Phytochemistry, 1979, Vol. 18, pp. 815–817. © Pergamon Ptess Ltd. Printed in England. 0031-9422/79/0501-0815 $02.00/0

ISOFLAVONOIDS FROM *MYROXYLON PERUIFERUM**

AURÉLIO MARANDUBA†, ALAÍDE B. DE OLIVEIRA, GEOVANE G. DE OLIVEIRA, JOÃO E. DE P. REIS and OTTO R. GOTTLIEB‡

Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil

(*Received* 25 *May* 1978)

Key Word Index—*Myroxylon peruiferum*; *M. balsamum*; Leguminosae–Lotoideae; isoflavonoids.

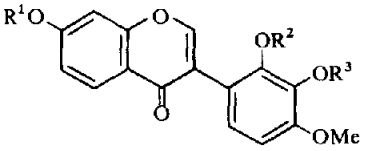
Abstract—Considerable differences in flavonoid composition of the trunkwood characterize different specimens of *Myroxylon balsamum* (L.) Harms. Only calycosin among the 11 flavonoids found in *M. peruiferum* L.f., presently considered synonymous with *M. balsamum*, had previously been located in the latter species. Two of these flavonoids, 2′-hydroxy-7,3′,4′-trimethoxyisoflavanone and 2′-hydroxy-7,3′,4′-trimethoxyisoflavone are new natural products.

INTRODUCTION

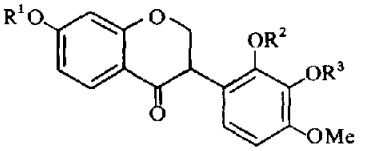
Although *ca* 6 species of the genus *Myroxylon* L.f. (Leguminosae–Lotoideae) have been described, Harms [2] recognized only *M. peruiferum* L.f. from Colombia to Bolivia and Brazil and *M. balsamum* (L.) Harms from Mexico to Venezuela and Colombia. These two species can be distinguished by their seeds, which have grooved and smooth cotyledons, respectively. According to this criterion, the copious Brazilian material belongs to *M. peruiferum* [3], the name referring to the country which exported its balsam following the arrival of the first Spanish explorers. The significance of the seed character for the distinction of otherwise morphologically indistinguishable species was later denied by Record and Hess [4] as well as by Ducke [5], who recognized only *M. balsamum* as a widespread, polymorphous species.

RESULTS AND DISCUSSION

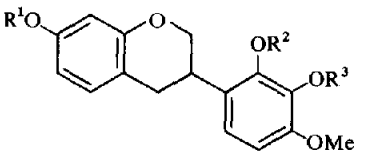
The trunkwood of a specimen earlier classified as *M. peruiferum* gave an essential oil composed predominantly of (+)-nerolidol [6]. The specimen analysed in the present work by solvent extraction, and also classified as *M. peruiferum* by Apparício Pereira Duarte from the Rio de Janeiro Botanical Garden, again contained nerolidol, in addition to vanillin and the flavonoids listed in Table 1 (specimen 1). Specimens 2 and 3 were originally classified by the same botanist as *M. balsamum*. Clearly, while specimens 1 and 2 are chemically related, specimen 3 shows a quite different composition. Indeed of 19 compounds, only one is shared by specimens 1 and 3. At this stage it is impossible to recheck the precise morphology of the analysed specimens. The present work is nevertheless useful, since it demonstrates the considerable differences which characterize different forms or species in the *M. balsamum* group.



1



2



3

a $R^1 = R^3 = Me$, $R^2 = H$
b $R^1 = R^2 = Me$, $R^3 = H$
c $R^1 = R^2 = R^3 = Me$
d $R^1 = R^3 = Bz$, $R^2 = Me$
e $R^1 = R^3 = H$, $R^2 = Me$
f $R^1 = R^3 = Me$, $R^2 = Ac$

The structure of **1a** (Table 1), $C_{15}H_6O_2.OH(OMe)_3$, was deduced by spectral evidence, including the diagnostic isoflavone H-2 PMR singlet at τ 2.2 of the acetate in $CDCl_3$ and the retro-Diels-Alder fragments *m/e* 151 and 178, which revealed the distribution of OMe vs $OH(OMe)_2$ respectively on rings A and B. The precise oxygenation pattern was ascertained by PMR data and

* Part LVI in the series "The Chemistry of Brazilian Leguminosae". For Part LV see ref. [1]. Based on theses submitted by A.M. and J.E. de P.R. to Universidade Federal de Minas Gerais, Belo Horizonte (1977). Sponsored by CNPq and FINEP through contract FNDCT No. 154.

