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Fatty Acid Esters from Betulinol

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ABSTRACT

Betulinol esters were prepared from stearic-, lauric-, palmitic-, oleic- and tall oil fatty acids via the acid-chloride and direct condensation routes. The degree of esterification was determined by high pressure liquid chromatography (HPLC), infrared (IR) and acid value measurements. The use of esters for air-dried, polyurethane and plastisol coatings was evaluated.

INTRODUCTION

The abundance and renewable source of the chemicals obtainable from tree bark are of increasing interest to both researchers and the chemical industry. The principal extractive component of birch bark is betulinol or betulin, which gives birch bark its white color. Betulinol is produced as a by-product in the new soap refining CSR-process (1).

Chemically, betulinol is a triterpene alcohol possessing two reactive hydroxyl groups that may be combined with fatty acids to produce esters. The work of Aslam et al. (2) indicates that betulinol can be esterified with linseed fatty acids to yield protective coating vehicles.

The object of this work was to extend knowledge on the preparation and characteristics of fatty acid esters from betulinol. Fatty acid esters were prepared from straight-chain fatty acids and betulinol via acid-chloride reaction route. Additional esters were made from some fatty acids and tall oil fatty acids using the direct condensation method. Potential use of the esters for coating applications was evaluated.

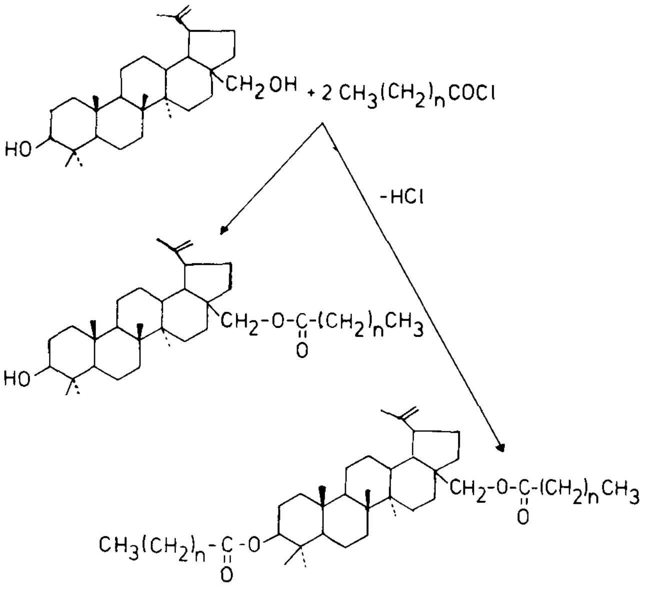
EXPERIMENTAL PROCEDURES

Betulinol was extracted from birch bark and purified by the method described elsewhere (3). The melting point of the purified betulinol was 258 C, which is in accordance with the literature values (4). The following fatty acids were used as esterifying reagents: stearic acid (mp 70 C), lauric acid (mp 44 C), palmitic acid (mp 63 C), oleic acid (mp 16 C) and a commercial fatty acid fraction of tall oil containing 95-97% fatty acids composed of 57% linoleic acids, 39% oleic acid and 4% saturated acids.

In the fatty acid chloride reaction route freshly distilled thionyl chloride (Merck p.a.) was used as a reagent. Dimethylacetamide and pyridine (Merck p.a.) were employed as solvents for betulinol.

Weighed amounts of fatty acid and excess thionyl chloride were reacted in a three necked flask equipped with a nitrogen inlet tube, a magnetic stirrer and a drying tube filled with $CaCl_2$. The mixture was heated at 80 C for 1.5 hr and unreacted thionyl chloride was removed by distillation. The amount of betulinol desired was placed in another flask and dissolved in pyridine or dimethylacetamide by bubbling nitrogen to the solution to avoid oxidation of betulinol. The formed fatty acid chlorides were added slowly to the betulinol solution. The mixture was heated at 70 C for 3 hr while bubbling nitrogen to the solution. After cooling, the reaction mixture was diluted with acetone and poured into water. The acidic water solution was extracted with ethyl ether or hexane. The separated solvent layer was

$$CH_3(CH_2)_nCOOH + SOCl_2 \longrightarrow CH_3(CH_2)_nCOCl + SO_2 + HCl$$



SCHEME I. Reaction scheme for the formation of the esters from betulinol and fatty acids via acid-chloride route.

dried with sodium bisulphate, filtered and evaporated in a rotavapor.

