pentayne (**1**) MS *m/e*: 162 M^+, UV $\lambda_{max}^{isopentane}$ nm: 251.5 (69), 256.5 (79), 264.0 (100), 270.0 (86), 285.5 (84), 327.5 (1.5), 351.0 (2), 377.0 (2) and 409 (1.5). 11Z-Trideca-1,11-diene-3,5,7,9-tetrayne (**2a**). MS *m/e*: 164M^+. UV$\lambda_{max}^{isopentane}$ nm: 257.5 (67), 270.0 (100), 287.0 (77), 314.5 (6), 336.0 (11), 361.0 (12) and 390.0 (8). 11E-Trideca-1,11-diene-3,5,7,9-tetrayne (**2b**). MS *m/e*. 164M^+. UV$\lambda_{max}^{isopentane}$ nm: 257.5 (73), 270.0 (100), 286.5 (75), 314.5 (6), 336.0 (10), 361.0 (12) and 390.0 (7). 3E-Trideca-1,3-diene-5,7,9,11-tetrayne (**3**). MS *m/e*. 164M^+. UV$\lambda_{max}^{isopentane}$ nm: 262.5 (35), 272.5 (56), 288.5 (100), 310.0 (10), 330.5 (15), 354.0 (18) and 382.0 (11). 3Z,11Z-Trideca-1,3,11-triene-5,7,9-triyne (**4a**). MS *m/e*: 166$^+$. UV$\lambda_{max}^{heptane}$ nm: 241.5 (51), 272.0 (100), 288.0 (95), 300.0 (23), 309.0 (16), 319.5 (25), 329.0 (18), 342.0 (52), 352.0 (13) and 368 (38). 3Z,11E-Trideca-1,3,11-triene-5,7,9-triyne (**4b**). MS *m/e*: 166M^+, UV$\lambda_{max}^{heptane}$ nm: 242.5 (52), 273.0 (100), 288.0 (93), 299.5 (24), 309.0 (18), 319.5 (39), 329.0 (19), 342.0 (54), 352.0 (13) and 367.5 (40). 3E,11E-Trideca-1,3,11-triene-5,7,9-triyne (**4c**). MS *m/e*: 166M^+, UV$\lambda_{max}^{heptane}$ nm: 243.0 (45), 273.0 (100), 288.5 (95), 300.0 (23), 310.0 (17), 320.0 (40), 329.5 (20), 343.0 (56), 353.0 (14) and 368.5 (41). Trideca-1,3,5-triene-7,9,11-triyene. A chromatographic fraction eluted after **4a–c** and along with **5c** showed a UV 283 nm peak [5]. Its MS, after subtraction of background due to **5c**, shows *m/e*: 166M^+ and a fragmentation pattern different from the mutually like patterns for **4a–c**. 3E,5Z,11E-Trideca-1,3,5,11-tetraene-7,9-diyne (**5a**). MS *m/e* 168M^+. UV$\lambda_{max}^{heptane}$ nm: 265.5 (78), 276.0 (60), 314.0 (76), 329.5 (100) and 354.0 (77). IR (CCl_4). 1623 and 1596 cm^{-1} (C=C stretch), 1002 cm^{-1} (—CH=CH_2, out-of-plane H deformation [o.o.p. H def.] of *trans* H's), 945 and 930 cm^{-1} (*trans* —CH=CH— o.o.p. H def.), 904 cm^{-1} (vinyl CH_2 wag) and 688 cm^{-1} (probable *cis* —CH=CH— o.o.p. H def.). 3Z,5E,11E-Trideca-1,3,5,11-tetraene-7,9-diyne (**5b**). MS *m/e*. 168M^+. UV$\lambda_{max}^{heptane}$ nm. 264.0 (61), 275.0 (51), 313.0 (70), 330.0 (100) and 354.5 (77). IR (CCl_4): 1623 and 1609 cm^{-1} (C=C stretch), 968 cm^{-1} (—CH=CH_2, o.o.p. H def of *trans* H's), 949 and 934 cm^{-1} (*trans* —CH=CH—, o.o.p. H def.), 910 cm^{-1} (vinyl wag) and 648 cm^{-1} (probable *cis* —CH=CH— o.o.p. H def.), 3E,5E,11E-Trideca-1,3,5,11-teraene-7,9-diyne (**5c**). MS *m/e*: 168M^+. UV$\lambda_{max}^{heptane}$ nm: 263.0 (57), 274.5 (49), 313.0 (69), 330.0 (100) and 354.0 (79). IR (CCl_4): 1623 and 1600 cm^{-1} (C=C stretch), 1002 cm^{-1} (—CH=CH_2, o.o.p. H def. of *trans* H's), 965 and 947 cm^{-1} (trans —CH=CH—, o.o.p. H def.) and 905 cm^{-1} (vinyl wag).

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1-(3′-FURYL)-6,7-DIHYDROXY-4,8-DIMETHYLNONAN-1-ONE, A STRESS METABOLITE FROM SWEET POTATOES (*IPOMOEA BATATAS*)

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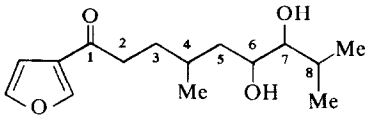
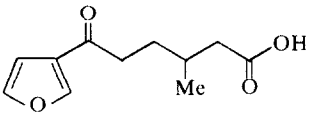
Key Word Index—*Impomoea batatas*; Convolvulaceae; sweet potatoes; sesquiterpene; stress metabolite.

