

## Phenolic Compounds from Various *Artemisia* species

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Many types of natural products have been reported from several species of the large genus *Artemisia* (Compositae). The diversity of this genus is reflected in the nature of major constituents. Sesquiterpene lactones are one of the major components which are characteristic to most investigated plants of the genus. Sesquiterpenoids from the genus *Artemisia* have already been compiled and reviewed [1-3]. On the other hand, plant phenolics, particularly flavonoids and coumarins are also another major class of secondary metabolites frequently isolated from *Artemisia*. Due to the phenolics widespread distribution within the genus and following our current research on the plants of this genus, we have now undertaken reviewing these secondary metabolites.

### Flavonoids

There is no general method for the isolation of flavonoids from their natural sources. Extraction by solvents is still, however, the usual procedure. The strongly polar flavonoids required alcohol or alcohol-H<sub>2</sub>O for extraction while the least polar flavonoids can be obtained from chloroform or acetone. The flavonoid extracts are chromatographed over silica gel, polyamide or sephadex LH-20. Further purification of some flavonoids may be carried out on prep. TLC or HPLC techniques. Ultraviolet spectroscopy has become a very useful technique for the structural analysis of various types of flavonoids. On the other hand, NMR is one of the most useful spectroscopic method for the structural determination. The latter method gives a very good information about the substituents of each ring in the flavone skeleton.

Table 1 contains more than 80 free aglycones which have been isolated from various *Artemisia* species, together with the naturally occurring glycosides from the same sources. The structures of these flavonoid aglycones are shown in Fig. 1 and

they are arranged in accordance with their oxygenation pattern. Only the well identified flavonoids (up to the end of 1989) have been presented in Fig. 1. However, flavonoids, both free and glycosides were detected in the extracts of four *Artemisia* species [4] and in seven other species [4a]. Further ten species of the *dracunculus* subgenus were investigated [5] for flavonoidal content. The latter species found to be different not only with regard to total flavonoids but also in relation to particular compound. Investigation of nine species of the *siriphidium* subgenus had shown similar flavonoid contents and the highest content was found in *A. sublessingiana* while the lowest was in *A. cina* [6].

As it could be noted from Table 1 and Fig. 1 flavonoid aglycones are di-, tri-, tetra-, penta- and hexa-oxygenated. Two dioxygenated flavones, pinocembrin (1) and pinostrobin (2) were obtained from *A. campestris* [27]. With the exception of the flavanone (42), all the flavanones isolated from the genus *Artemisia* were tri- and tetraoxygenated compounds (3-11) and they are restricted to *A. campestris* [25-28], *A. dracunculus* L. [35] and *A. sacoparia* [69]. Compound (3) is the only flavanone isolated from *Artemisia* species having 5,8,4'-substitution [28].

5,7,4'-Oxygenation pattern is found in each compound of the tetra-, penta- and hexaoxygenated except for transilutin (33) and arcapillin (52) which have been isolated from *A. transiliensis* [73,74] and *A. capillaris* [32] respectively. Of the nineteen flavonoids obtained from *A. ludoviciana* [57,58], compound (46) lacks the substitution at ring B. With the exception of cirsitakaogenin (23), substitution at positions 8 and/or 2 is found only in the penta- and hexaoxygenated flavones and represented by three and six members respectively (see Fig. 1). It is noteworthy that recent investigations on some *Artemisia* species have shown the multiplicity of flavonoids, for instance *A. annua* [17], *A. assoana*

Table 1: Flavonoids from *Artemisia* species.

| Species                                        | Flavonoid aglycones                                                                                                                                                                                                                                                                                                                                                                                                                           | Flavonoid glycosides                                                                                                                                                                                                                                     | References                          |
|------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| <i>A. absinthium</i> L.                        | Artemetin (81)                                                                                                                                                                                                                                                                                                                                                                                                                                | Rutin(Quercetin-3-rutinoside)<br>Quercetin-3-glucoside,<br>Isorhamnetin-3-glucoside,<br>Isorhamnetin-3-rhamnoglucoside,<br>Patuletin-3-glucoside,<br>Patuletin-3-rhamnoglucoside,<br>Spinacetin-3-glucoside and<br>Spinacetin-3-rhamnoglucoside<br>Rutin | 7<br>7,8<br>8<br>7<br>9             |
| <i>A. abrotanum</i> L.                         | Artemetin (81)                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                          |                                     |
| <i>A. adamsii</i>                              | Eupafolin (36) Jaceosidin (44)                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                          | 10-13                               |
| <i>A. annua</i>                                | Quercetagenin-6,7,3',4'-<br>tetramethyl ether (74)<br>Artemetin (81)<br>Chrysosplenetin (77)<br>Rhamnocitrin (19), Chrysoeriol (21),<br>Cirsimaritin (25), Rhamnetin (31),<br>Quercetin-3-methyl ether (34),<br>Tamarixetin (35), Cirsiliol (43),<br>Penduletin (47), Eupatorin (50),<br>Cirsilineol (51), Axillarin (59),<br>Chrysosplenol D (65),<br>Quercetagenin-3,4'-dimethyl ether<br>(57), and Compounds 60,70.<br>Arteanoflavone (79) |                                                                                                                                                                                                                                                          | 12-14<br>14-17                      |
| <i>A. anomala</i>                              |                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                          | 17                                  |
| <i>A. arborescens</i> L.                       | Artemetin (81)                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                          | 18                                  |
| <i>A. arctica</i>                              | Jaceosidin (44)                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                          | 19-21                               |
| <i>A. argentea</i>                             | Artemetin (81)                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                          | 22                                  |
| <i>A. assoana</i> Willk                        | Apigenin (12), Luteolin (16),<br>Chrysoeriol (21), Salvigenin (28),<br>Jaceosidin (44), Cirsilineol (51), 5-Hydroxy-<br>6,7,3',4'- tetramethoxyflavone (55),<br>6-Methoxytricin (68) and Artemetin (81)                                                                                                                                                                                                                                       |                                                                                                                                                                                                                                                          | 23                                  |
| <i>A. campestris</i>                           |                                                                                                                                                                                                                                                                                                                                                                                                                                               | Apigenin 7-rutinoside and<br>Luteolin 7-glucoside                                                                                                                                                                                                        | 24                                  |
| <i>A. campestris</i>                           |                                                                                                                                                                                                                                                                                                                                                                                                                                               | Rutin                                                                                                                                                                                                                                                    | 7                                   |
| <i>subsp. glutinosa</i>                        | 7,3'-Di-O-Methyl<br>dihydroquercetin (42)<br>Naringenin (4)<br>Sakuranetin (6)<br>Pinocembrin (1) and Pinostrobin (2)<br>Homoeriodictyol (8), 7-O-<br>Methyleeriodictyol (9),<br>Hispidulin (20) and Padmatin                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                          | 24<br>25,26<br>26,27<br>25,27<br>27 |
| <i>A. campestris</i><br><i>subsp. maritima</i> | 5,4',8-Trihydroxyflavanone (3),<br>5,6-Dihydroxy-4'-methoxyflavanone (5),<br>5,4'-Dihydroxy-7,3'-dimethoxyflavanone (11),<br>7,3-Di-O-Methyl dihydroquercetin (42) and<br>the flavone Cirsimaritin (25)<br>Chrysosplenetin (77)                                                                                                                                                                                                               |                                                                                                                                                                                                                                                          | 26<br>28<br>29                      |
| <i>A. cana</i> Pursh                           |                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                          |                                     |
| <i>A. capillaris</i><br>Thunb                  | Rhamnocitrin (19)<br>Cirsimaritin (25)<br>Eupatolitin (58) and Arcapiline (52)<br>5,2',4'-Trihydroxy-6,7,5'-trimethoxyflavone (70)<br>Jaceidin(67) and<br>Chrysosplenetin (77)                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                          | 30<br>31<br>32<br>33                |
| <i>A. copa</i>                                 |                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                          |                                     |
| <i>A. dracunculus</i> L.                       | Naringenin (4), 7-Methylaromadenderin (7) and<br>7,3-Di-O-Methyl dihydroquercetin (42)<br>5,3'-Dihydroxy-7,4'-dimethoxyflavanone (10)<br>Artemetin (81)<br>Quercetin (29)                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                          | 34<br>35<br>35<br>36<br>7           |
|                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                               | Hyperoside<br>(Quercetin-3-galactoside and<br>Isorhamnetin-7-galactoside-p-                                                                                                                                                                              |                                     |