† Instituto de Ciências Exatas, Universidade Federal de Juiz de Fora, Juiz de Fora, MG.

‡ Instituto de Química, Universidade de São Paulo, c.p. 20780, São Paulo, SP.

Table 1. Distribution of flavonoids in *Myroxylon*

Compound type name	Substitution pattern 5	6	7	8	2′	3′	4′	5′	Specimen 1	2 [7]	3 [1]
Chalcone											
Isoliquiritigenin*	—	—	OH	—	—	—	OH	—	+		
Aurone											
Sulfuretin†	—	—	OH	—	—	OH	OH	—	+		
Flavonol											
Fisetin	—	—	OH	—	—	OH	OH	—	+		
Isoflavones											
Biochanin-A	OH	—	OH	—	—	—	OMe	—	+		
Formononetin	—	—	OH	—	—	—	OMe	—			+
Texasin	—	OH	OH	—	—	—	OMe	—	+		
Afrormosin	—	OMe	OH	—	—	—	OMe	—	+	+	
Calycosin	—	—	OH	—	—	OH	OMe	—	+		+
Cabreuvin	—	—	OMe	—	—	OMe	OMe	—	+	+	
	—	—	OH	OMe	—	OH	OMe	—			+
1a	—	—	OMe	—	OH	OMe	OMe	—	+		
Isoflavanones											
	—	—	OH	—	—	—	OMe	—			+
	—	—	OH	—	—	OH	OMe	—			+
2a	—	—	OMe	—	OH	OMe	OMe	—	+		
Pterocarpans											
(+)-Medicarpin	—	—	OH	—	—	—	OMe	—			+
(−)	—	—	OMe	OMe	—	—	OMe	—	+		
Coumestans											
	—	—	OH	—	—	—	OMe	—			+
	—	—	OH	—	—	—	OMe	OMe			+
2-Arylbenzofuran	—	—	OH	—	—	—	OMe	OMe			+

*† According to the usual numbering system, respectively 4,2′,4′-trihydroxychalcone and 6,3′,4′-trihydroxyaurone.

confirmed by the identity of the methyl ether **1c** with an authentic sample prepared by oxidation of 7,3′-di-*O*-methylmucronulatol (**3c**) [8], whereby the isoflavanone **2c** was obtained as an intermediate. As shown by a positive Gibbs test [9], the hydroxyl can only be situated at C-2′ or C-3′, more probably at the former site in view of the relative abundances of the $[M-17]^+$ (16%) and $[M-31]^+$ (6%) MS fragments [10].

The constitution of **2a**, $C_{15}H_8O_2.OH(OMe)_3$, was also elucidated by spectra which again included the retro-Diels-Alder MS fragments, now at *m/e* 151 (100%) and 180 (16%), and identification of the methyl ether with **2c** [8]. Among the two possible positions for the hydroxyl, indicated by a positive Gibbs test [19], C-2′ was preferred in view of the structure of the co-occurring isoflavone **1a**.

The assignment of the hydroxyls to C-2′ in both natural compounds was compatible with the fact that the 3′-hydroxylated isomers **1b** and **2b** proved to be different from the natural isoflavone and isoflavanone respectively. The model compounds **1b** and **2b** were again prepared from mucronulatol (**3e**), this time by oxidation of the di-*O*-benzyl ether (**3d**) to the isoflavone **1d** via the intermediate isoflavanone **2d**, which both, upon debenzylation and selective methylation, gave the required products, respectively **1b** and **2b**.

