*-glucoside. (Lv)
(Williams 1979)

*Neomoorea wallisii***Flavone**

Luteolin glycoside. (Lv) (Williams 1979)

Dihydroflavonol

Dihydroquercetin glycoside. (Lv) (Williams 1979)

Neottianthe cucullata (ミヤマモジズリ)**Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Nephelaphyllum pulchrum***Anthocyanin**

Acylated cyanidin glycoside. (Lv) (Lowry and Keong 1973)

*Nigritella corneliana***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Nigritella lithopolitana***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Nigritella miniata***Anthocyanin**Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979)Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)*Nigritella nigra***Anthocyanin**Cyanidin 3-*O*-glucoside. (Fl) (Uphoff 1979, Strack *et al.* 1989)Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin

-(continued)-

Table 1.

-(continued)-

 oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)
Anthocyanin-flavonol complexCyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Nigritella rubra***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalyglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Oncidium excavatum***Flavone**Pectolarigenin 7-*O*-glucoside, Pectolarigenin 7-*O*-rutinoside, Hispidulin 7-*O*-rutinoside. (Lv) (Williams 1979)*Oncidium powellii***Anthocyanin**

Cyanidin glycoside, Peonidin glycoside. (Fl) (Arditti 1992)

*Oncidium sphacelatum***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3-*O*-arabinoside, Cyanidin 3-*O*-arabinoside-5-*O*-glucoside. (Fl) (Lowry and Keong 1973)**Flavone**Pectolarigenin 7-*O*-rutinoside, Hispidulin 7-*O*-rutinoside. (Lv) (Williams 1979)*Ophrys apifera***Anthocyanin**Cyanidin 3-*O*-glucoside. (Fl) (Uphoff 1979)**Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

*Ophrys bombyliflora***Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

*Ophrys ciliata***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalyglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Ophrys ferrum-equinum*, *O. fusca*, *O. lacaitae* and *O. lutea* subsp. *galilaea*

-(continued)-

Table 1.

-(continued)-

Anthocyanin

Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Ophrys holoserica and *O. morisii***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Ophrys insectifera***Anthocyanin**

Cyanidin 3-*O*-glucoside. (Uphoff 1979, Strack *et al.* 1989)

Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Ophrys phrygia***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Ophrys scolopax subsp. *cornuta***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Ophrys speculum***Anthocyanin**

Cyanidin 3-*O*-glucoside. (Fl) (Uphoff 1979)

*Ophrys sphegodes***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Ophrys straussii***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

-(continued)-

Table 1.

-(continued)-

Cyanidin oxaly1-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Ophrys tenthredinifera***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxaly1glucoside, Cyanidin oxaly1-3, 5-di-*O*-glucoside, Cyanidin oxaly1-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Flavonol

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

Orchis anatolica, *O. collina*, *O. coriophora*, *O. langei*, *O. laxiflora*, *O. olbiensis*, *O. palustris*, *O. papilionacea* subsp. *grandiflora*, *O. patens*, *O. prisca*, *O. pseudolaxiflora* and *O. spitzelii*

Anthocyanin

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxaly1glucoside, Cyanidin oxaly1-3, 5-di-*O*-glucoside, Cyanidin oxaly1-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxaly1-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Orchis aristata (ハクサンチドリ)**Anthocyanin**

Cyanidin dihexoside. (Fl) (Ueno *et al.* 1969)

*Orchis champagneuxii***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3-*O*-oxaly1glucoside, Cyanidin oxaly1-3, 5-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxaly1-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Orchis coriophora subsp. *fragrans***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxaly1glucoside, Cyanidin oxaly1-3, 5-di-*O*-glucoside, Cyanidin oxaly1-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxaly1-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

*Orchis italica***Flavonol**

Quercetin glycoside. (Lv) (Williams 1979)

*Orchis longicornu***Anthocyanin**

Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979)

Orchis mascula

-(continued)-

Table 1.

-(continued)-

Anthocyanin
Cyanidin 3, 5-di- <i>O</i> -glucoside. (Fl) (Harborne 1967a, Uphoff 1979, Strack <i>et al.</i> 1989)
Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3, 7-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 7-di- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
Cyanidin 3- <i>O</i> -[6- <i>O</i> -(oxalyl)-glucoside]. (Fl) (Strack <i>et al.</i> 1986)
Anthocyanin-flavonol complex
Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside-kaempferol 7- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
Flavonol
Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)
<i>Orchis militaris</i>
Anthocyanin
Cyanidin 3, 5-di- <i>O</i> -glucoside. (Fl) (Uphoff 1979, Strack <i>et al.</i> 1989)
Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3, 7-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 7-di- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
Cyanidin 3- <i>O</i> -[6- <i>O</i> -(oxalyl)-glucoside]. (Fl) (Strack <i>et al.</i> 1986)
Anthocyanin-flavonol complex
Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside-kaempferol 7- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
<i>Orchis morio</i>
Anthocyanin
Cyanidin 3, 5-di- <i>O</i> -glucoside. (Uphoff 1979, Strack <i>et al.</i> 1989)
Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3, 7-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 7-di- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
Cyanidin 3- <i>O</i> -[6- <i>O</i> -(oxalyl)-glucoside]. (Fl) (Strack <i>et al.</i> 1986)
Anthocyanin-flavonol complex
Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside-kaempferol 7- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
Flavonol
Quercetin 3- <i>O</i> -glucoside. (Lv) (Pagani 1976)
<i>Orchis papilionacea</i>
Anthocyanin
Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3, 5-di- <i>O</i> -glucoside, Cyanidin 3, 7-di- <i>O</i> -glucoside, Cyanidin 3- <i>O</i> -oxalylglucoside, Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 7-di- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
Anthocyanin-flavonol complex
Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside-kaempferol 7- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)
Flavonol
Quercetin glycoside. (Lv) (Williams 1979)
<i>Orchis purpurea</i>
Anthocyanin
Cyanidin 3- <i>O</i> -diglucoside. (Fl) (Uphoff 1979)
Cyanidin 3- <i>O</i> -glucoside, Cyanidin 3, 5-di- <i>O</i> -glucoside. (Fl) (Uphoff 1979, Strack <i>et al.</i> 1989)
Cyanidin 3, 7-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 5-di- <i>O</i> -glucoside, Cyanidin oxalyl-3, 7-di- <i>O</i> -glucoside. (Fl) (Strack <i>et al.</i> 1989)

-(continued)-

Table 1.

