Sapindaceen-Ölen, die mit einem hohen Anteil an $C_{18:1}$-, $C_{20.0}$- und $C_{20:1}$-Fettsäuren [10] Cyanolipid-Typ II kumulieren [3].

EXPERIMENTELLER TEIL

Gewinnung von **2**. **1** wurde wie bei [1] beschrieben isoliert. 46 mg **1** wurden mit 1 ml rauchender HCl (37%) 30 min auf 120° erhitzt, der Ansatz nach dem Erkalten dreimal mit EtOEt ausgeschüttelt, die EtOEt-Phase getrocknet und zur Trockne eingeengt.

Derivatisierung mit (−) *Menthol*. **2** sowie 2-Hydroxy-isovaleriansäure (Serva, Heidelberg, bezw. nach [5, 6] dargestellt und charakterisiert) werden in Mengen von *ca* 10 mg in 1 ml Benzol mit 25 mg (−) Menthol versetzt und unter Hinzufügung einer Spur *p*-Toluolsulfonsäure 12 hr am Rückfluß gekocht. Der Ansatz wird direkt zur GLC verwendet.

Gewinnung der Samenlipide. 20 g gepulverte Samen (bezogen von Nindethana Seed Service, Wellington, N.S.W. Australien und nach [13] als *Heterodendron*-Samen sowie Mustern des Royal Bot. Gardens and National Herb., Sidney identifiziert) wurden 2 mal 4 hr mit Petrol extrahiert. Der Petrol wurde abgedampft und der Rückstand bis zur Konstanz getrocknet.

HPLC-Bedingungen. Säule: μ Bondapak C-18; Fließmittel: CH_3CN–MeOH (17:3) isokratisch; 2 ml/min, Detektor: Refraktometer.

GLC-Bedingungen. Säule: FFAP (WGA, Griesheim) 10% auf Chromosorb HP-AW-DMCS 80–100 mesh, Stahl, 5 m × 2 mm i.d.; Ofentemperatur: 200° (Fettsäuremethylester) isotherm, 155° ((−) Menthylester) isotherm. Die Methylierung der Fettsäuren erfolgte nach [14].

^{1}H-NMR-Spektren. Varian T-60-NMR, jeweils *ca* 30 mg in $CDCl_3$. Gesamtöl-Spektren sind in [11], das Cyanolipid-Spektrum in [10] ausführlich diskutiert.

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POLYACETYLENES FROM *CARTHAMUS TINCTORIUS*

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Key Word Index—*Carthamus tinctorius*; Compositae; safflower; polyacetylenes; spore germination stimulator.

Polyacetylenes are found in safflower roots [1], aerial parts [1, 2], flowers [3, 4], immature seed [5] and *Phytophthora*-infected stems [6, 7]. In 4-day-old seedlings, there are about 175 nmol per seedling of polyacetylenic hydrocarbons, mostly in the cotyledons [8].

While trying to identify compounds in germinating safflower that stimulate fungal spore germination, we found and identified the polyacetylenic hydrocarbons **1–5**. Of the compounds identified, four (**2a**, **4a**, **5a** and **5b**) were not previously reported to be in safflower and three of these (**4a**, **5a** and **5b**) are herein first described as natural products. Data from UV and mass spectra also indicate the presence of trace amounts of trideca-1,3,5-triene-7,9,11-triyne, previously found in immature seed [5]. We have shown that polyacetylenes **1–5** potently stimulate germination of teliospores of the safflower rust *Puccinia carthami* [9].

EXPERIMENTAL

Seed of a commercial cultivar of safflower, soaked for 2 hr in H_2O, was allowed to germinate for 4 days in the dark on open trays to which water was occasionally added. Seedlings were then blended with Me_2CO. Solvent was removed from the Me_2CO extract and the residue was partitioned between Et_2O and H_2O. Saponification of the Et_2O extract gave nonsaponifiables. A short Si gel column removed polar compounds. Nonpolar nonsaponifiables were chromatographed on a 5 × 85 cm Sephadex LH-20 column with MeOH as eluting solvent and then repeatedly on a 2 × 95 cm Si gel H (dried at 120°) column with heptane as eluting solvent. To avoid isomerism of double bonds, operations were conducted in dim light or in darkness and peak positions were determined by UV analysis of aliquots of collected fractions. **1–5** were recognised by their distinctive UV spectra [5]. Purity of the isomers isolated was checked by HPLC on a Vydak reverse phase column. Electron ionization MS (70 eV) were recorded

Table 1 PMR data for polyacetylenic hydrocarbons 2–5 from *Carthamus tinctorius**

