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STRUCTURE DETERMINATION OF MELANERVIN, THE FIRST NATURALLY OCCURRING FLAVONOID OF THE TRIPHENYLMETHANE FAMILY

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Abstract—From the flowers of *Melaleuca quinquenervia* (Myrtaceae) besides the flavanones strobopinin and kryptostrobin a new 8-aryl-flavanone has been isolated and shown to be (2,4-dihydroxy-6-methoxy) tolyl-3-(5,7-dihydroxy-6-methyl) flavanonyl-8-phenylmethane, mainly by degradation, MS, ^{1}H- and ^{13}C-NMR-spectroscopy. The new flavanone represents the first naturally occurring triphenylmethane compound.

The leaves of the cajeput tree *Melaleuca quinquenervia S. T. Blake* (Myrtaceae) and its essential oil possess antiseptic, analgetic and vermifuge activities.[1] The oil is officinal in many pharmacopoeias. In the course of a program on anticancer-active principles in plants we investigated the flowers of *Melaleuca quinquenervia* and detected besides the well known flavanones strobopinin (**1**) and kryptostrobin (**2**)[2] another lipophilic flavonoid compound melanervin (**3**). As reported earlier[3] melanervin was isolated from $CHCl_3$ and petrolether extraction followed by silicagel chromatography with petrol-acetone-ether mixtures as a crystalline white substance, m.p. 193° and molecular formula $C_{31}H_{28}O_7$ (M^+ 512).

RESULTS AND DISCUSSION

The UV-spectrum in MeOH with maxima at 298 and 337 nm and the characteristic UV-shifts with NaOAc and $AlCl_3$ indicated a flavanone with free OH-groups in 5 and 7 position.[4] The ^{1}H-NMR-spectrum gave evidence for the following structural features: multiplets of an ABX-system at $\delta = 5.45$ and 3 ppm, singulets at $\delta = 7.08$ (broad) and 7.28 for two unsubstituted phenyl residues, two CH_3-groups ($\delta = 1.93$ and 1.96), one OCH_3-group ($\delta = 3.71$ ppm) and two protons in the aromatic region ($\delta = 6.16$ and 6.54 ppm). Melanervin forms a tetraacetate **4** and a triacetate **5** and a pentamethylether **6** with a chalcone structure when methylated with DMS. In alkaline medium melanervin can be transformed into a isomeric product isomelanervin (**7**), which was again acetylated to a tetraacetate **8** and a triacetate **9**. Since, by dehydrogenation with I_2/K_2CO_3[5] besides 2,3-dehydromelanervin (**10**), 5,7-dihydroxy-6-methyl-flavanone (strobopinin) (**1**) and 5,7-dihydroxy-6-methyl-flavonone (strobochrysin (**11**)[6] could be obtained, the flavanone part of **3** should have a methylpinocembrin structure, as confirmed by a *m/e* 270 ($C_{16}H_{14}O_4$) MS-fragment.

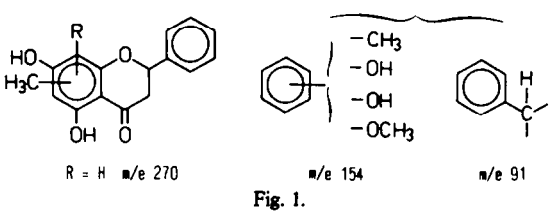


Fig. 1.

The remaining residue R ($C_{15}H_{15}O_3$), *m/e* 242 in MS, from the M.W. 512, which gave the MS-fragments *m/e* 91 and *m/e* 154 must include a phenyl residue ($\delta = 7.11$), one OCH_3-group (3.71), one CH_3-group on an aromatic nucleus (2.0), 2 protons at 6.62 and 6.13 ppm, the last of them exchangeable with CF_3CO_2D.

In addition to these major fragments, loss of water and phenyl from the molecular ion can be observed in the mass spectrum. Another intense peak was *m/e* 358, resulting from loss of *m/e* 154. RDA cleavage, stepwise splitting of CO and H-transfer as shown in Figs. I and II are typical for a polyphenolic compound.[7]

The substitution pattern in R could be deduced from the degradation products obtained by fission of **3** with 2N NaOH and $AlCl_3$. Alkaline degradation led to benzoic acid, cinnamic acid, C-methylphloroglucinol (**12**) and a methylphloroglucinolmonomethylether (*m/e* 154) all identified by GC-MS as the TMS-derivatives. The exact structure of the latter compound was elucidated by methylation[8] to 2,4,6-trimethoxy-toluene (**13**) and NMR-comparison (two meta-coupled aromatic H) with synthetic 2,4-dihydroxy-6-methoxytoluene[9] (**14**). Therefore the partial structure with *m/e* 154 must be in accord with the structure **14**.

Combination of **14** with the *m/e* 91 fragment gives rise to a diphenylmethyl residue. Since **3** could be split to C-methyl-phloroacetophenone (**15**) with $AlCl_3$, the methoxyl group has to be located in the diphenylmethyl residue. Similarly performed alkaline degradation of **6** resulted in diphenylmethane and triphenylmethane derivatives as fission products, which could be identified as 2,4,6-trimethoxy-3-methyl-phenyl-phenylmethane (**16**) *m/e* 272 and bis-(2,4,6-trimethoxy-3-methylphenyl)-phenylmethane (**17**) *m/e* 452. Another byproduct was the triphenylmethyl-acetophenone **18** *m/e* 494.

A decision between the two isomeric structures **19** and **20** and **3** and **7** respectively could be arrived at from detailed NMR-investigations of the compounds **6**, **4**, **5**, **8** and **9**. The compound **6** showed strong diamagnetic shift of only four methoxyl singulets.[10] This suggests the same shielding effect as observed for the o,o'-positioned methoxy protons in the synthetic bis-(2,4,6-trimethoxy-phenyl)-phenylmethane[11] (**21**). Therefore in **3** four methoxy groups in o-position must be shielded, whilst two appear almost uninfluenced. From this it follows that the methoxy group with the NMR signal at 3.71 ppm

