petrol–EtOAc mixtures and EtOAc, giving: herniarin (50 mg), naringenin (30 mg), dihydroquercetin-7,3′-dimethylether (63 mg), palmatin (210 mg), 5,3′-4′-trihydroxy-7-methoxyflavanone (50 mg), rhamnetin (90 mg), 2,4-diacetylanisole (195 mg), dehydroespeletone (600 mg) and glutinosol (155 mg).

2,4-*Diacetylanisole*. Mp 85° (EtOAc–hexane), UV λ_{max} nm: 273 (ε 10.000), 268 (ε 6.456), 310 (ε 1.349). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670 (C=O), 1600 (aromatic); ^{1}H NMR (Table 1); MS m/z (%) 192: $[M]^+$ (23), 177 $[M-Me]^+$ (100), 119 (44) and 91 (80).

Glutinosol (**1**). Mp 119°; UV λ_{max} nm: 252 (ε 27.542), 279 (ε 10.715), 320 (ε 4.570); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1660, 1640 (C=O), 1450 (Ph-OMe), 1360 (Ph-COMe); ^{1}H NMR (Table 1); MS m/z (%): 266 $[M]^+$ (5), 251 $[M-Me]^+$ (5), 248 $[M-H_2O]^+$ (2), 208 $[M-C_3H_6O]^+$ (10), 193 $[M-C_4H_9O]^+$ (100), 175 (37), 135 (9). Acetylation of 35 mg (Ac_2O–pyridine, 2 hr, 60°) yielded the starting product. With Ac_2O–NaOAc, 12 hr at 70°, two acetates were obtained, one being oily (21.3 mg) **2**; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (ester), 1685, 1610 (C=C), 1600 (aromatic); ^{1}H NMR ($CDCl_3$): δ 2.33 (3H, *s*); MS m/z (%): 290 $[M]^+$ (16), 248 (31), 247 (42), 233 (73), 231 (38), 230 (40), 215 (70), 205 (100), 193 (87), 175 (49). The other acetate was crystalline, **3** (15 mg), mp 78–80° (Et_2O–hexane); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (OH), 1770 (ester), 1680, 1600, 1460, 1360 and 1160; ^{1}H NMR ($CDCl_3$): δ 2.35 (3H, *s*); MS m/z (%): 308 $[M]^+$ (1), 266 (3), 251 (5), 247 (11), 248 (12), 233 (13), 208 (11), 205 (29), 193 (100), 175 (22), 149 (29), 91 (27).

Treatment of **1** (90 mg) with dry Me_2CO (5 ml), dry K_2CO_3 (0.5 g) and Me_2SO_4 (0.2 ml) with heating for 5 hr gave the Me ether, **4** (71 mg), mp 130–132° (EtOAc–hexane); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1650 (C=O), 1600 (aromatic), 1450 (-OMe); ^{1}H NMR (Table 1); $[M]^+$ 280 ($C_{15}H_{20}O_5$).

REFERENCES

1. Tutin, T. G. *et al.* (ed.) (1976) *Flora Europea* Vol 4, p. 186. Cambridge University Press, Cambridge.
2. Bhatt, M. R. and Shah, N. M. (1956) *J. Indian Chem. Soc.* **33**, 318.
3. Bohlmann, F. and Rao, N. (1973) *Chem. Ber.* **106**, 3035.
4. Bohlmann, F. and Mahanta, P. (1979) *Phytochemistry* **8**, 348.

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DIBENZYLBUTYROLACTONE LIGNANS FROM *VIROLA SEBIFERA**

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Key Word Index—*Virola sebifera*; Myristicaceae; seeds, pericarp; dibenzylbutyrolactone lignans.

Abstract—The fruits of *Virola sebifera* contain in the seed (2*R*, 3*S*)-3-(3,4-dimethoxybenzyl)-2-(3,4-methylenedioxybenzyl)-butyrolactone, and in the pericarp (2*R*, 3*R*)-3-(3,4-dimethoxybenzyl)-2-(3,4-methylenedioxybenzyl)-butyrolactone, (2*R*, 3*R*)-2,3-di-(3, 4-dimethoxybenzyl)-butyrolactone and (2*R*, 3*R*)-2,3-di-(3,4-methylenedioxybenzyl)-butyrolactone.

