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BENZOPYRANS FROM *MELICOPE PTELEFOLIA* LEAVES

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Key Word Index—*Melicope ptelefolia*; Rutaceae; leaves; 2,2-dimethyl-2H-1-benzopyrans.

Abstract—Investigation of leaves of *Melicope ptelefolia* afforded 18 2,2-dimethyl-2H-1-benzopyrans, consisting of 14 new members, including one benzodipyran and four known compounds. Their structures were established by mass and NMR spectroscopy, especially NOE and HMBC experiments.

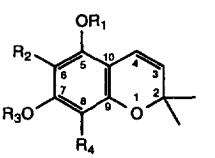
INTRODUCTION

Melicope ptelefolia (Champ. ex Benth.) Hartley [1], described by Ho still as *Euodia lepta* (Spreng.) Merr. (= *Evodia lepta* = *E. roxburghiana* Pierre) [2], is a 4–5 m high shrub growing in many areas of Vietnam. Leaves and twigs are used for the treatment of itch and wounds, whereas root and bark serve as an appetizer, digestive and emmenagogue [3]. Until now, only some alkaloids of the quinoline-, furoquinoline- and pyranoquinoline-type have been isolated from this species [4–6]. In the present study, we report on the isolation and structural elucidation of a series of benzopyrans from leaves of *M. ptelefolia*.

RESULTS AND DISCUSSION

A *n*-hexane extract of leaves afforded, upon repeated chromatographic separation (see Experimental), 14 new (**3–5**, **8–11**, **13–18**) and four known (**1**, **2**, **7** and **12**) 2,2-dimethyl-2H-1-benzopyrans. Their structures were established by mass and NMR spectroscopy, especially HMBC experiments (benzene ring with proton) or NOE difference spectra (benzene ring without proton). Carbon shifts were assigned using CH long-range correlations or by comparison with already assigned compounds. As no ^{13}C NMR reference data of the four known compounds are available in the literature, their structural elucidation and carbon shift assignment was done in the same way and their chemical shifts added in Tables 1–5.

All substances showed the typical NMR signals of 2,2-dimethyl-2*H*-1-benzopyrans (Tables 1–5): a *gem*-dimethyl group at δ_H 1.32–1.50 and δ_C 26.6–28.4, a quaternary carbon (C-2) at δ 76.4–79.1, two complementary proton doublets (J = 9.8–10.0 Hz) at δ 5.36–5.70 (H-3) and 6.54–6.77 (H-4) and the corresponding carbons at δ 124.6–129.9 (C-3) and 116.2–117.8 (C-4). The chemical shifts of the carbons of the benzene ring are dependent on the various substituents. The oxygen-substituted carbons in positions 5, 7 and 9 resonate between δ 142 and 166. From these



	R_1	R_2	R_3	R_4
1	CH_3	H	H	$COCH_3$
2	CH_3	H	CH_3	$COCH_3$
3	CH_3	H	CH_3	$CH(OH)CH_3$
4	CH_3	H	CH_3	$CH(OCH_3)CH_3$
5	CH_3	H	CH_3	$CH{=}CH_2$
6	CH_3	OCH_3	H	$COCH_3$
7	CH_3	OCH_3	CH_3	$COCH_3$
8	CH_3	OCH_3	CH_3	$CH(OH)CH_3$
9	H	CH_2-$CH{=}C(CH_3)_2$	H	$COCH_3$
11	H	$COCH_3$	CH_3	OCH_3
12	CH_3	$COCH_3$	CH_3	OCH_3
13	CH_3	$CH(OH)CH_3$	CH_3	OCH_3
14	CH_3	$CH(OCH_3)CH_3$	CH_3	OCH_3
15	CH_3	$CH(OCH_3)CH_3$	CH_3	H
16	CH_3	$CH(OC_{20}H_{39})CH_3$	CH_3	H
18	CH_3	H	CH_3	OH

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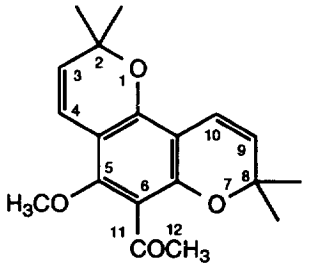

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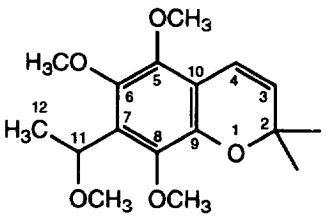

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structures, which were assigned by HMBC experiments, we could generalize that $\delta_{C\text{-}7} > \delta_{C\text{-}5} > \delta_{C\text{-}9}$ and that C-10 is always the quaternary aromatic carbon with the smallest chemical shift. Thus, the carbons of the residual compound could be assigned without HMBC. HMBC data of compounds **3**, **4**, **5**, **9**, **12** and **18** are summarized in Table 6. The $^1J_{CH}$-correlations were not completely suppressed in the HMBC experiment and could be observed in the spectra. They were useful for carbon assignment of the methoxyl groups, provided that the proton assignment was already known, thus revealing that the carbon shifts are affected by steric factors. Methoxyl carbons, which possess a substituent in each *ortho*-position resonate at δ 60–64. Where an *ortho*-position was unsubstituted there was a chemical shift of δ 55–57.

The first group of compounds with the two-carbon residue in position 8 were compounds **1**–**10** (Tables 1–3). Compound **1** ($C_{14}H_{16}O_4$, $[M]^+$ *m/z* 248) was identified as alloevodionol by analysis of its NOE interactions.

Compound **2** ($C_{15}H_{18}O_4$, $[M]^+$ *m/z* 262) is the *O*-methyl derivative of **1**, known as alloevodionol methyl ether. Its structure was also confirmed by its NOE effects.

