

CAROTENOID-LIKE COMPOUNDS FROM *TYPHA LATIFOLIA*¹

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ABSTRACT.—Blumenol A [1] and a new carotenoid-like compound, (3*R*,5*R*,6*S*,9*E*)-5,6-epoxy-3-hydroxy- β -ionol [2], were isolated from *Typha latifolia*.

In the course of our investigation on the chemical composition of aquatic plants, we have recently examined *Typha latifolia* L. (Typhaceae) (1), a plant showing an interesting antialgal activity due to the presence of some fatty acids and steroidal compounds (2).

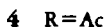
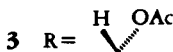
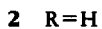
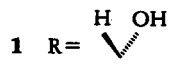
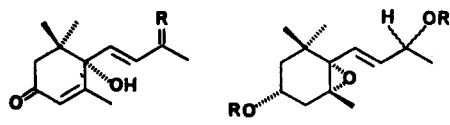
In this paper we describe the isolation and the characterization of two carotenoid-like compounds whose structures have been identified on the basis of physical data and by chemical correlation.

The MeOH extract of *T. latifolia* was distributed between EtOAc and H₂O. The organic layer gave a residue that was chromatographed on Si gel; elution with CHCl₃-Me₂CO (7:3) gave a mixture of hydroxylated compounds that was directly esterified with Ac₂O. The mixture of acetates was then chromatographed on Si gel to separate compounds 3 and 4.

Compound 3, after crystallization from MeOH, had mp 98–99°. The ms, ir, uv, and ¹H-nmr data, together with the ¹³C-nmr shieldings reported in

Table 1, suggested a gross structure of blumenol A acetate. Hydrolysis with 1 N NaOH in MeOH at room temperature gave a dihydroxy enone with all the physical features (mp, uv, ms, ¹H nmr, and cd) identical with those previously reported for blumenol A (3,4).

Compound 4 had a molecular ion at *m/z* 310, corresponding to a molecular formula C₁₇H₂₆O₅, and fragments at *m/z* 250, 208, 175 in its ms. The ¹H nmr showed an AB system (*J* = 15.4 Hz) centered at δ 5.797 attributable to the vinylic H-7 and H-8, the B part being split (*J* = 6.6 Hz) by coupling with the acetate gem proton. Two methines geminal with the acetate groups as multiplets centered a δ 5.383 and 4.875 were

TABLE 1. ¹³C-nmr Data of Compounds 3 and 4.

Carbon	Compound	
	3	4
C-1	41.15	34.28
C-2	49.65	41.25
C-3	197.85	67.58
C-4	162.06	36.84
C-5	127.15	65.20
C-6	78.99	69.86
C-7	131.21 ^a	126.99
C-8	131.46 ^a	133.61
C-9	70.19	70.58
C-10	20.48	19.95
C-11	24.06 ^b	25.31
C-12	22.87 ^b	28.40
C-13	18.91	20.57
MeCO	21.29	21.26, 21.28
MeCO	170.24	170.28, 170.32

^{a,b}Assignments bearing the same superscript may be reversed.

¹Part XV in a series of studies on aquatic plants. For Part XIV see Della Greca *et al.* (1).

attributable to H-9 and H-3, respectively. Four double doublets at δ 2.396 ($J = 4.3$ and 11.9 Hz), 1.782 ($J = 5.3$ and 11.9 Hz), 1.625 ($J = 3.2$ and 10.8), and 1.328 ($J = 7.6$ and 10.8) corresponded to H-4 β , H-4 α , H-2 β , and H-2 α , respectively. Two acetate methyls at δ 2.035 and 2.016, the H-10 methyl doublet at δ 1.326 ($J = 6.5$ Hz), and three methyl singlets at δ 1.186, 1.121, and 0.972 were attributable to H-13, H-12, and H-11, respectively.

Irradiation at δ 5.935 simplified the signal at δ 5.690, and the irradiation of the latter modified the protons at δ 5.935 and 5.383. Irradiation at δ 4.875 collapsed the four double doublets into four doublets. The ^{13}C -nmr spectrum showed 13 signals that through DEPT experiments were identified as four methyls, two methylenes, two methines, and two quaternary carbons bearing oxygen, a quaternary carbon, and two vinylic methines. Assignments of individual signals (Table 1) were based on two-dimensional heteronuclear chemical shift correlation.