Table 1: contd.

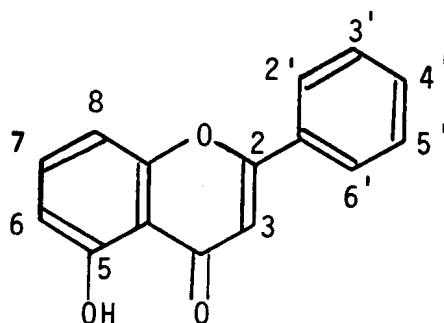
| Species                                              | Flavonoid aglycones                                                                                                                                                         | Flavonoid glycosides                                                                                                      | References |
|------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|------------|
|                                                      |                                                                                                                                                                             | hydrobenzoate                                                                                                             | 37         |
|                                                      |                                                                                                                                                                             | Kaempferol-3-rhamnoglucoside, Patuletin-3-glucoside and Patuletin-3-rhamnoglucoside                                       | 8          |
|                                                      |                                                                                                                                                                             | Bioquercetin and two Quercetin-3-glycosides                                                                               | 38         |
|                                                      |                                                                                                                                                                             | Rutin                                                                                                                     | 7,8        |
| <i>A. echegarayi</i>                                 | 6-Hydroxyluteolin (30) and Quercetagenin (56)                                                                                                                               | 7-glucosides of 30 and 56                                                                                                 | 39         |
| <i>A. frigida</i>                                    | 6-Methoxytricin (68) and flavone 72                                                                                                                                         |                                                                                                                           | 40         |
|                                                      | Luteolin (16) and Tricin (45)                                                                                                                                               |                                                                                                                           | 41,42      |
|                                                      | Cirsilineol (51)                                                                                                                                                            |                                                                                                                           | 42         |
|                                                      | Apigenin (12), Hispidulin (20), Chrysoeriol (21), Luteolin-3',4'-dimethyl ether (27), Eupafolin (36), Eupatilin (53), Quercetagenin-3,4'-dimethyl ether (57) and flavone 63 |                                                                                                                           |            |
|                                                      |                                                                                                                                                                             | Luteolin-7-glucoside                                                                                                      | 41         |
|                                                      |                                                                                                                                                                             | Schaftoside, Isoschaftoside and Vicenin 2                                                                                 | 43         |
| <i>A. glutinosa</i>                                  | Naringenin (4), 7-Methyleriodictyol (9), Rhamnetin (31)                                                                                                                     |                                                                                                                           | 44         |
|                                                      | 7,3'-Di-O-Methyl dihydroquercetin(42) and Palmatine                                                                                                                         |                                                                                                                           |            |
| <i>A. gmelinii</i>                                   | 7,4-Dimethylapigenin (15), Acacetin (14), Jaceosidin (44) and Velutin (24)                                                                                                  |                                                                                                                           | 45         |
| <i>A. herba-alba</i>                                 | Cirsilineol (51)                                                                                                                                                            |                                                                                                                           | 46,48      |
|                                                      | Artemetin (81)                                                                                                                                                              |                                                                                                                           | 49         |
|                                                      | Apigenin (12), Acacetin (14), Luteolin (16), Hispidulin (20), Cirsimaritin (25), Penduletin (47) and Flavone (72)                                                           |                                                                                                                           | 46         |
|                                                      |                                                                                                                                                                             | Quercetin                                                                                                                 |            |
|                                                      |                                                                                                                                                                             | 3-glucoside, 3-rutinoside                                                                                                 | 46,47      |
|                                                      |                                                                                                                                                                             | Patuletin                                                                                                                 |            |
|                                                      |                                                                                                                                                                             | 3-glucoside, 3-rutinoside                                                                                                 | 46,47      |
|                                                      |                                                                                                                                                                             | Isovitexin, Schaftoside and Isoschaftoside                                                                                | 46,47      |
| <i>A. hispanica</i> Lam.<br>(= <i>A. lucentica</i> ) | Cirsimaritin (25)                                                                                                                                                           |                                                                                                                           |            |
|                                                      | Apigenin (12), Jaceosidin (44), Penduletin (47), Cirsilineol (51), Axillarin (59), Chrysosplenol D (65), Chrysosplenetin (77), Arteanoflavone (79) and Flavones 63,72, 73   |                                                                                                                           | 50         |
|                                                      |                                                                                                                                                                             |                                                                                                                           | 51         |
|                                                      |                                                                                                                                                                             | Isoetin-5'-glucoside (Isoetin = 2',4',5',5'-Tetrahydroxy-7-methoxyflavone), Apigenin-7-glucoside and Luteolin-7-glucoside |            |
| <i>A. incanescens</i>                                | Quercetin-3-methyl ether (34), Quercetin-3,4-dimethyl ether (40), Penduletin (47), Santin (54), Axillarin (59), Centaureidin (66) and Casticin (76)                         |                                                                                                                           | 51         |
|                                                      | Acacetin (14)                                                                                                                                                               |                                                                                                                           |            |
| <i>A. judiaca</i>                                    | Hispidulin (20), Cirsimaritin (25), Pictolarigenin (26), Jaceosidin (44), Cirsilineol (51), Eupatilin (53) and Casticin (76)                                                |                                                                                                                           | 52         |
|                                                      | Chrysoeriol (21), Apigenin (12) and Luteolin (16)                                                                                                                           |                                                                                                                           | 46         |
|                                                      | Cirsitakaogenin (23)                                                                                                                                                        |                                                                                                                           |            |
|                                                      |                                                                                                                                                                             | Apigenin                                                                                                                  |            |
|                                                      |                                                                                                                                                                             | 7-glucoside, 7-glucuronide, 4'-glucoside, 7-gentiobioside, 7-diglucuronide and 7-rutinoside                               | 46         |