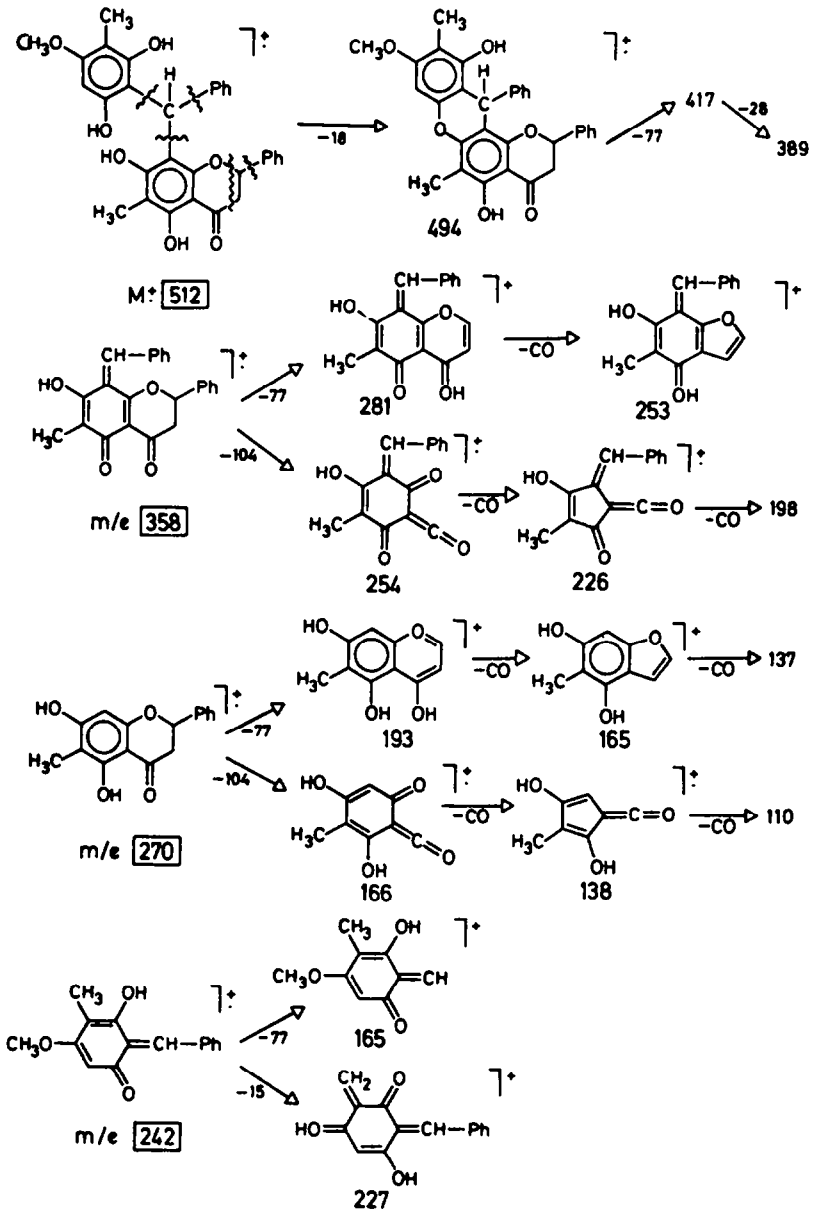
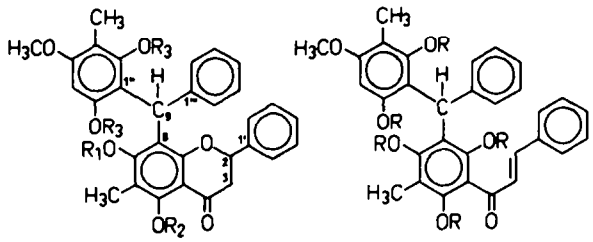


Fig. 2.

must be located originally in position para to the benzyl-C-atom as in **19**. Furthermore, in the NMR-spectrum of melanervintetraacetate (**4**), of the four acetoxy groups only one gives a signal at lower field than 1.9 (at δ = 2.42 ppm) and can be assigned to the C-5-OAc, since it is missing in the triacetate **5**. Generally acetoxy groups on aromatic rings, which give signals at higher field than 2.0 ppm are strongly shielded by adjacent aromatic rings.[12] The observation, that three OAc-groups are sterically hindered, is in accord with a substitution of the $C_{15}H_{15}O_3$-residue **19** in 8-position of melanervin. In the case of 6-substitution a strong diamagnetic shift would have been expected for the 5-OAc, too, as observed in the tetra-acetate of isomelanervin (**8**). In this respect, the ^{13}C-NMR-data of strobopinin ^{13}(**1**) and the triphenyl-methane-derivative **21** were also in good agreement compared with the data of **3**. A doublet in the off-resonance spectrum of **3** at δ = 34.2 ppm and of **21** at 37.2 ppm derives from the aliphatic methine C-9. The MS-fragmentation pattern of the derivatives and degradation products of **3** support also the postulated structure as 8-(2" 6"-dihydroxy-4"-methoxy-3"methyl)-diphenylmethyl-strobopinin or 2,4-dihydroxy-6-methoxy-tolyl - 3 - (5,7 - dihydroxy - 6 - methyl) - flavanonyl - 8 - phenyl - methane and the 6-diphenylmethane-isomer for isomelanervin. To our knowledge this is the first triphenyl-methane compound to be reported from the plant kingdom. Assuming that the C-2 in melanervin has S-configuration, as usual in flavanones[14], two epimeric forms can be described for the genuine compound. Further it can be deduced from NMR-temperature studies, that melanervin probably forms rotational conformers due to a restricted rotation. We received better information about the relative or absolute stereochemistry of melanervin from the total synthesis of melanervin, which is described in the next publication.

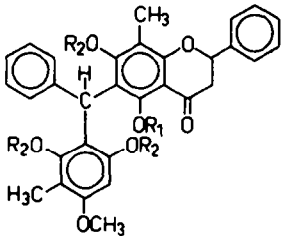


	R_1	R_2	R_3
(3)	H	H	H
(4)	Ac	Ac	Ac
(5)	Ac	H	Ac
(10)	H	H	H, 2,3-Dehydro-

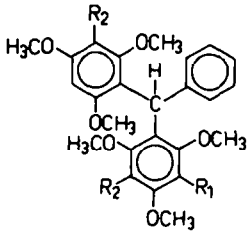
(6) R = Me

	R_1	R_2	R_3
(1)	Me	H	H
(2)	H	Me	H
(11)	Me	H	H, 2,3-Dehydro-

(a)

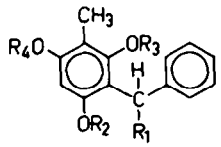


	R_1	R_2
(7)	H	H
(8)	Ac	Ac
(9)	H	Ac

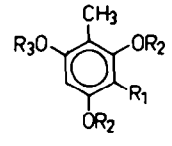


	R_1	R_2
(17)	H	Me
(18)	Ac	Me
(21)	H	H

(b)



	R_1	R_2	R_3	R_4
(16)	H	Me	Me	Me
(19)	-	H	H	Me
(20)	-	H	Me	H



	R_1	R_2	R_3
(12)	H	H	H
(13)	H	Me	Me
(14)	H	H	Me
(15)	Ac	H	H

(c)

Fig. 3.