In compound **3** ($C_{15}H_{20}O_4$, $[M]^+$ 264), the acetyl function occurs in its reduced form as 1-hydroxyethyl group consisting of one methyl doublet (δ 1.40, J = 6.7 Hz), one hydroxyl doublet (δ 3.58, J = 11.0 Hz) and one methine signal (δ 5.10; *dq*, J = 11.0 and 6.7 Hz). The other substituents are two methoxyl groups at δ 3.83 and 3.86 and one aromatic proton at δ 6.26. The substitution pattern, which is identical to that of **2**, and the chemical shift assignment was established by evaluation of the C–H long-range correlations from the HMBC experiment (Table 6) to yield the new structure 8-(1-hydroxyethyl)-5,7-dimethoxy-2,2-dimethyl-2H-1-benzopyran.

Compound **4** ($C_{16}H_{22}O_4$, $[M]^+$ *m/z* 278) is the methyl ether of **3**. The additional aliphatic methoxyl group resonates at δ 3.10. The NOE effects (2-Me_2/11-OMe, 11-OMe/7-OMe, 7-OMe/H-6, H-6/5-OMe, 5-OMe/H-4) lead to the structure 8-(1-methoxyethyl)-5,7-dimethoxy-2,2-dimethyl-2*H*-1-benzopyran. The carbon assignments are based on the C–H long-range correlations from HMBC (Table 6).

The molecular formula of compound **5** ($C_{15}H_{18}O_3$, $[M]^+$ *m/z* 246) corresponds with dehydrated **3**. The proton spectrum exhibits as in **3**, two methoxyl groups (δ 3.85 and 3.86) and one lone aromatic proton (δ 6.26). Instead of the hydroxyethyl group, it contains a vinyl function with signals at δ 6.86 (*dd*, J = 18.0 and 12.2 Hz), δ 6.01 (*dd*, J = 18.0 and 3.1 Hz) and δ 5.16 (*dd*, J = 12.2 and 3.1 Hz). Correlations from the HMBC experiment (Table 6) establish the structure as 8-vinyl-5,7-dimethoxy-2,2-dimethyl-2H-1-benzopyran.

The benzene ring substituents of **6** ($C_{15}H_{18}O_5$, $[M]^+$ *m/z* 278) are one acetyl group (δ 2.69), one chelated hydroxy group (δ 13.66) and two methoxyl groups (δ 4.03 and 3.82). From the NOE effects (2-Me_2/Ac, Ac/7-OH, 7-OH/6-OMe, 6-OMe/5-OMe, 5-OMe/H-4), the structure, 8-acetyl-7-hydroxy-5,6-dimethoxy-2,2-dimethyl-2H-1-benzopyran was deduced, hitherto only known as a synthetic precursor of alloevodione [7].

Compound **7** ($C_{16}H_{20}O_5$, $[M]^+$ *m/z* 292) was identified as alloevodione (the *O*-methylated form of **6**) from its NOE interactions.

Compound **8** ($C_{16}H_{22}O_5$ $[M]^+$ *m/z* 294) has three methoxyl groups (δ 3.80, 3.84 and 3.88) and one 1-hydroxyethyl group (δ 1.46, 3.62 and 5.08), which is, according to NOE effects (2-Me_2/H-11, H-11/7-OMe, 5-OMe/H-4), located in position 8. The structure, 8-(1-hydroxyethyl)-5,6,7-trimethoxy-2,2-dimethyl-2H-1-benzopyran, is the reduced form of alloevodione (**7**).

The characteristic feature of compound **9** ($C_{18}H_{22}O_4$, $[M]^+$ *m/z* 302) is the *iso*pentenyl group, with methyl singlets at δ 1.84 (*br s*) and 1.78 (*d*, J = 1.2 Hz), the olefinic proton at δ 5.27 (*tm*, J = 7.3 and 1.4 Hz) and the methylene group at δ 3.39 (*br d*, J = 7.3 Hz). The other substituents are one acetyl group (δ 2.67), one chelated (δ 14.13) and one non-chelated hydroxyl group (δ 6.32). Their positions and differentiation between the (*E*)- and (*Z*)-methyl group followed from NOE effects (2-Me_2/Ac, Ac/7-OH, 7-OH/H-1′, H-1′/6-OH and H-1′/3′-Me (*Z*)). From these data, compound **9** was regarded as 8-acetyl-5,7-

Table 1. ^{1}H NMR data of compounds **1–9**

	1[a,c]	**2**[a,c]	**3**[b,d]	**4**[a,d]	**5**[b,d]	**6**[a,c]	**7**[a,c]	**8**[a,d]	**9**[a,c,e]
3	5.42 *d* (10.0)	5.47 *d* (10.0)	5.52 *d* (9.9)	5.50 *d* (10.0)	5.52 *d* (9.8)	5.48 *d* (10.0)	5.57 *d* (10.0)	5.69 *d* (10.0)	5.44 *d* (9.9)
4	6.55 *d* (10.0)	6.57 *d* (10.0)	6.56 *d* (9.9)	6.56 *d* (10.0)	6.77 *d* (9.8)	6.54 *d* (10.0)	6.54 *d* (10.0)	6.56 *d* (10.0)	6.54 *d* (9.9)
6	6.01 *s*	6.01 *s*	6.26[f] *s*	6.24 *s*	6.26[g] *s*	—	—	—	—
11	—	—	5.10 *dq* (11.0/6.7)	4.89 *q* (6.7)	6.86 *dd* (18.0/12.2)	—	—	5.08 *dq* (10.5/6.6)	—
12	2.67 *s*	2.49 *s*	1.40 *d* (6.7)	1.45 *d* (6.7)	6.01 *dd* (18.0/3.1) 5.16 *dd* (12.2/3.1)	2.69 *s*	2.50 *s*	1.46 *d* (6.6)	2.67 *s*
2-Me$_2$	1.49 *s*	1.41 *s*	1.411 *s*	1.37 *s*	1.40 *s*	1.49 *s*	1.41 *s*	1.43 *s*	1.49 *s*
	1.49 *s*	1.41 *s*	1.409 *s*	1.37 *s*	1.40 *s*	1.49 *s*	1.41 *s*	1.43 *s*	1.49 *s*
5-OMe	3.84 *s*	3.85 *s*	3.83 *s*	3.83 *s*	3.86 *s*	4.03 *s*	3.89 *s*	3.84 *s*	—
6-OMe	—	—	—	—	—	3.82 *s*	3.83 *s*	3.80 *s*	—
7-OMe	—	3.81 *s*	3.86 *s*	3.81 *s*	3.85 *s*	—	3.88 *s*	3.88 *s*	—
5-OH	—	—	—	—	—	—	—	—	6.32 *s*
7-OH	13.83 *s*	—	—	—	—	13.66 *s*	—	—	14.13 *s*
11-OH	—	—	3.58 *d* (11.0)	—	—	—	—	3.62 *d* (10.5)	—
11-OMe	—	—	—	3.10 *s*	—	—	—	—	—

