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PYRONE DERIVATIVES FROM *PODOLEPIS HIERACIOIDES* AND SESQUITERPENE ACIDS FROM *CASSINIA LONGIFOLIA*

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Key Word Index—*Podolepis hieracioides*; *Cassinia longifolia*; Compositae; pyrone derivatives; sesquiterpenes; costic acid derivatives.

Abstract—The aerial parts of *Podolepis hieracioides* afforded eight γ-pyrones all derived from 2-methoxy-3,5-dimethyl-6-undecyl-γ-pyrone (podopyrone). The aerial parts of *Cassinia longifolia* gave in unusual high concentration two sesquiterpene acids, both related to costic acid. The structures were elucidated by highfield NMR spectroscopy. The structures of some previously reported pyrones are revised.

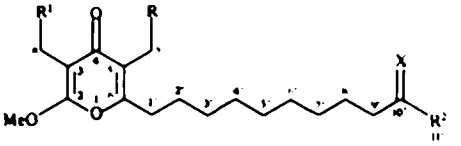
INTRODUCTION

The problems of the botanical relationships of the Australian members of the subtribe Gnaphaliinae (tribe Inuleae) have been discussed [1]. As little is known concerning their chemistry, we have started studying the chemistry of several of these genera. In this paper we report on the constituents of *Podolepis hieracioides* F. Muell. and *Cassinia longifolia* R. Br.

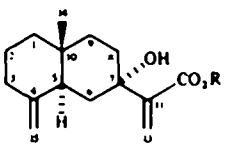
RESULTS AND DISCUSSION

The Australian genus *Podolepis* is placed in the subtribe Gnaphaliinae in a group together with parts of the genus *Athrixia* which is close to the Australian *Helichrysum* group [1]. So far none of the 18 species has been studied chemically. The aerial parts of *P. hieracioides* contain a complex mixture of compounds which by thin layer chromatography and reversed phase HPLC afforded nine compounds (**1**–**8** and **11**).

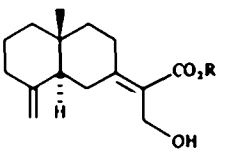
The ^{1}H NMR spectrum of **1** (see Experimental), molecular formula $C_{19}H_{32}O_3$, was not very conclusive. The presence of four methyl groups was indicated by singlets at δ1.92, 1.82 and 3.93 and by a triplet at δ0.86. The latter signal together with a broadened triplet, a triplet of triplets and a multiplet between δ1.35–1.20 (16H), showed the presence of a long chain saturated side chain. The IR band at 1670 cm^{-1} and the ^{13}C NMR spectrum (see Experimental) indicated the presence of a γ-pyrone ring system. However, the relative position of the substituents could not be deduced unambigiously from the data. A homoallylic coupling between the signals at δ2.57 and 1.92 showed that the aliphatic chain was in a position *ortho* to one of the methyl groups. Furthermore, clear NOEs were observed between H-7 and H-1′ as well as between H-8 and OMe while no NOE was present between H-7 and OMe. In agreement with all data therefore the structure **1** was proposed. A gated decoupled ^{13}C NMR spectrum confirmed the presence of a γ-pyrone. The signal at 162.2 ppm was a quartet of quartets which by irradiation of the methoxy carbon was changed to a quartet and therefore was due to C-1. This was also supported by the fragmentation pattern in the mass spectrum of **1**. The base peak was at *m/z* 168 ($C_9H_{12}O_3$) and was probably formed by a McLafferty-like



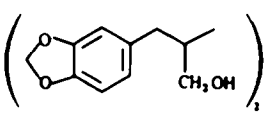
	1	2	3	4	5	6	7	8
R =	H	H	H	H	H	H	Me	H
R¹ =	H	H	H	Me	Me	Me	Me	H
R² =	Me	H	Me	Me	Me	Me	Me	CH_2OAc
X =	H_2	H_2	H,OAc	=O	OH,H	OAc,H	OAc,H	H_2



9a R = H
9b R = Me
9c R = Me, Δ⁴



10a R = H
10b R = Me



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fragmentation of the side chain with the ring oxygen. Compound **1** we have named podopyrone.

