A New Flavonol Glycoside Derivative from Leaves of *Moldenhawera nutans*

Ademir E. do Vale[a], Jorge M. David[a], Hugo N. Brandão[b], and Juceni P. David[b,*]

[a] Instituto de Química, Universidade Federal da Bahia, 40170-290 Salvador, BA, Brazil
[b] Faculdade de Farmácia, Universidade Federal da Bahia, 40170-290 Salvador, BA, Brazil. Fax: +55--71-2355166. E-mail: juceni@ufba.br

* Author for correspondence and reprint requests

Z. Naturforsch. **60c**, 45–49 (2005); received June 18/September 27, 2004

The ethyl acetate extract of leaves of *Moldenhawera nutans* Queiroz & Alkin (Leguminosae) furnished, besides methyl gallate and gallic acid, the flavonols named laricetrin, laricetrin 3-glucoside and laricetrin 3-galactoside as well as the new one named laricetrin 5-galloyl-3-β-D-xylopyranoside. It also was isolated from the hexane extract: β-sitosterol, lupenone, β-amyrinone, α-amyrinone, lupeol, β-amyrin, α-amyrin and α-tocopherol. The antioxidant activities of flavonoids were measured through DPPH radical scavenging and inhibition of auto-oxidation of β-carotene methods. The structures of the compounds were determined by analyses of spectral data. This is the first report dealing with phytochemical studies of leaves of *M. nutans*. In addition this current work describes the unequivocal attribution of ^{1}H NMR and ^{13}C NMR data of laricetrin.

Key words: Moldenhawera nutans, Antioxidant Activities, Flavonol Glycosides

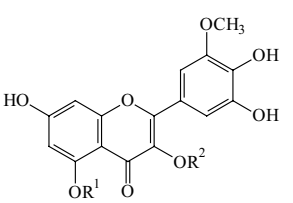
Introduction

Moldenhawera is a neotropical genera and it is distributed almost exclusively at the north coast of Brazil with significant taxa concentration in Bahia State. It is represented by approximately ten species (Queiroz *et al.*, 1999). The taxonomy of this genus is confusing, making the classification of the species difficult.

Moldenhawera nutans Queiroz & Alkin (Leguminosae) is a shrub apparently endemic of the coastal dunes of Salvador, Bahia. In a former phytochemical study with the stems of this species we reported the isolation and identification of labdenic diterpenes and a new dimeric diterpene (David *et al.*, 1999). There are no more studies dealing with species of this genus. The present paper reports the isolation and identification of β-sitosterol, lupenone, β-amyrinone, α-amyrinone, lupeol, β-amyrin, α-amyrin and α-tocopherol from the hexane extract of leaves of *M. nutans*. Furthermore it describes the isolation of methyl gallate, gallic acid and of the flavonols laricetrin, laricetrin 3-glucoside, laricetrin 3-galactoside and the new compound laricetrin 5-galloyl-3-β-D-xylopyranoside from the ethyl acetate extract.

Results and Discussion

All the substances were identified on the basis of chemical and spectral data. The ^{1}H NMR spectrum of compounds **1**–**4** (Fig. 1) presented characteristic signals of the flavonol skeleton. Two doublets observed at δ 6.18 and δ 6.39 indicated a 5,7-disubstituted flavonol. The doublets at δ 7.42 and δ 7.46 were attributed to the hydrogen of ring B of the AB system of the flavonol proving to place the methoxyl group (*ca.* δ 3.9) at C-3′. These observations allowed to identify the flavonol's aglycone in compounds **1**–**4** as laricetrin. The ^{13}C NMR spectra confirmed the previous statements by evidencing seven peaks for oxygenated carbons (see Experimental) and one carboxyl group (*ca.* δ 177.8). Detailed analysis of these spectra confirmed the substitution pattern of the rings A and



1 $R^1 = R^2 = H$
2 R^1 = Galloyl, R^2 = Xylopyranosyl
3 $R^1 = H$, R^2 = Glucosyl
4 $R^1 = R^2$ = Galactosyl

Fig. 1. Compounds isolated from leaves of *M. nutans*: laricetrin (**1**), laricetrin 5-galloyl-3-β-D-xylopyranoside (**2**), laricetrin 3-β-glucoside (**3**), laricetrin 3-β-galactoside (**4**).

