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AROMATIC SESQUITERPENOIDS FROM *EMMOTUM NITENS*[*]

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Key Word Index—*Emmotum nitens*; Icacinaceae; sesquiterpenoid tetralins; sesquiterpenoid naphthalenes; emmotin-A, -B, -C, -D; ^{13}C-NMR spectroscopy.

Abstract—The trunk wood of *Emmotum nitens* (Benth.) Miers (Icacinaceae) contains the aromatic sesquiterpenes 2-hydroxy-3-(2′-hydroxyisopropyl)-8-methoxymethyl-5-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene (emmotin-A), 2-hydroxy-5-hydroxymethyl-3-(2′-hydroxyisopropyl)-8-methoxymethyl-1-oxo-1,2,3,4-tetrahydronaphthalene (emmotin-B), 1,2-dihydroxy-8-formyl-3-isopropyl-5-methylnaphthalene (emmotin-C) and 8-carboxy-1,2-dihydroxy-3-(2′-hydroxyisopropyl)-5-methylnaphthalene γ-lactone (emmotin-D).

A SPECIMEN of *Emmotum nitens* (Benth.) Miers, an arboreous Icacinaceae species growing in the vicinity of Diamantina in the Brazilian state of Minas Gerais, was collected and identified by the botanist A. Pereira Duarte. A chemical investigation of the trunk wood has now revealed the presence of sitosterol and four crystalline compounds, designated emmotin-A, -B, -C, and -D.

Elemental analysis and MS MW determination of emmotin-A indicated its formula to be $C_{16}H_{22}O_4$. Its UV and IR spectra revealed the presence of an aryl ketone moiety and its PMR spectrum exhibited signals characteristic of two *ortho* hydrogens, aromatic methyl and methoxymethyl groups, a 2-hydroxyisopropyl function and a 3-carbon unit defined in part structure **1**. The relative substituent positions in the latter were determined from the shift and coupling behavior of its 4 hydrogens. The oxymethine hydrogen (4·43 ppm) was represented by a doublet of 12·5 Hz, the other methine hydrogen (2·21 ppm) by a double 1 : 2 : 1 triplet of 12·5, 12·5 and 4·5 Hz and the methylene hydrogens (2·53, 3·02 ppm) by two quartets of 16·5 and 12·5 Hz and of 16·5 and 4·5 Hz, respectively. The chemical shifts of the hydrogens of the 3-carbon system indicated the terminal carbons to be attached to the carbonyl group and aromatic ring and hence the central carbon to the hydroxyisopropyl group. The presence of an α-ketol function in emmotin-A, indicated by the deacetoxylation of the diacetate **2b** and formation of

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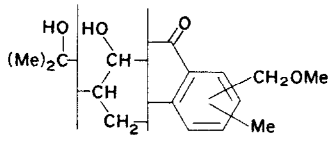
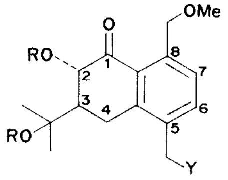
[*] Part I in the projected series "The Chemistry of Brazilian Icacinaceae", taken from part of the M. S. Thesis submitted by M. de L. M. F. to the Universidade Federal de Minas Gerais, and Part XXI in the series "^{13}C NMR Spectroscopy of Naturally Occurring Substances".

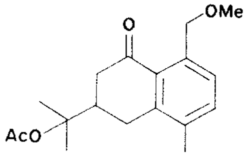
3 on reduction with zinc,[1] showed that the attachment of the 3-carbon unit to the remainder of the ring system could only be in the form depicted in 2a.



