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CHEMOSYSTEMATICS OF *RHABDODENDRON**

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Key Word Index—*Rhabdodendron macrophyllum*; *R. amazonicum*; Rhabdodendraceae; triterpenoids; *O*-methylflavellagic acids; dehydroxyflavellagic acid ether; Rosiflorae; Myrtiflorae.

Abstract—Analysis of *Rhabdodendron amazonicum* gave two new compounds, 5′-methoxy-3,4,5,3′-tetra-*O*-methylflavellagic acid and 3,3′-didehydroxy-5-*O*-methylflavellagic acid, and confirmed the triterpenoid and *O*-methylflavellagic acid based compositon of the Rhabdodendraceae. Chemically this family fits into the Rosiflorae or even better into the Myrtiflorae.

INTRODUCTION

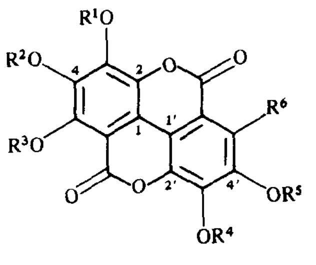
The family Rhabdodendraceae has a fascinating taxonomic history (Table 1). Its four species, collected in South America by Gardner and Spruce, were considered by Bentham in 1853 to be congeneric with De Candolle's genus *Lecostemon* and to belong to the Chrysobalanaceae of the order Rosales [9]. Although later authors called attention to the morphological distinctiveness of the group, placing it in its own subtribe, tribe, or subfamily and even referring it to the Phytolaccaceae, order Caryophyllales, the basic situation remained unchanged for about 50 years, when Gilg and Pilger renamed *Lecostemon sensu* Bentham *Rhabdodendron* and placed the genus near the tribe Cusparieeae of the Rutaceae, order Rutales. Although again later authors wished to separate the group into its own tribe or even subfamily, the situation remained practically unchanged for nearly 80 years. Meanwhile Prance excluded *Rhabdodendron* from both Chrysobalanaceae and Rutaceae and established a new family Rhabdodendraceae for it [9]. He also placed his family in the order Caryophyllales near to the Phytolaccaceae. However, the last word on the matter belongs to Cronquist [2, 10] who in 1981 placed Rhabdodendraceae into the Rosales. In spite of all this work, there are indications that the problem is still unresolved. Indeed Dahlgren accepts Gilg and Pilger's *Rhabdodendron*, Prance's Rhabdodendraceae and Bentham's and Cronquist's Rosales, but adds "position uncertain" [3].

In a previous paper we described a phytochemical analysis of *R. macrophyllum* [1]. The present paper reports our results on *R. amazonicum*, again in the hope that the chemical data will illuminate the problem of accommodation of the family into an appropriate order.

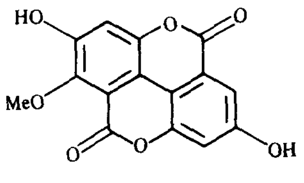
RESULTS

The comparison of the chemical composition of *R. macrophyllum* and *R. amazonicum* (Table 2) reveals the presence of the novel compounds **6c** and **7** in the latter.

The mass spectrum of **6c** shows the molecular ion peak at *m/z* 404, compatible with the formula $C_{19}H_{16}O_{10}$. The ^1H NMR spectrum consists of three singlets, one at low field (δ10.52) assigned to an aromatic hydroxyl and two



6a $R^1 = R^2 = R^4 = Me, R^3 = R^5 = R^6 = H$
6b $R^1 = R^2 = R^4 = Me, R^3 = R^5 = H, R^6 = OMe$
6c $R^1 = R^2 = R^3 = R^4 = Me, R^5 = H, R^6 = OMe$



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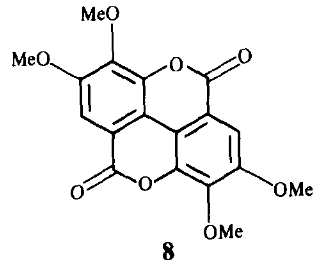

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*Part 2 in the series "The Chemistry of Brazilian Rhabdodendraceae". For Part 1 see ref. [1].

Table 1. Taxonomic history of the family Rhabdodendraceae Prance and the genus *Rhabdodendron* Gilg. & Pilg. (ex *Lecostemon sensu* Benth.)