EXPERIMENTAL

Plant origin

Flowers of *Melaleuca quinquenervia* were collected from wild growing trees in South Florida in June 1974. The dried drug was delivered by Andrew L. Manis, 13601 Old Cutter Rd. Miami, Florida 33158. We thank Prof. Dr. Julia Morton, Miami, for procuring the plant material.

Instruments, materials and methods

M.ps were determined on a Kofler block (corrected). H-NMR-spectra were recorded on a Varian A-60A spectrometer, ^{13}C-NMR spectra on a Bruker WX-90 FT at 22.63 MHz and a Varian XL-100 spectrometer at 25.2 MHz. Mass spectra were recorded with a Kratos MS-30 instrument. GC-separation was effected with a Erba Science Fractovap 2200, exit split 10:1. TLC was performed on silicagel layers of 0.05 and 0.1 mm with the following solvent systems: A: dichlorethane–ethylacetate–acetic acid 8:1:1; B: diethylether–petrol–acetone 5:5:1; C: benzene–acetone 9:1; D: toluene–ethylacetate 5:4.

Isolation of 3

300 g of the powdered drug were extracted in a Soxhlet with 3 l $CHCl_3$ for 10 hr and after concentration to a syrup successively digested with 5 × 100 ml petroleumether and filtered hot. On cooling, the yellow precipitates were collected with the crystalline product, resulting from repeated acetone extraction of the petroleumether residues. 1.5 g of the raw material were dissolved in 60% ethanol and washed with petroleumether. After concentration, pure melanervin crystallized from ethanolic solutions. The mother liquor was subjected to column chromatography on silicagel using B as eluent. The first 2–5 fractions yielded melanervin, further 3 fractions mixtures of stobopinin and kryptostrobin. On recrystallisation from EtOH/$CHCl_3$ 3:1 the melanervin fractions yielded 450 mg of white needles of melanervin–ethanolate m.p. 164°. Solvent free melanervin was prepared from benzene or $CHCl_3$/DMSO as prisms and plates m.p. 183°. HV-dried ethanolate of 3 lost ethanol to give 2.4-dihydroxy-6-methoxy-tolyl-3-(5., 7-dihydroxy-6-methyl)-flavanonyl-8-phenylmethane, m.p. 194° (HV, 120°) $C_{31}H_{28}O_7$ (512.53) Calc. C, 72.64; H, 5.50; found C, 72.60; H, 5.27%. Melanervin-ethanolate; m.p. 164° (EtOH–$CHCl_3$ 3:1). $C_{31}H_{28}O_7.C_2H_5OH$ (588.60). Calc. C, 70.95; H, 6.14; CH_3, 8.07; found C, 70.70; H, 5.91; CH_3, 7.76%. $[\alpha]_D^{23} = -4.8°$ (c = 0.807 in pyridine); R_f 0.79 (A), 0.35 (B), 0.33 (polyamide, MeOH)UV: (MeOH p.a.) λ_{max} (log ϵ) = 298 (4.086), 337 (4.001)nm (MeOH + NaOAc) 260 (sh), 337 nm; (MeOH + NaOMe 257 (sh), 338 nm (MeOH + $AlCl_3$) 319 nm. IR: (KBr) $\tilde{\nu} = 3420\,cm^{-1}$ (OH), 1615 (C=O), 1435, 1115 (CO) 800, 763, 750, 725, 692 (Ar); NMR: (^1H DMSO-d_6 + $CDCl_3$, TMS int.100°) δ = 1.93 ppm (s, 3H); 1.96 (s, 3H); CH_3–3", 6; 2.82–3.38 (m, 2H) CH_2–3; 3.71 (s, 3H) OCH_3; 5.45 (dd, J = 5.5 a. 10 Hz, 1 H) H–2; 6.16 (s, 1H) CH–9; 6.54 (s, 1H) H–3"; 7.08 (s_{br}, 5H) Ph'"; 7.28 (s, 5H) Ph'; 9.92 (br, 3H) OH–2", 6", 7; 12.70 (s, 1 H) OH–5; ^{13}C (DMSO-d_6, TMS int.) δ = 7.5 ppm C–6a; 8.7 C–3"a; 34.2 C–8a; 40.5 C–3; 55.2 C–4"a; 82.0 C–2; 92.6 C–3", 5", 102.2 C–10; 103.9 C–1"; 103.9 C–6; 106.2 C–8; 125.1 C–4'"; 126.6 C–2', 6'; 127.3 C–3'", 5'"; 128.3 C–2'", 6'"; 128.3 C–3', 4', 5'; 138.7 C–1'; 142.6 C–1'"; 153.8 C–2", 6"; 156.8 C–4"; 158.0 C–9: 159.2 C–5; 162.9 C–7; 197.2 C–4; MS (EI 70 eV, 4 KV, 100 μA, 130°; DI 100°, 10^{-6} T) *m/e* 512 M^+ (4% rel.int) 494 (1) 417 (3) 389 (2) 361 (3) 360 (20) 359 (10) 358 (8) 357 (8) 330 (6) 329 (7) 283 (6) 281 (5) 271 (22) 270 (100) 269 (47) 256 (10) 255 (9) 254 (4) 253 (10) 243 (12) 242 (19) 241 (24) 227 (15) 226 (5) 193 (51) 167 (13) 166 (59) 165 (12) 154 (45) 153 (19) 139 (16) 138 (44) 137 (15) 123 (18) 110 (13) 104 (10) 103 (11) 91 (8) 77 (13) 69 (23) 55 (13) 51 (17) 43 (15) 39 (23) 31 (34).

Isolation of 1 *and* 2

Fractions 5–8 of the isolation procedure described above were

concentrated under reduced pressure, separated by preparative TLC (A), eluted by acetone and crystallized from 70% EtOH to yield 60 mg strobopinin (1) and 46 mg kryptostrobin (2).