(1)

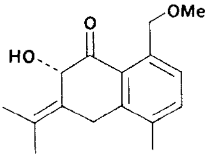


(2a) R = H ; Y = H
(2b) R = Ac; Y = H
(2c) R = H ; Y = OH
(2d) R = Ac; Y = OAc



(3)

The PMR spectrum of emmotin-A diacetate confirmed the structural environment of the nuclear hydroxy group by the *ca* 1 ppm paramagnetic shift experienced by the oxymethine hydrogen on acetylation. The side chain alcohol is tertiary and the natural product underwent dehydration on treatment with phosphorous oxychloride in pyridine. Although the resultant mixture could not be separated, its PMR spectrum revealed it to consist of olefins 4 and 5 by the methyl singlets (1·64, 1·73 ppm) of the isopropylidene unit of the former and the methyl singlet (1·57 ppm) and olefinic methylene multiplet (4·9–5·2 ppm) of the isopropenyl group of the latter. The methoxymethyl group was shown to be located *ortho* to the carbonyl function and its oxymethylene hydrogens deshielded by the latter, since sodium borohydride reduction of emmotin-A yielded a triol whose PMR spectrum revealed the oxymethylene hydrogen signal 0·9 ppm upfield of its earlier position. The combined PMR data for emmotin-A and its derivatives showed the natural product to possess structure 2a or 6a. While 2a was preferred on biogenetic grounds, its final proof depended on its ^{13}C NMR analysis (*vide infra*).



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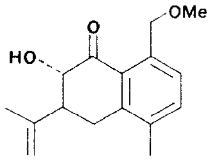

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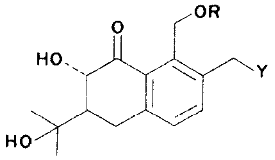

(6a) R = Me; Y = H
(6b) R = Me; Y = OH
(6c) R = H ; Y = OMe

The MS MW determination of emmotin-B showed it to be oxyemmotin-A, $C_{16}H_{22}O_5$. The PMR spectrum of emmotin-B resembled closely that of emmotin-A, differing mainly by the replacement of the aromatic methyl singlet (2·32 ppm) of the latter by an oxymethylene singlet (4·67 ppm). The presence of an extra hydroxy group was confirmed by the formation of a triacetate (2d) on acetylation of emmotin-B. The PMR spectrum of the acetate exhibited the new oxymethylene signal at expectedly lower field ($\Delta\delta$ 0·45). These facts support structure 2c, 2c with methoxymethyl and hydroxymethyl groups interchanged, 6b or 6c for emmotin-B.

The natural abundance ^{13}C NMR spectra of emmotin-A and emmotin-B yielded further insight into the structures of the two sesquiterpenes. Inspection of the proton-decoupled and the single-frequency, off-resonance decoupled spectra of the former in

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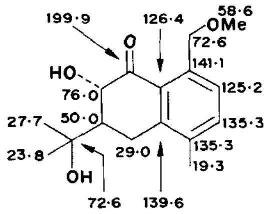
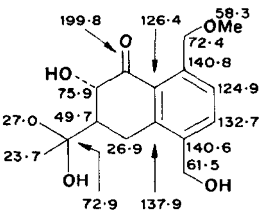
[1] Rosenfeld, R. S. and Gallagher, T. F. (1955) *J. Am. Chem. Soc.* 77, 4367.

$CDCl_3$ revealed one carbonyl, one quaternary sp^3 carbon and four quaternary aromatic carbon signals, two non-aromatic and two aromatic methine resonances, two methylene and four methyl signals, while a similar inspection of the spectra of emmotin-B in $CDCl_3$ showed the replacement of a methyl resonance by a methylene signal. The assignment of the chemical shifts of all non-aromatic carbons, indicated on formulas **7** and **8** for emmotin-A and emmotin-B, respectively, was based on chemical shift theory,[2] while that for the aromatic carbon shifts was founded on the following arguments. The difference of the methine carbon shifts is mainly due to the difference of the disposition of the carbons toward the carbonyl group, the *p*-carbon being deshielded strongly.[2] The latter as well as the quaternary centers under the aromatic methyl group and its *ortho* neighbour are the only aromatic carbons differing in chemical shift in the two compounds, hence revealing the presence of the extra oxygen in their vicinity in emmotin-B. The remaining two quaternary carbon shifts are assigned on the basis of expected similarity of the δ values of the two carbons *ortho* to the acylated carbon site.