EXPERIMENTAL

Isolation of the constituents. A trunkwood sample (11.5 kg) of *Myroxylon peruiferum*, collected in the Rio Doce region of Espirito Santo State, Brazil, was ground and extracted successively with hot C_6H_6 and EtOH. The C_6H_6 extract (313 g) was separated into petrol soluble and insoluble parts. The soluble part (178 g) was distilled (110–116°, 2 mm) to nerolidol (144 g). The insoluble part (99 g) was cryst. from EtOH. The crystals (31 g) were washed with 3% aq. NaOH. The insoluble part was cryst. repeatedly from EtOH to cabreuvin (24 g). The alkaline soln was acidified and extracted with Et_2O. Evapn of the Et_2O gave a residue which was separated into EtOH (room temp.) soluble and insoluble parts. Silica column chromatography of the soluble part gave, upon elution with C_6H_6, vanillin (428 mg). Silica column chromatography of the insoluble part gave, upon elution with C_6H_6–Me_2CO 9:1 initially **1a** (50 mg), next a mixture of **1a** and afrormosin (114 mg) and finally afrormosin (300 mg). Part (100 g) of the EtOH extract (628 g) was submitted to chromatography on a Si (500 g) column, eluting successively in 1 l. fractions with C_6H_6 (frs. 1, 2), C_6H_6–$CHCl_3$ 1:1 (frs. 3–6), $CHCl_3$ (frs. 7–20), $CHCl_3$–MeOH 95:5 (frs. 21–27). Frs. 4–7 were recryst. from EtOH to (−)-3,4,9-trimethoxypterocarpan (431 mg). Frs 8–10 were cryst. from EtOH to cabreuvin (5.4 g). The mother liquor was washed with 3% aq. NaOH. The insoluble part was cryst. from EtOH to cabreuvin (1.1 g). The alkaline solution was acidified and extracted with Et_2O. Evapn of the Et_2O gave a residue which was fractionally cryst. from EtOH to **2a** (12 mg). Frs. 11–14 were repeatedly recryst. from EtOH to afrormosin (455 mg). Frs. 23–25 were washed with petrol to a solid which was cryst. from EtOH to texasin (120 mg). The mother liquor was chromatographed on a Sephadex LH-20 column, MeOH eluting in order calycosin (6 mg) and 2 resins. Both were rechromatographed in the same way, the first giving texasin (608 mg) and calycosin (570 mg), the second giving isoliquiritigenin (150 mg). Frs. 26 and 27 were separately chromatographed on Sephadex LH-20, MeOH eluting, respectively, fisetin (385 mg) and sulfuretin (110 mg), and fisetin (160 mg) and biochanin-A (10 mg).

Identification of the known compounds relied on comparisons with authentic samples, with the exceptions of calycosin, which was characterized by spectra and methylation to cabreuvin, and sulfuretin which was characterized by physical constants and spectra.

2′-Hydroxy-7,3′,4′-trimethoxyisoflavone (**1a**). Mp 210–212° (Found: M (HRMS), 328.0941. $C_{18}H_{16}O_5$ requires: M,

328.0947). ν_{max} (KBr, cm^{-1}): 3440, 1620. λ_{max} (EtOH, nm): 248, 262 infl., 305 (ε 33400, 26500, 16400); no NaOAc or $AlCl_3$ shift; λ_{max} (EtOH + NaOH, nm): 236, 273, 297 (ε 44600, 21600, 21800). PMR (TFA): τ 1.64 (*s*, H-2), 1.97 (*d*, *J* = 8 Hz, H-5), 2.94 (*dd*, *J* = 8 and 2 Hz, H-6), 3.04 (*d*, *J* = 2 Hz, H-8), 3.27 (*d*, *J* = 8 Hz, H-6'), 3.64 (*d*, *J* = 8 Hz, H-5'), 6.34 (*s*, OMe), 6.38 (*s*, OMe), 6.42 (*s*, OMe). MS (*m/e*): 328 (100%) M, 313 (44), 311 (16), 310 (41), 309 (22), 281 (20), 280 (20), 267 (34), 253 (21), 214 (31), 198 (20), 178 (16), 151 (37), 136 (20), 134 (28). *Methyl ether* (**1c**). Mp 157–160° (Found: M (HRMS), 342.1087. $C_{19}H_{18}O_6$ requires: M, 342.1103). ν_{max} (KBr, cm^{-1}): 1645, 1630, 1610. PMR (100 MHz, $(CD_3)_2CO$): τ 1.88 (*d*, *J* = 9 Hz, H-5), 1.96 (*s*, H-2), 2.92 (*d*, *J* = 2 Hz, H-8), 2.94 (*dd*, *J* = 9 and 2 Hz, H-6), 2.98 (*d*, *J* = 8 Hz, H-6'), 3.17 (*d*, *J* = 8 Hz, H-5'), 6.01, 6.10, 6.16, 6.20 (4 *s*, 4 OMe). MS (*m/e*): 342 (100%) M, 311 (18). *Acetate* (**1f**). Mp 146–148°. ν_{max} (KBr, cm^{-1}): 1768, 1623. PMR ($CDCl_3$): τ 1.80 (*d*, *J* = 8 Hz, H-5), 2.20 (*s*, H-2), 2.93 (*d*), 3.13 (*d*) (AB system, *J* = 8 Hz, H-5', H-6'), 3.00 (*dd*, *J* = 8 and 2 Hz, H-6), 3.17 (*d*, *J* = 2 Hz, H-8), 6.07 (*s*, 2 OMe), 6.13 (*s*, OMe), 7.83 (*s*, OAc).