Fatty acid esters also were prepared from betulinol by direct condensation method in the temperature range of 180-260 C in a nitrogen atmosphere using the equipment described above. The crude esters were purified with SiO_2-activated carbon blend as described previously (5). The purified esters were used for the preparation of coatings.

The crude esters were characterized by high pressure liquid chromatography (HPLC), infrared (IR)-spectra and acid values.

RESULTS AND DISCUSSION

Properties of Esters

The reaction scheme for the formation of the esters from betulinol and fatty acids via acid-chloride route is illustrated in Scheme I. Mixtures of mono- and di-esters are expected to result because of the different reactivities of the primary and secondary hydroxyl groups in betulinol.

The products obtained in the esterification of betulinol via acid-chloride route are described in Table I. All reactions resulted in dark-colored oils whose acid values varied between 3.8 and 30.8.

The products obtained by direct condensation method are illustrated in Table II. As can be seen from Table II, an acid value of zero was obtained in sample DC4 prepared from tall oil fatty acids and excess betulinol. The acid value of 6.2 obtained in sample DC2 (Table II) points to a more complete esterification than that obtained by the acid-chloride route (sample AC4, Table I). The molecular weight of 978 obtained in sample DC2 indicates the diester formation on the basis of calculated value of 1002 obtained for the diester of betulinol and oleic acid.

Figure 1 shows a high pressure liquid chromatogram of betulinol-palmitic acid ester. In the chromatogram appear two peaks, which can be assumed to indicate the formation of mono- and diesters as illustrated in Scheme I owing to the different reactivities of the primary and secondary hydroxyl groups in betulinol.

Figure 2 shows IR-spectra of betulinol, betulinol-oleic acid ester and oleic acid. From IR-spectra it can be seen that the product had an intense band at 1730 cm^{-1}, which is characteristic for the ester group. The low acid values and

TABLE I

Preparation of Fatty Acid Esters from Betulinol by Acid-Chloride Route

Sample	Recipe	Acid value (mg KOH/g)	Remarks
AC1[a]	28.0 mM (8 g) stearic acid 62.0 mM (4.5 ml) SO Cl_2 14.0 mM (6.2 g) betulinol 434.0 mM (35 ml) pyridine	30.8	Dark-colored oil gradually changing to waxlike consistency
AC2	25.0 mM (5 g) lauric acid 69.0 mM (5 ml) SO Cl_2 6.8 mM (3 g) betulinol 430.0 mM (40 ml) dimethylacetamide	18.7	Brown oil
AC3	39.0 mM (10 g) palmitic acid 137.8 mM (10 ml) SO Cl_2 19.5 mM (8.6 g) betulinol 860.0 mM (80 ml) dimethylacetamide	3.8	Brown oil
AC4	51.3 mM (4.5 g) oleic acid 110.0 mM (8 ml) SO Cl_2 20.0 mM (8.8 g) betulinol 1075.0 mM (100 ml) dimethylacetamide	78.6	Dark brown oil

[a]AC refers to acid-chloride route.

TABLE II

Preparation of Fatty Acid Esters from Betulinol by Direct Condensation

Sample	Recipe	Conditions (temperature, °C)	Time (hr)	Acid value (mg KOH/g)	Remarks
DC1[a]	50.0 mM (10 g) lauric acid 13.6 mM (6 g) betulinol	220-260	8	37.0	Colorless, viscous oil
DC2	70.8 mM (20 g) oleic acid 35.0 mM (15.4 g) betulinol	240 260	3 2	6.2	Yellowish resin MW 978[b]
DC3	~176.0 mM (50 g) tall oil fatty acids 85.2 mM (37.5 g) betulinol	260	4	16.2	Red-brown resin
DC4	~ 22.0 mM (6.6 g) tall oil fatty acids 22.7 mM (10 g) betulinol	180 260	2 1	0	Red-brown resin

[a]DC refers to direct condensation.