-(continued)-

Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (FI) (Strack *et al.* 1986)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (FI) (Strack *et al.* 1989)

Orchis sambucina

Flavonol

Quercetin 3, 7-di-*O*-glucoside, Kaempferol 3-*O*-glucoside. (FI) (Dolci and Tira 1979)

Quercetin 3-*O*-glucoside. (FI) (Tira 1971)

Quercetin 3-*O*-glucoside, Quercetin 7-*O*-glucoside, Quercetin 3, 7-di-*O*-glucoside. (Lv) (Pagani 1976)

Orchis sancta

Anthocyanin

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (FI) (Strack *et al.* 1989)

Orchis simia

Anthocyanin

Cyanidin 3, 5-di-*O*-glucoside. (FI) (Uphoff 1979)

Orchis tridentata

Anthocyanin

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (FI) (Strack *et al.* 1989)

Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (FI) (Strack *et al.* 1986)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (FI) (Strack *et al.* 1989)

Orchis ustulata

Anthocyanin

Cyanidin 3-*O*-diglucoside. (FI) (Uphoff 1979)

Cyanidin 3-*O*-glucoside. (FI) (Uphoff 1979, Strack *et al.* 1989)

Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (FI) (Strack *et al.* 1989)

Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (FI) (Strack *et al.* 1986)

Flavonol

Quercetin glycoside. (Lv) (Williams 1979)

Paphiopedilum callosum

Anthocyanin

Cyanidin glycoside. (FI) (Arditti 1992)

Phaius minor

Anthocyanin

Cyanidin glycoside, Peonidin glycoside. (FI) (Arditti 1992)

Phalaenopsis equestris, *P. intermedia*, *P. leucorrhoda* and *P. sanderiana*

-(continued)-

Table 1.

-(continued)-

Anthocyanin
Cyanidin 3- <i>O</i> -glucoside-7, 3'-di- <i>O</i> -[6- <i>O</i> -(sinapyl)-glucoside], Cyanidin 3- <i>O</i> -[6- <i>O</i> -(malonyl)-glucoside]-7, 3'-di- <i>O</i> -[6- <i>O</i> -(sinapyl)-glucoside], Cyanidin 3- <i>O</i> -malonylglucoside-7, 3'-di- <i>O</i> -hydroxycinnamylglucoside. (Fl) (立澤 1996, Tatsuzawa <i>et al.</i> 1997)
<i>Phalaenopsis schilleriana</i>
Anthocyanin
Cyanidin 3- <i>O</i> -glucoside-7, 3'-di- <i>O</i> -[6- <i>O</i> -(sinapyl)-glucoside], Cyanidin 3- <i>O</i> -[6- <i>O</i> -(malonyl)-glucoside]-7, 3'-di- <i>O</i> -[6- <i>O</i> -(sinapyl)-glucoside], Cyanidin 3- <i>O</i> -malonylglucoside-7, 3'-di- <i>O</i> -hydroxycinnamylglucoside. (Fl) (立澤 1996, Tatsuzawa <i>et al.</i> 1997)
Cyanidin 3- <i>O</i> -trisinapylglucoside-7, 3'-di- <i>O</i> -glucoside. (Fl) (Griesbach 1990)
C-Glycosylflavone
Isovitexin 7- <i>O</i> -glucoside, Apigenin 6, 8-di- <i>C</i> -glucoside-7- <i>O</i> -glucoside. (Fl) (Griesbach 1990)
<i>Plantanthera bifolia</i>
Flavonol
Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)
<i>Plantanthera hyperborea</i> (シロウマチドリ)
Flavonol
Quercetin glycoside. (Lv) (Williams 1979)
<i>Pleurothallis cardiostola</i> , <i>P. dolichopos</i> , <i>P. revoluta</i> and <i>P. semipellucida</i>
Flavonol
Quercetin glycoside. (Lv) (Williams 1979)
<i>Pleurothallis gelida</i>
Flavonol
Quercetin 3- <i>O</i> -rutinoside. (Lv) (Williams 1979)
<i>Pogonia japonica</i> (トキノウ)
Anthocyanin
Cyanidin 3- <i>O</i> -glucoxyloside, Cyanidin monoglucoside. (Fl) (Ueno <i>et al.</i> 1969)
<i>Polystachya ashantensis</i> , <i>P. bella</i> , <i>P. hislopii</i> , <i>P. inconspicua</i> , <i>P. latilabris</i> , <i>P. laxiflora</i> and <i>P. megalogenys</i>
Flavonol
Quercetin glycoside. (Lv) (Williams 1979)
<i>Polystachya bicarinata</i> and <i>P. pubescens</i>
Flavonol
Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)
<i>Polystachya cultriformis</i>
Flavonol
Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)
Xanthone*

-(continued)-

Table 1.

-(continued)-

Mangiferin, Isomangiferin. (Lv) (Podzorski and Cribb 1978, Richardson 1983)

Polystachya fulvilabia and *P. galeata***Xanthone***

Mangiferin, Isomangiferin, Mangiferin *O*-glycoside, Isomangiferin *O*-glycoside. (Lv) (Podzorski and Cribb 1978, Richardson 1983, Williams 1979)

*Polystachya nyanzensis***Xanthone***

Mangiferin, Isomangiferin, Mangiferin sulphate. (Lv) (Podzorski and Cribb 1978, Richardson 1983, Williams 1979)

*Polystachya pachychila***Flavonol**

Kaempferol glycoside. (Lv) (Williams 1979)

Xanthone*

Mangiferin, Isomangiferin, Mangiferin sulphate. (Lv) (Podzorski and Cribb 1978, Richardson 1983, Williams 1979)

*Prasophyllum elatum***Anthocyanin**

Cyanidin di-monoside. (Fl) (Gascoigne *et al.* 1949)

*Restrepia elegans***Flavone**

Tricin 5-*O*-glucoside. (Lv) (Williams 1979)

C-Glycosylflavone

Luteolin *C*-glycoside, Apigenin di-*C*-glycoside. (Lv) (Williams 1979)

Proanthocyanin

Procyanidin. (Lv) (Williams 1979)

*Rhynchosstylis gigantea***Anthocyanin**

Cyanidin glycoside. (Fl) (Arditti 1992)

*Serapias cordigera***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Anthocyanin-flavonol complex

Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)

Flavonol

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

Serapias lingua

-(continued)-

Table 1.