Stropopinin (1). (5,7-dihydroxy-6-methyl-flavanone) m.p. 226° (EtOH 70% ig) $C_{16}H_{14}O_4$ (270.27) Calc. C, 71.10; H, 5.22; found C, 70.65; H, 5.35%. R_f 0.77 (A), 0.56 (B) 0.53 (polyamide, MeOH); UV: (MeOH) λ_{max} = 292, 340 (sh) nm (MeOH + NaOAc) 255 (sh), 295 (sh), 330 nm (MeOH + NaOMe) 223 (sh), 327 nm (MeOH + $AlCl_3$) 316, 385 nm. IR: (KBr) $\tilde{\nu}$ = 3100 cm^{-1} (OH), 1635 (C=O), 1575 (Ar), 1105 (CO), 815, 760, 704 (Ar). NMR: (^{1}H, $CDCl_3$, TMS int.) δ = 2.05 ppm (s, 3H) CH_3-6; 2.8–3.4 (m, 2H) CH_2-3; 5.42 (dd, J=5 a. 12 Hz, 1H) H-2; 6.02 (s, 1H) H-8; 7.40 (s, 5H) Ph; 9.5 (br, 1H) OH-7; 12.48 (s, 1H) OH-5; (^{13}C, DMSO-d_6, TMS int.) δ = 7.0 ppm C-6a; 42.2 C-3; 78.4 C-2; 94.5 C-8; 101.9 C-10; 102.1 C-6; 125.6 C-2', 6'; 128.5 C-3', 4' 5'; 139.5 C-1'; 160.0 C-5; 161.7 C-9; 165.2 C-7; 196.4 C-4; MS: (EI 70 eV, 4 KV, 300 μA, 200°; DI 180° 8.10^{-7}T) *m/e* 271 (15% rel.int.) 270 M^+ (100) 269 (45) 193 (61) 167 (22) 166 (85) 138 (50) 104 (20) 103 (15) 68 (18) 55 (26).

Kryptostrobin (2). (5,7-dihydroxy-8-methyl-flavanone) m.p. 203–205° (EtOH 70%) $C_{16}H_{14}O_4$ (270.27) Calc. C, 71.10; 5.22; found C, 71.30; H, 5.45%; R_f 0.68 (A); 0.51 (B); 0.60 (polyamide, MeOH); UV: (MeOH) λ_{max} = 290, 340 nm (MeOH + NaOAc) 255 (sh), 295 (sh), 332 nm (MeOH + NaOMe) 223 (sh), 328 nm (MeOH + $AlCl_3$) 316, 385 nm; IR: (KBr) $\tilde{\nu}$ = 3300 cm^{-1} (OH), 1620 (C=O), 1100, 1070, (CO), 818, 760, 693 (Ar); NMR ($CDCl_3$, TMS int.) δ = 2.05 ppm (s, 3H) CH_3-8; 2.8–3.4 (m, 2H) CH_2-3; 5.50 (dd, 5 a. 12 Hz, 1H) H-2; 6.02 (s, 1H) H-6; 7.42 (s, 5H) Ph; 9.0 (br, 1H) OH-7; 12.03 (s, 1H) OH-5.

Dehydration of 3 *with* I_2/*KOAc*

3 g dry KOAc were dissolved in 30 ml glacial acetic acid and 100 mg 3 were added to the hot solution. A solution of 300 mg I_2 in 20 ml HOAc was added dropwise to the solution within 30 min, the mixture was refluxed for 2 hr and stirred into water after cooling. The brown mixture was decolourised by treatment with solid Na_2SO_3. The precipitate was filtered, washed with water and heated in EtOH to give 60 mg of yellow crystalline product. This was dissolved in acetone, chromatographed by tlc(A) and three main zones were eluted and worked up to give strobochrysin R_f 0.61, strobopinin R_f = 0.76, dehydromelanervin R_f 0.85.

Strobochrysin (11)

M.p. 298–300° (EtOH 80%); UV: (MeOH) λ_{max} = 214, 248, 272, 318 nm NMR: (DMSO-d_6, TMS int.) δ = 7.70–8.00 ppm (m, 2H) H-2', 6'; 7.32–7.55 (m, 3H) H-3', 4', 5'; 6.79 (s, 1H) H-8; 6.47 (s, 1H) H-3; 2.02 (s, 3H) CH_3-6; 10.2 (br, 1H) OH-7; 13.1 (s, 1H) OH-5; MS: (EI 70 eV, 4KV, 100 μA, 190°; DI 170°, 10^{-6}T) *m/e* 268 M^+ (100% rel.int.) 240 (6) 239 (12) 213 (5) 193 (4) 166 (10) 165 (5) 138 (9) 137 (5) 134 (6) 123 (5) 110 (4) 102 (5) 77 (5) 69 (10) 55 (6) 51 (41).

Dehydromelanervin (10)

UV: (MeOH) λ_{max} = 249, 275, 320 nm; MS: (EI 70 eV, 4 KV, 100μA, 210°; DI 180°, 6.10^{-7}T) *m/e* 510 M^+ (rel. int. 3%) 492 (6) 415 (23) 368 (12) 360 (5) 268 (100) 240 (7) 239 (11) 193 (19) 166 (29) 138 (20).

Degradation of 3 *with* 2*N NaOH*

20 mg 3, dissolved in 20 ml NaOH were refluxed under N_2-flow to 100° for 1 hr. After cooling with ice the solution was acidified carefully with 5 ml 32% HCl. The product was extracted 4 times with Et_2O. The ether layers, dried with Na_2SO_4 were concentrated and analyzed by tlc(A). Under the same conditions a reductive alkaline degradation was performed by addition of 6 g powdered sodium amalgam. The main components 12 and 14 were isolated by preparative tlc as described before (system A). All compounds were identified by subjecting the mixture to GC–MS, trimethylsilylated in the usual manner. GC-conditions: 2m, 6 × 3 mm, 10% UCCW-982 column; Helium flow 50 ml/min; temperature programmed 140–250°, 5°/min; injection 280°; scan 0.5 cm/min; MS-conditions: ion source EI 70 eV, 4 KV 100 μA, 150–200°, direct inlet 150°, 5·10^{-7}–5·10^{-6}T, GC inlet and separator 200°, 30 ml He/min.

Benzoic acid

R_f 0.69; MS: *m/e* 122 M^+ (95% rel.int.) 105 (100) 77 (63) 51 (21); benzoic acid TMS-ester: retention time t_r = 1.2 min; *m/e* 194 M^+ (rel.int. 5%) 180 (16) 179 (100) 136 (75) 105 (68) 77 (30) 75 (8) 73 (7) 51 (8) 40 (15).

3-*Phenylpropanol*-1

R_f 0,67; MS: *m/e* 136 M^+ (rel.int. 28%) 118 (72) 117 (89) 92 (61) 91 (100) 69 (32) 57 (45); phenylpropanol-TMS-ether: t_r = 3.2 min; MS: *m/e* 208 M^+ (rel.int. 3%) 193 (16) 175 (5) 119 (10) 118 (100) 117 (75) 103 (6) 92 (14) 91 (39) 89 (56) 75 (26) 73 (25) 65 (9) 40 (12).

