27.4 (30-Me), 26.1 (28-Me), 21.1, 15.6 and 14.8 (18-, 19- and 29-Me).

Acetylation of compound **1**. Acetylation of **1** (Ac_2O–pyridine, 50°, 24 hr) gave 7α,12α-diacetoxy-1,2-dihydroazadirone. EIMS *m/z*: 496[M]$^+$, 436[M−AcOH]$^+$, 376[M−2AcOH]$^+$. IR ν_{max}^{KBr} cm^{-1}: 1740, 1720 (C=O) and 1250 (C–O); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.02 (6H), 1.04 (3H), 1.08 (3H), 1.19 (3H) [5 × Me], 1.91 (3H, *s*, 12Ac), 2.00 (3H, *s*, 7α-Ac), 2.99 (1H, *dd*, *J* = 9, 11 Hz, H-17), 5.07 (1H, *dd*, *J* = 7.8 Hz, H-12) 5.27 (1H, *m*, H-15), 5.48 (1H, *t*, *J* = 2.5 Hz, H-7), 6.27 (1H, *m*, H-22), 7.21 (1H, *m*, H-23) and 7.34 (1H, *m*, H-21).

Reaction of compound **1** with benzene seleninic anhydride. Compound **1** (100 mg) and benzene seleninic anhydride (80 mg) were refluxed for 30 min in chlorobenzene and the product, 12α-acetoxy-7-deacetylazadirone, purified by prep. TLC (silica gel, 20% EtOAc–hexane). EIMS *m/z*: 452[M]$^+$, 392[M−AcOH]$^+$, IR ν_{max}^{KBr} cm^{-1}: 3540 *br* (OH), 1730, 1670 (C=O), 1100 (C–O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.05 (3H), 1.09 (3H), 1.17 (3H), 1.19 (3H) [5 × Me], 1.93 (3H, *s*, Ac), 3.08 (1H, *dd*, *J* = 9, 10.8 Hz, H-17), 4.04 (1H, *t*, *J* = 2.8 Hz, H-7), 5.16 (1H, *dd*, *J* = 8.6, 9 Hz, H-12), 5.70 (1H, *dd*, *J* = 2, 3 Hz, H-15), 5.82 (1H, *d*, *J* = 10 Hz, H-1) 6.28 (1H, *m*, H-22), 7.02 (1H, *d*, *J* = 10 Hz, H-2), 7.23 (1H, *m*, H-23) and 7.36 (1H, *m*, H-21).

Acknowledgements—The authors thank Dr Ben Shoulders of the University of Texas for obtaining NMR spectra and the USDA (Grant 85-FSTY-0102) for financial support.

REFERENCES

1. Kokwaro, J. O. (1976) *Medicinal Plants of East Africa*, p.158. East African Literature Bureau, Nairobi, Kenya.
2. Akinniyi, J. A., Connolly, J. D., Mulholland, D. A., Rycroft, D. S. and Taylor, D. A. H. (1986) *Phytochemistry* **21**, 2187.
3. Taylor, D. A. H. (1983) in *Chemistry and Chemical Taxonomy of the Rutales* (Waterman, P. G. and Grundon, M. F., eds), p. 138. Academic Press, London.
4. Nakatani, M., Iwashita, T., Mizukawa, K. and Hase, T. (1987) *Heterocycles* **26**, 43.

Phytochemistry, Vol. 27, No. 7, pp. 2355–2357, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00

PREPHYTOENE ALCOHOL FROM *MYRIOPHYLLUM VERTICILLATUM**

PIETRO MONACO, MARINA DELLA GRECA, MARGHERITA ONORATO and LUCIO PREVITERA

Department of Organic and Biological Chemistry of the University Via Mezzocannone 16, 80134 Napoli, Italy

(*Received* 20 *October* 1987)

Key Word Index—*M. verticillatum*; Haloragaceae; carotenoids; prephytoene alcohol.