-(continued)-

AnthocyaninCyanidin 3-*O*-diglucoside. (Fl) (Uphoff 1979)Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside. (Fl) (Uphoff 1979, Strack *et al.* 1989)Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Flavonol**

Quercetin glycoside. (Lv) (Williams 1979)

*Serapias neglecta***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Serapias nurrica*, *S. olbia*, *S. parviflora*, *S. vomeracea* subsp. *laxiflora* and *S. vomeracea* subsp. *orientalis***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)*Serapias vomeracea***Anthocyanin**Cyanidin 3-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin 3-*O*-oxalylglucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Anthocyanin-flavonol complex**Cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside. (Fl) (Strack *et al.* 1989)**Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

*Sophranitella violacea***Anthocyanin**Cyanidin 3-*O*-glucoside-7-*O*-[6-*O*-(sinapyl)-glucoside]-3'-*O*-[6-*O*-(sinapyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(sinapyl)-glucoside]-3'-*O*-[6-*O*-(sinapyl)-glucoside]. (Fl) (立澤 1996)*Sophranitis coccinea* and *S. cernua***Anthocyanin**Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-*p*-coumaryl)-glucoside]. (Fl) (立澤 1996)

-(continued)-

Table 1.

-(continued)-

Sophronitis coccinea var. *tipo***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside]. (Fl) (立澤 1996)

*Sophronitis brevipedunculata***Anthocyanin**

Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(caffeyl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-caffeyl)-glucoside], Cyanidin 3-*O*-[6-*O*-(malonyl)-glucoside]-7-*O*-[6-*O*-(*p*-coumaryl)-glucoside]-3'-*O*-[6-*O*-(4-*O*-(6-*O*-(caffeyl)-glucosyl)-*p*-coumaryl)-glucoside]. (Fl) (立澤 1996)

*Sophronitis grandiflora***Anthocyanin**

Pelargonidin 3-*O*-bioside. (Fl) (Robinson and Robinson 1932, Lawrence *et al.* 1939)

*Sophronitis wittingiana***Anthocyanin**

Cyanidin 3, 7, 3'-*O*-glycoside. (Fl) (立澤 1996)

Spathoglottis plicata (コウトウシラン)**Anthocyanin**

Cyanidin glycoside. (Fl) (Forsyth *et al.* 1954)
Acylated cyanidin glycoside. (Fl) (Lowry and Keong 1973)

*Spiranthes aestivalis***Flavonol**

Quercetin glycoside, Kaempferol glycoside. (Lv) (Williams 1979)

*Stelis lutea***Flavonol**

Quercetin glycoside. (Lv) (Williams 1979)

*Thelymitra ixoides***Anthocyanin**

Cyanidin di-monoside. (Fl) (Gascoigne *et al.* 1949)

*Thelymitra venosa***Anthocyanin**

Cyanidin monoside. (Fl) (Gascoigne *et al.* 1949)

*Traunsteinera globosa***Anthocyanin**

Cyanidin 3-*O*-glucoside, Cyanidin 3, 5-di-*O*-glucoside, Cyanidin 3, 7-di-*O*-glucoside, Cyanidin oxalyl-3, 5-di-*O*-glucoside, Cyanidin oxalyl-3, 7-di-*O*-glucoside. (Fl) (Strack *et al.* 1989)
Cyanidin 3-*O*-[6-*O*-(oxalyl)-glucoside]. (Fl) (Strack *et al.* 1986)

-(continued)-

Table 1.

-(continued)-

Anthocyanin-flavonol complexCyanidin oxalyl-3, 5-di-O-glucoside-kaempferol 7-O-glucoside. (Fl) (Strack *et al.* 1989)*Vanda coerulea* and *V. coerulescens***Anthocyanin**

Cyanidin 3-O-glucoside-7-O-[6-O-(sinapyl)-glucoside]-3'-O-[6-O-(sinapyl)-glucoside], Cyanidin 3-O-[6-O-(malonyl)-glucoside]-7-O-[6-O-(sinapyl)-glucoside]-3'-O-[6-O-(sinapyl)-glucoside], Delphinidin 3, 7, 3'-O-glycoside. (Fl) (立澤 1996)

*Vanda tricolor***Anthocyanin**

Cyanidin glycoside. (Fl) (Arditti 1992)

(Fl) = flowers, (Lv) = leaves.

*Xanthenes which based C₆-C₁-C₆ are not flavonoids, but the distribution was listed in Table, because the compounds were biosynthetically related to the flavonoids.

(*Bletilla striata*), 数種の *Cattleya* 属, *Laelia* 属, *Sophoronitis* 属および *Vanda* 属植物の花から分離された種々の cyanidin 3, 7, 3'-O-配糖体である (Saito *et al.* 1994, 1995, Tatsuzawa *et al.* 1994, 1996a, 1996b, 1997, 立澤1996)。これらは cyanidin を基本骨格として, その 3-, 7- および 3'-位の水酸基にグルコースと芳香族有機酸の p-クマル酸, カフェー酸, シナピン酸など, および脂肪族有機酸のマロン酸が様々な組み合わせで複雑に結合しているものである。そのひとつの例を Fig. 2 に示す。これらのアントシアニンのように 3, 7, 3'-位が各種の糖やアシル基で置換された cyanidin 配糖体は以前に同じ単子葉のツルクサ科植物, *Zebrina pendula* の葉から分離同定されている (Idaka 1987)。このような多数の有機酸が結合した配糖体では分子内コピグメント作用が生じ, その結果として通常の cyanidin による花色よりも青みがかった色調を示し, より多彩な花色を表現する (Brouillard and Dangles 1994, 斎藤1995, 立澤1996)。しかし, このような 3, 7, 3'-配糖体はラン科では今までのところ cyanidin のみで報告されており, 他のアントシアニンからは知られていない。