(**7**)



(**8**)

The fact that only the shifts of the aromatic carbons in the neighbourhood of the aromatic methyl group of emmotin-A are changed in emmotin-B proves that the methyl function of the former and the hydroxymethyl group of the latter occupy the same position in the aromatic ring of the two substances. Furthermore, the shielding of the benzylic methylene group in the hydroaromatic ring on introduction of an oxygen onto the aromatic methyl group shows the *ortho* relationship between the two groups, excludes structures **6** for the emmotins and limits emmotin-A to structure **2a**. Finally, the nearly identical shifts of the methoxymethyl carbons and their aromatic neighbours in the two emmotins excludes the possibility of the methoxymethyl and hydroxymethyl units being interchanged in emmotin-B and limits the latter to structure **2c**.

The emmotins A and B coexist in the plant with structurally related, minor, naphthalenes. The PMR spectrum of one of the latter, emmotin-C ($C_{15}H_{16}O_3$), exhibited signals characteristic of three aromatic hydrogens, two hydroxy groups and one each of aldehyde, methyl and isopropyl functions, whose combination in light of a probable biogenetic relationship of emmotin-C with emmotin-A suggested structure **9** for the minor product. The aldehyde function (9·66 ppm singlet) was hydrogen-bonded to a hydroxyl group (12·3 ppm, *s*) and deshielded an *ortho* hydrogen (7·79 ppm) which was coupled strongly (8 Hz) to another hydrogen (7·24 ppm) whose PMR signal broadness revealed weak, long-range coupling with the neighbouring methyl group (*bs*. 2·77 ppm). These facts are in agreement with structure **9** for emmotin-C.

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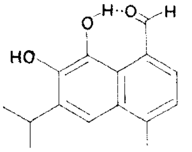
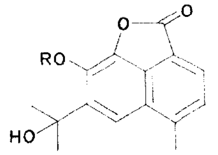
[2] STOTHERS, J. B. (1972) ^{13}C *NMR Spectroscopy*, Academic Press. New York; LEVY, G. C. and NELSON, G. L. (1972) ^{13}C *Nuclear Magnetic Resonance for Organic Chemists*, Wiley Interscience, New York.

The UV spectrum of another minor plant constituent, emmotin-D ($C_{15}H_{14}O_4$), showed it also to be a naphthalene, while its IR spectrum and that of its acetate (**10**b) and of its aryl methyl ether (**10**c), prepared *via* diazomethane, indicated it to possess a γ-lactone unit. The PMR spectra of emmotin-D and its derivatives revealed the plant product to contain two *ortho* hydrogens and another aromatic hydrogen, an aromatic methyl group, two hydroxy functions and two methyl groups, which, while deshielded, were reminiscent of those of the 2-hydroxyisopropyl unit of emmotins A and B. Attempted acetylation of **10**c gave a mixture of acetate and olefin. The isopropenyl unit (1·75 ppm methyl singlet, 5·0–5·2 ppm methylene multiplet) of the latter proved the presence of a 2-hydroxyisopropyl group in emmotin-D. These results and biogenetic considerations indicated structure **10**a for emmotin-D.

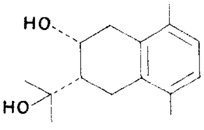


(9)

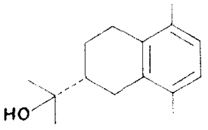


(10a) R = H
(10b) R = Ac
(10c) R = Me

The configurations of the four emmotins are related to the structures of rishitinol (**11**), recently isolated from diseased potato tubers,[3] and occidol (**12**).[4] Since the latter co-occurs in *Thuja occidentalis* L. with occidentalol (**13**),[5] a sesquiterpenic alcohol of the general eudesmane type, a 1-carbon shift seems to accompany the aromatization of sesquiterpenes obeying the Isoprene Rule.