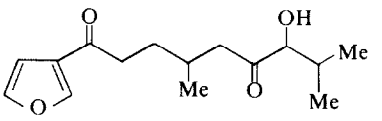
As part of our investigation of the stress metabolites of sweet potatoes we have isolated a new furanosesquiterpenoid from this source. The new compound (55 mg) was isolated from a MeOH–$CHCl_3$ extract of 2.1 kg of mercuric chloride treated sweet potato slices as an approximately 1:1 mixture with ipomeamaronol [1, 2] by Si gel chromatography (EtOAc–hexane, 1:2). Ipomeamaronol and compound **1** were separated by HPLC using a 60 cm C-18 μBondapak column (Waters Associates) eluted with MeOH–H_2O (1:1). The diol, $C_{15}H_{24}O_4$ (elemental analysis), crystallized from pentane–Et_2O, mp 70–71°, $[\alpha]_d^{26}$ + 17° (*c* = 1.57, MeOH). The presence of the keto-furan moiety was indicated by the UV, λ_{max}^{MeOH} 252 nm (ε = 2550), and the IR $\lambda_{max}^{CHCl_3}$ 1675 cm^{-1}. The broad absorption from 3700–3300 cm^{-1} in the IR verified the presence of hydroxyl groups. The PMR and MS of the compound were consistent with the proposed structure: PMR (100 M Hz, $CDCl_3$); δ 0.94 and 0.97 (9 H, superimposed *d*, *J* = 7 Hz, Me's), 2.20 (2 H, *br s*, OH), 2.82 (2 H, *t*, *J* = 7 Hz, C-2), 3.14 (1 H, *t*, *J* = 5 Hz, C-7), 3.75 (1 H, *m*, C-6), 6.84 (1 H, *m*, 4-furyl), 7.56 (1 H, *m*, 5-furyl), and 8.16 (1 H, *m*, 2-furyl). The other protons in the molecule were accounted for in a multiplet from 1.1 to 2.1 (6 H): MS (probe) 70 eV *m/e* (rel. int.); 268 [M^+] (4), 250 [$M^+ - H_2O$] (3), 232 [$M^+ - 2H_2O$] (2%), 225 [$M^+ - C_3H_7$] (3),



1



2



3

207 [$M^+ - C_3H_7 - H_2O$] (4), 196 [$M^+ - C_4H_8O$] (20), 195 [$M^+ - C_4H_9O$] (27), 177 [195 − H_2O] (22), 159 [cleavage at C-2, C-3] (6), 149 [cleavage at C-4, C-5] (22) 123 [cleavage of C-3, C-4] (59), 110 [McLafferty cleavage of C-2, C-3] (35), and 95 [cleavage of C-1, C-2] (100). Reaction of compound **1** with periodic acid followed by silver oxide oxidation gave the keto acid **2** (mp 46–47°, $[\alpha]_d^{25} = -12°$) which was identical to that obtained from periodic acid oxidation of 7-hydroxymyoporone, **3** [3].

To gain further information about the relative configuration of the hydroxyl groups in **1**, 100 mg of compound **3** was reduced with 1.9 eq of sodium *bis*(2-methoxyethoxy) aluminum hydride. The reduction gave a 4:1 mixture of ketodiols which were separated by HPLC using a 60 cm C-18 μBondapak column eluted with MeOH–H_2O (1:1). The major product, mp 94–95°, $[\alpha]_d^{25}$ + 26° was assigned the erythro configuration since reduction of α-ketols with hydride reagents has been shown to give predominantly the erythro isomer [4, 5]: PMR (100 MHz, $CDCl_3$) δ 0.89 and 1.02 (9 H, superimposed *d*, *J* = 7 Hz, Me's), 1.1–2.0 (6 H, *m*, C-3, C-4, C-5, C-8), 2.53 (2 H, *br s*, —OH), 2.82 (2 H, *t*, *J* = 7 Hz, C-2), 3.35 (1 H, *dd*, *J* = 4 and 8 Hz, C-7), 3.82 (1 H, *m*, C-6), 6.83 (1 H, *m*, 4-furyl), 7.50 (1 H, m, 5-furyl), and 8.13 (1 H, *m*, 2-furyl). The minor product, mp 45–47°, $[\alpha]_d^{25}$ −17°, was assigned the *threo* configuration: PMR (100 MHz, $CDCl_3$) δ 0.96 and 0.98 (9 H, superimposed *d*, *J* = 7 Hz, methyls), 1.1–2.1 (6 H, *m*, C-3, C-4, C-5, C-8), 2.84 (2 H, *t*, *J* = 7 Hz, C-2), 3.15 (1 H, *t*, *J* = 5 Hz, C-7), 3.84 (1 H, *m*, C-6), 6.82 (1 H, *m*, 4-furyl), 7.49 (1 H, *m*, 5-furyl), and 8.12 (1 H, *m*, 2-furyl). The IR and MS of both reduction products were indistinguishable from those of the natural product.

The PMR spectra of **1** most closely resembles the spectrum of the minor reduction product, especially the chemical shift and spin–spin coupling of the proton on C-7, and **1** is assigned the *threo* configuration at C-6 and C-7. We have shown that the keto-acid **2** from **3** is levorotatory [3], thus, the configuration at C-4 must be the same for all 3 keto-diols. The minor reduction product and **1** must have a mirror image relationship at C-6 and C-7. This relationship implies that **1** and **3** result from divergent biosynthetic pathways and that neither is the precursor of the other.

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