ランの花から分離されたもう一つの特有のフラボノイドはアントシアニンとフラボノール配糖体が有機酸を仲立ちとして結合している, いわゆるアントシアニン-フラボノール複合体で, cyanidin 3, 5-di-O-glucoside の 3-位のグルコースがシュウ酸 (oxalic acid) を仲立ちとして kaempferol 7-O-glucoside の 7-位のグルコースとエステル結合したもので, orchicyanin I と名づけられた (Strack *et al.* 1989)。これは *Dactylorhiza*, *Gymnadenia*, *Nigritella*, *Ophrys*, *Orchis*, *Serapias* 属など多くのラン科植物の花から分離されている。これもまた分子内コピグメント作用として, 本来のアントシアニンの色を深色移動させていると考えられる (Uphoff 1982)。上記のようなコピグメント作用の報告以外に, Griesbach (1990) は *Phalaenopsis schilleriana* でアントシアニン (cyanidin 3-O-trisinapylglucoside-7, 3'-di-O-glucoside) と 2 種類の C-グリコシルフラボン (isovitexin 7-O-glucoside と apigenin 6, 8-di-C-glucoside 7-O-glucoside) との間でコピグメント作用が生じていると報告した。

このように, ラン科植物のいくつかではアントシアニン (cyanidin 配糖体) と他のフラボノイドや有機酸との間で分子内および分子間コピグメント作用による花色の変異 (青色化) が認めら

-(continued)-

Table 2. The occurrence of floral anthocyanidins among the genera of Orchidaceae

Subfamily Genus	No.	Pg	Cy	Pn	Dp	Pt	Mv
Cypripedioideae							
<i>Cypripedium</i>	3		3				
<i>Paphiopedilum</i>	1		1				
Orchidoideae							
<i>Caladenia</i>	2		1				2
<i>Elythranthera</i>	2		2		2		
<i>Glossodia</i>	2				1	1	
<i>Caleana</i>	1		1				
<i>Acianthus</i>	1		1				
<i>Diuris</i>	3		1				2
<i>Thelymitra</i>	2		2				
<i>Prasophyllum</i>	1		1				
<i>Anacamptis</i>	1		1				
<i>Barlia</i>	2		2				
<i>Dactylorhiza</i>	17		17				
<i>Gymnadenia</i>	4		4				
<i>Hymantoglossum</i>	1		1				
<i>Neottianthe</i>	1		1				
<i>Nigritella</i>	5		5				
<i>Ophrys</i>	15		15				
<i>Orchis</i>	25		25				
<i>Serapias</i>	9		9				
<i>Traunsteinera</i>	1		1				
Epidendroideae							
<i>Cephalanthera</i>	2		2				
<i>Epipactis</i>	3		3				
<i>Limodorum</i>	1		1				
<i>Listera</i>	1		1				
<i>Calypso</i>	1		1				
<i>Bromheadia</i>	1		1				
<i>Dipodium</i>	1		1				
<i>Ansellia</i>	1		1	1			
<i>Cymbidium</i>	6		6	2			
<i>Grammatophyllum</i>	1		1				
<i>Catasetum</i>	1	1	1	1			
<i>Lycaste</i>	1		1	1			
<i>Miltonia</i>	1		1	1			
<i>Oncidium</i>	2		2	1			
<i>Bletilla</i>	1		1				
<i>Phaius</i>	1		1	1			
<i>Spathoglottis</i>	1		1				
<i>Brassavola</i>	1		1				
<i>Broughtonia</i>	3	3	1		1		
<i>Cattleya</i>	31		31				

-(continued)-

Table 2. -(continued)-

Subfamily Genus	No.	Pg	Cy	Pn	Dp	Pt	Mv
<i>Cattleyopsis</i>	1	1					
<i>Epidendrum</i>	3		3	1			
<i>Laelia</i>	19		19				
<i>Laeliopsis</i>	1	1					
<i>sophoronitella</i>	1		1				
<i>Sophoronitis</i>	6	1	5				
<i>Masdevallia</i>	1		1				
<i>Appendicula</i>	1		1				
<i>Dendrobium</i>	2		2				
<i>Aerides</i>	1		1				
<i>Ascocentrum</i>	1		1				
<i>Doritis</i>	1				1		
<i>Phalaenopsis</i>	5		5				
<i>Rhynchostylis</i>	1		1				
<i>Vanda</i>	3		3		1		
<i>Arundina</i>	1		1				
<i>Pogonia</i>	1		1				
total	207	7	198	9	5	2	4

Pg=pelargonidin, Cy=cyanidin, Pn=peonidin, Dp=delphinidin, Pt=petunidin and Mv=malvidin.

Arrangement according to Dressler (1993).

No.=Numbers of taxa were reported the presence of anthocyanins.

れている。

コピグメント作用以外にもう一つ知られている重要な花色の青色化現象はツククサ (*Commerina communis*) やアジサイ (*Hydrangea macrophylla*) に代表されるアントシアニンの金属との錯体の形成 (Hayashi and Takeda 1970, Takeda *et al.* 1985) であるが、ラン科植物の花色の変異に金属が関係するというような報告は今までのところまだない。

ラン科植物の花が多彩である他の原因として、カロチノイドとの共存があげられる。ランばかりでなく、植物界で花の色を構成する2大色素といえばアントシアニンとカロチノイドである。一般にアントシアニンが青、紫、赤系の花の主要色素であるのに対して、カロチノイドは黄色や橙色、時に赤色の花の主要色素であるといえる。ラン科植物でも今までに *Dendrobium* 数種の黄色花色素としてカロチノイドの zeaxanthin, lutein, neoxanthin, violaxanthin, antheraxanthin, β -carotene が (Thammasiri *et al.* 1986, 1987), *Cattleya aurantiaca* からは γ -carotene, lycopene, β -carotene, β -cryptoxanthin, rubixanthin, xanthophyll 類などが報告されている (Matsui *et al.* 1992)。また、カルコンやオーロンのような黄色系のフラボノイドやベタキササンチンなどはラン科からは報告されていないから、おそらくランの黄色花のほとんどすべてがカロチノイド色素によって発現されているものと推測される。