0939–5075/2005/0100–0045 $ 06.00

B of laricetrin (**1**) and its glycoside derivatives (**2**–**4**). The signals concerning the methine carbons registered between δ 95.1 and *ca.* δ 110.5 corroborated this observation. The chemical shifts observed in both ^{1}H and ^{13}C NMR spectra for the signals of ring B also established the localization of the methoxyl group at C-3′. The molecular ion peak of **1** registered in the mass spectrum at *m/z* 332 corroborated the molecular formula $C_{16}H_{12}O_8$ and confirmed compound **1** being laricetrin.

The detailed analysis of ^{13}C NMR spectra of **2** allowed to recognize besides the laricetrin moiety signals for a xylose and galloyl groups, suggesting that the substance was a flavonol glycoside esterifing gallic acid. The molecular ion peak $[M+Na]^+$ observed at *m/z* 639 in the mass spectrum (ESI) confirmed this statement and simultaneously with ^{1}H and ^{13}C NMR data pointed out the molecular formula $C_{28}H_{24}O_{16}$ for the isolate **2**. In comparison with compound **1** two significant differences were observed in aglycone peak displacements for C-3 ($\Delta\delta$ – 3 ppm) and for C-5 ($\Delta\delta$ – 3.1 ppm). The signals of C-3 were similar to the observed for flavonols bearing a glycosyl group at this position (Markham and Geiger, 1994; Markham *et al.*, 1978). The signal observed in the ^{1}H NMR spectrum for anomeric H-1″ at δ 5.7 as well as its coupling constant (J = 6.4 Hz) indicated that the sugar unit possessed the β-configuration (Markham and Geiger, 1994; Agrawal, 1992). The location of the xylopyranosyl group at C-3 and consequently the galloyl esterification at OH-5 were confirmed through a HMBC spectrum (Fig. 2) especially the correlation observed between H-1′ (δ 5.7) and C-3 (δ 135.2). On the other hand, the correlations observed between the oxymethylene hydrogen H-5″ (δ 3.5) and the anomer carbon atom (δ 100.1) made possible to confirm the pyranose form to xylose. Additional HMBC and HMQC data allowed to confirm the structure of compound **2** as being the new flavonol laricetrin 5-galloyl-3-β-D-xylopyranoside and all correlations observed were illustrated in Fig. 2.

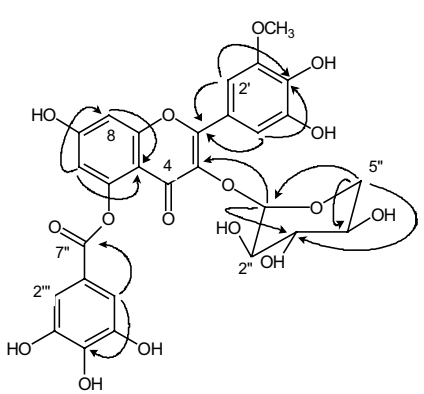


Fig. 2. Correlations observed for compound **2** in the HMBC spectrum.

The NMR spectral data of compounds **3** and **4** besides the signals regarding the laricetrin unit showed some differences especially in the region δ 60–80. Comparison with literature data (Markham and Geiger, 1994; Markham *et al.*, 1978) permitted to identify the glucosyl and galactosyl units of compounds **3** and **4**, respectively. The UV spectra recorded in the presence of shift diagnostic reagents ($AlCl_3$ and $AlCl_3$ + HCl) indicated the glycosylation in OH-3 even though the absence of a signal of the bonded hydrogen hydroxyl group in the ^{1}H NMR spectrum (Exarchou *et al.*, 2002). So, the compounds were identified as laricetrin 3-*O*-β-glucoside (**3**) and 3-β-galactoside (**4**). The mass spectra (ESIMS) of them showed the *quasi* molecular ion peak at *m/z* 493 $[M-1]^+$ in agreement with the proposed structures. These flavonol glycosides were previously isolated from *Picea abies* (Slimestad *et al.*, 1995) and from species of genera *Chondropetalum* (Harbone *et al.*, 1985), however this is their first occurrence in Leguminosae.