[a] 300 MHz.
[b] 500 MHz.
[c] In $CDCl_3$.
[d] In acetone-d_6.
[e] Isopentenyl moiety: 3.39 (2H, *br d*, J = 7.3 Hz, H-1′), 5.27 (1H, *tm* J = 7.3/1.4 Hz, H-2′), 1.84 (3H, *br s*, 3′-Me (*Z*)), 1.78 (3H, *d*, J = 1.2 Hz, 3′-Me (*E*)).
[f] In $CDCl_3$, δ 6.03.
[g] In $CDCl_3$, δ 6.04 ppm.

Table 2. ^{13}C NMR data of compounds **1–9** (75 MHz)

	1[a]	**2**[a]	**3**[b]	**4**[b]	**5**[d]	**6**[a]	**7**[a]	**8**[b]	**9**[a,c]
2	77.9	76.8	77.1	76.4	77.0	77.7	76.5	77.0	77.8
3	124.6	126.7	127.0	127.1	126.9	126.0	129.3	129.9	124.9
4	116.5	116.3	117.6	117.8	117.7	116.9	116.5	117.5	116.5
5	161.0	156.7	155.7	156.1	156.1	154.3	150.3	149.1	157.4
6	92.3	87.8	89.5	89.4	89.0	133.5	139.8	140.9	105.2
7	166.4	157.8	158.9	160.9	160.3	158.9	150.6	152.2	162.9
8	106.0	113.6	114.9	111.1	108.6	108.0	121.1	123.1	105.8
9	156.2	151.9	152.1	153.9	153.6	151.9	145.8	147.0	155.3
10	102.8	104.2	105.1	105.0	104.8	105.7	111.3	112.1	101.9
11	203.3	201.1	63.6	70.9	128.0	204.1	200.7	64.1	203.5
12	33.1	32.6	24.5	20.5	115.6	33.4	32.5	24.7	33.2
2-Me$_2$	27.8	27.6	27.9	27.8	27.9	27.8	27.6	27.8	27.8
	27.8	27.6	27.7	27.6	27.9	27.8	27.6	27.6	27.8
5-OMe	55.7	55.8*	56.0*	56.1*	56.0	61.2*	62.1*	61.7*	—
6-OMe	—	—	—	—	—	60.8*	61.4*	61.6*	—
7-OMe	—	55.6*	56.1*	55.9*	56.0	—	61.0*	61.0*	—
11-OMe	—	—	—	55.8*	—	—	—	—	—

[a] In $CDCl_3$.
[b] In acetone-d_6.
[c] Isopentenyl moiety: δ 21.5 (C-1′), 121.7 (C-2′), 136.6 (C-3′), 17.9 (3′-Me (*Z*)), 25.8 (3′-Me (*E*)).
* Assignment interchangeable in each column.

Table 3. NMR data of compound **10** in $CDCl_3$ (75/300 MHz)

	δ_C	δ_H	C–H long-range correlations
2	76.9	—	H-3, H-4, 2-Me_2
3	127.8	5.54 *d* (10.0)	2-Me_2
4	116.8	6.49 *d* (10.0)	
4a	108.2	—	H-3, H-4
5	153.7	—	H-4, 5-OMe
6	117.7	—	
6a	151.4	—	H-10
8	77.1	—	H-9, H-10, 8-Me_2
9	127.8	5.52 *d* (10.0)	8-Me_2
10	116.2	6.60 *d* (10.0)	
10a	106.5	—	H-9, H-10
10b	150.6	—	H-4
11	200.9	—	H-12
12	32.6	2.51 *s*	
2-Me_2	27.92	1.427* *s*	
8-Me_2	27.85	1.422 *s*	
5-OMe	63.6	3.75 *s*	

* Assignment interchangeable.

dihydroxy-6-isopentenyl-2,2-dimethyl-2H-1-benzopyran, previously known only as a synthetic side-product [8]. The assignment of the carbon shifts resulted from the HMBC correlations (Table 6). The substituents cause some additional correlations, *viz.*, C-5/H-1′, C-6/H-1′, C-7/H-1′, C-10/5-OH, C-2′/3′-Me_2, C-3′/H-1′ and C-3′/3′-Me_2.

Compound **10** ($C_{19}H_{22}O_4$ [M]$^+$ *m/z* 314) possesses two pairs of pyran protons (four doublets with J = 10.0 Hz at δ 5.52, 5.54, 6.49 and 6.60) and two *gem*-dimethyl groups (δ 1.42 and 1.43), which indicate a benzodipyran skeleton (Table 3). The two 3H singlets at δ 2.51 and 3.75 characterize an acetyl and a methoxyl substituent, respectively. The NOE effects (H-3/H4, H-4/5-OMe, 5-OMe/Ac, Ac/8-Me_2 and H-9/H-10) confirm the arrangement of the two pyran rings and the position of the substituents, as 6-acetyl-5-methoxy-2,2,8,8-tetramethyl-2H,8H-benzol[1,2-b:3,4-b′]dipyran. The carbon assignment followed from HMBC correlations (Table 3). Compound **10** might be formally deduced from **9** by ring-closure and *O*-methylation. After completion of this work, compound **10** was identified as a constituent of *Melicope erromangensis* (Rutaceae) [9].

The second group of compounds with the two-carbon residue in position 6 comprises compounds **11**–**16** (Tables 4 and 5). Compound **11** ($C_{15}H_{18}O_5$, [M]$^+$ *m/z* 278) is a regio-isomer of **6**. The substitution pattern was deduced from NOE experiments (2-Me_2/8-OMe, 8-OMe/7-OMe and 7-OMe/Ac), to yield the structure, 6-acetyl-5-hydroxy-7,8-dimethoxy-2,2-dimethyl-2H-1-benzopyran.