カロチノイドとアントシアニンとの共存は一部の赤色花種 (*Sophoronitis coccinea*, *Laelia milleri*)

-(continued)-

Table 3. The occurrence of flavonoid classes among the genera of Orchidaceae

Subfamily Genus	No.	An	Fl	Fn	Fv	Df	AF	CG	Pa	Xa
Cypripedioideae										
<i>Cypripedium</i>	3	3								
<i>Paphiopedilum</i>	1	1								
Spiranθοideae										
<i>Cyclopogon</i>	1		1							
<i>Spiranthes</i>	1		1							
Orchidoideae										
<i>Caladenia</i>	2	2								
<i>Elythranthera</i>	2	2								
<i>Glossodia</i>	2	2								
<i>Caleana</i>	1	1								
<i>Acianthus</i>	1	1								
<i>Diuris</i>	3	3								
<i>Thelymitra</i>	2	2								
<i>Prasophyllum</i>	1	1								
<i>Aceras</i>	1		1							
<i>Anacamptis</i>	1	1					1			
<i>Barlia</i>	2	2					2			
<i>Coenoglossum</i>	1		1							
<i>Dactylorhiza</i>	17	17	1				15			
<i>Gymnadenia</i>	4	4	2				2			
<i>Hymantoglossum</i>	1	1					1			
<i>Neottianthe</i>	1	1					1			
<i>Nigritella</i>	5	5					4			
<i>Ophrys</i>	16	15	3				5			
<i>Orchis</i>	26	25	6				19			
<i>Platanthera</i>	2		2							
<i>Leucorchis</i>	1		1							
<i>Serapias</i>	9	9	3				9			
<i>Trausteinera</i>	1	1					1			
Epidendroideae										
<i>Cephalanthera</i>	4	2	3				2			
<i>Epipactis</i>	5	3	4				1			
<i>Limodorum</i>	1	1					1			
<i>Listera</i>	1	1	1							
<i>Liparis</i>	1		1							
<i>Calypso</i>	1	1								
<i>Bromheadia</i>	1	1	1							
<i>Dipodium</i>	1	1								
<i>Ansellia</i>	1	1								
<i>Cymbidium</i>	7	6						2		
<i>Grammatophyllum</i>	1	1								
<i>Catasetum</i>	1	1								
<i>Anguloa</i>	1								1	
<i>Lycaste</i>	1	1								
<i>Neomoorea</i>	1			1		1				

-(continued)-

Table 3. -(continued)-

Subfamily Genus	No.	An	Fl	Fn	Fv	Df	AF	CG	Pa	Xa
<i>Maxillaria</i>	1									1
<i>Mormolyca</i>	1									1
<i>Lockhartia</i>	1		1							
<i>Miltonia</i>	1	1								
<i>Oncidium</i>	3	2		2						
<i>Bletilla</i>	1	1								
<i>Nephelaphyllum</i>	1	1								
<i>Phaius</i>	1	1								
<i>Spathoglottis</i>	1	1								
<i>Meiracyllium</i>	1								1	
<i>Anacheilium</i>	22					22				
<i>Brassavola</i>	1	1								
<i>Broughtonia</i>	3	3								
<i>Cattleya</i>	31	31						1		
<i>Cattleyopsis</i>	1	1								
<i>Epidendrum</i>	4	3							1	
<i>Laelia</i>	19	19								
<i>Laeliopsis</i>	1	1								
<i>Sophoronitella</i>	1	1								
<i>Sophoronitis</i>	6	6								
<i>Masdevallia</i>	1	1								
<i>Pleurothallis</i>	5		5							
<i>Restrepia</i>	1			1				1	1	
<i>Stelis</i>	1		1							
<i>Neobenthamia</i>	1		1							
<i>Polystachya</i>	14		11							5
<i>Eria</i>	1			1						
<i>Appendicula</i>	1	1								
<i>Dendrobium</i>	9	2	7							
<i>Epigeneium</i>	1								1	
<i>Bulbophyllum</i>	1		1							
<i>Aerides</i>	3	1	2				2			
<i>Ascocentrum</i>	1	1								
<i>Doritis</i>	1	1	1		1					
<i>Phalaenopsis</i>	5	5						1		
<i>Rhynchostylis</i>	1	1								
<i>Vanda</i>	3	3								
<i>Chamaeangis</i>	1							1		
<i>Arundina</i>	1	1								
<i>Pogonia</i>	1	1								
total	290	209	60	6	1	25	6	7	4	7

An=anthocyanin, Fl=flavonol, Fn=flavone, Fv=flavanone, Df=dihydroflavonol, AF=anthocyanin-flavonol complex, CG=C-glycosylflavone, Pa=proanthocyanin and Xa=xanthone.

No.=Numbers of taxa were observed for flavonoids.

Arrangement according to Dressler (1993).

や *Cattleya aurantiaca* の変種など) で報告され、赤色花の発現に重要な役割を果たしている (Griesbach 1984, Matsui and Nakamura 1988, Matsui 1988, 1992)。

花に含まれるアントシアニン以外のフラボノイドの報告は非常に少ない。報告されているものとしては *Dendrobium crumenatum* と *Bromheadia finlaysoniana* の白色花からフラボノールの quercetin 3-*O*-rutinoside (rutin) が (Lowry and Keong 1973), *Doritis pulcherrima* からフラボノールの quercetin 3, 4'-di-*O*-glucoside と quercetin 7, 4'-di-*O*-glucoside, フラバノンの naringenin 7-*O*-glucoside が (Harper 1974), *Gymnadenia conopsea* から kaempferol 3, 7-di-*O*-glucoside, quercetin 3, 7-di-*O*-glucoside など 4 種類のフラボノールが (Scönsiegel und Egger 1969), *Orchis sambucina* の黄色花から quercetin の 3-*O*-glucoside (isoquercitrin, Fig. 1) と 3, 7-di-*O*-glucoside および kaempferol 3-*O*-glucoside が (Tira 1971, Dolci and Tira 1979), そして前述のコピグメント作用を示すフラボノイドとして *Phalaenopsis schilleriana* から 2 種類の C-グリコシルフラボン (Griesbach 1990) が分離同定されているにすぎない。なお, *Doritis pulcherrima* からの naringenin 7-*O*-glucoside (Fig. 1) はラン科植物で唯一のフラバノンの報告である。