Hydrocinnamic acid

R_f 0,73; MS: *m/e* 150 M^+ (rel.int.48%) 133 (5) 132 (6) 131 (12) 105 (21) 104 (63) 91 (100) 78 (14) 77 (13) 65 (10) 51 (16); hydrocinnamic acid-TMS-ester: t_r = 4.2 min; MS: *m/e* 222 M^+ (rel.int. 17%) 208 (9) 207 (50) 189 (4) 132 (6) 131 (3) 105 (12) 104 (100) 103 (4) 91 (21) 77 (7) 75 (73) 73 (35).

Cinnam acid

R_f 0,66; MS: *m/e* 148 M^+ (90% rel.int.) 147 (100) 131 (26) 103 (54) 102 (27) 94 (18) 91 (30) 77 (48) 51 (36); cinnamic acid-TMS-ester: t_r = 6.2 min; MS: *m/e* 220 M^+ (rel.int. 23%) 206 (17) 205 (100) 161 (76) 145 (24) 135 (17) 131 (88) 103 (53) 102 (11) 77 (41) 75 (46) 73 (15).

Methylphloroglucinol-β-monomethylether (14)

(2,4-Dihydroxy-6-methoxytoluene) R_f 0.48; m.p. 113° IR: (KBr) $\tilde{\nu}$ = 3340 cm^{-1} (OH), 1610 (Ar), 1100 (CO); NMR: ($CDCl_3$ + DMSO-d_6, TMS int.); δ = 1.91 ppm (s, 3H) CH_3-Ar; 3.71 (s, 3H) OCH_3; 5, 2–5, 85 (br.1H) OH; 5.92 (d, J = 2.5 Hz, 1H) H-5; 6.05 (d, J = 2.5 Hz, 1H) H-3; MS: *m/e* 154 M^+ (rel.int. 100%) 153 (34) 139 (26) 125 (15) 123 (35) 69 (29) 55 (14); methylphloroglucinol-β-monomethylether-PTMS-ether: t_r = 8.3 min; MS: *m/e* 299 (rel.int. 26%) 298 M^+ (100) 297 (12) 284 (10) 283 (34) 269 (5) 268 (4) 251 (15) 209 (1) 147 (2) 133 (3) 119 (2) 89 (2) 75 (4) 73 (24) 45 (6).

Phloroglucinol

R_f 0,16; MS: *m/e* 127 (rel.int. 6%) 126 M^+ (100) 111 (5) 98 (4) 97 (7) 85 (15) 80 (10) 69 (11) 55 (5) 52 (9); phloroglucinol-PTMS-ether: t_r = 8.6 min; MS: 343 (rel.int. 18%) 342 M^+ (53) 328 (19) 327 (63) 268 (8) 253 (6) 147 (20) 133 (10) 75 (7) 74 (8) 73 (100) 45 (14).

Methylphloroglucinol (12)

R_f 0.25; m.p. 204–207° (EtOH); IR: (KBr) $\tilde{\nu}$ = 3420 cm^{-1} (OH) 1610 (Ar); 1130, 1075 (CO); NMR: (DMSO-d_6, TMS int.) δ = 1.81 ppm (s, 3H) CH_3-Ar; 5.80 (s, 2H) ArH; 8.4–8.6 (br, 3H) OH; MS: *m/e* 140 M^+ (rel. int. 100%) 139 (81) 123 (15) 122 (14) 111 (10) 85 (11) 69 (28) 55 (15); methylphloroglucinol-PTMS-ether t_r = 9.8 min; MS: *m/e* 357 (rel.int.33%) 356 M^+ (100) 341 (25) 327 (4) 283 (6) 268 (8) 253 (18) 251 (6) 147 (6) 133 (4) 75 (3) 74 (3) 73 (35) 45 (4).

Methylation of 14

A sample of 5 mg of isolated 14 was dissolved in 1 ml DMF and 50 mg dry K_2CO_3 and 2 ml MeI were added to the solution. After stirring for 5 hr the inorganic salts were filtered, washed with Et_2O, the filtrate concentrated and taken up in $CHCl_3$, finally washed with water and dried with Na_2SO_4, yielding an oily residue of 13.

2,4,6-*Trimethoxytoluene* (13)

R_f 0.63 (C); IR: (film on NaCl discs) $\tilde{\nu}$ = 2840 cm^{-1}, 2940 (CH), 1590 (Ar), 1125 (CO), NMR: ($CDCl_3$, TMS int.) δ = 2.0 ppm (s, 3H) CH_3-Ar; 3.75, 3.79 (s, 9H) OCH_3; 6.11 (s, 1H) ArH; MS: (EI 70eV, 4KV, 100 μA, 140°; DI 50°, 10^{-6} T) *m/e* 183 (rel.int.8%) 182 M^+ (100) 181 (22) 167 (17) 153 (20) 151 (23) 139 (12) 121 (15) 91 (6).

Degradation of 3 *with* $AlCl_3$

A sample of 3 (100 mg) was dissolved in 50 ml benzene and refluxed under stirring with 1 g dry $AlCl_3$ for 2 hr. After cooling the green solution was diluted with 80 ml 0.1 N HCl. The aqueous acid layer was washed with benzene and EtOAc and all benzenic

solutions combined. After concentration, the red organic layers were purified and fractionated in 50 ml portions by CC (A). Fractions 4–6 gave a crystalline product identified as **15**.

Methylphloracetophenone (**15**)

M.p. 203°; R_f 0.42 (A); UV: (MeOH λ_{max} = 210 (sh), 225, 289, 335 nm (MeOH + NaOAc) 298 (sh), 322 nm (MeOH + NaOMe) 324, 385 (sh) nm (MeOH + $AlCl_3$) 218, 242 (sh), 310, 382 nm; IR: (KBr) $\tilde{\nu}$ = 3200 cm^{-1} (OH), 1610 (C=O), 1105 (CO), 790 (Ar); NMR: (DMSO-d_6, TMS int.) δ = 1.87 ppm (s, 3H) CH_3–Ar; 2.58 (s, 3H) CH_3–CO; 6.03 (s, 1H) H-3; 10.32 (s_{br}, 1H); 10.55 (s, 1H) OH-2.6; 13.96 (s, 1H) OH-2; MS: (EI, 70 eV, 4 KV, 300 μA, 200° DI 170°, 8.10^{-7} T) *m/e* 182 M^+ (44% rel.int.) 167 (100) 153 (6) 83 (30); methylphloracetophenone-PTMS-ether, retention time t_r = 12.6 min (GC-conditions see above); MS: *m/e* 401 (3% rel.int.) 400 (15) 399 (36) 398 M^+ (100) 383 (4) 311 (4) 295 (3) 293 (2) 221 (2) 193 (2) 147 (5) 133 (4) 75 (6) 74 (3) 73 (40) 45 (8).