(±)-*2'-Hydroxy-7,3',4'-trimethoxyisoflavanone* (**2a**). Mp 155–157° (Found: M (HRMS): 330.1098. $C_{18}H_{18}O_6$ requires: 330.1103). ν_{max} (KBr, cm^{-1}): 3353, 1682, 1608. λ_{max} (EtOH, nm): 235 infl., 309, 370 (ε 16900, 12800, 8600); no NaOAc or $AlCl_3$ shift; λ_{max} (EtOH + NaOH, nm): 231, 305, 365 infl. (ε 24200, 11800, 8600). PMR ($(CD_3)_2CO$): τ 2.14 (*d*, *J* = 8 Hz, H-5), 3.24 (*s*, H-5', H-6'), 3.40 (*d*, *J* = 3 Hz, H-8), 3.50 (*dd*, *J* = 8 and 3 Hz, H-6), *ca* 5.4 (*m*, 2 H-2), *ca* 6 (overlapped by OMe signals, H-3), 6.10, 6.17, 6.19 (3 *s*, 3 OMe). MS (*m/e*): 330 (73%) M, 298 (39), 297 (21), 181 (69), 180 (82), 179 (23), 165 (72), 152 (75), 151 (100), 150 (57), 149 (20), 138 (22). *Methyl ether* (**2c**). Mp 133–134°, identical with an authentic sample [8].

Preparation of methyl ether **1c** *and* **2c**. To a soln of **3c** [8] (800 mg) in Me_2CO (150 ml) 5% aq. $KMnO_4$ soln (100 ml) was added portionwise (4 hr). Work up as described [11] gave **2c** (400 mg, 48%), identified by mmp and spectra. A soln of **2c** (20 mg) and DDQ (31 mg) in dioxane (15 ml) was maintained under reflux (96 hr). The solvent was evapd and the residue purified by Si chromatography to **1c** (6 mg, 30%), identified by mmp and spectra.

