REFERENCES

1. Bergmann, W. and Feeney, R. J. (1950) *J. Org. Chem.* **15**, 812.
2. Barton, D. H. R. (1946) *J. Chem. Soc.*, 1121.
3. Bhacca, N. S. and Williams, D. H. (1964) in *Applications of NMR Spectroscopy in Organic Chemistry*, p. 1924. Holden-Day, San Francisco.
4. Friedland, S. S. and Lane, G. H. (1959) *Analyt. Chem.* **31**, 169.
5. Nigam, S. K., Misra, G. and Mitra, C. R. (1971) *Phytochemistry* **10**, 1954.

Phytochemistry, 1978, Col. 17, pp. 2037–2038. © Pergamon Press Ltd Printed in England 0031-9422/78/1101-2037 $02.00/0

STRUCTURE OF THE CAROTENOID PHYSOXANTHIN*

CORNEL BODEA†, ARTHUR G. ANDREWES‡, GUNNER BORCH§ and SYNNØVE LIAAEN-JENSEN‡

†Department of Chemistry and Biochemistry, Institute of Agronomy, Cluj, Romania; ‡Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway and §Chemistry Department A, Technical University of Denmark, DK-2800 Lyngby, Denmark

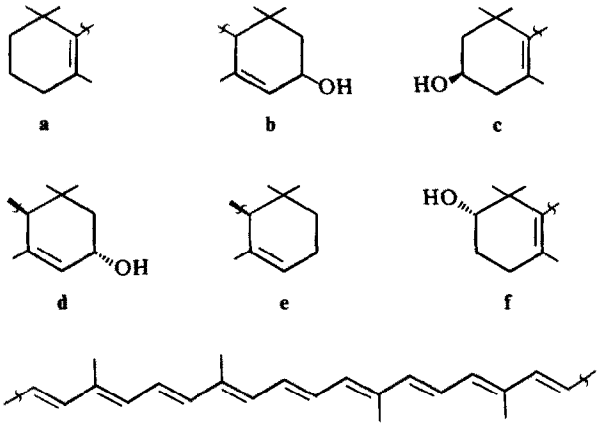
(*Received* 20 *April* 1978)

Key Word Index—*Physalis alkekengi*; Solanaceae: physoxanthin identity with 3*R*,6′*R*-β,ε-caroten-3-ol (α-cryptoxanthin).

Physoxanthin from *Physalis alkekengi* was assigned structure **1** by Bodea and Nicoara [1] on the basis of its electronic spectrum, polarity similar to cryptoxanthin (**2**) and ester formation. Location of the hydroxy function was based on the identification of a $KMnO_4$-oxidation product as an α-citraurin derivative on the basis of its electronic spectrum.

A small sample (0.1 mg) of physoxanthin was available for stereochemical studies. The absorption spectrum with λ_{max} (acetone) 423, 447 and 477, % III/II [2] 68 and λ_{max} (EPA = diethyl ether–isopentane–ethanol, 5:5:2) at 421, 445 and 478 nm, % III/II = 60, was consistent with the previously assigned β,ε-chromophore. MS confirmed the molecular weight: *m/e* 552, M − 92, M − 106. The CD spectrum (Fig. 1) gave a further clue to the structure of physoxanthin. It is now known that chiral centres at C-2 [3] or C-3 [4] in ε-rings do not contribute to the CD spectrum of carotenoids containing such end groups, e.g. decaprenoxanthin [3] and lutein (**3**) [4]. If physoxanthin were β,ε-caroten-3′(or 2′)-ol, its CD-spectrum should correspond to that of 6′*R*-β,ε-carotene (**4**) [5] or its enantiomer. On the other hand, provided physoxanthin were 3*R*,6′*R*-β,ε-caroten-3-ol (**5**) its CD spectrum should be very similar to that of lutein (**3**). Comparison of the CD spectra of physoxanthin, 6′*R*-β,ε-carotene (**4**) and lutein (**3**) in Fig. 1 reveals a clear agreement with the latter. This rules out C-3′ or C-2′ substitution of physoxanthin and is consistent with the formulation of physoxanthin as **5**. It should be noted that the CD contribution of end group **f** is equivalent to that of end group **c** [5], hence structure **6** cannot be ruled out. Compound **6** is the C-2 epimer of 2*R*,6′*R*-β,ε-caroten-2-ol present in the green alga *Trentepohlia iolithus* [5].

PMR data or kinetic acetylation studies on physoxanthin could clearly differentiate between structures **5** and **6**, and 4-substitution could be ruled by allylic oxidation. Attempts to reisolate physoxanthin in recent years have, however, failed because of poor growing conditions.



1 a—R—b
2 c—R—a
3 c—R—d
4 a—R—e
5 c—R—e
6 f—R—e
7 c—R—c

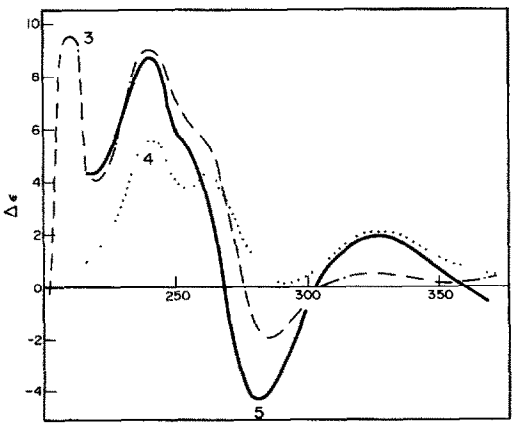


Fig. 1. CD spectra in EPA solution of physoxanthin (**5**), 6′*R*-β,ε-carotene (**4**) and lutein (**3**).