The seeds of *Virola sebifera* Aubl. were found to contain, besides the previously reported 1,11-diarylundecan-1-one and 4-aryltetralone neolignans [2], the *cis*-dibenzylbutyrolactone lignan, **1**. In the pericarp, however, two equally novel *trans*-dibenzylbutyrolactone lignans (**2a**, **2b**) were found to accompany (−)-hinokinine (**2c**).

The IR carbonyl absorptions (ν_{max} 1773 ± 6 cm^{-1}) of all four isolates suggested the presence of a butyrolactone system. Indeed, as ^{13}C NMR evidence (Table 1) suggests by comparison with the known derivative **2c** [3], all compounds must be 2,3-dibenzylbutyrolactones. The nature of the substituents at C-2 and C-3 can be determined by mass spectrometry [4] (Table 2). According to Corrie *et al.* [5], relative configurations in 2,3-dibenzylbutyrolactones are given by NMR comparison of the methylene protons at C-4. Equivalence of these protons corresponds to the *cis*-configuration, while non-equivalence corresponds to the *trans*-configuration. In this respect, **1** as well as the model compound **3** [5, 6], must be *cis*-oriented, while **2a**–**2c** as well as the model compound **2d** [4] must be *trans*-oriented (Table 3). Finally, the opposite ORD curves for the *cis*-derivative **1** ($[\phi]_{276}^{pk} -500$, $[\phi]_{300}^{tr} -2700$), and the model compound **3** ($[\phi]_{272}^{tr} +2300$, $[\phi]_{295}^{pk} +4500$) [6] establish the absolute configuration of the former. The ORD curves of the *trans*-derivatives **2a** and **2b** are comparable with the curves of the model compounds **2c** and **2d** [6].

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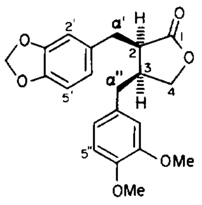
*Part XIX in the series "The Chemistry of Brazilian Myristicaceae". For Part XVIII see ref. [1]. Taken from part of the doctorate thesis presented by L. M. X. L. to the Universidade de São Paulo (1982).

Table 1. ^{13}C NMR data of dibenzylbutyrolactone lignans (20 MHz, $CDCl_3$, δ)

Carbons	1	2a	2b	2c [3]
1	178.0	177.5	178.0	177.9
2	46.1	45.5	46.1	46.1
3	41.0	40.5	40.7	41.0
4	70.8	70.3	70.7	70.7
α′	34.5	33.9	34.1	34.4
α″	37.9	37.2	37.7	37.9
1′	131.1	130.9	130.3*	131.2*
1″	130.3	130.1	130.0*	131.0*
2′	109.1	108.7	112.6	108.4
2″	111.9	111.6	112.0	109.0
3′	147.2	147.0	148.9	147.4
3″	149.0	148.5	148.9	147.4
4′	145.6	145.6	147.7	145.8
4″	147.2	147.3	147.7	146.0
5′	107.8	107.2	111.2	107.8
5″	111.5	111.2	111.4	107.8
6′	121.9	121.4	121.1	121.1
6″	120.4	120.0	120.3	121.8
CH_2O_2	100.6	100.6	—	100.6
CH_2O_2	—	—	—	100.6
MeO	55.8	55.1	55.5	—
MeO	55.7	55.0	55.5	—
MeO	—	—	55.5	—
MeO	—	—	55.5	—

*May be interchanged.



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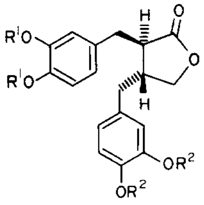
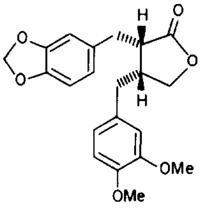


2a $R'–R'=CH_2$, $R^2=Me$
2b $R'=R^2=Me$
2c $R'–R'=R^2–R^2=CH_2$
2d $R'=Me$, $R^2–R^2=CH_2$



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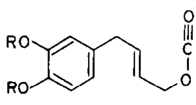

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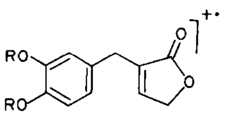

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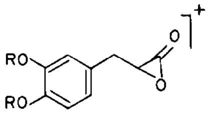

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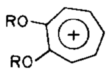

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Table 2. Mass spectral data of dibenzylbutyrolactone lignans [*m/z* (rel. int.)]