Although the exhibited ^{1}H NMR spectral data of compounds **1**, **3** and **4** have been compared with laricetrin and laricetrin-glycosides previously published (Niemann, 1973; Khetwal *et al.*, 1988), in this present paper their structures were confirmed by both HMBC and HMQC spectra. The chemical shifts observed in the ^{1}H NMR spectrum and attributed to H-2′ and H-6′ of laricetrin by Niemann (1973) and Khetwal *et al.* (1988) are inconsistent with the AB pattern expected for ring B for the laricetrin aglycone. So, the ^{1}H NMR spectral data proposed (Khetwal *et al.*, 1988) for the laricetrin aglycone is being reviewed.

In spite of the antioxidant ability of the flavonols to be plenty known (Pietta, 2000) this is the first report about the antioxidant ability of laricetrin (**1**) and its derivatives **2**–**4**. Even though compound **1** showed a high activity in the DPPH radicals scavenging test (Fig. 3), these compounds showed no significant activities in comparison with propyl gallate (IC_{50}= 0.26 μM) as well as with the commercially available antioxidants BHT and α-

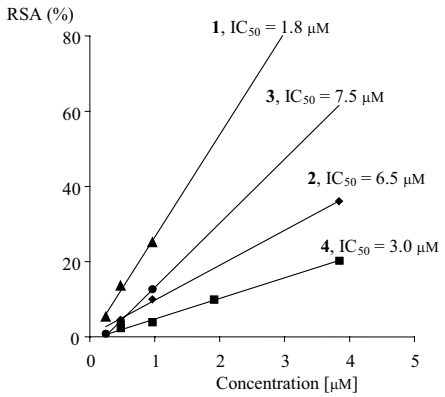


Fig. 3. IC_{50} values (μM) of the isolates in the DPPH radical scavenging activity (RSA) assay.

Table I. Antioxidant activity (AA)* observed in auto-oxidation of β-carotene assay of standards and compounds **1**–**4**.

Compound	AA
BHT	68.7 ± 5.9
α-Tocopherol	96.4 ± 9.1
1	15.5 ± 1.8
2	55.3 ± 1.1
3	17.8 ± 1.8
4	25.9 ± 2.8

* Values obtained at a concentration of 0.45 μM.

tocopherol in auto-oxidation of β-carotene assay (Table I).

Experimental

General procedures

^{1}H NMR (300 MHz); ^{13}C NMR and DEPT experiments (75 MHz); ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY: CD_3OD as internal standard; ESIMS (Quattro, Micromass, UK); UV spectra in MeOH. Silica gel (70–230 mesh; Merck); Sephadex LH-20 (Sigma); TLC: pre-coated sheets of silica gel 60 F_{254} (Merck); *n*-propyl gallate (Merck); DPPH (Sigma); β-carotene (Merck); linolenic acid (Aldrich); BHT (Merck); pyrogallol (Merck) and α-tocopherol previously isolated and characterized in our laboratory from *M. nutans*.

Plant material

The leaves of *Moldenhawera nutans* were collected in the "Reserva do Parque da Lagoa do Abaeté", Salvador (Bahia) and identified by Prof. Maria Lenise S. Guedes. A voucher is deposited at "Herbarium Alexandre Leal Costa" of Institute of Biology of Federal University of Bahia, under number 0290571.