Methylation of **15**

20 mg of the isolated compound **15** were methylated and purified as described above. The main product was eluted from tlc plates with $CHCl_3$ and concentrated to yield 2,4,6-trimethoxy-3-methyl-acetophenone R_f 0.60 (C) IR: (KBr) $\tilde{\nu}$ = 2840 cm^{-1}, 2940 (CH), 1680 (C=O), 1580 (Ar) 1103, 1135 (CO); NMR: ($CDCl_3$, TMS int.) δ = 2.05 ppm (s, 3H) CH_3–Ar; 2.49 (s, 3H) CH_3–CO; 3.70, 3.80, 3.83 (s, 9H) OCH_3; 6.23 (s, 1H) H-5; MS: (EI 70 eV, 4 KV, 100 μA, 180°; DI 150°, 10^{-6} T) *m/e* 224 M^+ (88% rel.int.) 209 (100) 194 (46) 136 (21) 91 (54).

Acetylation of **3**

A sample (50 mg) of **3** was acetylated in pyridine and Ac_2O at room temp. overnight and worked up as usual. Preparative tlc (system D) and elution with $CHCl_3$ yielded the tetraacetate **4** (11 mg) and the triacetate **5** (31 mg) and were recrystallized from 90% EtOH.

Melanervin-tetraacetate (**4**)

(2,4 - Diacetoxy-6-methoxy)-tolyl-3-(5,7 - diacetoxy-6-methyl)-flavanonyl-8-phenylmethane; m.p. 134° (colourless needles from EtOH); $C_{39}H_{36}O_{11}$ (680.68) Calc. C, 68.81; H, 5.33; found: C, 68.54; H, 5.17%; R_f 0.66 (D) UV: (MeOH) λ_{max} = 225 (sh), 263, 326 nm; IR: (KBr) $\tilde{\nu}$ = 1750 cm^{-1} (Ester C=O), 1675 (Flav. C=O), 1600 (Ar), 1180 (CO); NMR: ($CDCl_3$, TMS int.) δ = 1.65 ppm (s, 3H), 1.81 (s), 1.83 (s), 1.88 (s) 12H OAc + $ArCH_3$; 2.42 (s, 3H), OAc-5; 2.16–3.05 (m, 2H) CH_2-3; 3.78 (s, 3H) OCH_3; 5.25 (dd, J = 5 a. 12 Hz, 1H) H-2; 5.91 (s, 1H) CH-9; 6.32 (s, 1H) ArH; 6.9–7.45 (m, 10 H) Ph; MS: (EI 70 eV, 4 KV, 100 μA, 180°, DI 160°, 10^{-6} T) *m/e* 680 M^+ (rel.int. 10%) 639 (11) 638 (34) 637 (50) 620 (5) 597 (13) 596 (48) 595 (100) 580 (5) 579 (13) 578 (5) 577 (17) 576 (47) 554 (14) 553 (35) 538 (4) 537 (13) 536 (6) 535 (22) 534 (58) 512 (4) 511 (8) 495 (5) 494 (6) 493 (21) 492 (39) 459 (5) 450 (6) 433 (8) 417 (5) 407 (6) 391 (8) 390 (7) 389 (25) 363 (8) 361 (5) 359 (6) 357 (6) 313 (10) 309 (6) 285 (12) 284 (21) 283 (13) 281 (4) 255 (13) 253 (8) 243 (20) 242 (23) 241 (34) 227 (7) 225 (8) 167 (5) 166 (5) 154 (12) 153 (8) 139 (9) 131 (25) 105 (4) 104 (13) 103 (12) 91 (8) 83 (13) 78 (10) 77 (8) 69 (5) 55 (5) 44 (14) 43 (79) 42 (2).

Melanervin-7,2",6"-triacetate (**5**)

(2,4-Diacetoxy-6-methoxy)-tolyl-3-(5-hydroxy-7-acetoxy-6-methyl)-flavanonyl-8-phenylmethane; m.p. 128° (colourless splinters from EtOH–$CHCl_3$ 1:1); R_f 0.79 (D); $C_{37}H_{34}O_{10}$ 638.64; Calc. C, 69.58; H, 5.37; found C, 69.08; H, 5.35%; UV: (MeOH) λ_{max} 237 (sh), 279, 355 nm; (MeOH + NaOAc) 280, 348 nm; (MeOH + NaOMe) 285, 335 nm; (MeOH + $AlCl_3$) 280, 310, 350, 410 nm; IR: (KBr) $\tilde{\nu}$ = 2900 cm^{-1} (OH + CH), 1750 (Ester C=O) 1630 (Flav. C=O) 1166 (CO), 694 (Ar); NMR ($CDCl_3$ TMS int.) δ = 1.61 (s, 3H) OAc; 1.82 (s) 1.86 (s) 1.91 (s) 12H, OAc + $ArCH_3$; 2.55–3.35 (m, 2H) CH_2-3; 3.78 (s, 3H) OCH_3; 5.25 (dd, J = 5.5 a. 11 Hz, 1H) H-2; 5.87 (s, 1H) CH-9; 6.30 (s, 1H) ArH; 7.0–7.45 (m, 10 H) Ph; 12.21 (s, 1H) OH-5; MS: (EI 70 eV, 4 KV, 100 μA, 200°, DI 140° 10^{-6} T); *m/e* 638 M^+ (rel.int. 13%) 597 (17) 596 (50) 595 (100) 579 (21) 554 (15) 553 (33) 536 (16) 511 (11) 493 (25) 492 (46) 389 (26) 285 (15) 284 (21) 283 (17) 243 (20) 242 (23) 241 (47) 131 (25) 103 (12) 83 (16) 43 (79).

Methylation of **3**

A sample (100 mg) of **3** was dissolved in 15 ml acetone. 1 g K_2CO_3 and 5.0 ml dimethylsulphate were added dropwise. The mixture was refluxed and heated under stirring. After 40 min the yellow solution formed a colourless suspension, which was cooled and filtered to yield an orange oil after concentration. The oil was treated with hot 70% MeOH and the solution gave a pale yellow precipitate after cooling. The product was composed of 2 main components which were separated by tlc (syst. B). The upper zone (R_f 0.56) after elution yielded 15 mg of **6**, the lower zone (R_f 0.47) was a partially methylated product.