The ^{1}H NMR spectrum and the molecular formula of **2** clearly showed that this pyrone was a nor-derivative of **1**.

In the ^{1}H NMR spectrum of the main constituent (**6**), one methyl singlet in the spectrum of **1** was replaced by the signals of an ethyl group and the methyl triplet by a doublet at δ1.18. The latter was coupled with a lowfield signal at δ4.87. As an acetate methyl singlet was visible a 10'-acetoxy derivative was present. The position of the ethyl group followed from the ^{1}H NMR spectrum by the homoallylic couplings of H-1' with the methyl singlet. This was also supported by the ^{13}C NMR data (see Experimental).

The data of compounds **3** and **7** were close to those of **6**. However, the molecular formulae indicated that **3** had one methylene group less and **7** one more. The ^{1}H NMR spectra (see Experimental) showed that **3** was the 10'-acetoxy derivative of **1** and that **7** was the 7-methyl derivative of **6**.

The ^{1}H NMR spectrum of **4** (see Experimental) differed from that of **3** by the absence of the methyl doublet. Spin decoupling indicated that a second two proton triplet was due to a methylene group in the side chain. The presence of a methyl ketone was deduced from the methyl singlet at δ2.13 and from the IR band at 1720 cm^{-1}. Accordingly, all the data agreed with structure **4** which was further supported by the fragmentation pattern in the mass spectrum ([M − COMe]$^+$ and [M − CH_2COMe]$^+$).

All the data of compound **5** indicated it was the desacetyl derivative of **6**. As expected the H-10' signal was shifted upfield and the acetate methyl singlet was missing.

The molecular formula of **8** was identical with that of **3**. However, the ^{1}H NMR spectrum clearly differed. The presence of an isomeric primary acetate followed from the two proton triplet at δ4.05. Thus compound **8** was 11'-acetoxypodopyrone.

The pyrones **3a** and **5**–**7** are optically active. The absolute configuration was not determined. Comparison of the data of **1**–**8** with those of some methoxy pyrones from *Helichrysum* species indicated that these compounds are also γ-pyrones. Thus these structures have to be revised from α- to γ-pyrones (compounds **6**–**8** in [2], compounds **3**–**5** and **6** in [3] and compound **9** in [4]).

The lignane derivative **11** had been prepared by alanate reduction of the corresponding diester [5] and from a *Geigeria* species the diisobutyrate was reported [6].

The aerial parts of *Cassinia longifolia* gave large amounts of ledol and of γ- and δ-cadinene. In addition, mikanin and also in high concentration two isomeric costic acid derivatives (**9a** and **10a**) were isolated. The structure of **9a**, which was also transformed to the methyl ester **9b**, followed from the ^{1}H NMR spectrum (Table 1). All signals could be assigned by spin decoupling. Most were close to those of costic acid. However, the typical H-7 signals were missing and the chemical shifts of H-13 were perturbed. Accordingly, a hydroxy group, its presence already deduced from the IR spectrum, was at C-7. The stereochemistry was deduced from the downfield shift of H-5 and was established by NOE difference spectroscopy. Clear effects were observed between the hydroxyl proton, H-5 and H-13', between H-5, OH and H-3α as well as between H-14', H-2β, H-6β and H-8β. The ^{13}C NMR spectrum (see Experimental) also agreed with the proposed structure.

The ^{1}H NMR spectrum of **10b** (Table 1), which was prepared from the naturally occurring acid, was in part similar to that of **9b**. However, the presence of a primary alcohol followed from the broadened two proton singlets at δ4.33 and the signals of H-6 and H-8, especially that of H-8α were shifted downfield. This indicated the configuration of the 7,11-double bond. The ^{13}C NMR spectrum (see Experimental) also agreed with the proposed structure. Thus **10a** was the product of an allylic rearrangement of **9a** and therefore **10a** could be an artifact. This was excluded by the results of acid treatment of **9a**. In addition to elimination of water only the Δ^3 isomer of **9a** was obtained. The structure of which was easily deduced from the ^{1}H NMR spectrum (see Experimental).

