Short Communications

Alkali Isomerization of Methyl 9,12,15-Octadecatrienoate Geometrical Isomers

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ABSTRACT

Geometrical isomers of methyl 9,12,15-octadecatrienoate were subjected to alkali isomerization according to the official AOCS method. The *c,t,t* and *t,t,c* isomers gave higher specific extinction coefficients at 268 mμ than the all-*cis* isomer. The all-*trans* isomer was not completely conjugated. These results are in conformity with previous predictions based on theoretical and experimental evidence.

INTRODUCTION

Polyunsaturated fatty acids containing methylene-interrupted double bonds conjugate under the influence of strong alkali. This reaction forms the basis for estimation of linoleic, linolenic and other polyunsaturated acids which are conjugated under specified conditions, followed by measurement of absorption of conjugation in the ultraviolet (UV) region (1). The geometrical isomers of linoleate conjugate at different rates (2). For example, the *cis,cis* isomer is completely conjugated in 25-30 min at 180 C with KOH-ethylene glycol, whereas 150 and 360 min, respectively, are required for the *c,t* and *t,t* isomers. The official method (180 C; 25 min and KOH-ethylene glycol) will conjugate only a part of the geometrical isomers in the time allowed for the reaction. Linolenate and its geometrical isomers give rise to two different conjugated species, a conjugated triene and a conjugated diene with the third double bond separated by two methylene groups, and the ratio of these two isomers depends on the geometry of the double bonds involved (3). The geometrical configuration of the conjugated products depends on the geometry of the shifting double bond. When the bond involved in the shift is *cis*, the new bond formed assumes predominantly *trans* configuration, whereas a *trans* bond shifts to either a *trans* or a *cis* configuration (3). The different isomers of linolenate will thus give rise to conjugated dienes and conjugated trienes of differing geometrical configuration. This communication reports on the alkali conjugation of methyl linolenate and its geometrical isomers.

EXPERIMENTAL

The synthesis of all the available geometrical isomers of methyl 9,12,15-octadecatrienoate was reported previously (4). The samples were stored in isooctane solution at −40 C until used. Ten mg (±0.01) of each sample were isomerized according to the official AOCS method (1), and UV spectra were obtained on a Cary 219 spectrophotometer. The maxima at 268 and 233 mμ were due, respectively, to conjugated triene and conjugated diene.

RESULTS AND DISCUSSION

From experimental and theoretical considerations (3,5), it has been shown that a *cis* bond shifts much faster than a *trans* bond during alkali isomerization of polyunsaturated fatty acids. Based on this assumption, *t,c,t* isomer of linolenic acid should produce the most conjugated diene because the preferential shifting of the middle double bond in either direction results in the creation of an ethylene-interrupted *trans* bond which resists further conjugation. The results in Table I are in agreement with this assumption. On the other hand, *c,t,t* and *t,t,c* isomers are expected to form the most conjugated triene, since the preferential shifting of the end *cis* double bond towards the center results in conjugated diene that further isomerizes to conjugated triene. The results are in line with this prediction. Unfortunately, the *c,t,c* isomer was not available for this study; it can be expected to form also a high amount of conjugated triene. The all-*trans* isomer gave lower K values than the all-*cis* isomer for both conjugated triene and conjugated diene, indicating incomplete conjugation.

From the data in Table I, it is obvious that the official AOCS method would give erroneous results if geometrical isomers of linolenic acid are present in the sample.

TABLE I

Specific Extinction Coefficients (K Values) for Methyl 9,12,15-Octadecatrienoate and Its Geometrical Isomers after Alkali Isomerization[a]

Isomer (9,12,15)	Specific extinction coefficients[b]	
	268 mμ	233 mμ
c,c,c	48.3 (95.6)[c]	58.7
c,c,t	51.4 (101.8)	65.2
t,c,c	58.2 (115.2)	60.4
c,t,t	67.0 (132.7)	54.3
t,t,c	73.4 (145.3)	57.5
t,c,t	46.7 (92.5)	72.0
t,t,t	44.8 (88.7)	47.7

[a]Isomerized for 25 min at 180 C under nitrogen with 6.6% KOH in ethylene glycol reagent.

[b]Calculated on fatty acid basis.

[c]Values in parentheses are percent linolenic acid calculated according to the official AOCS method.

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