Melanervinchalcone pentamethylether (**6**)

2,4,6-Trimethoxytolyl-3-(2',4',6'-trimethoxy-3'methyl)-chalconyl-5'-phenylmethane; m.p. 70–75° amorphous; $C_{36}H_{38}O_7$ 582.66 calc. C, 74.20; H, 6.57; found C, 73.69; H, 6.61; R_f 0.56 (B); UV: (MeOH) λ_{max} = 285, 321, 372, (sh), nm; IR: (KBr) $\tilde{\nu}$ = 2930, 2820 cm^{-1} (CH), 1640 (C=O), 1580 (Ar), 1100 (CO), 690 (Ar); NMR: ($CDCl_3$, TMS int.); δ = 2.10 ppm (s, 3H); 2.19 (s, 3H) CH_3Ar; 3.12, 3.16, 3.22, 3.50, 3.71, 3.81 (s, 18H) OCH_3; 6.26, 6.31 (s, 2H) CH-9, Ar-H; 6.95 (d, J = 16 Hz, 1H) CH-α; 7.0–7.5 (m) Ph, 7.41 (d, J = 16 Hz, 1H) CH-β 11H; MS: (EI 70 eV, 4 KV, 100 μA, 200°, DI 180°, 10^{-6} T) *m/e* 582 M^+ (rel.int. 67%) 583 (25) 568 (20) 567 (54) 552 (19) 551 (37) 537 (9) 536 (37) 535 (100) 519 (13) 459 (20) 445 (6) 431 (12) 401 (5) 387 (10) 341 (4) 327 (5) 309 (8) 297 (8) 283 (14) 271 (17) 270 (35) 269 (12) 255 (15) 239 (40) 227 (15) 216 (12) 195 (37) 193 (42) 182 (16) 179 (20) 177 (8) 165 (41) 135 (12) 131 (41) 117 (21) 115 (12) 105 (20) 103 (46) 92 (8) 91 (66) 77 (21) 44 (87).

Alkaline fission of **6** *in alcoholic KOH*

A sample (5 mg) of **6** in 15 ml ethanol and 5 ml 50% KOH was refluxed for 5 hr analogous to the procedure described with 2 N NaOH. EtOH was destilled under diminished pressure and replaced by water. After extracting the acidified solution exhaustively with ether a syrupy product was obtained, which was examined by tlc (syst. B) and separated and identified by GC-MS and comparison with authentic samples. GD-conditions: Column 2m 6 × 3 mm 10% UCCW-982, He flow 65 ml/min; temperature programmed 150–250°, 5°/min; injection 290°; scan 0.5 cm/min; MS-conditions: ion source EI 70 eV, 4 KV, 300 μA, 150–200°; GC inlet 200°, separator 200°. 2,4,6-trimethoxytoluene (**13**). Retention time t_r = 6.1 min, R_f 0.88 (B); MS: *m/e* 182 M^+ (100% rel.int.) 181 (22) 167 (17) 153 (20) 151 (23) 139 (12) 121 (15) 91 (6) benzoic acid R_f 0.53; t_r = 8.5 min; MS: *m/e* 122 M^+ (95% rel.int.) 105 (100) 77 (68) 51 (30). Cinnamic acid. R_f 0.34; t_r = 14.0 min; MS: *m/e* 148 M^+ (84% rel.int.) 147 (100) 131 (30) 103 (55) 102 (25) 94 (18) 91 (45). 2,4,6-Trimethoxy-3-(methyl phenyl)-phenylmethane (**16**) R_f 0.70; t_r = 18.4 min; MS: *m/e* 273 (17% rel.int.) 272 M^+ (86) 257 (10) 243 (9) 241 (8) 227 (12) 225 (6) 195 (25) 181 (22) 167 (10) 165 (8) 119 (10) 109 (75) 108 (100) 91 (94) 79 (23) 67 (42) 55 (20). Bis-(2,4,6-trimethoxy-3-methylphenyl)-phenylmethane (**17**) R_f 0.60; t_r 51 min; MS: *m/e* 452 M^+ (rel.int. 28%) 437 (11) 423 (15) 421 (14) 375 (6) 361 (18) 345 (6) 315 (12) 298 (9) 284 (20) 270 (38) 255 (20) 241 (15) 239 (14) 227 (31) 207 (14) 195 (17) 193 (17) 193 (10) 182 (21) 180 (20) 168 (28) 167 (25) 165 (18) 151 (13) 119 (17) 109 (100) 108 (95) 95 (40) 91 (52) 69 (53) 55 (65). 2,4,6-Trimethoxy-5-methyl-3-(2,4,6-trimethoxy-tolyl-3)-benzylidene-acetophenone (**18**) R_f 0.77; t_r = 58 min; MS: (EI 70 eV, 4 KV, 100 μA, DI 200° 5·10^{-6} T) *m/e* 494 M^+ (rel.int. 88%) 479 (100) 447 (76) 371 (18) 355 (29) 298 (30) 297 (70) 270 (59) 195 (35) 193 (47) 165 (32) 147 (23) 91 (41) 73 (42).

Isolation of isomelanervin (**7**)

The $CHCl_3$ extract of the flowers of *Melaleuca quinquenervia*, after treatment with petroleum ether (see isolation of **3**) was dissolved in Et_2O and extracted with 2% NaOH-solution. The aqueous layer formed a light brown precipitate, which was filtered and rejected. The acidified (HCl) filtrate after standing for some days yielded a voluminous precipitate of raw isomelanervin, purified by CC as described above. (2,4-Dihydroxy-6-methoxy)-tolyl-3-(5,7-dihydroxy-6-methyl)-flavanonyl-6-phenylmethane; m.p. 235–237° (EtOH–$CHCl_3$ 1:1); $C_{31}H_{28}O_7$ 512.13; Calc. C, 72.64; H, 5.51; found C, 72.44, H, 5.47; R_f 0.81 (A) 0.40 (B); 0.20 (polyamide, MeOH); UV: (MeOH) λ_{max} = 299,

338 nm (MeOH + NaOAc) 257 (sh), 340 nm; (MeOH + NaOMe) 257 (sh), 329 nm; (MeOH + $AlCl_3$) 319, 400 nm (sh); IR (KBr) $\tilde{\nu}$ = 3430 cm^{-1} (OH), 2940; (CH), 1625 (C=O), 1123 (CO), 805, 750, 728, 694 (Ar); NMR: (^{1}H, DMSO-d_6 + $CDCl_3$, TMS int. 35°) δ = 2.02 ppm (s, 6H) CH_3-6, 3''; 2.82-3.38 (m, 2H) CH_2-3; 3.73 (s, 3H) OCH_3; 5.47 (dd, J = 5 a. 10 Hz, 1H) H-2; 6.12 (s, 1H) CH-9; 6.35 (s, 1H) H-3''; 7.15 (s, 5H) P''''; 7.41 (s, 5H) Ph'; 8.3–10.0 (br, 3H) OH-2'', 6'', 7; 13.66 (s, 1H) OH-5.