Synthesis of (±)-*3'-hydroxy-7,2',4'-trimethoxyisoflavanone* (**2b**). A. *Preparation of* (±)-*7,3'-dibenyloxy-2',4'-dimethoxyisoflavan* (**3d**) (±)-Mucronulatol (**3e**) [8] (200 mg), $PhCH_2Cl$ (0.2 ml) and K_2CO_3 (2 g) in Me_2CO (30 ml) (reflux, 72 hr) gave **3d** (287 mg, 90%), mp 90–91° (Et_2O). ν_{max} (KBr, cm^{-1}): 1621, 1585, 748, 695. λ_{max} (EtOH, nm): 283, 291 infl. (ε 13500, 11500). PMR (60 MHz, $CDCl_3$): τ 2.65 (*s*, 2 C_6H_5), 3.07 (*d*, *J* = 8 Hz, H-5), 3.22 (*d*, *J* = 8 Hz, H-6'), 3.40 (*d*, *J* = 8 Hz, H-5'), 3.49 (*dd*, *J* = 8 and 2 Hz, H-6), 3.57 (*d*, *J* = 2 Hz, H-8), 4.99 (*s*, 2 $PhCH_2$), 5.69 (*d*, *J* = 9 Hz, H_{eq}-2), 5.97 (*d*, *J* = 9 Hz, H_{ax}-2), 6.14 (*s*, OMe), 6.20 (*s*, OMe), 6.35–6.85 (*m*, H-3), 7.09 (*d*, *J* = 8 Hz, 2 H-4). MS (*m/e*): 482 (91%), M, 392 (67), 391 (83), 303 (47), 300 (66), 299 (31), 270 (50), 237 (32), 181 (55), 180 (69), 179 (51), 168 (75), 167 (88), 165 (25), 147 (51), 107 (26), 105 (28), 92 (92), 91 (100), 77 (42), 65 (93), 39 (34). B. *Preparation of* (±)-*7,3'-dibenzyloxy-2',4'-dimethoxyisoflavanone* (**2d**). A mixture of **3d** (130 mg) and DDQ (183 mg) in MeOH (6 ml) was kept at room temp. (24 hr). The solvent was evapd and the residue purified by Si chromatography to **2d** (110 mg, 82%), mp 109–112°. ν_{max} (KBr, cm^{-1}): 1682, 1651, 1602, 1568, 738, 695. λ_{max} (EtOH, nm): 233 infl., 274, 317 infl. (ε 39100, 32700, 20500). PMR (60 MHz, $CDCl_3$): τ 2.10 (*d*, *J* = 8 Hz, H-5), 2.62 (*s*, 2 C_6H_5), 3.19 (*d*, *J* = 8 Hz, H-6'), 3.42 (*d*, *J* = 8 Hz, H-5'), 3.49 (*dd*, *J* = 8 and 2 Hz, H-6), 3.55 (*d*, *J* = 2 Hz, H-8), 4.92 (*s*, $PhCH_2$), 5.04 (*s*, $PhCH_2$), 5.35–6.1 (*m*, 2 H-2, H-3), 6.22 (*s*, 2 OMe). MS (*m/e*): 496 (11%) M, 495 (45), 494 (89), 404 (81), 403 (91), 281 (36), 92 (57), 91 (100), 65 (58), 63 (25). C. *Preparation of* (±)-*7,3'-dihydroxy-2',4'-dimethoxyisoflavanone* (**2e**). A mixture of **2d** (20 mg) and AcOH HCl (aq.; conc.) 1:1 (6 ml) was kept slightly warm (3 hr) and inverted over ice. Extraction with $CHCl_3$ gave **2e** (8 mg, 63%), mp 200–204°. ν_{max} (KBr, cm^{-1}): 3420, 1667. λ_{max} (EtOH, nm): 279, 318 infl. (ε 10500, 8000); λ_{max} (EtOH + NaOH, nm): 250, 294 infl., 339 (ε 15000, 10500, 17300); λ_{max} (EtOH + AcONa, nm): 281 infl., 340 (ε 7400, 15000). D. *Preparation of* (±)-*3'-hydroxy-7,2',4'-trimethoxyisoflavanone* (**2b**). **2e** (4.5 mg), Me_2SO_4 (0.02 ml) and K_2CO_3 (100 mg) in Me_2CO (6 ml) (reflux, 20 min) gave **2b** (2.2 mg, 47%). (Found: M (HRMS), 330.1085. $C_{18}H_{18}O_6$ requires: M, 330.1103). ν_{max} (film, cm^{-1}): 3400, 1670. λ_{max} (EtOH, nm): 275, 317 infl. (ε 11200, 6700); λ_{max} (EtOH + NaOH, nm): 235, 275, 319 infl. (ε 9900, 9000, 4700); no NaOAc UV shift. The compound was not identical with **2a**.