Table 1: contd.

| Species                          | Flavonoid aglycones                                                                                                                                                                                                                                                                                                                                                                          | Flavonoid glycosides                                                                                                                                                                                                                                                           | References                                   |
|----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------|
|                                  |                                                                                                                                                                                                                                                                                                                                                                                              | 7-gentiobioside and 3',7-diglucoside<br>Chyrsoeriol<br>7-glucoside, 7-glucuronide, 4'-glucoside,<br>7-gentiobioside, 7-diglucuronide and<br>7-rutinoside<br>7-rhamnoglucoside<br>Vicenin 2, Lucenin 2, Schaftoside,<br>Isoschaftoside, Neoschaftoside and<br>Neoisoschaftoside | 46<br>46<br>53<br>46<br>54<br>55             |
| <i>A.klotzchiana</i> Begs        | Jaceosidin (44)                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                | 56                                           |
| <i>A.lanata</i> Willd            | Flavone 55, Casticin (76)<br>and Artemetin (81)                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                | 57                                           |
| <i>A.leucodes</i>                | Eupatilin (53)                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                | 57                                           |
| <i>A.ludoviciana</i><br>Nutt.    | Apigenin (12), Lutolin (16), Kaempferol-3-<br>methyl ether (18), Hispidulin (20)<br>Chyrsoeriol (21), Luteolin-3',4'-dimethyl<br>ether (27), Eupafolin (36), Jaceosidin (44),<br>Tricin (45), Eupatilin (53), Axillarin (59),<br>Selagin (37), 5,7,4'-Trihydroxy-<br>3,6-dimethoxyflavone (38),<br>Flavones ( 63),(64),(72),(75) and (78)<br>3,5-Dihydroxy-6,7,8-trimeth-<br>oxyflavone (46) |                                                                                                                                                                                                                                                                                | 57<br>57<br>58                               |
| <i>A.ludoviciana</i><br>Nutt.    |                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                |                                              |
| <i>A.mesatlantica</i>            | Apigenin (12), Chyrsoeriol (21),<br>Cirsimaritin (25), Tricin (45),<br>Cirsilineol (51) and<br>6-Methoxytricin (68)<br>4',5-Dihydroxy-3',5',6,7-<br>tetramethoxyflavone (80)                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                                                | 59<br>60                                     |
| <i>A.monosperma</i> Del.         | Cirsilineol (51) and Myricetin-<br>3,5'-dimethyl ether (61)<br>Diosmetin (22), Flavones (62), (69)<br>and 3,7,3'-Trimethoxyquercetin (49)                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                | 61<br>62                                     |
|                                  |                                                                                                                                                                                                                                                                                                                                                                                              | Acacetin<br>7-glucoside, 7-rutinoside<br>Quercetin<br>3-glucoside, 5-glucoside, 7-rutinoside<br>Patuletin<br>3-glucoside, 7-rutinoside<br>Isorhamnetin-5-glucoside<br>Vicenin 2, Lucenin 2<br>Luteolin-7-glucoside and Hyperoside                                              | 46,47<br>46,47<br>46,47<br>46,47<br>63<br>64 |
| <i>A.palustris</i>               | Luteolin (16), Quercetin (29)                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                                                | 65                                           |
| <i>A.pygmaea</i> Gray            | 7,3'-Di-O-Methyl dihydroquercetin (42)                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                                                                                                                | 66                                           |
| <i>A.rutifolia</i>               | Chyrsoeriol (21), Tricin (45),<br>Cirsilineol (51) and<br>Chrysosplenetin (77)                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                | 65<br>66                                     |
| <i>A.sacrorum</i>                | Genkwanin (13)                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                |                                              |
| <i>A.santolinifolia</i>          | Luteolin (16), Kaempferol (17)<br>and Quercetin (29)                                                                                                                                                                                                                                                                                                                                         | Rutin and Kaempferol-3-glucoside                                                                                                                                                                                                                                               | 67                                           |
| <i>A.santonium</i> L.            | Quercetin (29)                                                                                                                                                                                                                                                                                                                                                                               | Rutin and Kaempferol-3-glucoside                                                                                                                                                                                                                                               | 68                                           |
| <i>A.scoparia</i>                | 7-Methylaromadenderin (7),<br>Rhamnocitrin (19),<br>Cirsimaritin (25), Eupalitin (39)<br>and Eupatolitin (58)                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                                                | 69                                           |
|                                  |                                                                                                                                                                                                                                                                                                                                                                                              | Rutin, Quercetin-3-glucogalactoside,<br>Kaempferol-3-glucogalactoside,<br>Quercetin-3,7-rutinogalactoside and<br>Quercetin-3,7-rutinodigalactoside                                                                                                                             | 70                                           |
| <i>A.siversiana</i>              | Chrysosplenetin (77)                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                                                                                                                |                                              |
| <i>A.aurica</i> Willd            |                                                                                                                                                                                                                                                                                                                                                                                              | Axillarioside (7-glucoside-3',4',5'-<br>trihydroxy-3,6-dimethoxyflavone)                                                                                                                                                                                                       | 71<br>72                                     |
| <i>A.transiliensis</i><br>Poljak | Tansilitin (33)                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                | 73,74<br>75                                  |
|                                  |                                                                                                                                                                                                                                                                                                                                                                                              | Rutin<br>Transilin (3-O-Methylquercetin-7-<br>glucoside)                                                                                                                                                                                                                       | 73                                           |