(11)



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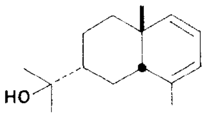

(13)

EXPERIMENTAL

Isolation of the constituents of Emmotum nitens. The trunk wood was separated into bark, heartwood and softwood and the ground heartwood (4·5 kg) extracted successively with benzene and EtOH in a Soxhlet. Chromatography of a portion (65 g) of the C_6H_6 extract (273 g) on silica (1·3 kg) and elution with C_6H_6 and C_6H_6–$CHCl_3$ (1 : 1) gave an oil and a solid, respectively, which were not investigated. Crystallization of the $CHCl_3$–C_6H_6 (3 : 2) eluate from Et_2O–petrol. (2 : 1) yielded emmotin-A (3·3 g), while crystallization of the $CHCl_3$–C_6H_6 (4 : 1) eluate from EtOH afforded emmotin-D (1·4 g). Crystallization of the $CHCl_3$–MeOH (9 : 1) eluate from EtOH led to emmotin-B (3·0 g). Chromatography of a portion (100 g) of the EtOH extract (310 g) on silica (1·0 kg) and rechromatography of the benzene eluate (2·5 g) on silica (50 g) gave a solid whose crystallization from 2 : 1 Et_2O–petrol. produced emmotin-C (52 mg). Extraction of the ground softwood (9·0 kg) with C_6H_6, chromatography of a portion (25 g) of the extract (210 g) on silica and crystallization of the C_6H_6–$CHCl_3$ (7 : 3) eluate from EtOH gave sitosterol (12 mg). Crystallization of the C_6H_6–$CHCl_3$ (1 : 1) eluate from 2 : 1 Et_2O–petrol. yielded more emmotin-A (735 mg), while crystallization of the $CHCl_3$–MeOH (20 : 1) eluate from EtOH afforded more emmotin-B (300 mg).

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[3] KATSUI, N., MATSUNAGA, A., IMAIZUMI, K., MASAMUNE, T. and TOMIYAMA, K. (1971) *Tetrahedron Lett.* 83.
[4] NAKAZAKI, M. (1962) *Chem. Ind.* 413.
[5] HORTMANN, A. and DE ROOS, J. B. (1969) *J. Org. Chem.* **34**, 736.

Emmotin-A (**2a**). Needles, m.p. 79° (Found: C, 69·00; H, 7·93. $C_{16}H_{22}O_4$ requires: C, 69·03; H, 7·97%). UV λ_{max}^{EtOH} (nm): 248, 254, 259, 303 (ε 9400, 11000, 9900, 2350). IR ν_{max}^{KBr} (cm^{-1}): 3470, 2960, 1675, 1575, 1475, 1400, 1100. PMR (δ): 1·33 (*s*, Me), 1·45 (*s*, Me), 2·21 (*td*, *J* 12·5, 12·5, 4·5 Hz, H-3), 2·32 (*s*, Me), 2·53 (*dd*, *J* 16·5, 12·5 Hz, H_{ax}-4), 3·02 (*dd*, *J* 16·5, 4·5 Hz, H_{eq}-4), 3·50 (*s*, OMe), 4·43 (*d*, *J* 12·5 Hz, H-2), 4·55 (*s*, OH), 4·62 (*s*, OH), 4·86, 4·93 (*d* each, *J* 16·5 Hz, AB of OCH_2), 7·46 (*d*, *J* 9·0 Hz, H-7), 7·54 (*d*, *J* 9·0 Hz, H-6). MS (m/e): 278 (35%) M, 260 (9), 232 (26), 231 (25), 229 (8), 228 (6), 227 (18), 220 (5), 204 (10), 203 (13), 202 (30), 201 (100), 200 (20), 199 (14), 189 (15), 188 (24), 187 (51), 186 (13), 185 (44), 183 (6), 176 (10), 175 (8), 174 (38), 173 (54), 172 (9), 171 (26), 170 (14), 169 (10), 161 (28), 160 (36), 159 (54), 158 (13), 157 (18), 156 (6), 149 (7), 148 (55), 146 (10), 145 (19), 141 (36), 133 (9), 132 (6), 131 (18), 130 (7), 129 (18), 128 (20), 127 (8), 118 (7), 117 (13), 116 (17), 115 (29), 105 (11), 103 (9), 91 (26).