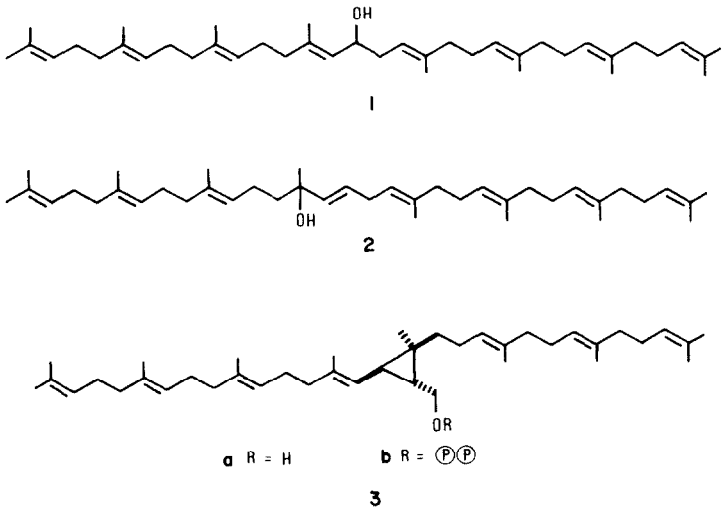
Abstract—Prephytoene alcohol, a biosynthetic intermediate of carotenoids, has been isolated from the aquatic plant *Myriophyllum verticillatum*.

In a previous paper [1] we reported the isolation from the aquatic plant *M. verticillatum* of two novel hydroxylated carotenoids which were attributed structures **1** and **2** on the basis of their chemical and physical features. These compounds may easily be considdred to arise through water addition to the cyclopropylcarbinyl cation intermediate produced by loss of pyrophosphate from prephytoene pyrophosphate (**3b**).

In pursuing the chemical investigation of this species we isolated a compound in small amount from the ethereal extract which has been identified as prephytoene alcohol (**3a**) on the basis of its spectroscopic features.

Compound **3a** had $[\alpha]_D$ + 37.5° and a molecular formula $C_{40}H_{66}O$. The IR spectrum indicated the presence of a hydroxyl group and isolated double bonds with absorptions at 3400 and 1660 cm^{-1}. The mass spectrum showed, beside the molecular peak at *m/z* 562, fragments at *m/z* 544 [M−H_2O]$^+$, 531 [M−CH_2OH]$^+$, 529 [M−H_2O−Me]$^+$, and the series of fragments due to allylic cleavages in the side chains at *m/z* 493 [M−C_5H_9]$^+$, 475 [M−H_2O−C_5H_9]$^+$, 425 [M−$C_{10}H_{17}$]$^+$, 407 [M−H_2O−$C_{10}H_{17}$]$^+$, 357 [M−$C_{15}H_{25}$]$^+$, 339 [M−H_2O−$C_{15}H_{25}$]$^+$, 271 [M−H_2O−$C_{20}H_{33}$]$^+$, 203 [M−H_2O−$C_{25}H_{41}$]$^+$, 137 [$C_{10}H_{17}$]$^+$ and 69 [C_5H_9]$^+$. The H NMR spectrum showed the presence of methyl singlets at δ1.15, 1.61 and 1.69 in a 1:6:3 ratio, a

*Part 8 in a series of studies on aquatic plants distributed in Italy. For part 7 see ref. [1].



hydroxyl bearing methylene as two double doublets (AB part of ABX system) centred at δ3.55 and 3.84, six olefinic protons at δ5.11, an olefinic proton as a doublet centered at δ4.95 and two cyclopropyl protons as multiplets at δ0.95 and 1.35. These data were identical with those reported by Campbell *et al.* [2] for synthetic (±) prephytoene alcohol. The ^{13}C NMR spectrum showed only 20 signals which were identified as carbon types by a DEPT experiment whereas an inverse gated decoupling experiment gave their relative intensities (Table 1). All the shieldings were attributed on the basis of the data reported by Crombie *et al.* [3] for presqualene esters and related cyclopropanes. The presence of two methines at δ28.61 and 34.85 and a quanternary carbon at δ23.71 confirmed the assigned structure.