These data suggested a gross structure of 3-acetoxy-5,6-epoxy- β -ionol acetate. The configuration *S* at C-6 and consequently *R* at C-5 was attributed by conversion of **4** into the already known (4,5) (6*S*)-bis-enone **5**. Compound **4** was hydrolyzed with 1 N NaOH in MeOH at room temperature to give the corresponding dihydroxy epoxide **2**, and this latter compound was treated with CrO_3 /pyridine. During the Sarett oxida-

tion the β,γ -epoxyketone intermediate was transformed (**6**) into **5** with retention of the configuration at C-6 (**7**). The assignment of the *R* configuration at C-3, as well as the full assignments of the ^1H -nmr signals, was then made on the basis of the coupling constants and *nOe* experiments (Figure 1) on the diacetate **4**. Although the stereomeric (3*S*,5*R*,6*S*,9*E*)-3-hydroxy- β -ionol has been already isolated from Japanese domestic Surfu tobacco (**8**), this is the first report of the presence of **2** in a natural source. (Compound **2** was formed during the synthesis of (3*S*,5*R*,6*S*)-3-hydroxy- β -ionol starting from 3-hydroxy- β -ionol (**7**); however, no physical data were reported.)

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.— ^1H -nmr spectra at 400 MHz and ^{13}C -nmr spectra at 100 MHz were obtained using CDCl_3 solution on a Bruker AM 400 spectrometer. One-bond 2D C-H COSY experiment was performed with the Bruker XHCCORR microprogram using delay $D_3 = 3.6$ msec (corresponding to $J_{\text{C,H}} = 140$ Hz). Eims spectra were recorded at 70 eV on a Kratos MS apparatus. Ir spectra were measured with a Perkin-Elmer model 1740 spectrometer. Uv spectra were recorded on a Perkin-Elmer LAMBDA 7 spectrophotometer.

PLANT MATERIAL.—The plants of *T. latifolia* were collected in July 1987, in a ditch near Naples. A voucher specimen is on deposit at the Botanical Garden of the University of Naples. The material was oven-dried at 40° for 7 days.

EXTRACTION, SEPARATION, AND ISOLATION.—The dried material (7 kg) was extracted with cold Et_2O and then with MeOH. The MeOH extract (170 g) was distributed between EtOAc and H_2O . The organic layer gave a residue (8 g) that was chromatographed on Si gel; CHCl_3 -

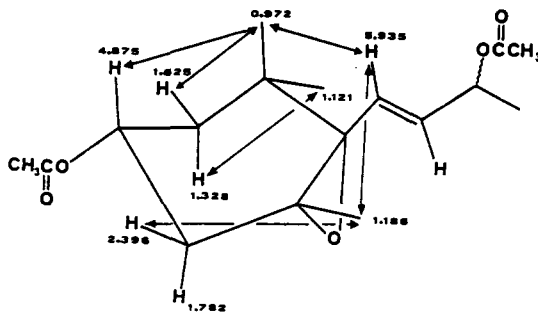


FIGURE 1. ^1H - ^1H *nOe*'s in compound **4**.

Me₂CO (7:3) (1200 ml) gave a mixture of hydroxylated compounds (500 mg) directly esterified with Ac₂O (1 ml) in dry pyridine (10 ml). Si gel chromatography of the resulting mixture gave **3** [20 mg, hexane-EtOAc (19:1)] and **4** [40 mg, hexane-EtOAc (7:3)] besides a mixture of acylated steroidal glycosides (300 mg).

Compound 3.—After crystallization from MeOH: mp 98–99°; ir ν (max) 3350, 1729, 1680 cm⁻¹; ms m/z 266, 223, 206, 150, 135, 124, 107, 94, 79, 43; uv λ max (MeOH) 236 nm (ϵ 13,000); ¹H nmr δ 0.994 (3H, s, H-11), 1.072 (3H, s, H-12), 1.324 (3H, d, J = 6.5 Hz, H-10), 1.833 (3H, d, J = 1.4 Hz, H-13), 2.004 (3H, s, Ac), 2.319 (2H, AB system, J = 17.0 Hz, H-2), 5.381 (1H, m, H-9), 5.781 and 5.916 (3H, ss, H-4, H-7, and H-8).