Synthesis of 3'-hydroxy-7,2',4'-trimethoxyisoflavone (**1b**). A. *Preparation of 7,3'-dibenzyloxy-2',4'-dimethoxyisoflavone* (**1d**). A mixture of **2d** (see above) (130 mg) and DDQ (200 mg) in dioxane (10 ml) was heated under reflux (26 hr). The solvent was evapd and the residue purified by Si chromatography to **1d** (73 mg, 56%), mp and lit. [12] mp 145–147°. ν_{max} (KBr, cm^{-1}): 1626. λ_{max} (EtOH, nm): 241 infl., 249 infl., 308 (ε 14400, 13800, 6100). PMR (60 MHz, $CDCl_3$): τ 1.84 (*d*, *J* = 8 Hz, H-5), 2.14 (*s*, H-2), 2.60 (*s*, 2 C_6H_5), 2.95 (*d*, *J* = 8 Hz, H-6'), 2.99 (*d*, *J* = 8 Hz, H-5'), 3.32 (*dd*, *J* = 8 and 2 Hz, H-6), 3.39 (*d*, *J* = 2 Hz, H-8), 4.85 (*s*, $PhCH_2$), 4.95 (*s*, $PhCH_2$), 6.15 (*s*, OMe), 6.22 (*s*, OMe). MS (*m/e*): 494 (14%) M, 406 (29), 405 (71), 403 (31), 377 (33), 270 (41), 227 (50), 180 (25), 179 (45), 119 (30), 92 (60), 91 (100), 65 (59). B. *Preparation of 7,3'-dihydroxy-2',4'-dimethoxyisoflavone* (**1e**). Acid hydrolysis of **1d** (40 mg) according to the procedure described above gave **1e** (20 mg, 79%), mp and lit. [12] mp 251–252°. ν_{max} (KBr, cm^{-1}): 3420, 1628. λ_{max} (EtOH, nm): 240 infl., 249 infl., 309 infl. (ε 7500, 3800); λ_{max} (EtOH + NaOH, nm): 228, 256 infl., 346 infl. (ε 14000, 12200, 6900). λ_{max} (EtOH + NaOAc, nm): 260 infl., 355 infl. (ε 7700, 3900). PMR (60 MHz, TFA): τ 1.15 (*s*, H-2), 1.50 (*d*, *J* = 8 Hz, H-5), 2.50 (*dd*, *J* = 8 and 2 Hz, H-6), 2.57 (*d*, *J* = 2 Hz, H-8), 3.00 (*s*, H-5',6'), 5.97 (*s*, OMe), 6.04 (*s*, OMe). C. *Preparation of 3'-hydroxy-7,2',4'-trimethoxyisoflavone* (**1b**). **1e** (16 mg), Me_2SO_4 (0.02 ml) and K_2CO_3 (300 mg) in Me_2CO (12 ml) (reflux, 3 hr) gave **1b** (9 mg, 54%), mp 150–153° (Found: M (HRMS), 328.0900. $C_{18}H_{16}O_6$ requires: M, 328.0947). ν_{max} (KBr, cm^{-1}): 3348, 1650, 1627, 1612. λ_{max} (EtOH, nm): 240 infl., 248, 269 infl., 308 infl. (ε 32400, 30500, 19000, 14700); λ_{max} (EtOH + NaOH, nm): 247, 305 (ε 37700, 19300); no NaOAc UV shift. PMR (60 MHz, TFA): τ 1.05 (*s*, H-2), 1.49 (*d*, *J* = 8 Hz, H-5), 2.47 (*dd*, *J* = 8 and 2 Hz, H-6), 2.54 (*d*, *J* = 2 Hz, H-8), 2.95 (*s*, H-5',6'), 5.84 (*s*, OMe), 5.95 (*s*, OMe), 6.02 (*s*, OMe). The compound was not identical with **1a**.

Acknowledgement—The authors wish to thank Dr. P. M. Baker, NPPN, Universidade Federal do Rio de Janeiro, for the 100 MHz PMR and the HRM spectra.

REFERENCES

1. Oliveira, A. B. de, Madruga, M. I. L. M. and Gottlieb, O. R. (1978) *Phytochemistry* **17**, 539.
2. Harms, H. (1908) *Notizblatt Bot. Gart. Mus. Berl.* **5**, 85.
3. Rizzini, C. T. (1971) *Árvores e Madeiras Úteis do Brasil, Editora da Universidade de São Paulo.*
4. Record, S. J. and Hess, R. W. (1943) *Timbers of the New World*. Yale University Press.
5. Ducke, A. (1949) *As Leguminosas da Amazonia Brasileira*, 2nd Edn, p. 160. Boletim Técnico do Instituto Agronômico do Norte, Belém, Pará, Brasil.
6. Naves, Y.-R. (1947) *Helv. Chim. Acta* **30**, 278.
7. Gottlieb, O. R. and Magalhães, M. T. (1959) *An. Assoc. Bras. Quím.* **18**, 89.
8. Kurosawa, K., Ollis, W. D., Sutherland, I. O., Gottlieb, O. R. and Oliveira, A. B. de (1978) *Phytochemistry* **17**, 1405.
9. Mesquita, A. A. L., Corrêa, D. de B., Gottlieb, O. R. and Magalhães, M. T. (1968) *Anal. Chim. Acta* **42**, 311.
10. Mabry, T. J. and Markham, K. R. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.) p. 78. Chapman & Hall, London.
11. McGookin, A., Robertson, A. and Whalley, W. B. (1940) *J. Am. Chem. Soc.* **62**, 792.
12. Farkas, L., Gottsegen, A., Nogradi, M. and Antus, S. (1974) *J. Chem. Soc. Perkin Trans.* 1, 305.