Table 1: contd.

| Species               | Flavonoid aglycones                                                                  | Flavonoid glycosides                                                                      | References |
|-----------------------|--------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|------------|
|                       | Genkwanin (13), Acacetin (14) and 3-O-Methylquercetin (34)                           |                                                                                           | 74         |
| <i>A. tridentata</i>  |                                                                                      | Apigenin-6-C-glucoside and vicianin 2 (Apigenin-6,8-C-diglucoside)                        | 76         |
| <i>Vaseyana</i>       | Luteolin (16), Eupafolin (36) and Axillarin (59)                                     |                                                                                           | 77         |
| <i>A. vulgaris</i> L. | Ayanin (48)                                                                          | Luteolin-7-O-glucoside                                                                    | 78         |
|                       |                                                                                      | Rutin, Quercetin-3-glucoside, Isorhamnetin-3-glucoside and Isorhamnetin-3-rhamnoglucoside | 8          |
| <i>A. xerophytica</i> | Luteolin (16), Cirsimaritin (25) Pictolarigenin (26) Jaceosidin (44) and Tricin (45) |                                                                                           | 79         |

Fig.1: Structures of the flavonoids isolated from *Artemisia* species.

|                               | 3   | 6   | 7   | 8   | 2' | 3'  | 4'  | 5' |
|-------------------------------|-----|-----|-----|-----|----|-----|-----|----|
| Di, Tri and Tetra-oxygenated  |     |     |     |     |    |     |     |    |
| 1. Pinocembrin                | -   | -   | OH  | -   | -  | -   | -   | -  |
| 2. Pinostrobin                | -   | -   | OMe | -   | -  | -   | -   | -  |
| 3. Naringenin                 | -   | -   | OH  | OH  | -  | -   | OH  | -  |
| 4. -                          | -   | OH  | -   | -   | -  | -   | OMe | -  |
| 5. Sakuranetin                | -   | -   | OMe | -   | -  | -   | OH  | -  |
| 6. 7-Methylaromadenderin      | -   | OH  | OMe | -   | -  | -   | OH  | -  |
| 7. Homoeriodictyol            | -   | -   | OH  | -   | -  | OH  | OH  | -  |
| 8. 7-Methyl eriodictyol       | -   | -   | OMe | -   | -  | OH  | OH  | -  |
| 9. -                          | -   | -   | OMe | -   | -  | OH  | OMe | -  |
| 10. Apigenin                  | -   | -   | OH  | -   | -  | -   | OH  | -  |
| 11. Genkwanin                 | -   | -   | OMe | -   | -  | -   | OH  | -  |
| 12. Acacetin                  | -   | -   | OH  | -   | -  | -   | OMe | -  |
| 13. 7,4'-Dimethyl-apigenin    | -   | -   | OMe | -   | -  | -   | OMe | -  |
| 14. Luteolin                  | -   | -   | OH  | -   | -  | OH  | OH  | -  |
| 15. Kaempferol                | OH  | -   | OH  | -   | -  | -   | OH  | -  |
| 16. Kaempferol-3-methyl ether | OMe | -   | OH  | -   | -  | -   | OH  | -  |
| 17. Rhamnocitrin              | OH  | -   | OMe | -   | -  | -   | OH  | -  |
| 18. Hispidulin                | -   | OMe | OH  | -   | -  | -   | OH  | -  |
| 19. Chrysoeriol               | -   | -   | OH  | -   | -  | OMe | OH  | -  |
| 20. Diosmetin                 | -   | -   | OH  | -   | -  | OH  | OMe | -  |
| 21. Cirsitakaogenin           | -   | -   | OH  | OMe | -  | -   | OMe | -  |
| 22. Velutin                   | -   | -   | OMe | -   | -  | OMe | OH  | -  |
| 23. Cirsimaritin              | -   | OMe | OMe | -   | -  | -   | OH  | -  |