Compound **12** ($C_{16}H_{20}O_5$, [M]$^+$ *m/z* 292), a regioisomer of **7**, was identified as evodione, the *O*-methyl derivative of **11**, by analysis of NOE effects. Carbon assignments were deduced from a HMBC experiment (Table 6).

Compound **13** ($C_{16}H_{22}O_5$, [M]$^+$ *m/z* 294) has the same substituents as compound **8**. From NOE effects (2-Me_2/8-OMe, 7-OMe/H-11, H-11/5-OMe and 5-OMe/H-4), it was proved to be 6-(1-hydroxyethyl)-5,7,8-trimethoxy-2,2-dimethyl-2H-1-benzopyran, which represents the reduced form of evodione (**12**).

Compound **14** ($C_{17}H_{24}O_5$, [M]$^+$ *m/z* 308) is the *O*-methyl derivative of **13**. Analysis of NOE interactions

Table 4. ^{1}H NMR data of compounds **11**–**18**

	11[a,d]	**12**[a,c]	**13**[a,d]	**14**[a,c]	**15**[a,d]	**16**[a,d,e]	**17**[a,c]	**18**[b,d]
3	5.66 *d* (10.0)	5.62 *d* (9.9)	5.70 *d* (9.9)	5.59 *d* (9.8)	5.60 *d* (10.0)	5.59 *d* (9.9)	5.57 *d* (9.9)	5.50 *d* (9.9)
4	6.63 *d* (10.0)	6.50 *d* (9.9)	6.51 *d* (9.9)	6.52 *d* (9.8)	6.50 *dd* (10.0/0.5)	6.51 *dd* (9.9/0.6)	6.56 *d* (9.9)	6.55 *d* (9.9)
6	—	—	—	—	—	—	—	6.23 *s*
8	—	—	—	—	6.23 *s*	6.23 *s*	—	—
11	—	—	5.07 *dq* (8.4/6.6)	4.75 *q* (6.7)	4.80 *q* (6.8)	4.96 *q* (6.7)	4.89 *q* (6.8)	—
12	2.62 *s*	2.51 *s*	1.49 *d* (6.6)	1.60 *d* (6.7)	1.49 *d* (6.8)	1.50 *d* (6.7)	1.57 *d* (6.8)	—
2-Me_2	1.49 *s*	1.48 *s*	1.43 *s*	1.49 *s*	1.40 *s*	1.40 *s*	1.41 *s*	1.37 *s*
	1.49 *s*	1.48 *s*	1.43 *s*	1.47 *s*	1.39 *s*	1.38 *s*	1.40 *s*	1.37 *s*
5-OMe	—	3.73 *s*	3.71 *s*	3.72 *s*	3.72 *s*	3.74 *s*	3.88 *s*	3.76 *s*
6-OMe	—	—	—	—	—	—	3.87 *s*	—
7-OMe	4.03 *s*	3.90 *s*	3.90 *s*	3.88 *s*	3.78 *s*	3.78 *s*	—	3.81 *s*
8-OMe	3.78 *s*	3.85 *s*	3.79 *s*	3.85 *s*	—	—	3.84 *s*	—
11-OMe	—	—	—	3.26 *s*	3.12 *s*	—	3.23 *s*	—
5-OH	13.70 *s*	—	—	—	—	—	—	—
8-OH	—	—	—	—	—	—	—	6.70 *s*

[a] 300 MHz.
[b] 500 MHz.
[c] In $CDCl_3$.
[d] In acetone-d_6.
[e] Shifts of phytyl moiety are in Experimental.

Table 5. ^{13}C NMR data of compounds **11**–**18**

	11[a,d]	**12**[a,c]	**13**[a,d]	**14**[a,c]	**15**[a,d]	**16**[a,c]	**17**[a,c]	**18**[b,d]
2	79.1	76.8	76.8	76.1	76.7	76.7	75.7	76.6
3	127.8	129.3	129.9	128.8	128.1	128.1	129.3	127.4
4	116.4	116.5	117.9	117.2	117.8	117.9	117.0	117.8
5	156.7	148.4	150.2	150.7	157.3	157.5	148.7*	148.8
6	109.0	122.8	124.7	120.3	116.4	117.2	153.3	90.8
7	157.0	150.4	153.0	152.9	160.5	160.4	118.8	149.2
8	135.3	138.1	139.6	138.7	97.1	97.1	140.1	130.4
9	154.7	148.4	146.9	146.5	155.1	155.1	147.5*	141.9
10	106.5	111.9	112.5	111.7	108.8	109.0	111.2	105.5
11	204.6	201.3	64.0	71.8	71.6	69.3	71.1	—
12	32.2	32.6	24.8	20.5	20.5	20.8	20.2	—
2-Me_2	28.4	27.6	27.8	27.9	28.2	28.2	27.6	27.7
	28.4	27.6	27.7	27.5	27.8	27.8	27.4	27.7
5-OMe	—	63.7	63.3	62.8	62.9	63.0	61.4*	56.3*
6-OMe	—	—	—	—	—	—	61.2*	—
7-OMe	61.6*	61.9	61.8	61.3*	56.1	56.2	—	56.6*
8-OMe	61.2*	61.0	60.9	60.8*	—	—	60.8*	—
11-OMe	—	—	—	56.4	56.1	—	56.3	—

[a] 300 MHz.
[b] 500 MHz.
[c] In $CDCl_3$.
[d] In acetone-d_6.
* Assignment interchangeable in each column.

Table 6. ^1H-^{13}C long-range correlation (HMBC) map of compounds **3**, **4**, **5**, **9**, **12** and **18**

	C-2	C-3	C-5	C-7	C-8	C-9	C-10	C-11	2-Me_2
H-3							×		×
H-4	×		×			×			
H-6			×	×	×		×		
H-11				×	×[b]	×			
H-12					×[c]			×	
2-Me_2	×	×							×
5-OR[a]			×						
7-OR[a]				×					
11-OMe								×	

[a] R=H or OH.
[b] Missing in **5**.
[c] Missing in **12**, because of different substitution pattern.

