

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Dimers of Aleuritic Acid Derivatives

Mahendra Kumar Mishra^a

^a Chemistry Division Indian Lac Research Institute Nakum, Ranchi, India

To cite this Article Mishra, Mahendra Kumar(1983) 'Dimers of Aleuritic Acid Derivatives', Journal of Macromolecular Science, Part A, 20: 5, 619 — 625

To link to this Article: DOI: 10.1080/00222338308061796

URL: <http://dx.doi.org/10.1080/00222338308061796>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Dimers of Aleuritic Acid Derivatives

MAHENDRA KUMAR MISHRA

Chemistry Division
Indian Lac Research Institute
Namkum, Ranchi 834010, India

ABSTRACT

The unsaturated esters of aleuritic acid have been prepared by the condensation method and their oligomerization has been effected by free-radical initiation. The results show that the dimers of unsaturated esters of aleuritic acid were obtained.

INTRODUCTION

Aleuritic acid (9,10,16-trihydroxy palmitic acid) is the most important constituent of shellac. It is used as a basic material in the synthesis of civetone, ambrettolide, and other perfumary compounds [1-6]. Recently, the oligomerization of vinyl monomers has attracted increasing interest since they are effective tools in organic synthesis and for obtaining insight into the mechanism and the stereochemistry of polymerization [7-15]. Thus an attempt was made to obtain oligomers from unsaturated esters of aleuritic acid which may find use as intermediates, as well as to obtain insight into stereochemistry in perfumary synthesis.

EXPERIMENTAL

Materials

Aleuritic acid (crude) was recrystallized from an alcohol-water mixture [16], mp 101°C. Thiophene-free benzene was prepared by a method available in the literature [17]. Benzoyl peroxide was recrystallized by a chloroform-methanol mixture [18]. Concentrated hydrochloric acid, allyl alcohol, crotonic acid, and cinnamic acid were of analytical reagent grade.

TechniquePreparation of Allyl Aleuritite

Aleuritic acid (10 g) was refluxed with allyl alcohol (25 mL) in the presence of conc HCl (1%) under anhydrous conditions for 1 h at 84°C. The excess of alcohol and HCl was distilled off. The residue was washed with distilled water and extracted with ether and dried with anhydrous sodium sulfate. Ether was evaporated and the product was then freed of moisture under vacuum.

Preparation of Aleurityl Crotonate and Aleurityl Cinnamate

Aleuritic acid (1 mol) was refluxed separately with crotonic acid (1 mol) and cinnamic acid (1 mol) in the presence of conc HCl (1%) for 1 h at 84°C in benzene (100 mL) under anhydrous conditions. The benzene together with the catalyst (HCl) was then distilled off. The residue was washed with distilled water (to free the catalyst), extracted with ether, and dried with anhydrous sodium sulfate. Ether was evaporated and the product was freed of moisture under vacuum.

The yield of monomers was calculated on the basis of the weight of aleuritic acid (Table 1).

Oligomerization Procedure

Allyl aleuritite, aleurityl crotonate, and aleurityl cinnamate (2.5 and 5.7% each) [19], in thiophene-free benzene (100 mL) were separately oligomerized with benzoyl peroxide (1%) for 6 h at $80 \pm 1^\circ\text{C}$ under an inert atmosphere of nitrogen gas. It is difficult to separate the oligomer because both the oligomer and monomer were soluble in organic solvents. The method of fractional crystallization was, however, adopted to this end. The oligomerized product was present in the first fraction.

The monomers and oligomerized products were subjected to physicochemical analysis. The results are recorded in Tables 1 and 2.

The molecular weight of the oligomer was determined by vapor phase-osmometer.

The infrared spectra were run on a Perkin-Elmer model 700 spectrometer.

TABLE I. Characteristics of the Monomers (unsaturated esters)

Monomers	mp (°C)	Yield (%)	Iodine value		Acid value		Hydroxyl value	
			Theoretical	Practical	Theoretical	Practical	Theoretical	Practical
Allyl aleuritrate	53	58	73.78	70.05	Nil	Nil	489.2	462.0
Aleurityl crotonate	52	45	58.5	52.00	151.0	149.3	303.3	293.0
Aleurityl cinnamate	160	39	68.45	60.3	127.0	120.0	258.5	234.7

TABLE 2. Characteristics of the Dimers

Dimer	Yield (%)	Molecular weight	Iodine value		Acid value		Hydroxyl value	
			Theoretical	Practical	Theoretical	Practical	Theoretical	Practical
Di(allyl aleuritane)	2.0	569	Nil	Nil	Nil	Nil	489.2	462.0
Di(aleurithyl crotonate)	3.4	400	Nil	Nil	151	145.6	303.3	299.6
Di(aleurithyl cinnamate)	3.0	546	Nil	Nil	127	117.6	258.5	243.6

RESULTS AND DISCUSSION

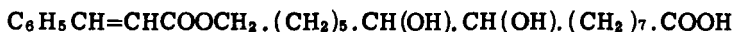
In the present study allyl aleuritite (I), aleurityl crotonate (II), and aleurityl cinnamate (III), i.e., unsaturated esters (monomers), were prepared by reaction of aleuritic acid with allyl alcohol, crotonic acid, and cinnamic acid, respectively. The prepared unsaturated esters (I-III) were white-brown, solid materials, soluble in benzene and dioxane. Only monoesters were obtained, indicating a 1:1 molar combination. This view is supported by iodine, acid, and hydroxyl values. Table 3 shows the important bands in their IR spectra which confirm the assigned structures.