[b]Determined by Vapour Pressure Oscometer calibrated by benzil.

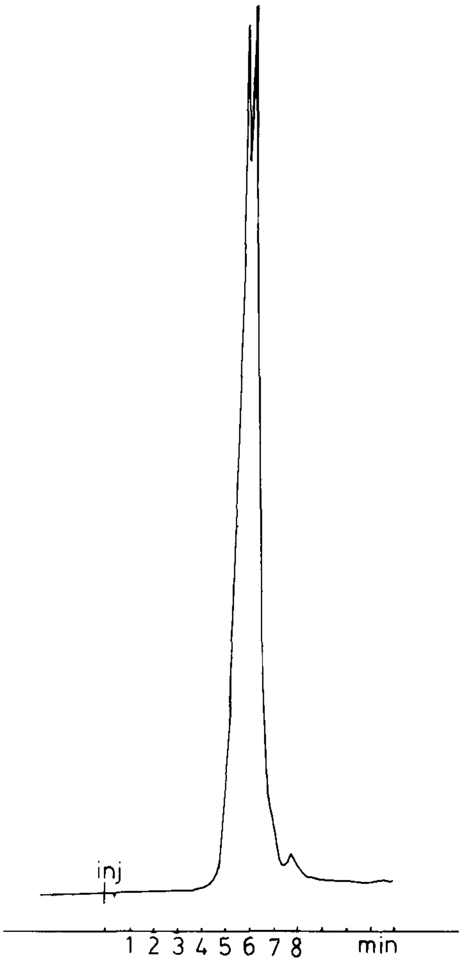


FIG. 1. HPLC of betulinol-palmitic acid ester. Column, 250 x 4.6 mm; packing, Partisil PXS 10/25 ODS (Whatman); flow rate, 1 ml/min and eluent, THF.

the disappearance of acid band at 1700 cm^{-1} in samples of AC2 and AC3 indicates the advanced degree of esterification, whereas in samples of AC1 and AC4 high acid values and the presence of acid and ester bands point to the incomplete esterification.

Preparation of Coatings

A 50% solution of purified ester (sample DC3, Table II) in hexane was prepared to which 2.0 wt% of drier solution in toluene was added (10% Co-naphthenate in toluene). Films were drawn from the solution on a glass plate. The data regarding the drying properties of the films are given in Table III. The films dried after treatments showed yellow appearance. The pencil hardness of the films was H. After 2 hr immersion in water the films became turbid except the one treated at 150 C. All films showed poor resistance to organic solvents.

As the ester product is a mixture of mono- and diesters, free OH-groups are available to react with isocyananates to form polyurethanes. Therefore, an attempt was made to prepare a coating using the following mixture: palmitic acid-betulinol ester (4.0 g), Desmodur N 75% (2.4 g) and ethyl acetate (20 ml). Desmodur N is a commercial aliphatic tri-isocyanate used for making light-resistant coatings. The blend was refluxed in a nitrogen atmosphere for 1 hr, and the solvent was evaporated. A yellow viscous resin was obtained. A film drawn from ethyl acetate on a glass plate and heated at 150 C for 0.5 hr was colorless and transparent, showing pencil hardness of 2 H and fair resistance to organic solvents. The disappearance of NCO peaks at 2280 cm^{-1} in the IR-spectra of film indicates complete reaction between OH and NCO groups of the ester and Desmodur N.