(2-Me_2/8-OMe, 7-OMe/H-11, H-11/5-OMe and 5-OMe/H-4), establishes its structure as 6-(1-methoxyethyl)-5,7,8-trimethoxy-2,2-dimethyl-2H-1-benzopyran.

Compound **15** ($C_{16}H_{22}O_4$, $[M]^+$ *m/z* 278) possesses one 1-methoxyethyl group (δ 1.49, 3.12 and 4.80), two aromatic methoxyl groups (δ 3.78 and 3.72) and one lone aromatic proton (δ 6.23). NOE effects (2-Me_2/H-8, H-8/7-OMe, H-11/5-OMe and 5-OMe/H-4) reveal the structure 6-(1-methoxy-ethyl)-5,7-dimethoxy-2,2-dimethyl-2H-1-benzopyran, which is a regioisomer of **4**.

The ^1H and ^{13}C NMR spectra of compound **16** ($C_{35}H_{58}O_4$, $[M]^+$ *m/z* 542) exhibit all signals of compound **15**, with nearly the same chemical shifts. Differences are found only at positions 6 and 11; the 11-methoxyl group is missing. Additionally, all signals of phytol are present. This indicates that the 11-methoxyl group of **15** has been exchanged by a phytyl residue. This derivative might have formed during extraction, because the methoxyethyl group is unstable and phytol has also been found in the extract (see Experimental).

The ^1H and ^{13}C NMR spectra (Tables 4 and 5) of **17** ($C_{17}H_{24}O_5$, $[M]^+$ *m/z* 308) are similar to those of **14**. NOE interactions (2-Me_2/8-OMe, 8-OMe/11-OMe, 11-OMe/6-OMe and 5-OMe/H-4) reveal an unusual substitution pattern, with the two-carbon side-chain in position 7. The structure, 7-(1-methoxyethyl)-5,6,8-trimethoxy-2,2-dimethyl-2H-1-benzopyran, was confirmed by HMBC data. Besides the expected cross-peaks for the dimethylbenzopyran moiety (Table 6), the following correlations were observed: C-5/H-11, C-6/H-11, C-7/H-12 and C-9/H-11.

Compound **18** ($C_{13}H_{16}O_4$ $[M]^+$ *m/z* 136) is the only compound isolated without the two-carbon residue. The proton spectrum displays two methoxyl groups (δ 3.76 and 3.81), one non-chelated hydroxyl group (δ 6.70) and one lone aromatic proton (δ 6.23). Their locations were established by the HMBC experiment (Table 6), leading to the structure, 8-hydroxy-5,7-dimethoxy-2,2-dimethyl-2H-1-benzopyran.

Those compounds, which possess a hydroxyethyl or methoxyethyl group, are unstable in $CDCl_3$, normally containing traces of DCl, with formation of a blue-coloured solution. Thus, decomposition can be avoided using neutral $CDCl_3$. One of the decomposition products of **3** and **4**, is the vinylic compound **5**, ident-

ified by comparison of its ^{1}H spectrum with that of the pure compound. On prolonged standing, **5** undergoes polymerization, indicated in the ^{1}H-NMR spectrum, by additional olefinic signals and some very broad signals. Compound **15**, the regioisomer of **4**, also formed its corresponding vinyl derivative.

Compounds **3**, **4**, **8** and **13**–**17** possess a chiral centre at C-11 but only **8** and **13** exhibit an appreciable optical rotation. Addition of $Eu(TFC)_3$, as lanthanide shift reagent (see Experimental), revealed in ^{1}H NMR spectra, that **8** is optically pure and that **13** contains 86% of a main enantiomer. Monitoring the optically inactive compounds **4**, **14**, **15** and **17** in the same way showed, that they are *ca* 1:1 mixtures of enantiometers.

Melicope species are known to contain the 6- and 8-acetyl-2,2-dimethyl-2*H*-1-benzopyrans, evodionol, alloevodionol, isoevodionol, evodionol methyl ether, alloevodionol methyl ether, evodione and alloevodione, in their essentiall oil [10, 11]. Benzopyrans have also been found in the Asteraceae. Mostly, they possess an acetyl group at position 6 or 8 [12]. The benzopyran spectrum of *M. ptelefolia* is characterized by 6- and 8-acetyl compounds co-occurring with reduced 6- or 8-hydroxyethyl or methoxethyl forms. They differ from the known dimethylbenzopyrans by another substitution pattern and/or a large number of substituents. All benzopyrans, except compound **17**, possess two oxygen substituents at positions 5 and 7, according to phloroglucinol oxidation pattern. The two-carbon side-chain may also appear as a vinyl group, as in compound **5**. Compound **18** is the only member lacking the two-carbon side-chain, representing a very rare structural type [13].

EXPERIMENTAL

Mps: uncorr. EIMS: 70 eV. CC: silica gel 60, 230–400 mesh ASTM (Merck). TLC: precoated silica gel plates 60 F_{254} (Merck), detection, UV-light, spray reagent, vanillin–H_2SO_4. Lanthanide shift expts (500 MHz): *tris*[3(2,2,2-trifluor-1-hydroxyethyliden)-*d*-camphorato]-europium ($Eu(TFC)_3$) with a molar ratio between the compound and $Eu(TFC)_3$ of *ca* 1.5:1; the ratio of enantiomers was calculated from the ^{1}H integrals (accuracy ±5–10%).

Plant material. Leaves and branches of *M. ptelefolia* were collected in Lao cai, North Vietnam, in June 1994, and identified by Dr T. D. Dai. A voucher specimen (No. 382) is deposited in the Institute of Ecology and Natural Resources, National Centre for Scientific Research and Technology, Hanoi, Vietnam.