|      |                                                     |     |     |     |     |    |     |     |     |
|------|-----------------------------------------------------|-----|-----|-----|-----|----|-----|-----|-----|
| 26.  | Pictolarigenin-                                     | -   | OMe | OH  | -   | -  | -   | OMe | -   |
| 27.  | Luteolin-3',4'-<br>dimethyl ether                   | -   | -   | OH  | -   | -  | OMe | OMe | -   |
| 28.  | Salvigenin                                          | -   | OMe | OMe | -   | -  | OMe | OMe | -   |
| 29.  | Pentaoxy-<br>genated<br>Quercetin                   | OH  | -   | -   | OH  | -  | OH  | OH  | -   |
| 30.  | 6-Hydroxy-<br>luteolin                              | -   | OH  | OH  | -   | -  | OH  | OH  | -   |
| 31.  | Rhamnetin                                           | OH  | -   | OMe | -   | -  | OH  | OH  | -   |
| 32.  | Isorhamnetin                                        | OH  | -   | OH  | -   | -  | OMe | OH  | -   |
| 33.  | Quercetin-3-<br>methyl ether                        | OMe | -   | OH  | OH  | -  | OH  | OH  | -   |
| 34.  | Tamarixetin                                         | OMe | -   | OH  | -   | -  | OH  | OH  | -   |
| 35.  | Eupafolin                                           | OH  | -   | OH  | -   | -  | OH  | OMe | -   |
| 36.  | Selagin                                             | -   | OMe | OH  | -   | -  | OH  | OH  | -   |
| 37.  | Eupalitin                                           | -   | -   | OH  | -   | -  | OH  | OH  | OMe |
| 38.  | Quercetin-3,4'-<br>dimethyl ether                   | OMe | OMe | OH  | -   | -  | -   | OH  | -   |
| 39.  | Quercetin-7,3'-<br>dimethyl ether                   | OH  | OMe | OMe | -   | -  | -   | OH  | -   |
| 40.  | 7,3'-Di-O-Methyl<br>dihydroquercetin                | OMe | -   | OH  | -   | -  | OH  | OMe | -   |
| 41.  | Cirsiliol                                           | OH  | -   | OMe | -   | -  | OMe | OH  | -   |
| *42. | Jaceosidin                                          | OH  | -   | OMe | -   | -  | OMe | OH  | -   |
| 43.  | Tricin                                              | -   | OMe | OMe | -   | -  | OH  | OH  | -   |
| 44.  | Penduletin                                          | -   | OMe | OH  | -   | -  | OMe | OH  | -   |
| 45.  | Ayanin                                              | -   | -   | OH  | -   | -  | OMe | OH  | OMe |
| 46.  | 3,7,3'-Trimethyl<br>quercetin                       | OH  | OMe | OMe | OMe | -  | -   | -   | -   |
| 47.  | Eupatorin                                           | OMe | OMe | OMe | -   | -  | -   | OH  | -   |
| 48.  | Cirsiliniol                                         | OMe | -   | OMe | -   | -  | OH  | OMe | -   |
| 49.  | Arcapillin                                          | OMe | -   | OMe | -   | -  | OMe | OH  | -   |
| 50.  | Eupatilin                                           | -   | OMe | OH  | -   | -  | OMe | OMe | -   |
| 51.  | Santin                                              | -   | OMe | OMe | -   | -  | -   | OMe | -   |
| 52.  | Hexaoxygenated<br>Quercetagenin                     | OMe | OMe | OMe | -   | -  | OMe | OMe | -   |
| 53.  | Quercetagenin-3,4'-<br>dimethyl ether               | -   | OMe | OH  | -   | -  | OH  | OH  | -   |
| 54.  | Patuletin                                           | OH  | OMe | OMe | -   | -  | OH  | OH  | -   |
| 55a. | Eupatolitin                                         | OH  | OMe | OMe | -   | -  | OH  | OH  | -   |
| 56.  | Axillarin                                           | OMe | OMe | OH  | -   | -  | OH  | OH  | -   |
| 57.  | 5,7,8,3'-Tetrahydro-<br>xy-3,4'-dimethyl<br>flavone | OMe | -   | OH  | -   | OH | OMe | -   | -   |
| 58.  | Myricetin-3,5-<br>dimethyl ether                    | OMe | -   | OH  | -   | -  | OH  | OH  | OMe |
| 59a. | Spinacetin                                          | OH  | OMe | OH  | -   | -  | OMe | OH  | -   |
| 60.  | Chrysosplenol D                                     | OH  | -   | OH  | -   | -  | OMe | OH  | OMe |
| 61.  | Centaureidin                                        | -   | OMe | OH  | -   | -  | OH  | OH  | OMe |
| 62.  | Jaceidin                                            | -   | OMe | OH  | -   | OH | -   | OH  | OMe |
| 63.  | 6-Methoxytricin                                     | -   | OMe | OH  | -   | -  | OH  | OH  | OMe |
| 64.  | 5,2',4'-Trihydroxy-<br>6,7,5-trimethoxy<br>flavone  | OMe | OMe | OMe | -   | -  | OH  | OH  | -   |
| 65.  | Quercetagenin-6,7<br>3,4-tetramethyl ether          | OMe | OMe | OH  | -   | -  | OH  | OMe | -   |
| 66.  |                                                     | -   | OMe | OH  | -   | -  | OMe | OH  | OMe |
| 67.  |                                                     | -   | OMe | OH  | -   | -  | OH  | OMe | OMe |
| 68.  |                                                     | -   | OMe | OMe | -   | -  | OH  | OH  | OMe |
| 69.  |                                                     | OH  | OMe | OMe | -   | -  | OMe | OMe | -   |
| 70.  |                                                     | -   | OMe | OMe | -   | -  | OH  | OH  | OMe |
| 71.  |                                                     | -   | OMe | OH  | -   | -  | OH  | OMe | OMe |
| 72.  |                                                     | -   | OMe | OH  | -   | -  | OH  | OMe | OMe |
| 73.  |                                                     | -   | OMe | OMe | -   | -  | OH  | OH  | OMe |
| 74.  |                                                     | OH  | OMe | OMe | -   | -  | OMe | OMe | -   |

|     |                                             |     |     |     |     |   |     |     |     |
|-----|---------------------------------------------|-----|-----|-----|-----|---|-----|-----|-----|
| 75. | Quercetagenin-3,6<br>3,4'-tetramethyl ether | OMe | OMe | OH  | -   | - | OMe | OMe | -   |
| 76. | Casticin                                    | OMe | OMe | OMe | -   | - | OH  | OMe | -   |
| 77. | Chrysosplenetin                             | OMe | OMe | OMe | -   | - | OMe | OH  | -   |
| 78. |                                             | OMe | OMe | OH  | OMe | - | -   | OMe | -   |
| 80. |                                             | -   | OMe | OMe | -   | - | OMe | OH  | OMe |
| 81. | Artemetin                                   | OMe | OMe | OMe | -   | - | OMe | OMe | -   |