Extraction and isolation

The dried leaves were powdered (358.32 g) and the powdered material was submitted for maceration in methanol. The methanol extract obtained (18.13 g) was partitioned among hexane/MeOH/H_2O (9:1), $CHCl_3$/MeOH/H_2O (6:4) and AcOEt/H_2O. The ethyl acetate extract (7.76 g) was fractionated by column chromatography (CC) using silica gel as adsorbent and mixtures of $CHCl_3$/EtOAc and EtOAc/MeOH with increasing polarity as eluent. The methyl gallate (2.65 g) was obtained from main CC in the fraction eluted with $CHCl_3$/EtOAc (1:1 v/v) and the gallic acid (1.95 g) was obtained in the fraction eluted with EtOAc followed by subsequent purification through CC on silica gel using $CHCl_3$/MeOH/EtOAc (90:9:1) as eluent. The pure laricetrin (**1**; 19.5 mg) was obtained from main CC in the fraction eluted with EtOAc followed by new CC on silica gel eluted with $CHCl_3$/EtOAc (8:2), and the fractions obtained were purified on Sephadex LH-20 gel permeation using $CHCl_3$/MeOH (1:4) as eluent. From the main CC fraction eluted with EtOAc/MeOH (9:1) laricetrin 5-galloyl-3-β-D-xylopyranoside (**2**; 9.0 mg) was also obtained after CC eluted with $CHCl_3$/MeOH (8:2) followed by gel permeation on Sephadex LH-20 using as mobile phase 20% $CHCl_3$ in MeOH. The substances laricetrin 3-glucoside (**3**; 11.1 mg) and laricetrin 3-galactoside (**4**; 9.8 mg) were purified from main CC using the fraction eluted with EtOAc/MeOH (1:1), after CC on polyamide using MeOH/H_2O (1:1) followed by CC on silica gel and Sephadex LH-20 both eluted with $CHCl_3$/MeOH (1:1) and (1:4), respectively.

Scavenging DPPH radical test

The test to evaluate the ability scavenging to radicals was adapted of that proposed by Malterud *et al.* (1993). This method evaluated the ability of the substance to scavenge the 1,2-diphenyl-2-picryl-hydrazyl (DPPH) free radicals and was carried out according to an established protocol. Briefly the DPPH methanolic solution (45 μg/ml) was mixed with samples in four concentrations and compared with the reference compound (pyrogal-

lol, 5 mg/ml in CH_3OH), which is able to scavenge 100% of DPPH radicals. For each concentration the compounds were evaluated in triplicate. The antioxidant capacity was compared with that observed for standard *n*-propyl gallate and concentration decreasing of DPPH radicals was monitored by a spectrophotometer (λ_{max} = 517 nm) after 15 min and the percentage of inhibition by sample treatment was calculated. The diagram (Fig. 3) of the activity (%) *versus* concentration was plotted and the linear regression was applied to determine the line equation. The extrapolation of the line for 50% of scavenging allowed to determine the concentration of the sample necessary to scavenge 50% (IC_{50}) of DPPH radicals (μM).

Auto-oxidation of β-carotene method

The methodology used in the test of antioxidant activity (AA) was adapted from that previously described by Hidalgo *et al.* (1994). This method of evaluation of the antioxidant activity is based on the inhibition of the auto-oxidation reaction of β-carotene in a linolenic acid solution. The auto-oxidation reaction was recorded by a spectrophotometer at λ_{max} = 470 nm and the activity was compared with 0.45 μM solutions of compounds **1**–**4** and the commercially available antioxidants BHT and α-tocopherol (Table I). The antioxidant percentage was calculated by the equation $AA = 100\,[1-(A_{60}-A_0)/(A°_{60}-A°_0)]$, where A and $A°$ are the measured intensities in the presence and absence of the additive, respectively, and the subindices mean the measured intensities at initial and final (60 min) incubation times.

Methyl gallate ($C_7H_8O_5$): Yellow amorphous powder. – MS: *m/z* (rel int.) = 184 (50), 153 (100), 125 (25), 79 (12). – ^{1}H NMR [300 MHz, CD_3OD, δ (ppm), multiplicity, J (Hz)]: δ = 3.80 (s, $CO_2C\underline{H}_3$), 7.05 (s, H-2 and H-6). – ^{13}C NMR [75 MHz, CD_3OD, δ (ppm)]: δ = 110.1 (C-2, C-6), 121.4 (C-1), 139.7 (C-4), 146.4 (C-3, C-5), 169.1 ($\underline{C}O_2CH_3$), 52.3 ($CO_2\underline{C}H_3$). NMR data are in accordance with the literature (Haddock *et al.*, 1982).