Prephytoene alcohol (**3a**) and its pyrophosphate (**3b**) have been well known from a long time and they have been the subjects of biochemical [4] and chemical [5] investigations. However, this is the first report of the isolation of prephytoene alcohol from a natural source.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were measured at 270 and 50.28 MHz, respectively, in $CDCl_3$. The deuterium resonance was used as lock signal. MS were recorded at 70 eV with the source of 150° on a Kratos MS 80 apparatus.

Isolation of prephytoene alcohol (**3a**). Fresh plants of *M. verticillatum* (2 kg) were homogenized and lyophilized to afford material which was extracted with cold Et_2O. The ethereal extract was treated with 2 N NaOH and then neutralized with 2 N H_2SO_4 and evapd to give a residue (500 mg) which was chromatographed on silica gel column. Elution with petrol–Et_2O (9:1, 90 ml) gave crude **3a** (14 mg) which after purification by prep. TLC (petrol–Et_2O 4:1) had $[\alpha]_D$ + 37.5° ($CHCl_3$; *c* 0.7); MS *m/z* (rel. int.): 562 (4), 544 (9), 531 (12), 529 (17), 493 (15), 475 (18), 425 (16), 407 (21), 357 (17), 339 (12); 271 (20), 203 (27), 137 (43), 69 (100); ^{1}H NMR: δ0.95 (*m*, 1H), 1.15 (*s*, 3H), 1.35 (*m*, 1H), 1.61 (*s*, 18H), 1.69 (*s*, 9H), 2.01 (*br*, 24H), 3.53 (*dd*, 1H, *J* = 8.5 and 11 Hz), 3.82 (*dd*, 1H, *J* = 6 and 11 Hz), 4.95 (*d*, 1H, *J* = 8 Hz), 5.11 (*br*, 6H).

Table 1. ^{13}C NMR data of prephytoene alcohol (**3a**)*

C		C		C		C	
1	131.18 *s*	11	26.62 *t*[b]	20′	17.83 *q*	10′	124.05 *d*[a]
2	124.31 *d*[a]	12	39.68 *t*[c]	19′	15.93 *q*	9′	134.85 *s*
3	26.70 *t*[b]	13	136.70 *s*	18′	15.93 *q*	8′	39.68 *t*[c]
4	39.70 *t*[c]	14	123.32 *d*	17′	25.67 *q*	7′	26.62 *t*[b]
5	134.85 *s*	15	34.85 *d*	16′	17.65 *q*[d]	6′	124.18 *d*[a]
6	124.18 *d*[a]	16	17.65 *q*[d]	15′	63.72 *t*	5′	134.85 *s*
7	26.62 *t*[b]	17	25.67 *q*	14′	28.61 *d*	4′	39.70 *t*[c]
8	39.68 *t*[c]	18	15.93 *q*	13′	23.71 *s*	3′	26.70*t*[b]
9	134.85 *s*	19	15.93 *q*	12′	37.03 *t*	2′	124.31 *d*[a]
10	124.05 *d*[a]	20	16.61 *q*	11′	26.62 *t*[b]	1′	131.18 *s*

*The numbering system used for **3a** is according to the IUPAC rules for carotenoids. Assignments bearing the same superscript may be reversed.

Acknowledgement —This work was supported by M.P.I. (Ministero della Pubblica Istruzione).

REFERENCES

1. Lanzetta, R., Monaco, P., Previtera, L. and Simaldone, A. (1988) *Phytochemistry*, (in press).
2. Campbell, R. V. M., Crombie, L., Findley, D. A. R., King, R. W., Pattenden, G. and Whiting, D. A. (1975) *J. Chem. Soc. Perkin I* 897.
3. Crombie, L. King, R. W. and Whiting, D. A. (1975) *J. Chem. Soc. Perkin I* 913.
4. Altman, L. J., Ash, L., Kowerski, R. C., Epstein, W. W., Larsen, B. R., Rilling, H. C., Muscio, F. and Gregonis, D. E. (1972) *J. Am. Chem. Soc.* 3257.
5. Altman, L. J., Kowersky, R. C. and Laungani, D. R. (1978) *J. Am. Chem. Soc.* 6174.