Table 1. ^{1}H NMR spectral data of compounds **9a/b** and **10a/b** (400 MHz, $CDCl_3$, TMS as internal standard)

H	**9a**	**9b**	**10a**	**10b**
1α	1.33 *m*	1.26 *m*	1.25 *ddd*	1.24 *ddd*
1β	1.45 *m*	1.42 *m*	1.50 *d*(*br*)	1.47 *b d* (*br*)
2α	1.60 *m*	1.60 *m*	1.64 *m*	1.60 *m*
2β				
3α	2.04 *ddd*	2.02 *ddd* (*br*)	1.97 *ddd* (*br*)	1.95 *m*
3β	2.31 *dt*	2.27 *dt*	2.33 *dt*	2.30 *dt*
5	2.37 *dd* (*br*)	2.36 *dd* (*br*)	1.89 *d* (*br*)	1.85 *d* (*br*)
6α	1.62 *m*	1.60 *m*	2.72 *ddd*	2.65 *dt*
6β			2.04 *dd*	1.98 *dd*
8α	1.33 *m*	1.30 *m*	3.38 *dddd*	3.05 *dddd*
8β	1.75 *m*	1.75 *m*	2.16 *ddd*	2.13 *ddd*
9α	1.87 *m*	1.83 *m*	1.38 *ddd*	1.34 *ddd*
9β	1.40 *m*	1.30 *m*	1.64 *m*	1.60 *m*
13	6.38 *s*	6.15 *s*	4.40 *s* (*br*)	4.33 *s* (*br*)
13'	5.94 *s*	5.81 *s*		
14	0.73 *s*	0.70 *s*	0.86 *s*	0.83 *s*
15	4.71 *q*	4.66 *q*	4.79 *q*	4.76 *q*
15'	4.38 *q*	4.33 *q*	4.48 *q*	4.46 *q*
OMe	—	3.75 *s*	-	3.76 *s*

J [Hz]: Compounds **9a/b**: 2α,3α = 7; 2α,3β = 12; 2α,3β = 2β,3β = 3; 3α,3β = 5,6β = 8β,9α = 9α,9β = 13; 3,15 = 5,15 = 1; compounds **10a/b**: 1α,1β = 3α,3β = 6α,6β = 13; 1α,2α = 6; 3,15 = 5,15 = 1; 1α,2β = 12; 2α,3α = 7; 2β,3α = 12; 2α,3β = 2β,3β = 3.5; 5,6β = 12; 5,6α,8α = 2; 8α,8β = 8α,9β = 9α,9β = 13; 8β,9β = 4.5.

The chemistry of the *Podolepis* species investigated indicated no relationship with the South African *Athrixia* species where diterpenes and thymol derivatives are common [7, 8]. It would be of interest to study the Australian *Athrixia* species which are placed in one group with *Podolepis*, unlike the South African *Athrixia* species which are members of another subtribe. As the rare substituted pyrones have been reported so far only from *Helichrysum* [2–4] and *Gnaphalium* [9 and unpublished results] the pyrones **1**–**8** may support the proposed close relationship of these genera [1].

The constituents from *Cassinia*, where so far only polyacetylenes were reported [10], show no clear relationship to other genera. Acids derived from eudesmane are widespread in the Compositae. However, the unusual high concentration of **9a** and **10a** in *C. longifolia* is remarkable. Clearly many more of the Australian species have to be investigated to get a better picture.