Gallic acid ($C_6H_6O_5$): White amorphous powder. – ^{1}H NMR [300 MHz, CD_3OD, δ (ppm), multiplicity, J (Hz)]: δ = 7.06 (s, H-2 and H-6). – ^{13}C NMR [75 MHz, CD_3OD, δ (ppm)]: δ = 110.9 (C-2, C-6), 122.7 (C-1), 140.1 (C-4), 146.9 (C-3, C-5), 171.0 ($\underline{C}O_2H$). NMR data are in accordance with the literature (Sun *et al.*, 1988; Nawwar *et al.*, 1982).

Laricetrin (**1**; $C_{16}H_{12}O_8$): Yellow amorphous powder. – UV (CH_3OH): λ_{max} = 260.6, 270, 358 nm. – MS: *m/z* (rel. int.) = 332 (100), 317 (7), 303 (9), 289 (5), 262 (14), 205 (7), 136 (14), 107 (14), 97 (10), 69 (40), 55 (35). – ^{1}H NMR [300 MHz, CD_3OD, δ (ppm), multiplicity, J (Hz)]: δ = 6.18 (d, J = 2.0, H-6), 6.39 (d, J = 2.0, H-8), 7.42 (d, J = 1.8, H-6′), 7.46 (d, J = 2.1, H-2′), 3.90 (s, OCH_3). – ^{13}C NMR [75 MHz, CD_3OD, δ (ppm)]: δ = 57.4 ($O\underline{C}H_3$), 95.1 (C-8), 99.9 (C-6), 104.9 (C-10), 105.5 (C-2′), 110.5 (C-6′), 123.6 (C-1′), 138.2 (C-3), 138.4 (C-4′), 148.5 (C-5′), 149.9 (C-3′), 158.4 (C-2), 162.8 (C-9), 165.9 (C-5), 169.7 (C-7), 177.9 (C-4).

Laricetrin 5-galloyl-3-β-D-xylopyranoside (**2**; $C_{28}H_{24}O_{16}$): Yellow amorphous powder. – $[\alpha]_D^{25}$ – 120° (c 1.0 × 10^{-4}, CH_3OH). – UV (CH_3OH): λ_{max} = 269.0, 359.0 nm; ($AlCl_3$): λ_{max} = 269.0, 419.0 nm; ($AlCl_3$ + HCl): λ_{max} = 270.1, 272.0, 363.1, 419.9 nm. – ESIMS: *m/z* (rel. int.) = 639 $[M+Na]^+$ (100). – ^{1}H NMR [300 MHz, CD_3OD, δ (ppm), multiplicity, J (Hz)]: δ = 6.2 (d, J = 2.2, H-6), 6.4 (d, J = 1.9, H-8), 7.13 (s, H-2‴ and H-6‴), 7.22 (d, J = 1.9, H-6′), 7.55 (d, J = 1.9, H-2′), 5.7 (d, J = 6.4, H-1″), 5.54 (dd, J = 6.4, 1.4, H-2″), 3.99 (s, OCH_3), 3.91 (indt., H-3″), 3.89 (indt., H-4″), 3.54 (dd, J = 10.0, 1.0, H-5″). – ^{13}C NMR [75 MHz, CD_3OD, δ (ppm)]: δ = 57.7 ($O\underline{C}H_3$), 66.7 (C-5″), 69.2 (C-4″), 72.1 (C-3″), 74.0 (C-2″), 94.6 (C-8), 99.8 (C-6), 100.1 (C-1″), 105.9 (C-10), 106.9 (C-2′), 110.4 (C-2‴ and C-6‴), 110.8 (C-6′), 121.8 (C-1‴), 121.9 (C-1′), 135.2 (C-3), 138.8 (C-4′), 139.0 (C-4‴), 146.0 (C-3‴ and C-5‴), 146.3 (C-5′), 149.2 (C-3′), 158.3 (C-2), 158.5 (C-9), 162.9 (C-5), 163.7 (C-7), 168.9 (C-7‴), 179.1 (C-4).