\*2,3-Dihydro(flavanone type  
@ 5-Dihydro derivatives

Table 2: Natural Coumarins from *Artemisia* species

| Species                        | Coumarins                                                                                                                                                                                                                | References                   |
|--------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| <i>A.abrotanum</i> L.          | Coumarin (82)<br>Esculetin (85)                                                                                                                                                                                          | 80<br>7                      |
|                                | Umbelliferone (83), Scopoletin (87)                                                                                                                                                                                      |                              |
| <i>A.annua</i> L.              | Isofraxidin (97) and Scopolin (105)<br>Coumarin (82)<br>Scopoletin (87), Scoparone (91),<br>5,6-Dimethyl-7-hydroxycoumarin(96)<br>and Isofraxidin (97)                                                                   | 81-84<br>12,13,85a<br><br>17 |
| <i>A.apiacea</i> Hance         | Scopoletin (87) and Scopolin (105)<br>Herniarin (84), Daphnetin (86),<br>Daphnetin-8-methyl ether (90),<br>Daphnetin dimethyl ether (92),<br>Daphnetin methylene ether (93) and<br>7-Isopentenoxo-8-methoxycoumarin (95) | 12,85<br><br><br>86,87       |
| <i>A.adamsii</i>               | Scopoletin (87)                                                                                                                                                                                                          | 87a                          |
| <i>A.armeniaceum</i>           | Armin (94)                                                                                                                                                                                                               | 9                            |
| <i>A.assoana</i> Willk         | Umbelliferone (83), Scopoletin (87)<br>and Isofraxidin (97)                                                                                                                                                              | 88<br>24                     |
| <i>A.comphorata</i> Vill       | Isofraxidin (97)                                                                                                                                                                                                         | 81                           |
| <i>A.capillaris</i> Thunb      | Coumarin (82) and Scopoletin (87)<br>Scoparone (91)                                                                                                                                                                      | 30<br>30,33                  |
| <i>A.carruthii</i> Wood        | 6-Methoxy-7,8-methylen ether (99)                                                                                                                                                                                        | 89                           |
| <i>A.chamaemelifolia</i>       | I. Scopoletin (87) and Scopolin (105)                                                                                                                                                                                    | 90                           |
| <i>A.compacta</i> Fisch        | Umbelliferone (83) and Scopoletin (87)                                                                                                                                                                                   | 91                           |
| <i>A.caurifolia</i>            | Daphnetin-7-methyl ether (89),<br>Daphnetin dimethyl ether (92) and<br>Daphnetin methylene ether (93)                                                                                                                    |                              |
| <i>A.diffusa</i>               | Herniarin (84)                                                                                                                                                                                                           | 92<br>93                     |
| <i>A.dracunculus</i> L.        | Herniarin (84) and Scoparone (91)<br>Esculetin (85)<br>Scoparone (91)                                                                                                                                                    | 94-96<br>7<br>36             |
| <i>A.dracunculoides</i>        | Scopoletin (87), Daphnetin-7-methyl<br>ether(89), Scoparone (91), Daphnetin<br>methylene ether (93), 7-Isopentenoxo-8<br>methoxycoumarin (95) and<br>6-Methoxy-7,8-methylene ether (99)                                  |                              |
| <i>A.feddei</i> Lev.           | Herniarin (84), Scopoletin (87),<br>Scoparone (91) and Isofraxidine (97)                                                                                                                                                 | 22<br>30,97,98               |
| <i>A.glutinosa</i>             | Herniarin (84)                                                                                                                                                                                                           | 44,                          |
| <i>A.gmelinii</i>              | Scopoletin (87)                                                                                                                                                                                                          | 45,99                        |
| <i>A.herba-alba</i>            | Scopoletin (87)                                                                                                                                                                                                          | 100                          |
| <i>A.hispanica</i>             | Esculetin (85)                                                                                                                                                                                                           | 51                           |
| <i>A.incanescens</i><br>Jordan | Umbelliferone (83), Scopoletin (87)<br>and Isofraxidin (97)                                                                                                                                                              |                              |
| <i>A.ircyniana</i>             | Scopoletin (97)                                                                                                                                                                                                          | 52                           |
| <i>A.japonica</i>              | Coumarin (82), Herniarin (84),<br>Scoparone (91) and Isofraxidin (97)                                                                                                                                                    | 101<br>30,101                |
| <i>A.lactiflora</i> Wall       | Coumarin (82), Herniarin (84) and<br>Umbelliferone (83)                                                                                                                                                                  |                              |
| <i>A.monosperma</i> Del.       | Umbelliferone (83), Herniarin (84)<br>and Scopoletin (87)                                                                                                                                                                | 102,103<br>104               |

Table 2: contd.