Acetylation of **7**

40 mg of **7** were suspended in 2 ml Ac_2O and 20 mg dry NaOAc. The mixture was refluxed for 15 hr and worked up in the usual way to yield compound **8** (18 mg) and **9** (16 mg). As with **4** and **5**, the acetates were separated by tlc. Isomelanervin-7,2'',6''-triacetate (**9**), (2,4-Diacetoxy-6-methoxy)-tolyl-3-(5-hydroxy-7-acetoxy-8-methyl)-flavanonyl-6-phenylmethane had m.p. 133–134° (colourless plates from ethanol-chloroform 3:1) $C_{37}H_{34}O_{10}$ (638.64) calc. C, 69.58; H, 5.37; found C, 69.65; H, 5.22%; R_f 0.77 (D); UV: (MeOH) λ_{max} = 279 nm, 355; (MeOH + NaOMe) 255 (sh), 330 nm; (MeOH + NaOAc) 278, 344 nm; (MeOH + $AlCl_3$) 279, 355 nm; IR: (KBr) $\tilde{\nu}$ = 2930 cm^{-1} (CH), 2500–3100 (OH), 1750 (Ester C=O) 1625 (Flav. C=O), 1177, 1115 (CO), 694 (Ar); NMR ($CDCl_3$, TMS int.) δ = 1.70 ppm (s), 1.73 (s) OAc; 1.90, 1.95 (s, 12H) OAc + CH_3-Ar; 2.70–3.50 (m, 2H) CH_2-3; 3.80 (s, 3H) OCH_3; 5.50 (dd, J = 5 a. 12 Hz, 1H) H-2; 6.09 (s, 1H) CH-9; 6.52 (s, 1H) ArH-5'' 7.18 (m, 5H) Ph''''; 7.48 (s, 5H) Ph'; 12.3 (s, 1H) OH-5; MS: (EI 70 eV, 4 KV, 300 μA 210°; DI 190°; 10^{-6} T) *m/e* 638 M^+ (rel.int. 25%) 597 (15) 596 (46) 595 (54) 579 (11) 553 (21) 535 (24) 501 (27) 493 (24) 459 (27) 417 (13) 389 (35) 359 (15) 357 (12) 313 (26) 295 (12) 285 (24) 284 (91) 283 (22) 255 (19) 253 (12) 243 (37) 242 (60) 241 (100) 225 (13) 154 (30) 139 (16) 131 (51) 103 (27) 91 (13) 83 (43) 77 (16) 69 (59) 32 (> 100).

Isomelanervin-tetraacetate (**8**)

(2, 4-Diacetoxy-6-methoxy)-tolyl-3-(5, 7-diacetoxy-8-methyl)-flavanonyl-6-phenylmethane; m.p. 147° (colourless splinter from ethanol-chloroform 3:1); $C_{39}H_{36}O_{11}$ (680.68) Calc. C, 68.81; H, 5.33; found: C, 68.53 H, 5.12%; R_f 0.70 (D); UV: (MeOH) λ_{max} = 225 (sh), 265, 330 nm; IR: (KBr) $\tilde{\nu}$ = 2930 cm^{-1} (CH), 1750 (Ester C=O), 1680 (Flav. C=O), 1590 (Ar), 1165 (CO), 695, 750 (Ar); NMR: ($CDCl_3$; TMSint.) δ = 1.95 ppm, 1.97 (s, 18H) OAc + CH_3-Ar; 2.55–3.40 (m, 2H) CH_2-3; 3.82 (s, 3H) OCH_3; 5.50 (dd, J = 5 a. 12 Hz, 1H) H-2; 5.95 (s, 1H) CH-9; 6.53 (s, 1H) ArH-5''; 7.20 (s, 5H) Ph''''; 7.48 (s, 5H) Ph'; MS: (EI 70 eV, 4 KV, 300 μA, 210°, DI 190°, 10^{-6} T) *m/e* 680 M^+ (rel.int. 4%) 639 (25) 638 (67) 637 (37) 597 (23) 596 (66) 595 (79) 579 (12) 578 (14) 577 (21) 554 (17) 553 (31) 531 (18) 536 (27) 535 (56) 519 (17) 501 (29) 493 (44) 477 (15) 459 (27) 431 (12) 417 (16) 390 (15) 389 (54) 359 (17) 357 (15) 313 (28) 285 (31) 284 (56) 283 (28) 255 (23) 253 (17) 243 (37) 242 (58) 241 (100) 227 (13) 225 (14) 154 (31) 139 (19) 131 (54) 103 (23) 91 (14) 83 (44) 43 (> 100).

Synthesis of Bis-(2,4,6-trimethoxyphenyl)-phenylmethane (**21**)

5 ml 32% HCl were slowly poured to 3 g 1,3,5-trimethoxybenzene and 1 g benzaldehyde. The resulting precipitate was treated twice with 5 ml water and decanted. The white crystalline product was filtered and washed free from acid. After drying and recrystallization from EtOH 3,15 g of colourless plates were obtained. m.p. 190° (EtOH); UV (MeOH) λ_{max} = 244 (sh), 265, 273 nm; IR: (KBr) $\tilde{\nu}$ = 3000 cm^{-1}, 2940, 2850 (CH), 1580 (Ar), 1115 (CO), 695, 810 (Ar); R_f 0.55 (B); NMR: (^{1}H, $CDCl_3$, TMS int.) δ = 3.50 ppm (s, 12H) OCH_3-2, 2', 6, 6'; 3.78 (s, 6H)OCH_3-4, 4'; 6.11 (s, 4H) H-3, 3', 5, 5'; 6.23 (s, 1H) CH; 7.09 (s, 5H) Ph; NMR: (^{13}C, $CDCl_3$, TMS int.) δ = 37.0 ppm C-8a; 54.9 C-4''a; 91.7 C-3'', 5''; 114.0 C-1''; 123.6 C-4''; 126.5 C-3''', 5'''; 127.3 C-2''', 6'''; 145.1 C-1'''; 158.6 C-4''' 159.2 C-2'', 6''.; MS: (EI 70 eV, 4 KV, 100 μA, 180°, DI 120°, 8.10^{-7} T) *m/e* 425 (rel.int. 20%) 424 M^+ (72) 409 (7) 393 (18) 247 (15) 331 (10) 301 (6) 257 (29) 256 (100) 255 (28) 241 (17) 228 (21) 227 (16) 226 (11) 225 (23) 212 (13) 196 (12) 181 (41) 180 (16) 179 (94) 168 (10) 165 (13) 151 (19) 121 (17) 91 (42) 78 (6) 77 (5) 69 (6).

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