Phytochemistry, Vol. 27, No. 7, pp. 2357–2358, 1988.
Printed in Great Britain.

0031–9422/88 $3.00+0.00

COUMARINS FROM THE LEAVES OF *MURRAYA PANICULATA*

TIAN-SHUNG WU

Department of Applied Chemistry, Providence College of Arts and Science, Taichung, Taiwan 40211, Republic of China

(*Revised received* 23 *December* 1987)

Key Word Index—*Murraya paniculata* var. *omphalocarpa*; Rutaceae; coumarins; murrayanone; murraculatin.

Abstract—Two new coumarins, murrayanone and murraculatin, together with seven known coumarins have been isolated from the leaves of *Murraya paniculata* var. *omphalocarpa*. The structures of murrayanone and murraculatin were elucidated by spectroscopic methods.

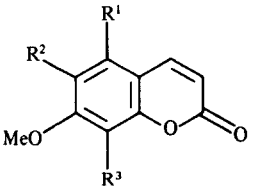
INTRODUCTION

In a previous paper [1], the isolation of a new coumarin, omphamurin, from the leaves of *Murraya paniculata* var. *omphalocarpa Hayata* was reported. Further examination of the leaves of this plant has now resulted in the isolation of 10 further coumarins, two (**1** and **2**) of which are new coumarins.

RESULTS AND DISCUSSION

Murrayanone (**1**), $C_{17}H_{20}O_6$ ($[M]^+$, *m/z* 306), gave IR absorption bands at 1710 (saturated ketone), 1695 (conjugated δ-lactone) and 1590 cm^{-1} (aromatic). Its UV spectrum [λ_{max} 230.5 (sh), 253.5 (sh) and 305.5 nm] was very similar to that of murragleinin [2], i.e. characteristic of a 5,6,7-trioxygenated coumarin (5,6,7-trimethoxycoumarin): λ_{max}^{MeOH} nm: 224 (sh), 253 (sh), 322; λ_{min}^{MeOH} nm: 262. 5,7,8-Trimethoxycoumarin: λ_{max}^{MeOH} nm: 222 (sh), 260, 318; λ_{min}^{MeOH} nm: 236, 273). The ^1H NMR spectrum of **1** had a pair of doublets ($J = 9.7$ Hz) at δ 6.25 and 7.94. The downfield signal (δ 7.94) confirmed the coumarin moiety and the presence of an oxygen in position 5 [3]. Three sharp singlets at δ 3.87, 3.90 and 4.01 due to nine protons suggested the presence of three methoxy groups. A 3-methyl-2-oxobutyl side chain was indicated by the ^1H NMR data [δ 1.23 (6H, *d*, $J = 6.9$ Hz), 2.85 (1H, *hept*, $J = 6.9$ Hz) and 3.96 (2H, *s*)] and mass fragmentation ions at *m/z* 249 $[M-COCH(Me)_2]^+$ and 235 $[M-CH_2COCH(Me)_2]^+$. According to the above data, murrayanone could be formulated as 5,6,7-trimethyoxy-8-(3′-methyl-2′-oxobutyl) coumarin (**1**).

Murraculatin (**2**), $C_{16}H_{18}O_6$, showed the UV absorption characteristics of a 7-alkoxycoumarin [4, 5]. Strong IR absorption bands at 3400 (OH) and 1705 cm^{-1} were indicative of a carboxylic group, and bands at 1690 and 1595 cm^{-1} confirmed the presence of a δ-lactone group



1 $R^1 = R^2 = OMe$, $R^3 = CH_2COCH(Me)_2$
2 $R^1 = OMe$, $R^2 = H$, $R^3 = CH_2C(Me)_2COOH$
3 $R^1 = OMe$, $R^2 = H$, $R^3 = CH_2C(Me)_2COOMe$
7 $R^1 = R^2 = H$, $R^3 = CHCOCH(Me)_2$ | $OCOCH_2CH(Me)_2$