Laricetrin 3-β-glucoside (**3**; $C_{22}H_{22}O_{13}$): Yellow amorphous powder. – $[\alpha]_D^{25}$ + 187.5° (c 1.6 × 10^{-4}, CH_3OH). – UV (CH_3OH): λ_{max} = 257.0, 264.1, 361 nm; ($AlCl_3$): λ_{max} = 270.1, 272.0, 435.9 nm; ($AlCl_3$ + HCl): λ_{max} = 270.0, 272.0, 361.0.1, 402.0 nm. – ESIMS: *m/z* (rel. int.) = 493 $[M-H]^+$ (100). – ^{1}H NMR [300 MHz, CD_3OD, δ (ppm), multiplicity, J (Hz)]: δ = 6.14 (d, J = 2.0, H-6), 6.32 (d, J = 2.0, H-8), 7.28 (d, J = 1.8, H-6′), 7.50 (d, J = 1.8, H-2′), 3.91 (s, OCH_3), 5.34 (d, J = 6.0, H-1″), 3.55–3.63 (m, H-2″, H-3″, H-5″), 3,52 (t, J = 6.0 , H-4″), 3.58 (dd, J = 12.3, indt., H-6″), 3.62 (dd, J = 12.3, indt., H-6″). – ^{13}C NMR [75 MHz, CD_3OD, δ (ppm)]: δ = 57.0 ($O\underline{C}H_3$), 94.8 (C-8), 99.9 (C-6), 105.6 (C-10), 106.8 (C-2′), 111.1 (C-6′), 121.8 (C-1′),

135.6 (C-3), 138.7 (C-4′), 146.0 (C-5′), 148.9 (C-3′), 158.2 (C-2), 158.6 (C-9), 162.8 (C-5), 165.8 (C-7), 179.2 (C-4), 62.5 (C-6″), 71.3 (C-5″), 75.8 (C-2″), 78.0 (C-3″), 78.3 (C-4″), 103.9 (C-1″).

Laricetrin 3-β-galactoside (**4**; $C_{22}H_{22}O_{13}$): Yellow amorphous powder. – $[\alpha]_D^{25}$ – 10.0° (*c* 2.0 × 10^{-4}, CH_3OH). – UV (CH_3OH): λ_{max} = 257.9, 260.0, 362.0 nm; ($AlCl_3$): λ_{max} = 270.1, 274.0, 419.1 nm; ($AlCl_3$ + HCl): λ_{max} = 270.1, 274.0, 363.1, 409.0 nm. – ESIMS: *m/z* (rel. int.) = 493 $[M-H]^+$ (100). – ^{1}H NMR [300 MHz, CD_3OD, δ (ppm), multiplicity, *J* (Hz)]: δ = 6.14 (d, *J* = 2.0, H-6), 6.32 (d, *J* = 2.0, H-8), 7.34 (d, *J* = 1.8, H-6′), 7.54 (d, *J* = 1.8, H-2′), 3.91 (s, OCH_3), 5.24 (d, *J* = 7.5, H-1″), 3.55–3.63 (m, H-2″, H-3″, H-5″), 3,83 (dd, *J* = 4.2, 2.1, H-4″), 3.73 (dd, *J* = 10.0, 5.4, H-6_a″), 3.77 (dd, *J* = 10.0, 2.4, H-6_b″). – ^{13}C NMR [75 MHz, CD_3OD, δ (ppm)]: δ = 57.1 ($O\underline{C}H_3$), 94.8 (C-8), 99.9 (C-6), 105.6 (C-10), 106.8 (C-2′), 111.1 (C-6′), 121.7 (C-1′), 135.7 (C-3), 138.7 (C-4′), 145.9 (C-5′), 148.8 (C-3′), 158.1 (C-2), 158.5 (C-9), 162.8 (C-5), 165.8 (C-7), 179.2 (C-4), 61.8 (C-6″), 69.7 (C-4″), 72.9 (C-2″), 74.7 (C-3″), 76.8 (C-5″), 104.8 (C-1″).