EXPERIMENTAL

The air dried plant material was collected in February 1986 near Canberra, Australia, and worked-up as reported previously [11]. CC of the defatted extract of the aerial parts of *Cassinia longifolia* (760 g, voucher Robinson 86-0064, all deposited in the U.S. National Herbarium) gave four fractions (1: petrol and Et_2O–petrol, 1:20, 2: Et_2O–petrol, 1:3, 3: Et_2O–petrol, 1:1 and 4: Et_2O). PTLC (silica gel, PF 254, Et_2O petrol, 1:9) of fraction 1 gave 1.6 g ledol and a mixture of hydrocarbons, one tenth of which was separated on $AgNO_3$ coated silica gel (Et_2O petrol, 1:100) affording 50 mg δ-cadinene (R_f 0.75) and 50 mg γ-cadinene (R_f 0.50). PTLC of fraction 2 (Et_2O petrol, 1:3) gave 1 g ledol and 1 g **9a**. Fraction 3 contained 7.6 g **9a**. Fraction 4 gave by flash chromatography (silica gel ϕ 30–60 μ) 200 mg **9a**, 2 g **10a** and 300 mg mikanin. CC of the defatted extract of the aerial parts of *Podolepis hieracioides* (470 g, voucher Robinson, 86-0068) gave three fractions (1: petrol, 2: Et_2O–petrol, 1:1 and Et_2O, 3: Et_2O–MeOH, 9:1). Fraction 1 gave by TLC (petrol) 20 mg squalene. HPLC of fraction 2 (RP 8, MeOH–H_2O, 17:3, *ca* 100 bar) afforded 300 mg **6** (R_t 2.6 min), 55 mg **2** (R_t 3.9 min), 80 mg **1** (R_t 4.9 min) and crude **7** which gave after repeated HPLC (same conditions) 20 mg **7** (R_t 3.0 min). PTLC of fraction 3 (Et_2O–petrol, 3:1) gave two bands (3/1 and 3/2). HPLC of 3/1 (RP 8, MeOH–H_2O, 4:1) gave 6 mg **4** (R_t 3.6 min), 16 mg **3** (R_t 5.0 min) and 1 mg **8** (R_t 6.5 min). HPLC of 3/2 (same conditions) gave 3 mg **5** (R_t 3.8 min) and crude **11** (R_t 1.2 min) which gave by PTLC (Et_2O–petrol, 3:1, two developments, R_f 0.4) 40 mg **11**.

Podopyrone (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1670, 1610 (γ-pyrone); MS *m/z* (rel. int.): 308.235 [M]$^+$ (48) (calc. for $C_{19}H_{32}O_3$: 308.235), 293 [M – Me]$^+$ (35), 181 $[C_{10}H_{13}O_3]^+$ (70), 168.079 $[C_9H_{12}O_3]^+$ (100); ^{1}H NMR ($CDCl_3$): δ 1.82 (*s*, H-7), 1.92 (*s*, H-8), 2.57 (*t*, H-1′), 1.63 (*tt*, H-2′), 1.35–1.20 (*m*, H-3′–H-10′), 0.86 (*t*, H-11′), 3.93 (*s*, OMe) (*J* [Hz]: 1′,2′ = 7.5; 10′,11′ = 6.5); ^{13}C NMR ($CDCl_3$, C-2–C-8): 162.2 *s*, 99.3 *s*, 181.2 *s*, 118.2 *s*, 159.5 *s*, 9.7 *q*, 6.8 *q*; OMe: 55.2 *q*; C-1′–C-11′: 27.0, 29.0, 29.3, 29.4, 30.6, 29.4, 29.3, 29.2, 28.9, 22.6 *t*, 15.3 *q*. Gated decoupling: C-2 *qq*, C-3 *q*, C-4 *qq*, C-5 *tq*, C-6 *tq* (*J* [Hz]: C-2, H-8 = C-2, OMe = 4; C-3, H-8 = 6.5; C-4, H-7 = C-4, H-8 = 3; C-5, H-7 = 6; C-5, H-1′ = 3; C-6, H-7 = C-6, H-1′ = 5).

nor-Podopyrone (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1665, 1605 (γ-pyrone); MS *m/z* (rel. int.): 294.220 [M]$^+$ (21) (calc. for $C_{18}H_{30}O_3$: 294.220), 279 [M – Me]$^+$ (28), 195 (25), 181 (52), 168 (100); ^{1}H NMR as **1**, except 0.87 (*t*, H-10′).