		Fragment ions				
Compound	$M^{+\cdot}$	4	5	6	7	
1	370 (25)	219 (3)	218 (10)	192 (15)	151 (75)	135 (100)
2a	370 (50)	219 (10)	218 (2)	192 (6)	151 (88)	135 (100)
2b	386 (30)	235 (7)	234 (5)	208 (3)	151 (100)	135 (2)
2c	354 (45)	219 (10)	218 (8)	192 (14)	—	135 (100)

Table 3. ^1H NMR data of dibenzylbutryolactone lignans (**2d** at 100 MHz, all others at 60 MHz, $CDCl_3$, single δ values refer to singlets and ranges to multiplets; *br* indicates broad singlet)

Protons	1	3 [5]	2a	2b	2c	2d [4]
2, 3 α′, α″	2.3–3.2	2.2–3.3	2.2–2.9	2.3–3.1	2.2–3.0	2.2–3.2
4	3.90 *br*	4.04 *br*	3.5–4.1	3.7–4.3	3.5–4.2	4.0–4.2
Ar	6.4–6.8	6.5–7.0	6.3–6.7	6.4–6.9	6.2–6.7	6.4–6.8
CH_2O_2	5.88	5.97	5.83	—	5.83	5.88
CH_2O_2	—	—	—	—	5.83	—
MeO	3.80	3.83	3.67	3.84	—	3.82
MeO	3.83	3.83	3.65	3.84	—	3.82
MeO	—	—	—	3.84	—	—
MeO	—	—	—	3.84	—	—

EXPERIMENTAL

Isolation of constituents. Fractionation of a seed extract [2] was carried out by dry CC. The column was cut into 33 portions. Portions 15–23, purified by repeated TLC, gave a major constituent (2.1 g [2]). Elution of one of the remaining bands on the plate gave **1** (35 mg). An additional quantity of fruits was collected from a specimen growing near Cajuru, São Paulo State, by Hipolito F. Paulino Filho, UNESP, Araraquara. The seeds were removed and the pericarp was dried, reduced to powder (1 kg) and extracted with C_6H_6 at room temp. The solvent was evaporated and the residue (31 g) crystallized from MeOH to give acylglycerols (10 g). The mother liquor was evaporated and the residue (21 g) submitted to dry CC (400 g Si gel, $CHCl_3$–EtOAc, 19:1). The column was cut into three equal portions which were extracted with MeOH. Evaporation of the solns gave three residues corresponding to the lower (L), the middle (M) and the top (T) portions of the column. The residue L (7.1 g) was, in part (1.6 g), separated by TLC (Si gel, $CHCl_3$–EtOAc, 9:1) into **2a** (130 mg) and **2c** (120 mg). The residue M (6.8 g), chromatographed on a Si gel column, gave **2b** (300 mg); besides other products which, as also the residue T (5.5 g), were not further examined.

(2R, 3S)-3-(3,4-*Dimethoxybenzyl*)-2-(3,4-*methylenedioxybenzyl*)-*butyrolactone* (**1**). Mp 125–126° (MeOH). UV λ_{max}^{MeOH} nm: 230, 279 (ε 22 000, 10 900). IRν_{max}^{film} cm^{-1}: 1767, 1590, 1485, 1440, 1235, 935. $[\alpha]_D^{25}$ $-8.8°$ ($CHCl_3$; c 0.114). ORD (dioxane; c 0.003): $[\phi]_{240}^{tr}$ $-13\,600$, $[\phi]_{276}^{pk}$ -500, $[\phi]_{300}^{tr}$ -2700.