Emmotin-A diacetate (**2b**). Crystals, m.p. 98–99° (Et_2O–petrol.). IR ν_{max}^{KBr} (cm^{-1}): 2920, 1740, 1730, 1680, 1575, 1477, 1463, 1370, 1260, 1236. PMR (δ): 1·55 (*s*, Me), 1·61 (*s*, Me), 2·01 (*s*, OAc), 2·25 (*s*, OAc), 2·29 (*s*, Me), 2·74 (*dd*, *J* 16, 12·5 Hz, H_{ax}-4), 3·06 (*dd*, *J* 16, 4·5 Hz, H_{eq}-4), 3·25 (*td*, *J* 12·5, 12·5, 4·5 Hz, H-3), 3·46 (*s*, OMe), 4·72, 5·11 (*d* each, *J* 15 Hz, AB of OCH_2), 5·47 (*d*, *J* 12·5 Hz, H-2), 7·37 (*d*, *J* 8 Hz, H-7), 7·53 (*d*, *J* 8 Hz, H-6). MS (*m/e*); [362 (0%) M], 273 (2), 201 (100).

Reduction of emmotin-A. A mixture of emmotin-A (293 mg) and $NaBH_4$ (500 mg) in H_2O (5 ml) was stirred at room temp. (4 hr), then acidified with conc. HCl and diluted with H_2O (20 ml). It was concentrated under reduced pressure and the residue extracted with $CHCl_3$. The extract was washed with H_2O, dried and evaporated and the oily residue (192 mg) purified by silica chromatography. IR ν_{max}^{KBr} (cm^{-1}): 3310, 2950, 1460, 1450, 1380, 1260, 1080, 820. PMR (δ): 1·33 (*s*, Me), 1·36 (*s*, Me), *ca* 1·9 (*m*, H-3), 2·22 (*s*, Me), 2·36 (*m*, H-4), 2·85 (*m*, H-4), 3·40 (*s*, OMe), 3·70 (*b s*, OCH_2), 3·95 (*b s*, 2 OH), 4·15 (*t*, *J* 11 Hz, H-2), 4·90 (*s*, OH), 5·13 (*d*, *J* 11 Hz, H-1), 7·11 (*s*, H-6, H-7).

Deoxyemmotin-A acetate (**3**). A mixture of emmotin-A diacetate (59 mg) and Zn (60 mg) in HOAc (15 ml) was refluxed for 7 hr and then filtered. The filtrate was diluted with Et_2O and the solution washed with 5% aqueous NaOH and with H_2O and dried. Evaporation yielded an oil (49 mg), a single component by TLC. IR ν_{max}^{film} (cm^{-1}): 3450, 2975, 2920, 1740, 1680, 1580, 1480, 1375, 1260, 1140, 1110. PMR (δ): 1·59 (*s*, 2 Me), 2·03 (*s*, OAc), 2·34 (*s*, Me), 2·5–2·9 (*m*, 2 H-2, 2 H-4), 3·49 (*s*, OMe), 4·71 (*b s*, OCH_2), 7·35 (*d*, *J* 8 Hz, H-7), 7·54 (*d*, *J* 8 Hz, H-6).