To consider the use of fatty acid derivatives as plasticizers in plastisol coatings, an attempt was made to prepare polyvinyl chloride (PVC) paste where half of the primary plasticizer was replaced by palmitic acid-betulinol as follows: E-grade PVC (7.0 g), dioctylphtalate (3.5 g), betulin palmitate (3.5 g) and DBTDL (dibutyltin-dilaurate) (0.07 g).

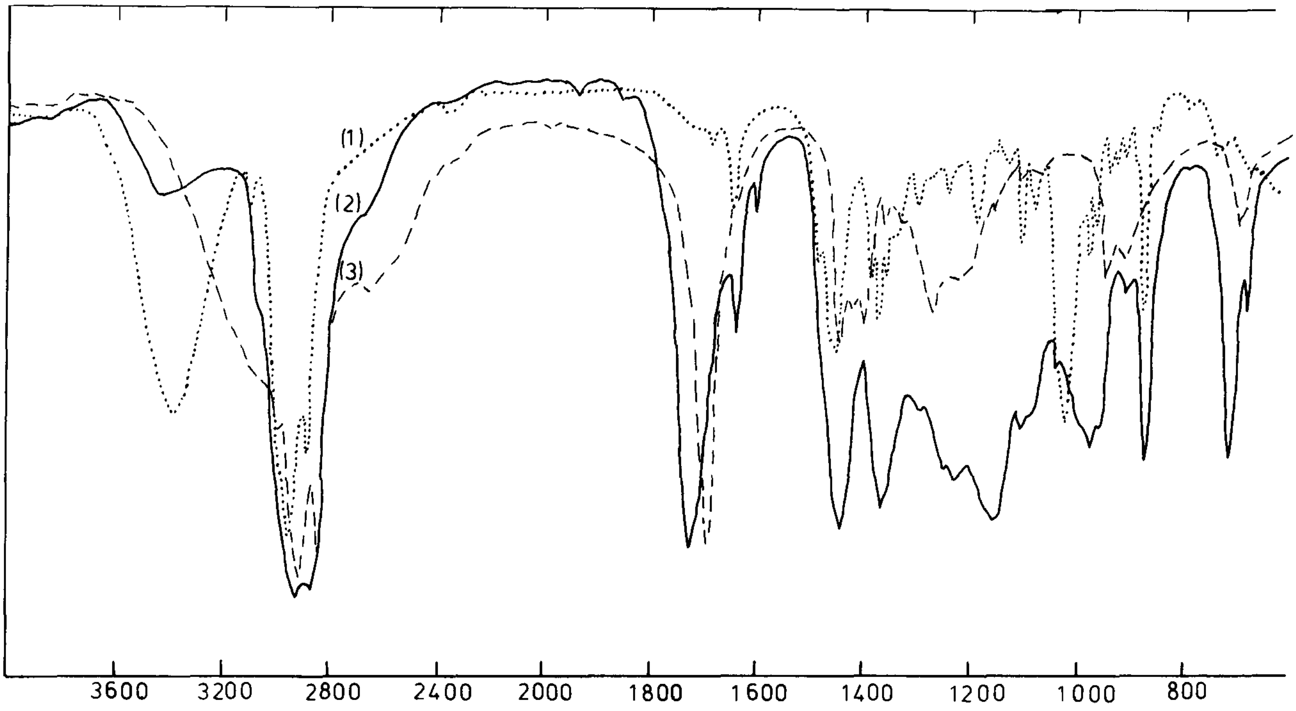


FIG. 2. IR-spectra of betulinol (··············), betulinol-oleic acid ester (————) and oleic acid (— — — —).

TABLE III

Drying Properties of Tall Oil Fatty Acid-Betulinol Esters

	Treatment			
	25 C	100 C	150 C	Ultraviolet light
Dry to touch	2 hr	1.5 hr	0.5 hr	1 hr
Tack free	2 days	1.5 hr	0.5 hr	1 hr
Hard dry	2 days	1.5 hr	1 hr	1 hr

It was observed that betulin palmitate was compatible in this mixture, giving a free-flowing paste. The paste was homogenized in a three-roll mill and a 2-mm plastisol layer was cast into the mold and gelled for 10 mins at 180 C. The resulting film was soft, transparent and brown. After one month's storage at room temperature no exudation of betulin palmitate from the film was observed.

