séchage, R_f CCM de polyamide Macherey Nagel DC 11. C_6H_6–MeCOEt–MeOH 4:3:3: 0,27; DC-Alufolien Cellulose Merck, AcOH 60%: 0,45; Si gel 60F-254, C_6H_6–Diox–AcOH 90:25:4: 0,10. λ_{max} en nm, MeOH: 252 sh, 262 sh, 268, 300 sh, 350; +NaOAc: 273, 322, 373; +NaOAc + H_3BO_3: 256, 270 sh, 376; +$AlCl_3$: 272, 308 sh, 350 sh, 426; +$AlCl_3$ + HCl: 275, 303 sh, 363, 386; +NaOH: 266, 277 sh, 324 sh, 408, stable. SM: pics principaux en valeurs *m/e*: 316 (100%), 273 (5%), 164 (7%), 153 (17%), 138 (15%). RMN* *in* CD_3OD XL-100 TF, O-Me (*s*, 4,00); *H*-6 (*d*, 6,22; *J* 2,5 Hz); H-8 (*d*, 6,46 *J* 2,5 Hz); H-3 (*s*, 6,58); H-2′, H-6′ (*d* 7,123 et 7,127).

Synthèse. Chlorure de diacétoxy-3, 4 *méthoxy*-5 *benzoyle.* 2,7 g d'acide diacétoxy-3, 4 méthoxy-5 benzoïque, préparés à partir de l'acide gallique selon Scheline (8) et Bradley [9], additionnés de 5 cm^3 de chlorure de thionyle et portés à reflux pendant 2 h, conduisent à 2,5 g de chlorure de diacétoxy-3, 4 méthoxy-5 benzoyle. F = 106-108° Litt. F = 109° [9]).

Tri(diacétoxy-3′, 4′ *méthoxy*-5′ *benzoyloxy*)-2, 4, 6 *acétophénone.* A 500 mg (2,9 mmoles) de phloracétophénone dissous dans la pyridine anhydre sont ajoutés 2,5 g (8 mmoles) de chlorure de diacétoxy-3, 4 méthoxy-5 benzoyle fraîchement préparé, dissous dans la pyridine anhydre. Le mélange abandonné 48 h à température ambiante est ensuite versé sur de la glace additionnée d'HCl 6 N (pH du milieu voisin de 7). Le précipité formé est essoré, lavé à l'eau puis séché sous vide (P_2O_5). On obtient 1,55 g de produit sec que l'on soumet directement au traitement de transposition de Baker-Venkataraman.

Tétrahydroxy-3′, 4′, 5, 7 *méthoxy*-5′ *flavone* (sélagine). (a) La totalité du produit sec précédemment obtenu est dissoute dans environ 15 cm^3 de DMSO anhydre et additionnée d'environ 10 g de NaOH pulvérisée sous Et_2O anhydre. Le mélange laissé sous agitation, à température ambiante, pendant 15 mn est versé sur glace puis abandonné pendant 1 h, pour la saponification, avant d'être neutralisé par AcOH à froid. La solution verdâtre obtenue est extraite par AcOEt et l'extrait est lavé à l'eau puis mis à sec. (b) Le résidu sec est dissous dans environ 8 cm^3 d'AcOH auxquels on ajoute 1 cm^3 de H_2SO_4 36 N, puis porté au bain marie pendant 5 mn. Après refroidissement le milieu est neutralisé avec NaOH et on obtient, après lavage à l'eau et essorage, 200 mg de précipité En CCM, la tétrahydroxy-3′, 4′, 5, 7 méthoxy-5′ flavone, révélée en jaune après vaporisation de Na_2CO_3 10%, apparaît en quantité majeure avec des traces d'impuretés: cellulose A 1440 Schleicher et Schüll, AcOH 60%, R_f 0,45; gel de silice A 1500 Schleicher et Schüll, C_6H_6–Me_2CO (7:3), R_f 0,35. (c) La totalité du précipité ci-dessus obtenu, acétylé par $(MeCO)_2O$ (10 cm^3) en présence d'NaOAc (1,5 g), conduit à 155 mg de sélagine acétylée après deux cristallisations dans l'acétone (rendement 13%). F = 228–230°; analyse: $C_{24}H_{20}O_{11}$ cal. C 59,50%, H 4,16%; tr. C 59,68%, H 4,04%. (d) 50 mg de sélagine acétylée, additionnés de 3 cm^3 de MeOH, sont traités à température ambiante, pendant 15 mn, par 2 cm^3 de NaOH 2 N. Le précipité fin formé après neutralisation du milieu, essoré, lavé à l'eau, est cristallisé dans MeOH et donne 20 mg de sélagine (rendement 62%). Spectres UV-visible, RMN sont identiques à ceux de la sélagine naturelle. F = 320–325° (déc.).