Isolation. Dried leaves (500 g) were extracted ×3 with 80% aq. MeOH at room temp and the organic solvent removed under red. pres. The aq. residue was extracted ×3 with *n*-hexane, EtOAc and *n*-BuOH, successively, to give 17.3 g hexane extract. This was sepd by chromatography on silica gel 60 (200 g, 70–200 mesh) with increasing amounts of EtOAc in *n*-hexane as eluent (2–100% EtOAc, 237 frs, each 20 ml). Frs 1–20 (402 mg) were further purified by CC on silica gel (80 g) with *n*-hexane–EtOAc (19:1), giving 7.3 mg of **5**. Frs 21–37 (369 mg) yielded 192 mg of **1** after purification by CC with *n*-hexane–EtOAc (9:1). Further purification of frs 38–47 (417 mg), gave 183 mg of **6** (CC with *n*-hexane–$CHCl_3$ 1:1), 18 mg of **11** (CC with *n*-hexane–EtOAc, 4:1) and 4 mg of **9** (prep. TLC with *n*-hexane–CH_2Cl_2, 1:1), CC of frs 67–87 (1.86 g) using CH_2Cl_2–EtOAc (19:1) yielded 50 mg of **7** and some other frs, which were further purified and afforded 24 mg of **17** (CC with *n*-hexane–EtOAc, 4:1) and 15 mg of **15** (prep. TLC with *n*-hexane–Me_2CO (9:1)). From frs 89–113 (650 mg), were isolated 101 mg of **14** (CC with *n*-hexane–EtOAc, 4:1), 21 mg of phytol (CC with CH_2Cl_2–EtOAc, 19:1) and 25 mg of **12** (CC with *n*-hexane–EtOAc, 4:1). Frs 114–136 (1.47 g) afforded 51 mg of **8** (CC with *n*-hexane–EtOAc, 4:1) and 17 mg of **4** (prep. TLC with *n*-hexane–EtOAc, 4:1). Purification of frs 137–153 (939 mg) yielded 56 mg of **13** (CC with $CHCl_3$–EtOAc, 9:1) and 10 mg of **16** (prep. TLC with *n*-hexane–EtOAc, 4:1). **10** (6 mg) was obtained by prep. TLC of frs 154–166 (1.29 g) using *n*-hexane–EtOAc (7:3). Frs 167–194 (401 mg) gave 3 mg of **18** (CC and prep. TLC with *n*-hexane–EtOAc, 7:3), 20 mg of **3** (CC with CH_2Cl_2–EtOAc, 49:1) and 257 mg of **2** (CC with *n*-hexane–EtOAc, 4:1).

Alloevodionol (**1**). Yellow crystals from *n*-hexane, mp 68–69°. R_f 0.56 (*n*-hexane–EtOAc, 7:3). UV λ_{max}^{MeOH} nm (log ε): 276 (4.48), 221 (3.10). IR ν_{max}^{KBr} (cm^{-1}): 3446, 3051, 2969, 2865, 1638, 1611, 1587, 1365, 1267, 1122, 900, 820, 692, 583. MS *m/z* (rel. int.): 248 $[M]^+$ (50), 234 $[M-CH_2]^+$ (30), 233 $[M-Me]^+$ (100), 215 $[M-Me-H_2O]^+$ (34), 202 $[M-3Me]^+$ (10), 200 $[M-2Me-H_2O]^+$ (15).

Alloevodionol methyl ether (**2**). Crystals from *n*-hexane, mp 103–104°. R_f 0.56 (CH_2Cl_2–EtOAc, 25:1). UV λ_{max}^{MeOH} nm (log ε): 278 (4.28), 204 (4.27). IR ν_{max}^{KBr} (cm^{-1}): 3002, 2986, 2964, 2945, 2845, 1705, 1636, 1607, 1582, 1469, 1413, 1334, 1265, 1216, 1157, 1125–1100, 909, 881, 795, 771, 560. MS *m/z* (rel. int.): 262 $[M]^+$ (15), 247 $[M-Me]^+$ (100), 232 $[M-2Me]^+$ (5), 217 $[M-3Me]^+$ (16), 116 (10).

8-(1-*Hydroxyethyl*)-5,7-*dimethoxy*-2,2-*dimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**3**). Crystals from *n*-hexane, mp 75–76°. R_f 0.43 (CH_2Cl_2–EtOAc, 25:1). $[\alpha]_D^{30}$ −0.7° ($CHCl_3$, *c* 0.38). UV λ_{max}^{MeOH} nm (log ε): 286 (4.19), 227 (4.42), 203 (4.26). IR ν_{max}^{KBr} (cm^{-1}): 3538, 2966, 2842, 1636, 1607, 1465, 1324, 1211, 1145–1070, 879, 795, 772. MS *m/z* (rel. int.): 264 $[M]^+$ (12), 249 $[M-Me]^+$ (100), 231 $[M-Me-H_2O]^+$ (12), 219 $[M-3Me]^+$ (12); HRMS 264.1370 $[M]^+$ ($C_{15}H_{20}O_4$ requires 264.1362).

8-(1-*Methoxyethyl*)-5,7-*dimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**4**). Amorphous solid. R_f 0.34 (*n*-hexane–EtOAc, 7:3). $[\alpha]_D^{25}$ +2.2°, (MeOH, *c* 0.33). UV λ_{max}^{MeOH} nm (log ε): 287 (4.88), 229 (5.12), 204 (4.91). IR ν_{max}^{KBr} (cm^{-1}): 2971, 2924, 1638, 1602, 1581, 1466, 1326, 1253, 1214, 1145–1090, 853, 773. MS *m/z* (rel. int.): 278 $[M]^+$ (35), 263 $[M-Me]^+$ (84), 246 (24),

231 (100), 216 (12), 201 (12); HRMS 278.1515 $[M]^+$ ($C_{16}H_{22}O_4$ requires 278.1518).

8-*Vinyl*-5,7-*dimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**5**). Amorphous solid. R_f 0.22 (*n*-hexane–EtOAc, 19:1). UV λ_{Max}^{MeOH} nm (log ε): 260 (4.48), 204 (4.28). IR ν_{max}^{KBr} (cm^{-1}): 2926, 1641, 1605, 1125. MS *m/z* (rel. int.): 246 $[M]^+$ (36), 232 $[M-CH_2]^+$ (15), 231 $[M-Me]^+$ (100), 216 $[M-2Me]^+$ (8), 201 (7); HRMS 246.1260 $[M]^+$ ($C_{15}H_{18}O_3$ requires 246.1256).