10′-Acetoxypodopyrone (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735, 1240 (OAc), 1670, 1610 (γ-pyrone); MS *m/z* (rel. int.): 366.241 [M]$^+$ (32) (calc. for $C_{21}H_{34}O_5$: 366.241), 323 [M – COMe]$^+$ (62), 307 [M – OAc]$^+$ (28), 306 [M – HOAc]$^+$ (21), 195 (32), 181 (86), 168 (100); ^{1}H NMR ($CDCl_3$) as **1**, except 4.87 (*tq*, H-10′, *J* = 7 and 6 Hz), 1.19 (*d*, H-11′), 2.02 (*s*, OAc), 1.57 (*m*, H-9′); $[\alpha]_D^{24°} = -1$ $[\alpha]_{436}^{24°} = -4$ ($CHCl_3$; *c* 1.6).

10′-Oxo-8-methylpodopyrone (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 (C=O), 1670, 1605 (γ-pyrone); MS *m/z* (rel. int.): 336.230 [M]$^+$ (72) (calc. for $C_{20}H_{32}O_4$: 336.230), 321 [M – Me]$^+$ (100), 293 [321 – CO]$^+$ (12), 279 [M – CH_3COMe]$^+$ (21), 195 (30), 182 $[C_{10}H_{14}O_3]^+$ (31); ^{1}H NMR ($CDCl_3$) as **1**, except 2.39 (*q*, H-8), 1.03 (*t*, H-9), 1.57 (*m*, H-8′), 2.41 (*t*, H-9′), 2.13 (*s*, H-11′) (*J* [Hz]: 8,9 = 8′,9′ = 7).

10′-Hydroxy-8-methylpodopyrone (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640 (OH), 1665, 1605 (γ-pyrone); MS *m/z* (rel. int.): 338.246 [M]$^+$ (41) (calc. for $C_{20}H_{34}O_4$: 338.246), 323 [M – Me]$^+$ (26), 305 [323 – H_2O]$^+$ (78), 195 (62), 182 (62), 55 (100); ^{1}H NMR ($CDCl_3$) as **1**, except 2.39 (*q*, H-8), 1.03 (*t*, H-9), 1.60 (*m*, H-9′), 3.78 (*tq*, H-10′, *J* = 6 and 6 Hz), 1.09 (*d*, H-11′, *J* = 6 Hz).

10′-Acetoxy-8-methylpodopyrone (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1240 (OAc), 1670, 1605 (γ-pyrone); MS *m/z* (rel. int.): 380.256 [M]$^+$ (64) (calc. for $C_{22}H_{36}O_5$: 380.256), 337 [M – COMe]$^+$ (26), 321 [M – OAc]$^+$ (24), 320 [M – HOAc]$^+$ (19), 305 [320 – Me]$^+$ (100), 195 (38), 182 (41); ^{1}H NMR ($CDCl_3$) as **3**, except 2.38 (*q*, H-8) and 1.01 (*t*, H-9, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$, C-2′–C-9′): 162.0 *s*, 105.2 *s*, 180.3 *s*, 118.4 *s*, 158.2 *s*, 9.7 *q*, 25.2 *t*, 12.7 *q*; C-1′ C-11′: OMe: 55.1 *q*; OAc: 170.5 *s*, 21.2 *q*; C-1′ C-11′: 26.9, 28.9, 29.2, 29.3, 30.6, 29.2, 29.1, 15.1, 35.7 *t*, 70.8 *d*, 19.8 *q*.

10′-Acetoxy-7,8-dimethylpodopyrone (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1240 (OAc), 1670, 1605 (γ-pyrone); MS *m/z* (rel. int.): 394.272 [M]$^+$ (12) (calc. for $C_{23}H_{38}O_5$: 394.272), 335 [M – OAc]$^+$ (10), 334 [M – HOAc]$^+$ (9), 209 (100), 196 (40); ^{1}H NMR ($CDCl_3$) as **6**, except 2.42 (*q*, H-7) and 1.05 (*t*, H-10, *J* = 7 Hz).