*Part 11 in the series "Carotenoids of Higher Plants". For Part 10 see (1976) *Helv. Chim. Acta* **59**, 1360.

¶Present address: Chemistry Department, Saginaw Valley State College, University Center, MI 48710, U.S.A.

The possibility of physoxanthin being a mono-*cis* isomer of β-cryptoxanthin (**2**) [6, 7] is inconsistent with its electronic spectrum and chiroptical properties. Mono-*cis*-**2** is predicted to show opposite Cotton effect of all-*trans*-**2** [4].

In conclusion, the CD data of physoxanthin evaluated in relation to accumulated knowledge on CD properties of carotenoids is taken to disprove a mono-*cis* form of **2** and 3′ (or 2′) hydroxylation of the ε-ring, and is compatible with physoxanthin being identical with α-cryptoxanthin (**5**) [8]. The occurrence in *Physalis alkekengi* of other carotenoids with end group **c**, namely cryptoxanthin (**2**), zeaxanthin (**7**) and lutein (**3**) supports the preference for a 3-hydroxy-β-ring in physoxanthin. Although the reported melting points for α-cryptoxanthin (**5**) [9] from *Capsicum annuum* and physoxanthin [10], differed, this is not uncommon, and failure to separate them chromatographically also favours the assignment of identical structures.

Acknowledgements—A grant from the Norwegian Research Council of Science and the Humanities to S.L.J. was used for the support of A.G.A.

REFERENCES

1. Bodea, C. and Nicoara, E. (1957) *Ann. Chem.* **609** 181.
2. Ke, B., Imsgard, F., Kjøsen, H. and Liaaen-Jensen, S. (1970) *Biochim. Biophys. Acta* **210**, 139.
3. Andrewes, A. G., Liaaen-Jensen, S. and Weeks, O. B. (1975) *Acta Chem. Scand.* **B29**, 884.
4. Hertzberg, S., Borch, G. and Liaaen-Jensen, S. *Acta Chem. Scand.* (in press).
5. Kjøsen, H., Arpin, N. and Liaaen-Jensen, S. (1972) *Acta Chem. Scand.* **26**, 3053.
6. Straub, O. (1976) *Key to Carotenoids*, p. 20. Birkhaüser, Basel.
7. Cholnoky, L. and Szabolcs, J. (1959) *Ann. Chem.* **626**, 207.
8. Bartlett, L., Klyne, W., Mose, W. P., Scopes, P. M., Galasko, G., Mallams, A. K., Weedon, B. C. L., Szabolcs, J. and Tóth, G. (1969) *J. Chem. Soc. C.*, 2527.
9. Cholnoky, L., Szabolcs, J. and Nagy, E. (1958) *Ann. Chem.* **616**, 207.
10. Bodea, C. and Nicoara, E. (1959) *Ann. Chem.* **622**, 188.

Phytochemistry, 1978, Vol. 1, pp. 2038–2039. © Pergamon Press Ltd. Printed in England. 0031-9422/78/1101-2038 $02.00/0

BENZOFURANOID NEOLIGNANS FROM *LICARIA ARMENIACA**

CACILDA J. AIBA†, OTTO R. GOTTLIEB†, JOSÉ G. S. MAIA‡, FRIDA M. PAGLIOSA† and MASSAYOSHI YOSHIDA†

†Instituto de Química, Universidade de São Paulo, c.p. 20780, São Paulo; ‡Instituto Nacional de Pesquisas da Amazônia, Conselho Nacional de Desenvolvimento Científico e Tecnológico, Manaus, Brazil

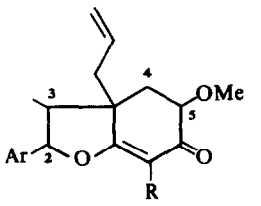
(*Received* 28 *March* 1978)

Key Word Index—*Licaria armeniaca*; Lauraceae: hexahydro-6-oxobenzofuran neolignans: structural determination.

Abstract—The trunkwood of *Licaria armeniaca* (Nees) Kosterm. (Lauraceae) contains sitosterol, 6,7-dimethoxycoumarin and two novel benzofuranoid neolignans: (2*S*, 3*S*, 3a*R*, 5*R*)-3a-allyl-5-methoxy- and 5,7-dimethoxy-2-(3′, 4′-methylenedioxyphenyl)-3-methyl-2,3,3a,4,5,6-hexahydro-6-oxobenzofurans.

Wood of the Amazonian Lauraceae species *Licaria armeniaca* (Nees) Kosterm. contains, besides sitosterol and 6,7-dimethoxycoumarin, two novel compounds, $C_{18}H_{17}O_2 \cdot OMe$ (**1a**) and $C_{18}H_{16}O_2 \cdot O_2CH_2(OMe)_2$ (**1b**). Spectral data indicate both to belong to the small group of hexahydro-6-oxobenzofuran neolignans, represented so far only by canellin-B (**1c**) [1] and porosin (**1d**) [2].

Concerning the aliphatic C_6C_3-moiety, **1d** is a useful model for **1a**, both showing the H-7 PMR singlet at



	Ar	Me	Al	OMe	R
1a	α-Pi	β	α	β	H
1b	α-Pi	B	α	β	OMe
1c	α-Pi	β	β	α	OMe
1d	α-Ve	α	β	α	H
1e	β-Pi	β	α	β	H

Ar = aryl, Me = methyl, Al = allyl, Pi = piperonyl, Ve = veratryl.

* Part 52 in the series "The Chemistry of Brazilian Lauraceae". For Part 51 see ref. [1]. Based on part of the Doctorate thesis submitted by F. M. P. to Universidade de São Paulo (1978). Sponsored by Fundação de Amparoã Pesquisa do Estado de São Paulo.