Dehydration of emmotin-A. A mixture of emmotin-A (100 mg) and $POCl_3$ (2 ml) in pyridine (1 ml) was kept at room temp. (2 hr). It was poured into ice water and the ppt., needles m.p. 144–150°, filtered. The latter was a two-component mixture (**4** and **5**) of close R_fs by TLC, which could not be separated by preparative TLC (silica-$AgNO_3$). PMR (δ): 1·57 (*s*, Me), 1·64 (*s*, Me), 1·73 (*s*, Me), 2·28 (*s*, Me), 2·5–3·0 (*m*), 3·44 (*s*, OMe), 4·75 (*b s*, OCH_2), 4·9–5·2 (*m*, olefinic CH_2), 7·40 (*d*, *J* 8 Hz, H-7), 7·54 (*d*, *J* 8 Hz, H-6).

Emmotin-B (**2c**). Needles, m.p. 138–140°. UV λ_{max}^{EtOH} (nm): 253, 299 (ε 12690, 28180). IR ν_{max}^{KBr} (cm^{-1}): 3450, 3430, 3350, 1685, 1675, 1575, 1450, 1425, 1390, 1275, 1100, 1070, 1030, 1025. PMR (δ): 1·28 (*s*, Me), 1·41 (*s*, Me), 2·01 (*td*, *J* 12·5, 12·5, 4·5 Hz, H-3), 2·59 (*dd*, *J* 16·5, 12·5 Hz, H_{ax}-4), 3·16 (*dd*, *J* 16·5, 4·5 Hz, H_{eq}-4), 3·49 (*s*, OMe), 4·38 (*d*, *J* 12·5 Hz, H-2), 4·55 (*s*, OH), 4·67 (*s*, $HOCH_2$), 4·67, 4·87 (*d* each, *J* 15 Hz, AB of $MeOCH_2$), 7·49 (*s*, H-6, H-7). MS (*m/e*): 294 (5%) M, 276 (4), 259 (5), 258 (27), 243 (5), 231 (9), 230 (100), 229 (8), 217 (7), 215 (7), 211 (9), 208 (5), 204 (5), 201 (5), 200 (6), 199 (22), 198 (5), 189 (6), 187 (7), 186 (15), 185 (9), 173 (5), 172 (6), 169 (6), 159 (6), 158 (13), 157 (12), 145 (8), 129 (11), 128 (12), 127 (7), 120 (5), 117 (6), 115 (11), 105 (8), 91 (10). (Found: M 294·1456. $C_{16}H_{22}O_5$ requires: M 294·1467).

Emmotin-B triacetate (**2d**). Needles, m.p. 125–126° (EtOH). IR ν_{max}^{KBr} (cm^{-1}): 1745, 1725, 1690, 1375, 1260, 1240. PMR (δ): 1·54 (*s*, Me), 1·62 (*s*, Me), 2·01 (*s*, OAc), 2·10 (*s*, OAc), 2·25 (*s*, OAc), 2·3–3·4 (*m*, H-3, 2 H-4), 4·71, 4·91 (*d* each, *J* 15 Hz, $MeOCH_2$), 5·11 (*s*, $AcOCH_2$), 5·49 (*d*, *J* 11 Hz, H-2), 7·56 (*d*, *J* 8 Hz, H-7), 7·70 (*d*, *J* 8 Hz, H-6). MS (*m/e*): 420 (0%) M, 361 (1), 199 (100).