Compound	C-13 methyl	H-12	H-11	H-6	H-5	H-4	H-3	H-2	H-1 *cis*	H-1 *trans*
2a†	1.87 *dd* (7.0, 1.8)	6.20 *dq* (10.8, 7.0)	5.44 *dq* (10.8, 1.8)							
2b†	1.83 *dd* (7.0, 1.8)	6.46 *dq* (16.0, 7.0)	5.54 *dq* (16.0, 1.8)							
3†	1.98 *s*					5.60 *d* (15.6)	6.78 *dd* (15.6, 10.6)	6.36 *ddd* (16.5, 10.6, 10.0)		
4a‡	1.96 *dd* (7.0, 1.7)	6.20 *dq* (10.6, 7.0)	5.54 *dq* (10.5, 1.5)			5.49 *d* (10.0)	6.52 *dd* (11.0, 10.0)	6.88 *ddd* (16.5, 11.0, 9.5)	5.34 *d* (9.5)	5.40 *d* (16.5)
4b†	1.86 *dd* (7.0, 1.7)	6.42 *dq* (16.0, 7.0)	5.56 *dd* (16.0, 1.7)			5.50 *d* (11.0)	6.57 *dd* (11.0, 10.0)	6.89 *ddd* (16.5, 10.0, 10.0)	5.38 *d* (10.0)	5.45 *d* (16.5)
4c‡	1.86 *dd* (7.0, 1.6)	6.43 *dq* (16.0, 7.0)	5.53 *dq* (16.0, 1.6)			5.63 *d* (15.5)	6.74 *dd* (15.5, 11.0)	6.36 *ddd* (16.0, 11.0, 9.5)	5.20 *d* (9.5)	5.35 *d* (16.0)
5a‡	1.87 *dd* (7.0, 1.7)	6.28 *dq* (15.8, 7.0)	5.57 *dq* (15.8, 1.7)	5.46 *d* (9.5)	7.28 *dd* (10.5, 9.5)	6.42§ *m* (13.5, 10.0)	6.42§ *m* (13.5, 10.0)	6.68§ *ddd* (16.0, 10.5, 10.0)	5.18 *d* (10.5)	5.26 *d* (16.0)
5b‡	1.86 *dd* (7.0, 1.7)	6.27 *dq* (15.5, 7.0)	5.56 *dq* (15.5, 1.7)	5.64 *d* (15.5)	7.15 *dd* (15.5, 10.0)	6.01 *dd* (10.5, 10.0)	6.01 *dd* (10.5, 10.0)	6.83 *ddd* (16.5, 10.0, 10.0)	5.22 *d* (10.0)	5.25 *d* (16.5)
5c‡	1.86 *dd* (7.0, 1.7)	6.26 *dq* (15.5, 7.0)	5.56 *dq* (15.5, 1.7)	5.63 *d* (15.0)	6.67 *dd* (15.0, 10.5)	6.0–6.5 *m*	6.0–6.5 *m*	6.0–6.5 *m*	5.17 *d* (9.8)	5.26 *d* (15.0)

* Spectra were determined at 100 MHz. Chemical shift values are expressed relative to TMS; coupling constants are shown in parentheses (Hz); *s* = singlet, *d* = doublet, *dd* = double doublet, *ddd* = double double doublet, *dq* = double quartet, *m* = multiplet. † In $CDCl_3$ ‡ In CCl_4. § Assignments are best guess.

$$Me(C{=}C)_5CH{=}CH_2$$

1

$$Me\,CH{=}CH(C{=}C)_4CH{=}CH_2$$

2a: 11Z
2b. 11E

$$Me(C{=}C)_4CH{=}CH{-}CH{=}CH_2$$

3. 3E

$$Me\,CH{=}CH(C{=}C)_3CH{=}CH{-}CH{=}CH_2$$

4a: 3Z, 11Z
4b. 3Z, 11E
4c. 3E, 11E

$$Me\,CH{=}CH(C{=}C)_2CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

5a: 3E, 5Z, 11E
5b. 3Z, 5E, 11E
5c. 3E, 5E, 11E

on a 21-110A (C.E.C.) or MM 70/70F (Vacuum Generators, Ltd.) mass spectrometer using a cooled direct introduction probe. PMR spectra were determined at 100 MHz on a Varian HR-100 equipped with a field-frequency internal lock in CCl_4 or $CDCl_3$ with TMS as int. stand. and decoupling was used to verify assignments (Table 1). UV spectra of heptane or isopentane solns were obtained for the 240–420 nm region. Because molar absorptivity values are uncertain, the relative intensities of UV peaks are reported. Assignment of *cis* (Z) or *trans* (E) configuration to the olefinic bonds in compounds **5a–c** required correlation of PMR and IR data. For each compound, the PMR spectrum indicated that the C-11 double bond was *trans*. There was a 15.5 Hz *trans* coupling constant [10a] for C-11 and C-12 protons and the chemical shift for the methyl protons was δ 1.86 rather than δ 1.96 observed for the *cis* bond in **4a**. This difference is attributable to long range anisotropic shielding by the acetylenic bond of the methyl protons for the *trans* compounds and deshielding for the *cis* compound [10b]. The configurations of the C-3 and C-5 double bonds could be deducted from inspection of the —C≡C— stretching band near 1600 cm^{-1} and of the out-of-plane vinyl hydrogen deformation bands at 900–1000 cm^{-1}. The bands in the 1590–1630 cm^{-1} region for **5b** and **5c** are weak whereas **5a** shows a much stronger band at 1590 cm^{-1}. This band intensity increase indicates that **5a** is more asymmetrical and thus the *cis* double bond must be nearer the center of the molecule, that is, at the C-5 position. The strong band at 1002 cm^{-1} for **5a** and **5c** is due to coupling between *trans* out-of-plane hydrogen deformations of C-3 and the vinyl group. There is no such coupling of vibrations when a *cis* configuration is conjugated with a vinyl. This must be the case for **5b** where the band has dropped in frequency to 968 cm^{-1}. Therefore, the C-3 double bond of **5a** and **5c** is *trans* and that of **5b** is *cis*. A band in the region 648–688 cm^{-1} for **5a** and **5b**, but not for **5c**, probably indicates out-of-plane hydrogen deformation on a *cis* double bond. This suggests an all-*trans* double bond configuration for **5c**. Assignments of configuration for C-3 and C-5 double bonds from PMR data, based on double irradiation experiments, are in accord. 1-Tridecene-3,5,7,9,11-

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),