* Déplacements chimiques en ppm (échelle δ) par rapport au TMS.

BIBLIOGRAPHIE

1. Voirin, B., Jay, M. et Hauteville, M. (1975) *Phytochemistry* **14,** 257.
2. Audier, H. (1966) *Bull. Soc. Chim. Fr.* 2892.
3. Jurd, L. (1962) in *The Chemistry of Flavonoid Compounds* (Geissman, T. A. ed.), p. 107, Pergamon Press, Oxford.
4. Markham, K. R. and Mabry, T. J. (1968) *Phytochemistry* **7,** 1197.
5. Hauteville, M., Chadenson, M. et Chopin, J. (1973) *Bull. Soc. Chim. Fr.* 1781.
6. Hauteville, M., Chadenson, M. et Chopin, J. (1973) *Bull. Soc. Chim. Fr.* 1784.
7. Hauteville, M., Chadenson, M. et Chopin, J. (1974) *C. R. Acad. Sci. Paris* **278,** 471.
8. Scheline, R. R. (1966) *Acta Chem. Scand.* **20,** 1182.
9. Bradley, W., Robinson, R. et Schwarzenbach, G. (1930) *J. Chem. Soc.* 793.
10. Lebreton, Ph., Jay, M., Voirin, B. et Bouchez, M. P. (1967) *Chim. Anal. Fr.* **49,** 375.

Phytochemistry, 1976, Vol. 15, pp. 841–842. Pergamon Press Printed in England.

BUTYLATE, PEBULATE, AND VERNOLATE INHIBITION OF PLANT FATTY ACID BIOSYNTHESIS

ROBERT E. WILKINSON and ALBERT E. SMITH
Department of Agronomy, Georgia Station, Experiment, GA 30212, USA

(*Received* 3 *November* 1975)

Key Word Index—*Spinacia oleracea*; Chenopodiaceae; spinach; fatty acids; inhibition; butylate; pebulate; vernolate.

Abstract—Incorporation of 2-^{14}C-acetate into fatty acids of isolated spinach chloroplast was inhibited by μM concentrations of *S*-ethyl diisobutylthiocarbamate (butylate), *S*-propyl dipropylthiocarbamate (vernolate), and *S*-propyl butylethylthiocarbamate.

Incorporation of 2-^{14}C-acetate and 2-^{14}C-malonate into the fatty acyl units associated with thio- and oxygen-esters was inhibited by the herbicide *S*-ethyl dipropylthiocarbamate (EPTC) [1]. The inhibition of fatty acid synthesis was postulated as the mode of action for EPTC [1]. Resolution of this response as an isolated effect of a single herbicide or as a general action by a whole group of herbicides was necessary.

Butylate, pebulate, and vernolate (80 μM) inhibited the incorporation of 2-^{14}C-acetate into the total fatty acids of isolated spinach chloroplasts (Table 1). Incorporation of 2-^{14}C-acetate into saturated fatty acids was inhibited by 0.8 μM pebulate. Incorporation of 2-^{14}C-acetate into monoenoic and dienoic fatty acids was inhibited at the 80 μM concentration level in all three compounds. Thus, the inhibition of fatty acid synthesis is not restricted to a single member of the thiocarbamate group.

Stokes and Stumpf demonstrated a nonenzymatic acy-

Table 1. Incorporation of acetate-2-^{14}C into the fatty acids of isolated spinach chloroplasts in thiocarbamate bathing solution