Hydrolysis of 3.—Compound **3** (10 mg) was treated with 1 N NaOH in MeOH (5 ml) at room temperature for 3 h. Usual workup gave blumenol A [**1**] mp 114–115°; ir ν max 3380, 1665 cm⁻¹; uv λ max (MeOH) 236 (ϵ 12,900); ms m/z 224, 168, 124; ¹H nmr δ 0.989 (3H, s), 1.065 (3H, s), 1.266 (3H, d, J = 6.5 Hz), 1.875 (3H, d, J = 1.4 Hz), 2.320 (2H, AB system, J = 17.0 Hz), 4.371 (1H, m), 5.803 (2H, m), 6.004 (1H, bs); cd (MeOH) $\Delta\epsilon_{242}$ +9.7, $\Delta\epsilon_{319}$ -0.40.

Compound 4.—After crystallization from MeOH: mp 72–74°; ir ν max 3689, 1729, 1255 cm⁻¹; ms m/z 310, 267, 250, 208, 194, 175, 125, 107; ¹H nmr δ 0.972 (3H, s, H-11), 1.121 (3H, s, H-12), 1.186 (3H, s, H-13), 1.326 (3H, d, J = 6.5 Hz, H-10), 1.328 (1H, dd, J = 7.6 and 10.8 Hz, H-2 α), 1.625 (1H, dd, J = 3.2 and 10.8 Hz, H-2 β), 1.782 (1H, dd, J = 5.3 and 11.9 Hz, H-4 α), 2.016 and 2.035 (2 \times 3H, ss, Ac), 2.396 (1H, dd, J = 4.3 and 11.9 Hz, H-4 β), 4.875 (1H, m, H-3), 5.383 (1H, m, H-9), 5.657 (1H, dd, J = 6.6 and 15.4 Hz, H-8), 5.935 (1H, d, J = 15.4 Hz, H-7).

Hydrolysis of 4.—Pure **4** (15 mg) was hydrolyzed at room temperature with 1 N NaOH in MeOH (5 ml) for 2 h to give **2** (13 mg): ms m/z 208, 181, 125, 107; ir ν max 3380, 1660, 1359

cm⁻¹; ¹H nmr δ 0.991 (3H, s, H-11), 1.115 (3H, s, H-12), 1.198 (3H, s, H-13), 1.318 (3H, d, J = 7.0 Hz, H-10), 1.330 (1H, dd, J = 7.5 and 11.2 Hz, H-2 α), 1.553 (1H, dd, J = 3.4 and 11.2 Hz, H-2 β), 1.790 (1H, dd, J = 5.4 and 12.2 Hz, H-4 α), 2.292 (1H, dd, J = 4.4 and 12.2 Hz, H-4 β), 3.850 (1H, m, H-3 β), 4.428 (1H, m, H-9), 5.891 (2H, m, H-7 and H-8).

Conversion of 2 into 5.—Pure **2** (12 mg) in dry pyridine (2 ml) was added to CrO₃ (15 mg) in pyridine (2 ml). The mixture was kept overnight and then poured into Et₂O; the solution was washed with 2 N H₂SO₄ and then with 2 N Na₂CO₃. Preparative tlc [hexane-Et₂O (9:1)] gave the bis-enone **5** (8 mg): ir ν max 3490, 1639, 1630, 1290 cm⁻¹; ¹H nmr δ 1.047 (3H, s, H-11), 1.138 (3H, s, H-12), 1.916 (3H, d, J = 1.5 Hz, H-13), 2.302 (3H, s, H-10), 2.428 (2H, AB system J = 16.8 Hz, H-2), 6.055 (1H, bs, H-4), 6.570 (1H, d, J = 16.2 Hz, H-8), 7.033 (1H, d, J = 16.2 Hz, H-7); cd (MeOH) $\Delta\epsilon_{207}$ -30.2, $\Delta\epsilon_{242}$ +37.5, $\Delta\epsilon_{320}$ -3.2.

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