11′-Acetoxypodopyrone (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1250 (OAc), 1670, 1610 (γ-pyrone); MS *m/z* (rel. int.): 366.241 [M]$^+$ (28) (calc. for $C_{21}H_{34}O_5$: 366.241), 323 [M – COMe]$^+$ (27), 307 [M – OAc]$^+$ (33), 195 (36), 181 (74), 168 (100); ^{1}H NMR ($CDCl_3$) as **1**, except 4.05 (*t*, H-11′, *J* = 6.5 Hz).

7-Hydroxyeudesm-4(15),11(13)-dien-12-acid (**9a**). Colourless crystals, mp 220°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3500–2600, 1700, 1650 (C=CCO_2H); $[\alpha]_D^{24°} = +21$ ($CHCl_3$; *c* 3.03); Addition of CH_2N_2 in Et_2O gave the methyl ester **9b**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1725, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 264.173 [M]$^+$ (0.8) (calc. for $C_{16}H_{24}O_3$: 264.173), 246 [M – H_2O]$^+$ (100), 231 [246 – Me]$^+$ (76), 218 (52), 214 (29), 187 (68), 186 (62), 171 (62), 123 (98), 95 (62), 93 (68), 91 (62), 79 (64), 55 (66); ^{13}C NMR ($CDCl_3$, C-1–C-15): 41.3 *t*, 23.4 *t*, 36.8 *t*, 150.3 *s*, 43.7 *d*, 34.3 *t*, 72.9 *s*, 31.3 *t*, 35.9 *t*, 35.4 *s*, 146.7 *s*, 167.8 *s*, 123.3 *t*, 15.4 *q*, 105.1 *t*; OMe: 51.7 *q*. 50 mg **9a** in 5 ml dioxane were heated 4 hr with 5 ml 1M H_2SO_4 at 80°. After addition of CH_2N_2 to the crude reaction product PTLC (Et_2O–petrol, 1:3) gave a mixture of isomeric trienes and 20 mg of **9c**. ^{1}H NMR ($CDCl_3$): 2.07 (*dd* (*br*), H-3α), 1.90 (*d* (*br*), H-3β), 2.72 (*dd*, H-6α), 2.37 (*d* (*br*), H-6β), 2.12 (*dd*, H-9α), 6.20 (*d*, H-13), 5.92 (*d*, H-13′), 1.08 (*s*, H-14), 1.84 (*s* (*br*), H-15) (*J* [Hz]: 2β,3α = 10; 3α,3β = 18; 6α,6β = 14.5; 6α,8α = 2.5; 8β,9α = 9α,9β = 13.5; 8α,9α = 4; 6β,13 = 0.7.

13-Hydroxyeudesm-4(15),7(11)-dien-12-acid (**10a**). Colourless crystals, mp 156°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 3500–2600, 1695, 1650 (C=CCO_2H); MS *m/z* (rel. int.): 250.157 [M]$^+$ (3) (calc. for $C_{15}H_{22}O_3$: 250.157), 232 [M – H_2O]$^+$ (100), 217 [M – Me]$^+$ (56), 204 (42), 187 (36), 121 (66), 93 (80), 91 (82); $[\alpha]_D^{24°} = +21$ ($CHCl_3$; *c* 0.22). Addition of CH_2N_2 gave **10b**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1725, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 264.173 [M]$^+$ (3) (calc. for $C_{16}H_{24}O_3$: 264.173), 246 [M – H_2O]$^+$ (100), 231 (66), 218 (32), 214 (26), 187 (58), 186 (48), 171 (52), 93 (82), 91 (81); ^{13}C NMR ($CDCl_3$, C-1–C-15): 41.0 *t*, 29.4 *t*, 41.8 *t*, 149.8 *s*, 50.6 *d*, 27.4 *t*, 154.0 *s*, 23.1 *t*, 36.4 *t*, 36.1 *s*, 125.1 *s*, 169.7 *s*, 59.0 *t*, 15.9 *q*, 105.8 *t*; OMe: 51.5 *q*.

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