(I)



(II)



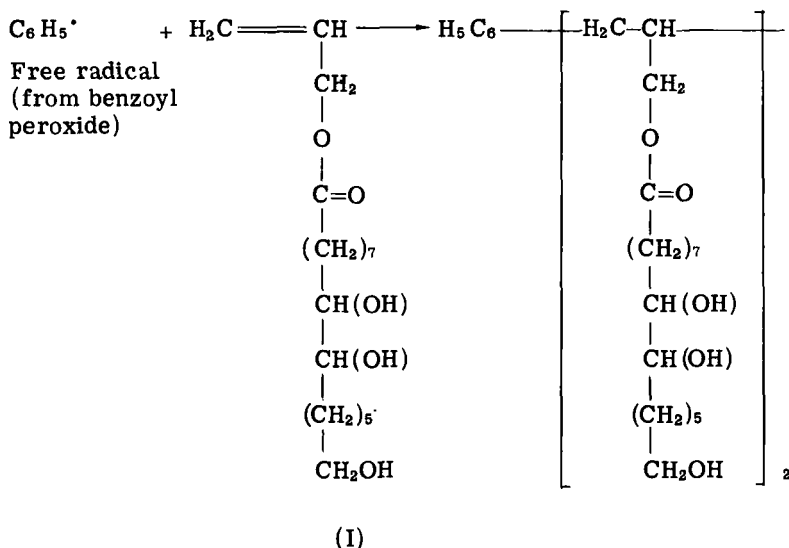
(III)

Further, the free-radical initiated (benzoyl peroxide initiated) addition polymerization of allyl aleuritite, aleurityl crotonate, and aleurityl cinnamate resulted in the formation of only a low molecular weight oligomer as obtainable in the case of allyl monomers [20, 21]. This was

TABLE 3. IR Spectral Data of Monomers (esters) and Dimers

Component	IR $\nu(\text{cm}^{-1})$		
	-C=C-	-C=O	-CH ₂ stretching
Allyl aleuritite	1680	1700	2935
Aleurityl crotonate	1680	1720	2940
Aleurityl cinnamate	1680	1700	2941
Di(allyl aleuritite)	Absent	1700	2975
Di(aleurityl crotonate)	Absent	1724	2941
Di(aleurityl cinnamate)	Absent	1761	2950

because of the extensive occurrence of chain transfer reactions [20], which terminate the growing polymer chain without terminating the kinetic chain [20, 21]. The dimers were white-brown, solid materials, soluble in dioxane at 74°C. The reaction mechanism of the oligomerization of allyl aleuritrate (similar for other monomers) is



The iodine, acid, and hydroxyl values of the oligomers (Table 2) show that a dimer is formed. This view is supported by IR spectral analysis (Table 3) and the molecular weight.

Further work to increase the yield and to obtain insight into the oligomerization of unsaturated esters of the aleuritic acid is in progress.

ACKNOWLEDGMENT

The author is grateful to Dr T. P. S. Teotia, director of this institute, for his kind interest in this work.

REFERENCES

- [1] P. C. Mitter and B. K. Bhattacharya, *J. Indian Chem. Soc.*, **19**, 69 (1942).
- [2] H. Hunsdiecker, *Naturwissenschaften*, **30**, 587 (1942).
- [3] H. H. Mathur and S. C. Bhattacharya, *J. Chem. Soc.*, **1**, 114 (1963).

- [4] H. H. Mathur and S. C. Bhattacharya, J. Chem. Soc., 2, 2477 (1963).
- [5] H. H. Mathur and S. C. Bhattacharya, J. Chem. Soc., 3, 3505 (1963).
- [6] R. N. Majee, J. N. Chatterjea, S. C. Sengupta, and S. N. Mukherjee, Chem. Ind. In Press.
- [7] T. Higashimura and M. Hiza, J. Polym. Sci., Polym. Chem. Ed., 19, 1957 (1981).
- [8] T. E. Hogen-Esch and C. F. Tien, Ibid., 17, 281 (1979).
- [9] S. Fujishige, Makromol. Chem., 179, 2251 (1978).
- [10] M. Aldissi and F. Schue, Ibid., 181, 1413 (1980).
- [11] Y. Yamamoto, M. Miko, and K. Hayashi, Makromoleculen, 14, 208 (1981).
- [12] T. Suzuki, Y. Tsuji, Y. Watanabe, and Y. Takegame, Polym. J., 11, 937 (1979).
- [13] M. Takahashi, T. Satoh, and T. Toya, Polym. Bull., 2, 215 (1980).
- [14] L. Lochmann and J. Trekoval, Makromol. Chem., 182, 1951 (1981).
- [15] M. Stichler, Ibid., 181, 131 (1980).
- [16] C. D. Harries and W. Nagel, Ber., 55B, 3833 (1923).
- [17] N. G. Gaylord and F. R. Eirich, J. Am. Chem. Soc., 74, 334 (1952).
- [18] M. Litt and F. R. Eirich, J. Polym. Sci., 45, 379 (1960).
- [19] L. Gindin, S. Medvedev, and E. Fleshler, Zh. Obschch. Khim., (J. Gen. Chem.), 19, 1694 (1949).
- [20] C. Walling, Free Radicals in Solution, Wiley, New York, 1957, p. 175.
- [21] P. B. Bartlett and A. Aitshul, J. Am. Chem. Soc., 67, 812, 816 (1945).

Accepted by editor January 24, 1983

Received for publication February 27, 1983