Acknowledgements

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), IMSEAR (Instituto do Milênio do Semi-Árido) and to Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB) for financial support and fellowship. We were in debt to Prof. Dr. Norberto P. Gallegari (FCF-USPRP) for ESIMS and to Prof. Dr. Edilbero R. Silveira (CENAUREAMN-UFC) for the bidimensional spectra.

Agrawal P. K. (1992), NMR spectroscopy in the structural elucidation of oligosaccharides and glycosides. Phytochemistry **31**, 3307–3330.

David J. P., David J. M., Yang S. W., and Cordell G. A. (1999), A bis-labdenic diterpene from *Moldenhawera nutans*. Phytochemistry **50**, 443–447.

Exarchou V., Troganis A., Gerothanassis I. P., Tsimidou M., and Boskou D. (2002), Do strong intramolecular hydrogen bonds persist in aqueous solution? Variable temperature gradient ^{1}H, ^{1}H–^{13}C GE-HSQC and GE-HMBC NMR studies of flavonols and flavones in organic and aqueous mixtures. Tetrahedron **58**, 7423–7429.

Haddock E. A., Gupta R. K., Al-Shafi S. M. K., Haslam E., and Magnolato D. (1982), The metabolism of gallic acid and hexahydroxydiphenic acid in plants. 1. Introduction – Naturally-occurring galloyl esters. J. Chem. Soc. Perkin Trans. 1, 2515–2524.

Harbone J. B., Boaedley M., and Linder H. P. (1985), Variations in flavonoid patterns within the genus *Chondropetalum* (Restionaceae). Phytochemistry **24**, 273–278.

Hidalgo M. E., Fernández E., Quilhot W., and Lissi E. (1994), Antioxidant activity of depsides and depsidones. Phytochemistry **37**, 1585–1587.

Khetwal K. S., Manral K., and Verma D. L. (1988), Flavonoids from the roots of *Sedum cressipes*. Planta Med. **54**, 89–90.

Malterud K. E., Farbrot T. L., Huse A. E., and Sund R. B. (1993), Antioxidant and radical scavenging effects of anthraquinones and anthrones. Pharmacology **47**, 77–85.

Markhan K. R. and Geiger H. (1994), ^{1}H nuclear magnetic resonances spectroscopy of flavonoids and their glycosides in hexadeuterodimethylsulfoxide. In: The Flavonoids – Advances in Reseach since 1986 (Harbone J. B., ed.). Chapman & Hall, New York, pp. 441–498.

Markhan K. R., Ternai B., Stanley R., Geiger H., and Mabry T. J. (1978), Carbon-13 NMR studies of flavonoids. – III. Naturally occuring flavonoid glycosides and their acylated derivatives. Tetrahedron **34**, 1389–1397.

Nawwar M. A. M., Buddrus J., and Bauer H. (1982), Dimeric phenolic constituents from the roots of *Tamarix nilotica*. Phytochemistry **21**, 1755–1758.

Niemann G. J. (1973), Flavonoids from needles of *Larix leptolepis*. Phytochemistry **12**, 2056.

Pietta P. G. (2000), Flavonoids as antioxidants. J. Nat. Prod. **63**, 1035–1042.

Queiroz L. P., Lewis G. P., and Allkin R. (1999), A revision of the genus *Moldenhawera* Schrad (Leguminosae – Caesalpinoideae). Kew Bulletin **54**, 817–852.

Slimestad R., Andersen O. M., Francis G. W., Marston A., and Hostettmann K. (1995), Syringetin 3-*O*-(6″-acetyl)-β-glucopyranoside and other flavonols from needles of Norway spruce, *Picea abies*. Phytochemistry **40**, 1537–1542.

Sun D., Zhao Z., Wong H., and Foo L. Y. (1988), Tannins and other phenolics from *Myrica esculaenta* Bark. Phytochemistry **27**, 579–583.