フラボンやフラボノールを中心としたこれらのフラボノイドはコピグメント物質として花色の変異に重要な役割を果たすものが多いばかりでなく、白色の花にもハチなどの昆虫が飛来するのは、紫外域に吸収をもつこれらのフラボノイドを識別するからだといわれている (Harborne 1993)。ラン科でも *Anacheilium* 属数種の花に結晶の形で存在するジヒドロフラボノール (3, 5, 7, 3'-tetrahydroxy-4'-methoxydihydroflavonol 3-*O*-rutinoside, Fig. 1) が、このような役割を果たしていると推定されている (Pabst *et al.* 1981, Ferreira *et al.* 1986)。植物界では一般に、アントシアニン以外のフラボノイドが花に存在しないことは極めてまれで、実際にラン科植物の花を予備的に分析すると、ほとんどの花に紫外線吸収物質が含まれていることが判明している (立澤, 私信)。

ランの花に含まれる色素成分のうち、アントシアニンについてはその構造の複雑さにもかかわらず、近年解明されはじめ、その機能、分布などについて総説されたが (Arditti 1969b, Withner 1974, Arditti and Fisch 1977, Ernst and Rodriguez 1984), 他のフラボノイド成分についてはほとんど未知のままであり、花色との関係や昆虫との相互進化におけるフラボノイドの役割の解明、あるいは化学分類学的指標としての応用などのためにも花に含まれるフラボノイド成分のいっそうの分離同定が必要とされる。

フラボノイドを指標としたラン科の化学分類学的知見

前にも述べたように、含有されているフラボノイドの組成が完全あるいは部分的にせよ明らかになっているランは著者の知る限り 82 属 290 種類である (Table 1)。これは仮にラン科の種が約 1 万 7 千種と最も少なく見積もっても、僅か全体の 2% に満たない種しかフラボノイド組成に関する調査が行われていない事になる。従って、これだけのデータからラン科を化学分類学的に処理しようとする事には無理がある。しかし、あえてここでは今まで得られている情報を基に若干の化学分類学的知見を述べることにする。

ラン科でフラボノイドを指標とした化学分類学的知見を述べたものは一部のアントシアニンに関して Arditti and Ernst (1969a) が著わした以外、ラン科全体を取り扱ったものは Williams (1979) の論文だけと思われる。彼女は 75 属 142 種 (フラボノイドを定性できなかった種も含む) のラン科植物の葉に含まれるフラボノイドを調査した。その結果、53% の種で C-グリコシルフラボンを、37% の種でフラボノールを検出した。それらは従来のラン科の分類などとはあまり強い相関はなかったが、Dressler に従った分類の Epidendroid および Vandoid の連の熱帯および亜熱帯の種に C-グリコシルフラボンが一般的で、Neottoid の連ではフラボノール配糖体を含むものが多いことが特徴的であると指摘している。これらの C-グリコシルフラボンやフラボノール

はそのほとんどがアグリコン部分だけなどの部分的な同定であるが、いくつかの稀な、あるいは新規化合物については完全な同定がなされた。例えば、*Oncidium excavatum* と *O. sphacelatum* からの hispidulin 7-O-rutinoside (Fig. 3), 同じく *O. excavatum* と *Eria javanica* からの pectolinarigenin 7-O-glucoside (Fig. 3), *Listera ovata* から luteolin 3', 4'-di-O-glucoside (Fig. 3) は従来ラン科はもとより自然界で報告のなかったフラボノイド配糖体である (Williams 1979)。彼女はこの他に、プロアントシアニン、ジヒドロフラボノール、さらにはフラボノイド (C₆-C₃-C₆ が基本骨格) とは極めて生合成的に関連しているキサントン (C₆-C₁-C₆ が基本骨格) の mangiferin や isomangiferin (Fig. 4) などいくつかの植物から検出している。フラボノイドに関連するフェノール化合物としてはこの他に *Dendrobium densiflorum* から 2-(β-D-glucopyranosyloxy) 4, 5-dimethoxy-trans-cinnamic acid (densifloroside) が新規化合物として分離同定されている (Dahmén et al. 1975)。

Williams (1979) のデータも含めた今までに知られているラン科のフラボノイドの報告を Table 1 に、またラン科の属の間でのフラボノイドのクラスの分布を Table 3 に示した。アントシアニンは最も多くの植物で検出されているが (290種中209種)、特に花の場合、多形性 (polymorphism) の結果として発現する事も多く、必ずしも分類とは一致しない (Bohm 1987)。その中で近年、立澤ら (Tatsuzawa et al. 1994, 1996a, 1996b, 1997, 立澤1996, Saito et al. 1994, 1995) が分離同定したいくつかの複雑にアシル化された cyanidin の 3, 7, 3'-配糖体は他の植物群ではほとんど見出されておらず、ラン科でも *Cattleya* などいくつかの属に包含される種の花から検出されたのみである。これらのアントシアニンがラン科の中でどのように分布しているかは今後検討されなければならないところである。

ラン科で検出されたアントシアニン以外のフラボノイドで注目されるのは pectolinarigenin (5, 7-dihydroxy-6, 4'-dimethoxyflavone), scutellarein (5, 6, 7, 4'-tetrahydroxyflavone), hispidulin (5, 7, 4'-trihydroxy-6-methoxyflavone) のような 6-位に水酸基やメトキシ基の結合しているフラボンで (Fig. 4 参照), 一般的にキク科などのより進化していると考えられる植物群で従来報告されている化合物である (岩科ら1988, Iwashina et al. 1995)。これらは配糖体として *Eria javanica*, *Oncidium excavatum*, *O. sphacelatum* から完全な分離同定がなされている他に、*Odontoglossum* 属数種にも存在している (Williams 1979)。