Order	Family	Additional information	Species	References
Rosales	Chrysobalanaceae		1–4	Bentham 1853
		Chrysobalaneae		Mueller 1858
		Chrysobalanoideae*		Baillon 1868
		separate tribe		Fritsch 1888
		separate tribe		Hallier 1903
		Chrysobalaninae*		Focke 1888
			5	Gleason 1927
	Rhabdodendraceae			Cronquist 1981 [2]
	Rhabdodendraceae	position uncertain		Dahlgren 1983 [3]
Rutales	Rutaceae	Cusparieae	7	Gilg, Pilger 1905
		Rhabdodendreae	6, 8, 10	Huber 1909
		idem		Krause 1914
		idem	2	Ducke 1922
		Rhabdodendroideae		Engler 1931
			6 (=5), 9, 10	Sandwith 1943
				Maguire 1948
				Takhtajan 1969 [4]
				Dahlgren 1980 [5]
				Puff, Weber 1976 [6]
		Rhabdodendroideae		Thorne 1983 [7]
	Rhabdodendraceae			Takhtajan 1980 [8]
Caryophyllales	Phytolaccaceae			Record 1934
	Rhabdodendraceae		6, 8–10	Prance 1968 [9]

Notes: For all refs to material published prior to 1968 see Prance [9].

*Affinity with Phytolaccaceae suggested; *Lecostemon* species: 1 *amazonicum*, 2 *crassipes*, 3 *gardneranum*, 4 *macrophyllum*, 5 *sylvestre*; *Rhabdodendron* species: 6 *amazonicum*, 7 *columnare*, 8 *crassipes*, 9 *gardneranum*, 10 *macrophyllum*, 11 *sylvestre*.

Table 2. Constituents of *Rhabdodendron* species

	R. macrophyllum [1]			*R. amazonicum*		
	Leaves	Branches	Roots	Leaves	Branches	Roots
Dry powdered plant material	3.6 kg	0.5 kg	1.4 kg	0.4 kg	0.6 kg	2.4 kg
EtOH extract	13 g	26 g	76 g	15 g	30 g	128 g
Triterpenoids						
24-methylenecycloartenol (**1**)	875 mg			1.4 g		
oleanolic acid* (**2**)	1 g	3.9 g	4.9 g	1.7 g	4.3 g	1.5 g
3-*O*-acetylaleuritolic acid (**3**)		1.9 g	6 g		2.6 g	6.5 g
hederagenin* (**4**)		86 mg	76 mg		50 mg	20 mg
arjunolic acid* (**5**)		380 mg			100 mg	40 mg
Ellagic acids						
3,4,3′-tri-*O*-methylflavellagic acid (**6a**)			157 mg			210 mg
5′-methoxy-3,4,3′-tri-*O*-methylflavellagic acid (**6b**)			280 mg			280 mg
5′-methoxy-3,4,5,3′-tetra-*O*-methylflavellagic acid (**6c**)						30 mg
3,3′-didehydroxy-5-*O*-methylflavellagic acid (**7**)						50 mg
3,4,3′,4′-tetra-*O*-methylellagic acid† (**8**)			20 g			4 g

*After hydrolysis of glycosides.

†After *O*-methylation of a mixture.

at δ4.30 and 4.06 assigned respectively to six and nine methoxyl protons. Hence the formula can be expanded to $C_{14}O_4OH(OMe)_5$. The compound is thus an ellagic acid derivative, as was confirmed by IR and UV spectra. Among the three alternative structures only **6c** is compatible with several additional facts: two and not only one methoxyl is strongly deprotected (δ4.30) byadjacent carbonyls. Besides, the UV spectrum was unchanged in the presence of NaOAc or $AlCl_3$ + HCl. Thus the hydroxyl cannot be situated at C-3′ or C-5′. Its placement at C-4′

was confirmed by a strong bathochromic UV shift upon addition of NaOEt [11].

As shown by IR and UV spectra, **7** is again of the ellagic acid structural type. The MS of its diacetate showed a molecular ion peak at *m/z* 384, compatible with the formula $C_{19}H_{12}O_9$ or, in expanded form, $C_{14}H_3O_4OMe(OAc)_2$. One of the aromatic protons must be located at C-5′, the adjacent carbonyl being responsible for the one proton resonance at low field (δ7.86). Thus C-5 cannot have a proton attached. As no UV shift is observed upon addition of $AlCl_3 + HCl$ to the original compound **7**, C-5 can also not be hydroxylated and must consequently be substituted by the methoxyl. No *ortho* splitting of the aromatic proton signals is observed and the acetoxyls (or hydroxyls in **7**) must hence occupy positions 4 and 4′. In consequence the two remaining aromatic protons are nearly symmetrical. Evidence for this fact is given by the ^1H NMR spectrum of the diacetate in which both are represented by a sole signal at δ6.25.