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Correlation of Gas Liquid Chromatographic Volatiles with Flavor Intensity Scores of Stored Sunflower Oils

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ABSTRACT

Samples of sunflower salad oil from seed produced in the northern United States containing butylated hydroxyanisole, butylated hydroxytoluene, tert-butylhydroquinone and propyl gallate were stored in flintglass and amber bottles in the presence and absence of light for 16 wk. Using Dupuy's direct gas liquid chromatography method, correlations were made between pentane and flavor intensity scores and total volatiles and flavor intensity scores as well as flavor intensity values (FIV). Samples stored in clear bottles exposed to light had higher scores and pentane content than those stored in amber bottles or in the dark. Peroxide values were highest for samples stored in amber bottles. High correlation was found between flavor intensity scores and pentane and between pentane and FIV for rancid and painty flavor descriptors. Indications from the chemical and sensory data suggested that the addition of antioxidants had little effect on flavor scores when the oil was stored in the absence of light.

INTRODUCTION

Sunflower production in the United States has grown from somewhat less than a million acres in 1976 to over five million acres in 1979. With this expansion in production has come an increased and constant supply of oil for domestic use and the availability of sunflower salad oil on the grocer's shelves.

Initial oil quality, antioxidant efficacy and packaging affect flavor characteristics and ultimately consumer acceptance. One of the more recently developed methods for evaluating oil quality is the direct gas liquid chromatographic (GLC) measurement of volatiles (1,2). Several laboratories have used this approach, or variations thereof, as a quality control tool with a variety of products and have found high correlations with flavor scores (3-9).

In this study, a commercially prepared sunflower salad oil was evaluated by direct GLC, chemical analyses and by a sensory evaluation panel for the effects of antioxidants, packaging containers and light on oil quality. Correlations were established between volatiles and flavor intensity scores and flavor intensity values (FIV).

MATERIALS AND METHODS

Sample Preparation and Storage Treatment

The sunflower oil used was commercially prepared; contained no antioxidants; and had a fatty acid composition of 7.2% palmitic, 4.7% stearic, 14.0% oleic and 74.0% linoleic. Antioxidants were added to four 2.5-liter aliquots of oil at concentrations of 0.076% Tenox 6, 0.076% Tenox 26, 0.10% Tenox 20-A and a control containing no antioxidant. The Tenox series are mixtures of antioxidants (Eastman): Tenox 6 contains butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and propyl gallate; Tenox 26 contains BHA, BHT and tert-butylhydroquinone (TBHQ); Tenox 20-A contains only TBHQ. Flint clear glass and amber bottles (8 oz) washed with alcoholic KOH, dilute HCl and distilled water were filled with 180 ml of oil, their caps were tightened and the bottles were stored. For each antioxidant treatment, one set of four flint glass bottles was stored in the dark and a second set was stored on a rack exposed to light. In addition a third set of amber bottles were stored exposed to light. The light received was a combination of fluorescent and indirect sunlight with an intensity of 130 footcandles. Every 4 wk for 16 wk, samples stored in the dark and those stored in the light in clear and amber bottles for each treatment were frozen until chemical and sensory evaluations were conducted. Each oil sample was evaluated for Lovibond color, peroxide value (PV) (10), fatty acid composition (11) and direct GLC volatiles (12).

Gas Liquid Chromatography

Direct GLC volatiles were determined using a Tracor MT220 GLC equipped with a Hewlett Packard 3385-A integrator-recorder. A 6 ft. x 1/8 in. id stainless steel column packed with 7% Poly MPE on 60/80 mesh Tenax GC was used for the analysis. In preparing this column, chloroform, the solvent recommended by the manufacturer for Poly MPE, was found to polymerize the Tenax gas chromatography (GC) packing material. When ethylacetate