| Species                    | Coumarins                                                                                                                                                                        | References |
|----------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| <i>A. montana</i>          | Coumarin (82), Herniarin (84), Scopoletin (87), Scoparone (91) and Isofraxidin (97)                                                                                              | 30         |
| <i>A. palustris</i>        | Umbelliferone (83)                                                                                                                                                               | 63         |
| <i>A. parviflora</i> Roxb. | Esculetin (85), Scopoletin (87) and Scoparone (91)                                                                                                                               | 105        |
| <i>A. persica</i>          | Scopoletin (87) and Scopolin (105)                                                                                                                                               | 106,107    |
| <i>A. porrecta</i> Var.    | Herniarin (84)                                                                                                                                                                   | 108        |
| <i>A. princeps</i>         | Coumarin (82), Herniarin (84), Scopoletin (87), Scoparone (91) and Isofraxidin (97)                                                                                              | 30         |
| <i>A. ramosa</i>           | Umbelliferone (83), Scopoletin (87) and Isofraxidin (97)                                                                                                                         | 109        |
| <i>A. sacrorum</i>         | Umbelliferone (83)                                                                                                                                                               | 66         |
| <i>A. santolinaefolia</i>  | Umbelliferone (83) and Scopoletin (87)                                                                                                                                           | 107,110    |
| <i>A. scoparia</i> Waldst  | Scopoletin (87), Esculetin 7-methyl ether (88) and Scoparone (91)                                                                                                                | 69,111     |
| <i>A. scotina</i>          | Umbelliferone (83), Scopoletin (87), Isofraxidin (97) and Fraxidin (98)                                                                                                          | 112,113    |
| <i>A. silvatica</i>        | Herniarin (84)                                                                                                                                                                   | 101        |
| <i>A. siversiana</i>       | Esculetin (85)                                                                                                                                                                   | 71         |
| <i>A. stelleriana</i>      | Coumarin (82), Herniarin (84), Scopoletin (87), Scoparone (91) and Isofraxidin (97)                                                                                              | 30         |
| <i>A. stolonifera</i>      | Herniarin (84)                                                                                                                                                                   | 101        |
| <i>A. tridentata</i> Nutt. | Umbelliferone (83), Esculetin (85), Scopoletin (87), Isoscapoletin (88), Scoparone (91), Artelin (100), Skimmin (101), Cichoriin (102), Esculin (103) and 7-Methyl esculin (104) | 77,114     |
| <i>A. vulgaris</i>         | Coumarin (82), Umbelliferone (83), Esculetin (85), Scopoletin (87) and Esculin (103)                                                                                             | 115        |

[24], *A. herba-alba* [46] and *A. judaica* [46]. 14 known methoxylated flavonoids were isolated from *A. annua* [17] along with three new flavones (57), (60) and (70). However, the flavone (70) has been reported earlier from *A. capillaris* [33].

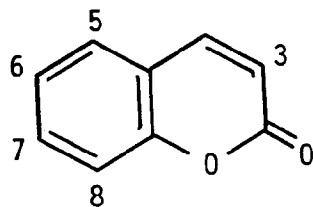
Flavonoid glycosides obtained from 19 *Artemisia* species belong to the common flavonols, kaempferol (17), quercetin (29), isorhamnetin (32) and patuletin (57a) and to the flavones apigenin (12), luteolin (16) and chrysoeriol (21). More than 50 flavonoid O-glycosides (acidic hydrolysable) have been isolated from various *Artemisia* species (Table 1). Rutin (quercetin 3- rutinoside) is found in most flavonoid O-glycoside containing species. Apigenin 7-rutinoside was recently isolated [24] for the first time from the genus *Artemisia*. The majority of the isolated O-glycosides are O-monosides and O-biosides with  $\beta$ -D-glucose being the frequently occurring monosaccharide. Acylated glycosyl flavonoids were only represented by one

compound which co-occur with other glycosides in *A. dracunculus* [37]. Flavonol-5-O-glucosides were only reported from *A. monosperma* [46,47].

Little has been reported on flavonoid C-glycosides (resistant to acidic and enzymatic hydrolysis). This type of glycosides are represented by totally 7 compounds, isolated from five *Artemisia* species, namely, *A. frigida* [43], *A. herba-alba* [46,47], *A. judaica* [46], *A. monosperma* [46,47] and *A. transilien-sis* [76]. All C-glycosides obtained from *Artemisia* species are 6-C and/or 8-C glycosyl of apigenin (12) and luteolin (16), and the sugar moiety in all of them is glucose and arabinose. These glycosides are schaftoside (6-C-glucosyl-8-C- $\alpha$ -arabinosylapigenin) (6-C- $\alpha$ -arabinosyl-8-C-glucosyl-apigenin), neoschaftoside (6-C-glucosyl-8-C- $\beta$ -arabinosylapigenin), neoisoschaftoside (6-C- $\beta$ -arabinosyl-8-C-glucosylapigenin), isovitexin (apigenin-6-C-glucoside), lucenin 2 (luteolin-6,8-C-diglucoside) and vicenin 2 (apigenin-6,8-C-diglucoside).

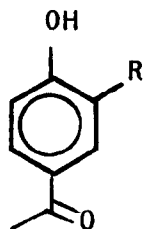


Fig.2: Structure of the coumarins isolated from *Artemisia* species.



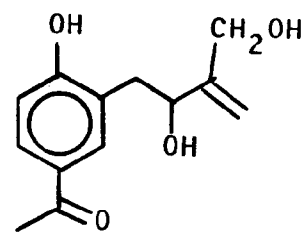
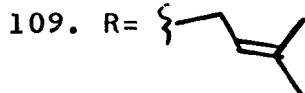
|       |                                  | 5   | 6      | 7                    | 8   |
|-------|----------------------------------|-----|--------|----------------------|-----|
| 82.   | Coumarin                         | -   | -      | -                    | -   |
| 83.   | Umbelliferone                    | -   | -      | OH                   | -   |
| 84.   | Herniarin                        | -   | -      | OMe                  | -   |
| 85.   | Esculetin                        | -   | OH     | OH                   | -   |
| 86.   | Daphnetin                        | -   | -      | OH                   | OH  |
| 87.   | Scopoletin                       | -   | OMe    | OH                   | -   |
| 88. @ | Esculetin 7-methyl ether         | -   | OH     | OMe                  | -   |
| 89.   | Daphnetin 7-methyl ether         | -   | -      | OMe                  | OH  |
| 90.   | Daphnetin 8-methyl ether         | -   | -      | OH                   | OMe |
| 91.   | Scoparone                        | -   | OMe    | OMe                  | -   |
| 92.   | Daphnetin Di-methyl ether        | -   | -      | OMe                  | OMe |
| 93.   | Daphnetin methylene ether        | -   | -      | -O-CH <sub>2</sub> - | O-  |
| 94.   | Armin                            | -   | -      | *                    | OH  |
| 95.   | 7-Isopentenoxo-8-methoxycoumarin | -   | -      | **                   | OMe |
| 96.   | 5,6-Dimethoxy-7-hydroxycoumarin  | OMe | OMe    | OH                   | -   |
| 97.   | Isofraxidin                      | -   | OMe    | OH                   | OMe |
| 98.   | Fraxidin                         | -   | OH     | OMe                  | OMe |
| 99.   | 6-Methoxy-7,8-methylene ether    | -   | OMe    | O-CH <sub>2</sub> -  | O-  |
| 100.  | Artelin                          | OMe | OMe    | OMe                  | OMe |
| 101.  | Skimmin                          | -   | -      | O-glu.               | -   |
| 102.  | Cichorin                         | -   | OH     | O-glu.               | -   |
| 103.  | Esculin                          | -   | O-glu. | OH                   | -   |
| 104.  | 7-Methylesculin                  | -   | O-glu. | OMe                  | -   |
| 105.  | Scopolin                         | -   | OMe    | O-glu.               | -   |
| 106.  | Daphnin                          | -   | -      | O-glu.               | OH  |