8-*Acetyl*-7-*hydroxy*-5,6-*dimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**6**). Yellow oil. R_f 0.55 (*n*-hexane–EtOAc, 7:3). UV λ_{max}^{MeOH} nm (ε): 369 (3.54), 280 (4.40), 220 (4.28). IR ν_{max}^{KBr} (cm^{-1}): 3434, 2975, 2934, 1639, 1615, 1580, 1426, 1361, 1318, 1279, 1211, 1142, 1044, 905, 863, 742, 622. MS *m/z* (rel. int.): 278 $[M]^+$ (58), 263 $[M-Me]^+$ (100), 248 $[M-2Me]^+$ (10), 245 $[M-Me-H_2O]^+$ (11), 233 $[M-3Me]^+$ (7); HRMS 278.1152 $[M]^+$ ($C_{15}H_{18}O_5$ requires 278.1254).

Alloevodione (**7**). Amorphous solid. UV λ_{max}^{MeOH} nm (log ε): 321 (3.59), 222 (4.41), 252 (4.22). IR ν_{max}^{KBr} (cm^{-1}): 2973, 2936, 2852, 1706, 1589, 1458, 1414, 1293, 1135, 1051. MS *m/z* (rel. int.): 292 $[M]^+$ (31), 277 $[M-Me]^+$ (100), 261 $[M-2Me]^+$ (2), 247 $[M-3Me]^+$ (16), 229 (3).

8-(1-*Hydroxyethyl*)-5,6,7-*trimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**8**). Oil. R_f 0.38 (*n*-hexane–EtOAc, 7:3). $[\alpha]_D^{25}$ −24.4° (MeOH, *c* 0.33). UV λ_{max}^{MeOH} nm (log ε): 272 (3.87), 231 (4.39). IR ν_{max}^{KBr} cm^{-1}: 3547, 3019, 2978, 2938, 2876, 2852, 2832, 1639, 1595, 1466, 1419, 1344, 1281, 1131, 1033, 966. MS *m/z* (rel. int.): 294 $[M]^+$ (27), 279 $[M-Me]^+$ (100), 261 $[M-OMe]^+$ (21), 249 (8), 231 (8), 85 (42), 83 (68); HRMS 294.1478 $[M]^+$ ($C_{16}H_{22}O_5$ requires 294.1467).

8-*Acetyl*-5,7-*dihydroxy*-6-*isopentenyl*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**9**). Amorphous solid. R_f 0.53 (*n*-hexane–EtOAc, 7:3). UV λ_{max}^{MeOH} nm (log ε): 283 (4.50), 222 (4.42), 205 (4.44). IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 3590, 3364, 2979, 2928, 2856, 1644, 1612, 1430, 1365, 1134, 1085. MS *m/z* (rel. int.): 302 $[M]^+$ (56), 287 $[M-Me]^+$ (60), 259 $[M-Ac]^-$ (8), 247 $[M-C_4H_7]^+$ (11), 246 (9), 231 $[M-C_4H_7-Me]^+$ (100), 213 $[231-H_2O]^+$ (16); HRMS 302.1531 $[M]^+$ ($C_{18}H_{22}O_4$ requires 302.1518).

6-*Acetyl*-5-*methoxy*-2,2,8,8-*tetramethyl*-2*H*,8*H*-*benzo* [1,2-*b*:3,4-*b'*]-*dipyran* (**10**). Oil. R_f 0.54 (*n*-hexane–EtOAc, 7:3). UV λ_{max}^{MeOH} nm (log ε): 257 (4.44). IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 2979, 2937, 2858, 1692, 1640, 1591, 1577, 1465, 1363, 1300, 1215, 1135, 1001, 883. MS *m/z* (rel. int.): 314 $[M]^+$ (19), 299 $[M-Me]^+$ (100), 281 (4), 269 (4), 267 (4), 142 (6), 124 (4); HRMS: 314.1503 $[M]^+$ ($C_{19}H_{22}O_4$ requires 314.1518).

6-*Acetyl*-5-*hydroxy*-7,8-*dimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**11**). Oil. R_f 0.64 (*n*-hexane–EtOAc, 3:2). UV λ_{max}^{MeOH} nm (log ε): 310 (4.04), 262 (4.61). IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 3016, 2983, 2937, 1640, 1610, 1459, 1378, 1282, 1132, 1119, 1055, 979, 890. MS *m/z* (rel. int.): 278 $[M]^+$ (31), 263 $[M-Me]^+$ (100), 248 $[M-2Me]^+$ (4), 245 $[M-Me-H_2O]^+$ (8), 233 $[M-3Me]^+$ (7), 230 $[M-2Me-H_2O]^+$ (8); HRMS 278.1152 $[M]^-$ ($C_{15}H_{18}O_5$ requires 278.1154).

Evodione (**12**). Oil. R_f 0.40 (*n*-hexane–EtOAc, 7:3). UV λ_{max}^{MeOH} nm (log ε): 260 (4.17), 204 (4.00). IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 2978, 2939, 1697, 1590, 1470, 1375, 1296, 1239, 1133, 1059. MS *m/z* (rel. int.): 292 $[M]^+$ (43), 277 $[M-Me]^+$ (100), 247 $[M-3Me]^+$ (19), 107 (4).

6-(1-*Hydroxyethyl*)-5,7,8-*trimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**13**). Oil. R_f 0.37 (*n*-hexane–EtOAc, 3:2). $[\alpha]_D^{25}$ −14.1°, (MeOH, *c* 0.36). UV λ_{max}^{MeOH} nm (log ε): 274 (3.78), 228 (4.29). IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 3543, 2980, 2938, 2838, 1636, 1596, 1472, 1376, 1233, 1134, 1059, 1015, 975. MS *m/z* (rel. int.): 294 $[M]^+$ (19), 279 $[M-Me]^+$ (100), 261 $[M-Me-H_2O]^+$ (9), 249 $[M-3Me]^+$ (19), 231 $[M-3Me-H_2O]^+$ (3); HRMS 294.1439 $[M]^+$ ($C_{16}H_{22}O_5$ requires 294.1467).