DISCUSSION

We have now shown that from the chemosystematic point of view the Rhabdodendraceae does not fit into either the Rutales [12] or the Caryophyllales [1]. The inclusion of the family in the Rosales is more consistent with our data. Indeed ellagic acid is the classical systematic marker of this order [13]. However, *O*-alkylated ellagic acid derivatives are of restricted occurrence [1] and are accumulated chiefly in the major families of the Myrtales (Combretaceae, Melastomataceae. Myrtaceae, Punicaceae, Sonneratiaceae) and the Rhizophorales (Rhizophoraceae) [14]. Dahlgren considers that there is a strong affinity between the Rosiflorae and the Myrtiflorae [5] and it is in the latter superorder that it would be appropriate to include the Rhabdodendraceae on the basis of their micromolecular composition.

EXPERIMENTAL

Isolation and identification of the constituents. Material of *Rhabdodendron amazonicum* was collected near Itacoatiara, Manaus, Amazonas, and identified by Dr. William A. Rodrigues (Voucher: INPA Herbarium no 93.911). Leaves, branches and roots were worked-up and compounds **1–5**, **6a**, **6b** and **8** were identified as described for *R. macrophyllum* [1].

5′-Methoxy-3,4,5,3′-tetra-O-methylflavellagic acid (**6c**). Mp 218–220° dec. (dioxane, MeOH). IR λ_{max}^{KBr} cm^{-1}: 3300, 1715, 1698, 1612, 1580, 1520, 1480, 1456, 1428, 1387, 1352, 1240, 1200, 1160, 1080, 1050, 980, 950, 770. UV λ_{max}^{EtOH} nm (ε): 249 (31 800), 370 (9700), 382 (9450); $\lambda_{max}^{EtOH + NaOH}$ nm (ε): 246 (36650), 418 (11000); $\lambda_{max}^{EtOH + AlCl_3}$ nm (ε) : 249 (35 050), 411 (11 800); no NaOH + HCl, NaOAc and $AlCl_3 + HCl$ shifts. ^1H NMR (60 MHz, $CDCl_3$) : 10.52 (*s*, ArOH), 4.30 (*s*, 2 OMe), 4.06 (*s*, 3 OMe). MS *m/z* (rel. int.): 404 (M^+, 11), 389 (22), 374 (100), 346 (33), 331 (27), 301 (12), 373 (51).

3,3′-Didehydroxy-5-O-methylflavellagic acid (**7**). Mp 306–309° dec. (MeOH). UV λ_{max}^{EtOH} nm (ε): 250 (38 700), 348 infl. (8600), 360 (10 850); no NaOAc, $H_3BO_3 + NaOAc$ and $AlCl_3 + HCl$ shifts. Diacetate. Mp 239–241° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 1760, 1725, 1618, 1589, 1492, 1410, 1340, 1250, 1180, 1150, 1097, 897. ^1H NMR (60 MHz, $CDCl_3$) δ: 7.86 (*s*, H-5′), 6.25 (*s*, H-3,3′), 4.17 (*s*,OMe), 2.37, 2.29 (2*s*, 2 OAc). MS *m/z* (rel. int.): 384 (M^+, 22), 342 (100), 327 (18), 300 (13), 299 (12), 285 (13), 257 (11).

REFERENCES

1. Wolter-Filho, W., Rocha, A. I. da, Yoshida, M. and Gottlieb, O. R. (1985) *Phytochemistry* **24,** 1991.
2. Cronquist, A. (1981) *An Integrated System of Classification of Flowering Plants*, p. 585. Columbia University Press, New York.
3. Dahlgren, R. (1983) *Nord. J. Bot.* **3,** 119.
4. Takhtajan, A. (1969) *Flowering Plants – Origin and Dispersal*, p. 225. Smithsonian Institution Press, Washington.
5. Dahlgren, R. (1980) *Bot. J. Linn. Soc.* **80,** 91.
6. Puff, G. and Weber, A. (1976) *Pl. Syst. Evol.* **125,** 195.
7. Thorne, R. F. (1983) *Nord. J. Bot.* **3,** 85.
8. Takhtajan, A. (1980) *Bot. Rev.* **46,** 225.
9. Prance, G. T. (1968) *Bull. Jard. Bot. Natl Belg.* **38,** 127.
10. Cronquist, A. (1983) *Nord. J. Bot* **3,** 75.
11. Scott, A. I. (1964) *Interpretation of the Ultraviolet Spectra of Natural Products*, p. 145. Pergamon Press, Oxford.
12. Silva, M. F. das G. F. da, Gottlieb, O. R. and Ehrendorfer, F. (1988) *Plant Syst. Evol.* **161,** 97.
13. Bate-Smith, E. C. (1984) *Phytochemistry* **23,** 945.
14. Lowry, J. B. (1968) *Phytochemistry* **7,** 1803.