Me = CH<sub>3</sub>, glu = glucoside; @ = Isoscopoletin  
 \* = O-CH<sub>2</sub>MeCHCH<sub>2</sub>OH; \*\* = OCH<sub>2</sub>CH = CMe<sub>2</sub>

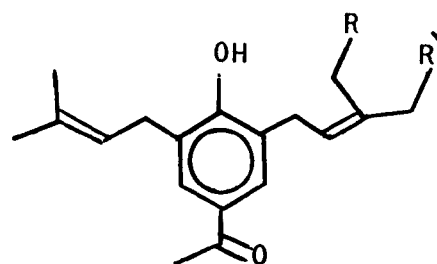


107. R = H

108. R = Ac

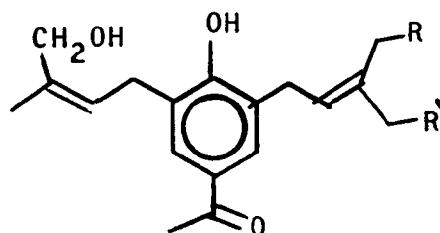


110



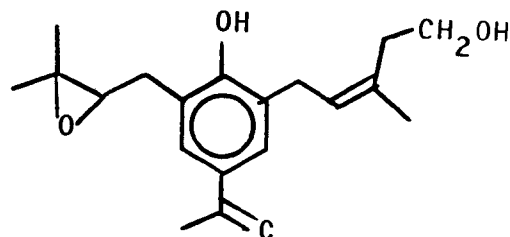
111. R = OH, R' = H

112. R = H, R' = OH

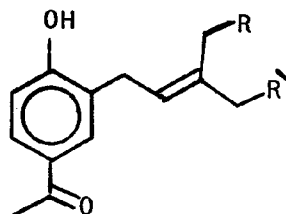


113. R = OH, R' = H

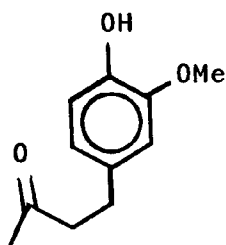
114. R = H, R' = OH



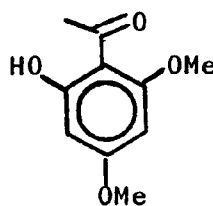
115



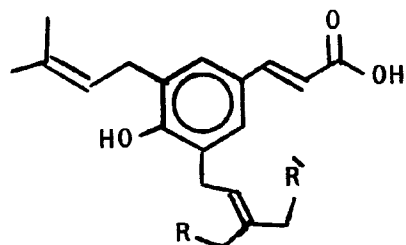
116.  $R=OH$ ,  $R'=H$   
 117.  $R=OAc$ ,  $R'=H$   
 118.  $R=H$ ,  $R'=OAc$   
 119.  $R=H$ ,  $R'=OH$   
 120.  $R=CHO$ ,  $R'=H$



121. Zingerone



122



123.  $R=R'=H$   
 124.  $R=H$ ,  $R'=OH$   
 125.  $R=OH$ ,  $R'=H$

### Coumarins

Coumarins are also common constituents of the plants of the genus *Artemisia*. More than forty five *Artemisia* species have been found to contain coumarins. Table 2 contains the coumarins isolated from various *A.* species and their structure are given in Fig. 2. Scopoletin (87) is the more common compound since it occurred in many *A.* species as shown in Table 2. All the coumarins isolated from *Artemisia* species are not substituted in the lactone

ring (i.e. at position 3 and 4). In addition to the coumarins listed in Fig. 2, many sesquiterpene coumarin ethers were obtained from different *Artemisia* species [80, 122-124].

### Miscellaneous

Acetophenone derivatives frequently occur in most the phenolic containing *Artemisia* species. Pascual-T *et al* [25,117,118] have isolated several acetophenones (107-119) from *A. campestris* subsp. *glutinosa*. The phenic compound (109) was also isolated from *A. campestris* subsp. *maritima* [28]. p-Hydroxyacetophenone (107) has been obtained from different *Artemisia* species [24,51, 120]. The two phenolics, (119) [119] and (120) [140] were obtained from *A. monosperma*. Zingerone (121) was isolated from two *Artemisia* plants [51,52] while the acetophenone derivative (122), as far as we know, was only reported once from *A. gypsacea* Krasch [121]. On the other hand, several phenolic acids were found to occur in some *Artemisia* species. Mixtures of straightchain n-alkyl p-coumarates have been reported from *A. assoana* Willk [24] and from *A. campestris* [116]. Such latter derivatives were isolated from *A. monosperma* [125]. p-Coumaric acids (123-125) were obtained from *A. patustris* L. [120]. Caffeic acid and its methyl ester occurred in some *A.* species [24,45,51,71]. Finally, Namba *et al* [33] have isolated two known chromene derivatives from *A. capillaris*.

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