Emmotin-C (**9**). Needles, m.p. 121–124° (Found: C, 73·69; H, 6·60. $C_{15}H_{16}O_3$ requires: C, 73·74; H, 6·61%). UV λ_{max}^{EtOH} (nm): 232, 254, 335, 374 (ε 23400, 18650, 2500, 2700); $\lambda_{max}^{EtOH+NaOH}$ (nm): 262, 344 (ε 12100, 1900); $\lambda_{max}^{EtOH+NaOH+HCl}$ (nm): 232, 252, 335, 374 (ε 23500, 15200, 2500, 2100). IR ν_{max}^{KBr} (cm^{-1}): 3440, 1650, 1570, 1450, 1360, 1330. PMR (δ); 1·43 (*d*, *J* 6 Hz, 2 Me), 2·77 (*s*, Me), 3·54 (sept., *J* 6 Hz, *i*-Pr CH), 6·69 (*s*, OH), 7·24 (*d*, *J* 8 Hz, H-6), 7·47 (*s*, H-4), 7·79 (*d*, *J* 8 Hz, H-7), 9·66 (*s*, CHO), 12·30 (*s*, OH). MS (*m/e*): 244 (24%) M, 243 (76), 242 (38), 241 (11), 229 (13), 228 (85), 226 (38), 215 (30), 214 (28), 210 (31), 200 (24), 199 (11), 197 (15), 187 (13), 184 (17), 183 (81), 182 (10), 173 (11), 169 (14), 168 (24), 157 (13), 156 (16), 155 (100), 154 (20), 153 (35), 152 (28), 145 (10), 143 (10), 142 (10), 141 (24), 139 (17), 129 (38), 128 (57), 127 (29), 116 (11), 115 (54), 91 (21).

Emmotin-D (**10a**). Needles, m.p. 209–210° (Found: C, 69·72; H, 5·45. $C_{15}H_{14}O_4$ requires: C, 69·74; H, 5·47%). UV λ_{max}^{EtOH} (nm): 226, 249, 254, 260, 338, 360 (ε 10550, 13950, 16200, 15550, 350, 750). IR ν_{max}^{KBr} (cm^{-1}): 3420, 3120, 1745, 1645, 1427, 1320, 1265, 1052, 750. PMR (d_6-acetone, δ): 1·94 (*s*, 2 Me), 2·87 (*s*, Me), 7·58 (*d*, *J* 7 Hz, H-6), 7·87 (*s*, H-4), 8·03 (*d*, *J* 7 Hz, H-7). MS (*m/e*): 258 (29%) M, 242 (14), 241 (63), 240 (100), 239 (59), 225 (44), 211 (10), 185 (14), 184 (86), 183 (17), 169 (20), 156 (17), 155 (18), 141 (42), 139 (13), 128 (16), 116 (10), 115 (56), 114 (12).

Emmotin-D monoacetate (**10b**). Crystals, m.p. 174–175° (Et_2O–petrol.). IR ν_{max}^{KBr} (cm^{-1}): 3440, 1786, 1735, 1670, 1500, 1380, 1260, 1190. PMR (δ): 1·92 (*s*, Me), 2·02 (*s*, Me), 2·45 (*s*, OAc), 2·81 (*s*, Me), 7·76 (*d*, *J* 7 Hz, H-6), 7·82 (*s*, H-4), 7·96 (*d*, *J* 7 Hz, H-7). MS (*m/e*): [300 (0%) M], 241 (20), 240 (100).

Emmotin-D methyl ether (**10c**). Needles, m.p. 171–172° (EtOH). IR ν_{max}^{KBr} (cm^{-1}): 3470, 1754, 1640, 1490, 1405, 1250, 1080, 798. PMR (δ): 1·76 (*s*, 2 Me), 2·77 (*s*, Me), 3·55 (*s*, OH), 4·38 (*s*, OMe), 7·43 (*d*, *J* 7 Hz, H-6), 7·83 (*s*, H-4), 7·93 (*d*, *J* 7 Hz, H-7). MS (*m/e*): 272 (42%) M, 258 (100).

NMR instrumentation. The PMR spectra were determined for $CDCl_3$ solutions (except **10a**) containing TMS as internal standard ($\delta = 0$ ppm) on Varian DP-60 and HR-220 spectrometers. The CMR spectra of $CDCl_3$ solutions in spinning 13 mm o.d. tubes were recorded on a spectrometer operating at 15·08 MHz with a Varian DP-60 magnet working at 14 kg. The δ values on **7** and **8** are in ppm downfield from TMS, $\delta^{TMS} = \delta^{CDCl_3} + 76{\cdot}9$ ppm, the solvent being used as the internal reference.