他のまれなフラボンとして、ラン科では唯一 *Restrepia elegans* で検出された triclin 5-O-glucoside (Fig. 1) がある (Williams 1979)。フラボンやフラボノールのような 4-位にカルボニル基を有するフラボノイドはアントシアニンのような、これを有しないフラボノイドとは異なり、4-位のカルボニル基と隣接する 5-位の水酸基との間で、フラボノイド骨格が形成される時点で水素結合が成立し、結果として、5-位の水酸基に糖が結合することは稀である (Harborne 1976b, 岩科ら1989)。そのため、フラボノイド生合成の最終段階で行われる 7-位などへの糖の結合とは異なり、同じ糖の結合でありながら、フラボノイド骨格が出来上がる前後ですでに 5-位に糖が結合すると推定される。したがって、この配糖体を合成する能力のある種は、他のフラボノイド配糖体を合成する種とは比較的離れていると考えられるが、ラン科では今まで唯一 *R. elegans* で報告されたのみでいっそうの分析が待たれる。

最初に述べたように、どんなに少なく見積もっても 1万をはるかに越える種を有し、しかも地球上の植物の中で最も進化している種群と考えられるラン科は、その受粉様式において、少なくとも花の形態的多様性においてはかなり進んでいる。当然、形態とともに昆虫を誘引する花の色についても多様な分化が生じていると予想され、わずかにラン科の数パーセントの種が分析されただけでも、花の主要色素であるアントシアニンはもとより、フラボノール、フラボン、フラバ

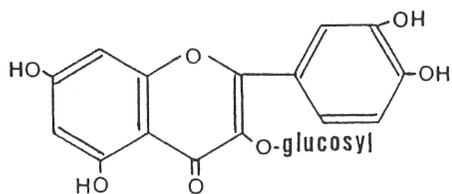
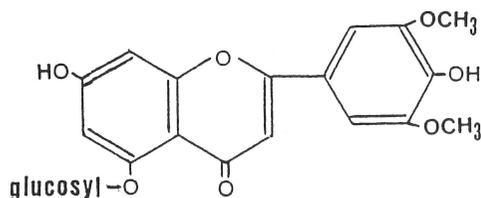
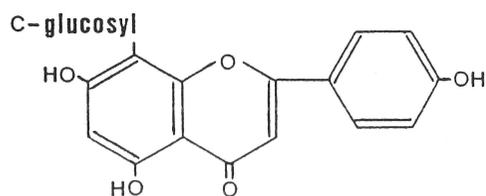
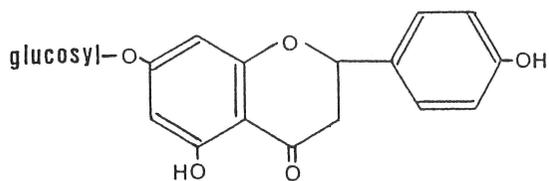
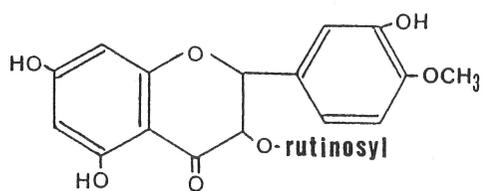
quercetin 3-*O*-glucoside (flavonol)tricetin 5-*O*-glucoside (flavone)vitexin (*C*-glycosylflavone)naringenin 7-*O*-glucoside (flavanone)3, 5, 7, 3'-tetrahydroxy-4'-methoxydihydroflavonol
3-*O*-rutinoside (dihydroflavonol)

Fig. 1. Chemical structures of the representative flavonoids which were isolated from orchids.

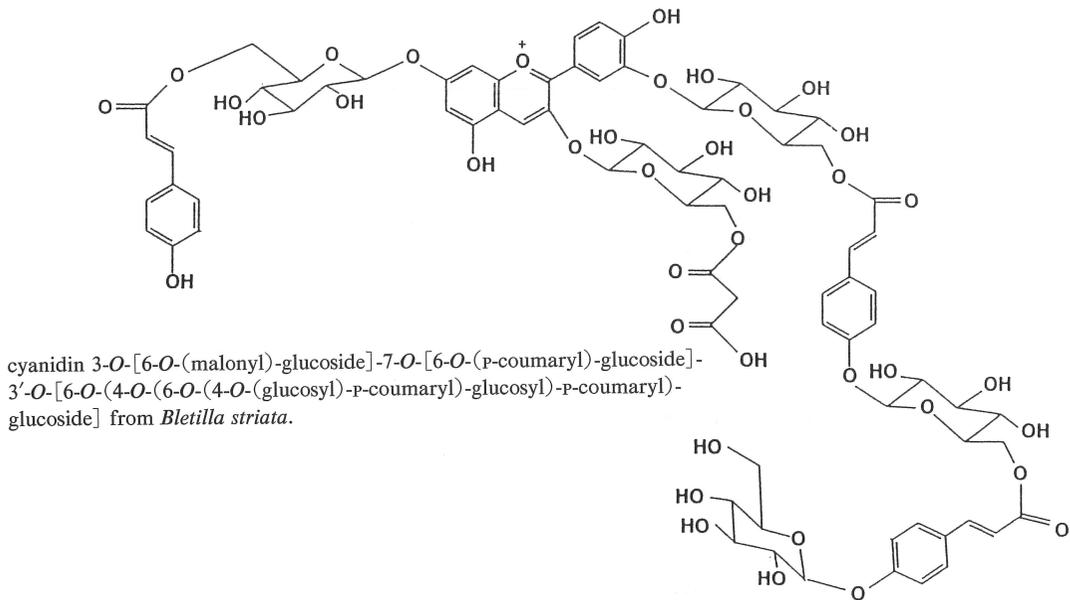


Fig. 2. Chemical structure of a representative cyanidin 3,7,3'-O-glycoside in orchids (modified from 立澤 1996).