Compound Name	Conc.	Incorporation of Ac* into fatty acids: Saturated		Monoenoic		Dienoic		Total	
	(μM)	(CPM) (X10^2)	(%)	(CPM) (X10^2)	(%)	(CPM) (X10^2)	(%)	(CPM) (X10^2)	(%)
Butylate	0	49a*	(100)	47a	(100)	22a	(100)	118a	(100)
	0.8	30b	(62)	26b	(56)	21a	(97)	78b	(66)
	8	29b	(59)	24bc	(51)	18a	(84)	72b	(61)
	80	10c	(21)	5c	(12)	4b	(20)	20c	(17)
Pebulate	0	50a	(100)	47a	(100)	22a	(100)	118a	(100)
	0.8	46a	(92)	45a	(95)	32a	(146)	122a	(103)
	8	40a	(80	38a	(81)	21a	(96)	99a	(83)
	80	15b	(29)	8b	(16)	7a	(31)	29b	(24)
Vernolate	0	50a	(100)	47a	(100)	22a	(100)	118a	(100)
	0.8	44ab	(88)	49a	(104)	23a	(105)	115b	(98)
	8	37b	(76)	40a	(85)	26a	(121)	104c	(87)
	80	12c	(24)	7b	(16)	9b	(22)	24d	(20)

* Values in a column in a box followed by the same letter or letters are not significantly different at the 5% level. Each value is the average of ten determinations.

lation of dithiothreitol by acyl coenzyme A that was ether-soluble and destroyed by saponification [2]. The saponification prior to extraction and esterification conducted in these experiments precluded the measurement of such dithiothreitol artifacts. Although trienes compose the majority of spinach leaf fatty acids [3], demonstration of the formation of α-linolenic acid by subcellular spinach chloroplast fractions was reported in 1973 [4–6].

EXPERIMENTAL

Chloroplast extraction and experimental conditions were described previously [1]. 2-^{14}C-acetate (0.1 μCi) (6.11 mCi/mM) per treatment was applied. Lipids were saponified with 1 ml 40% NaOH at 85° for 1 hr. After acidification with 2 ml conc HCl, total fatty acids were extracted with petrol (bp 30 to 60°). Fatty acids were methylated in 14% BF_3-MeOH, separated into saturation subclasses by argentation TLC [7], and counted by liquid scintillation [1]. Each treatment was repeated ten times, and the data were analyzed by analysis of variance on a randomized block design.

REFERENCES

1. Wilkinson, R. E. and Smith, A. E. (1975) *Weed Sci.* **23,** 100.
2. Stokes, G. B. and Stumpf, P. K. (1974) *Arch. Biochem. Biophys.* **162,** 638.
3. Debuck, H. (1961). *Z. Naturforsch* **166,** 561.
4. Jacobson, B. S., Kannangara, C. G. and Stumpf, P. K. (1973) *Biochem. Biophy. Res. Commun.* **51,** 487.
5. Jacobson, B. S., Kannangara, C. G. and Stumpf, P. K. (1973) *Biochem. Biophy. Res. Commun.* **52,** 648.
6. Jacobson, B. S., Kannangara, C. G. and Stumpf, P. K. (1973) *Biochem. Biophy. Res. Commun.* **52,** 1190.
7. Mangold, H. K. (1969) *Thin-Layer Chromatography,* E. Stahl (ed.) 1041 pp. pp. 363–421. Springer-Verlag, New York.

Phytochemistry, 1976, Vol 15, pp 842–844 Pergamon Press. Printed in England.

THE ORIGIN OF CYANOLIPIDS IN *KOELREUTERIA PANICULATA*

D. S. SEIGLER* and C. S. BUTTERFIELD†
*Department of Botany, The University of Illinois, Urbana, IL 61801, U.S.A.;
†Department of Biochemistry and Biophysics, The University of California, Davis, CA 95616, U.S.A.

(*Received* 26 *October* 1975)

Key Word Index—*Koelreuteria paniculata*; Sapindaceae; cyanolipids; biosynthesis; origin from leucine.

Cyanolipids (**1** and **2**) were first discovered in *Koelreuteria paniculata* (Sapindaceae) by Mikolajczak [1,2] and coworkers in 1970. Unlike those of several other Sapindaceous seed oils, the compounds isolated from *Koelreuteria* do not possess the ability to liberate HCN upon hydrolysis. However, they are related to such compounds from *Ungnadia speciosa* (**3**) and *Cardiospermum halicacabum* [2] (**4**). The latter are derivatives of α-hydroxynitriles which possess the ability to liberate hydrogen cyanide under mild or enzymatic conditions. Compounds **1** and **2** appear to be structurally related to the cyanogenic compounds **3** and **4** respectively by an allylic rearrangement.

The aglycones of several cyanogenic glycosides have