(2R, 3R)-3-(3,4-*Dimethoxybenzyl*)-2-(3,4-*methylenedioxybenzyl*)-*butyrolactone* (**2a**). Viscous oil. UV λ_{max}^{MeOH} nm: 229, 280 (ε 15 800, 8250). IR ν_{max}^{film} cm^{-1}: 1774, 1590, 1500, 1450, 1250, 945. $[\alpha]_D^{25}$ $-26.3°$ ($CHCl_3$; c 0.144). ORD (dioxane; c 0.004): $[\phi]_{240}^{tr}$ $-13\,650$, $[\phi]_{283}^{pk}$ -250, $[\phi]_{300}^{tr}$ -2950.

(2R, 3R)-2,3-*Di*-(3,4-*dimethoxybenzyl*)-*butyrolactone* (**2b**). Mp 127–128° (MeOH). UV λ_{max}^{MeOH} nm: 229, 277 (ε 17 400, 7150). IR ν_{max}^{film} cm^{-1}: 1778, 1590, 1510, 1450, 1250. $[\alpha]_D^{25}$ $-39.0°$($CHCl_3$; c 0.180). ORD (dioxane; c 0.006): $[\phi]_{243}^{tr}$ $-12\,700$, $[\phi]_{280}^{pk}$ -600, $[\phi]_{297}^{tr}$ -3200.

(2R, 3R)-2,3-*Di*-(3,4-*methylenedioxybenzyl*)-*butyrolactone* ((−)-*hinokinin* [7], **2c**). Mp 92–95° (MeOH). UV λ_{max}^{MeOH} nm: 232, 284 (ε 13 500, 10 600). IR ν_{max}^{film} cm^{-1}: 1778, 1590, 1500, 1250. $[\alpha]_D^{25}$ $-26.3°$ ($CHCl_3$; c 0.123). ORD (dioxane; c 0.004): $[\phi]_{250}^{tr}$ $-10\,900$, $[\phi]_{282}$ 0, $[\phi]_{285}^{pk}$ $+400$, $[\phi]_{287}$ 0, $[\phi]_{300}^{tr}$ -4850.

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REFERENCES

1. Braz Fo., R., Carvalho, M. G. de and Gottlieb, O. R. *Acta Amazonica* (in press).
2. Lopes, L. M. X., Yoshida, M. and Gottlieb, O. R. (1982) *Phytochemistry* **21**, 751.
3. Wenkert, E., Gottlieb, H. E., Gottlieb, O. R., Pereira, M. O. da S. and Formiga, M. D. (1976) *Phytochemistry* **15**, 1547.
4. McDoniel, P. B. and Cole, J. R. (1972) *J. Pharm. Sci.* **61**, 1992.
5. Corrie, J. E. T., Green, G. H., Ritchie, E. and Taylor, W. C. (1970) *Aust. J. Chem.* **23**, 133.
6. Burden, R. S., Crombie, L. and Whiting, D. A. (1969) *J. Chem. Soc. C* 693.
7. Haworth, R. D. and Woodcock, D. (1938) *J. Chem. Soc.* 1985.

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A BIFLAVONOID FROM *SEMECARPUS ANACARDIUM**

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Key Word Index—*Semecarpus anacardium*; Anacardiaceae; biflavanones; ^{1}H NMR and mass spectra; semecarpuflavanone.

Abstract—A new biflavonoid, semecarpuflavanone, has been isolated from the nut shells of *Semecarpus anacardium*. Its structure has been assigned on the basis of chemical and spectroscopic evidence.

Two new compounds **4** and **5**, besides the three known biflavanones [1] **1**–**3**, have been isolated from the acetone soluble fraction of an ethanolic extract of the defatted nut shells of *Semecarpus anacardium* L. The structure of **4** has already been assigned [2]. The present study deals with the structural determination of **5**.

Compound **5** appeared as a micro-crystalline pale yellow powder from acetone, $C_{30}H_{22}O_{10}$, mp 248–249° and has been named semecarpuflavanone. It gave a greenish-violet ferric reaction, a pinkish-red colour with

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*Part 4 in the series "Naturally Occurring Biflavonoid Derivatives". For Part 3 see ref. [2].

†Chemical shifts throughout this communication in δ values.