ノン、ジヒドロフラボノール、C-グリコシルフラボン、プロアントシアニンと、多くの種類のフラボノイドおよびそれに関連するキサントンが知られている。これらのいくつかは花ではなく、葉でのみ検出されたものもあるが、今後の分析が進むにつれて、花でも検出される可能性が高い。その時、これらがいったいランの進化、特に受粉のための昆虫の誘引などどのように関わっているのかなどが明らかになってくるであろう。非常に興味深いところである。

謝 辞

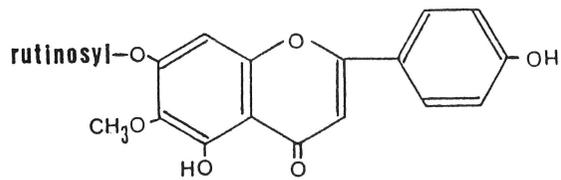
本総論を執筆するにあたり、著者はラン科の分類・系統に関してご指導頂いた国立科学博物館筑波実験植物園橋本保園長に驚く感謝の意を表す。本総論は氏の筑波実験植物園の退官を記念して、専門分類群の一つ、ラン科についてそのフラボノイドと花色への貢献および分布を著したものである。

著者はまた多くのラン科植物のフラボノイドに関する情報を与えられた千葉大学園芸学部立澤文見博士にも併せて謝意を表す。

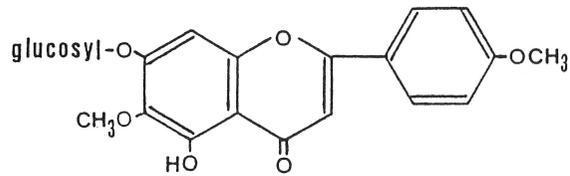
Summary

The family Orchidaceae is big family containing about 17,000~20,000 or more species. In this review, the flavonoids which have been reported from the family are mentioned, and are discussed their contribution to flower colours and chemotaxonomic significance.

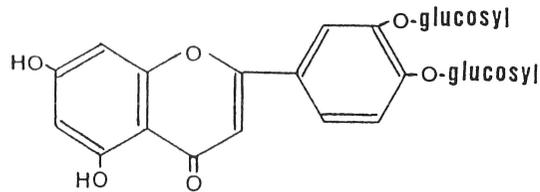
Two hundred-ninety taxa (82 genera) of the Orchidaceae have been surveyed for flavonoids. The anthocyanins which were reported from many orchids as flower pigments, flavonols, flavones, C-



hispidulin 7-*O*-rutinoside (from *Oncidium excavatum* and *O. sphacelatum*)

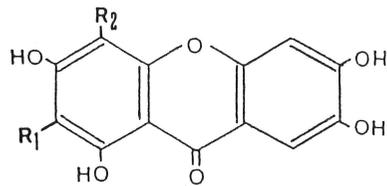


pectolarigenin 7-*O*-glucoside (from *Oncidium excavatum* and *Eria javanica*)



luteolin 3', 4'-*O*-glucoside (from *Listera ovata*)

Fig. 3. New flavone glycosides which were isolated from orchids.



$R_1 = C\text{-glucosyl}$, $R_2 = H$: mangiferin

$R_1 = H$, $R_2 = C\text{-glucosyl}$: isomangiferin

Fig. 4. Chemical structures of xanthones from orchids.

glycosylflavones, flavanone, dihydroflavonols, proanthocyanins and rare anthocyanin-flavonol complex have been found from the flowers and leaves. Related xanthenes were also detected. But, isoflavone, flavane 3, 4-diol, biflavone, chalcone and aurone are not reported.

In almost cases, flavonoid survey have been performed in relation to flower colours. Thus, six common anthocyanidins, pelargonidin, cyanidin, peonidin, delphinidin, petunidin and malvidin were detected from orchid flowers. But, almost anthocyanins which were found in orchids were cyanidin glycosides. The very unique cyanidin glycosides, which complicatedly attached some glucose and organic acid moieties such as *p*-coumaric, caffeic, sinapic or malonic acids to 3-, 7- and 3'-positions, were isolated from *Bletilla striata*, some *Cattleya*, *Laelia*, *Sophoronitis* and *Vanda* species by Tatsuzawa, Saito and co-workers (Tatsuzawa *et al.* 1994, 1996a, 1996b, 1997, 立澤1996, Saito *et al.* 1994, 1995). Their acylated cyanidin glycosides represent more bluish flower colour due to intramolecular co-pigments with organic acids than simple cyanidin glycosides. Another intramolecular co-pigmented anthocyanin was an anthocyanin-flavonol complex, i. e., cyanidin oxalyl-3, 5-di-*O*-glucoside-kaempferol 7-*O*-glucoside, and was named as orchicyanin I. The complex was found in *Dactylorhiza*, *Gymnadenia*, *Nigritella*, *Ophrys*, *Orchis*, *Serapias* species etc. (Strack *et al.* 1989).

Other flavonoids, i. e., quercetin 3-*O*-rutinoside from *Bromheadia finlaysoniana* and *Dendrobium curmenatum* (Lowry and Keong 1973), quercetin 3, 4'-di-*O*-glucoside, quercetin 7, 4'-di-*O*-glucoside and naringenin 7-*O*-glucoside from *Doritis pulcherrima* (Harper 1974), kaempferol 3, 7-di-*O*-glucoside and quercetin 3, 7-di-*O*-glucoside from *Gymnadenia conopsea* (Schönsiegel und Egger 1969), quercetin 3-*O*-glucoside, quercetin 3, 7-di-*O*-glucoside and kaempferol 3-*O*-glucoside from *Orchis sambucina* (Tira 1971, Dolci and Tira 1979), isovitexin 7-*O*-glucoside and apigenin 6, 8-di-*C*-glucoside 7-*O*-glucoside from *Phalaenopsis schilleriana* (Griesbach 1990), and 3, 5, 7, 3'-tetrahydroxy-4'-methoxy-dihydroflavonol 3-*O*-rutinoside from some *Anacheilium* species (Ferreira *et al.* 1986), were also isolated as flower pigments.

Chemotaxonomically, the flavonoids have been surveyed less than 2% of orchids. Williams (1979) has found *C*-glycosylflavones and flavonols as most common orchid flavonoids except anthocyanins. She also found new flavonoid glycosides from some species. Thus, hispidulin 7-*O*-rutinoside from *Oncidium excavatum* and *O. sphacelatum*, pectolinarigenin 7-*O*-glucoside from *O. excavatum* and *Eria javanica*, and luteolin 3', 4'-di-*O*-glucoside from *Listera ovata* were isolated as foliar flavonoids. Xanthenes (mangiferin and the related compounds) were also detected from some orchids.

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