6-(1-*Methoxyethyl*)-5,6,8-*trimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**14**). Amorphous solid. R_f 0.58 (*n*-hexane–EtOAc, 3:2). $[\alpha]_D^{32}$ −3.2° ($CHCl_3$, *c* 0.24). UV λ_{max}^{MeOH} nm (log ε): 274 (3.99), 229 (4.52). IR ν_{max}^{KBr} (cm^{-1}): 2970, 2932, 2833, 1636, 1591, 1472, 1376, 1137, 1077, 1050, 1012, 981, 928, 874. MS *m/z* (rel. int.): 308 $[M]^+$ (35), 293 $[M-Me]^+$ (100), 277 $[M-OMe]^+$ (6), 261 $[M-Me-MeOH]^+$ (16), 247 (5), 245 (4), 231 (4), 83 (6); HRMS 308.1637 $[M]^+$ ($C_{17}H_{24}O_5$ requires 308.1624).

6-(1-*Methoxyethyl*)-5,7-*dimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**15**). Amorphous solid. R_f 0.48 (*n*-hexane–EtOAc, 7:3). $[\alpha]_D^{24}$ −1.5° (MeOH, *c* 0.32). UV λ_{max}^{MeOH} nm (log ε): 285 (3.68), 228 (4.28). IR ν_{max}^{KBr} (cm^{-1}): 2967, 2932, 2839, 1605, 1572, 1471, 1447, 1357, 1285, 1257, 1200, 1150–1080, 1010, 819, 745. MS *m/z* (rel. int.): 278 $[M]^+$ (23), 263 $[M-Me]^+$ (100), 247 $[M-OMe]^+$ (12), 233 $[M-3Me]^+$ (10), 231 $[M-Me-MeOH]^+$ (8), 217 $[M-2Me-OMe]^+$ (9), 124 (6); HRMS 278.1518 $[M]^+$ ($C_{16}H_{22}O_4$ requires 278.1518).

11-O-*Phytyl*-6-(1-*hydroxyethyl*)-5,7-*dimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**16**). Oil. R_f 0.80 (*n*-hexane–EtOAc, 3:2). $[\alpha]_D^{25}$ 0.9° ($CHCl_3$, *c* 0.30). UV λ_{max}^{MeOH} nm (log ε): 286 (4.21), 232 (4.86), 203 (4.63). IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 3010–2830, 1668, 1634, 1606, 1572, 1465, 1362, 1191, 1150–1080, 1045, 1017, 887, 828. MS *m/z* (rel. int.): 542 $[M]^+$ (11), 527 $[M-Me]^+$ (16), 322 (7), 279 (6), 249 (20), 248 (18), 247 (35), 246 (28), 231 (100), 215 (26); HRMS: 527.4111 $[M-Me]^+$ ($C_{34}H_{55}O_4$ requires 527.4100). ^{13}C and ^1H NMR (75/300 MHz, acetone-d_6) of the phytyl moiety: δ_C: 138.9 (C-3′), 123.3 (C-2′), 65.5 (C-1′), 40.4 (C-4′), 40.1 (C-14′), 38.1 (C-8′, C-10′), 38.0 (C-12′), 37.3 (C-6′), 33.5 (C-11′), 33.4 (C-7′), 28.6 (C-15′), 25.8 (C-5′), 25.5 (C-13′), 25.1 (C-9′), 23.0 (C-16′), 22.9 (C-20′), 20.1 (C-18′, C-19′), 16.3 (C-17′); δ_H: 5.30 (1H, *td*, J = 6.6 and 1.2 Hz, 2′-H), 3.82 (2H, *t*, J = 6.6 Hz, 1′-H_2), 1.97 (2H, *td*, J = 7.3 and 1.2 Hz, 4′-H_2), 1.55 (3H, *s*, 3′-Me) 1.5–1.0 (19H, *m*, 5′-H-15′-H), 0.872 (6H, *d*, J = 6.6 Hz, Me_2), 0.866 (3H, *d*, J = 6.6 Hz, Me).

7-(1-*Methoxyethyl*)-5,6,8-*trimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**17**). Amorphous solid. R_f 0.64 (*n*-hexane–EtOAc, 3:2). $[\alpha]_D^{31}$ −1.5° ($CHCl_3$, *c* 0.31). UV λ_{max}^{MeOH} nm (log ε): 315 (3.65), 272 (4.01), 231 (4.54). IR ν_{max}^{KBr} (cm^{-1}): 3427, 2923, 2850, 1465, 1419, 1136–1084, 1043. MS *m/z* (rel. int.): 308 $[M]^+$ (25), 293 $[M-Me]^+$ (100), 277 $[M-OMe]^+$ (5), 263 $[M-3Me]^+$ (9), 261

$[M-Me-MeOH]^+$ (16); HRMS 308.1600 $[M]^+$ ($C_{17}H_{24}O_5$ requires 308.1623).

8-*Hydroxy*-5,7-*dimethoxy*-2,2-*dimethyl*-2*H*-1-*benzopyran* (**18**). Amorphous solid. R_f 0.25 (*n*-hexane–EtOAc, 7:3). UV λ_{max}^{MeOH} nm (log ε): 284 (3.94), 221 (4.16). IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 3548, 2976, 2937, 2842, 1628, 1505, 1465, 1438, 1341, 1252, 1229, 1136, 1104, 1042, 925, 877. MS *m/z* (rel. int.): 236 $[M]^+$ (92), 222 $[M-CH_2]^+$ (37), 221 $[M-Me]^+$ (100), 206 $[M-2Me]^+$ (49), 191 $[M-3Me]^+$ (18); HRMS 236.1031 $[M]^+$ ($C_{13}H_{16}O_4$ requires 236.1049).

Phytol. Carbon shifts of isolated compound were in agreement with ref. [14].

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