0.05% for forced draft oven method.

In the oil analysis of sunflower seed by the AOCS Official Method Ai 3-75 and NIR method, the sample must be ground. Using KF and vacuum oven methods to measure moisture contents, sunflower seed were found to lose moisture (0.6% moisture from a sample containing 8.9% moisture) when grinding the sample with Hyflo Super Cel as in the AOCS official method (Table III). The loss was statistically significant and varies depending on the variety of seed and temperature and relative humidity of the laboratory during grinding. Therefore, moisture data obtained by instruments in which the seed have to be ground such as NIR may not be very accurate. Since sunflower seed are high in oil content (ca. 40-45%) and the oil has a high content of polyunsaturated fatty acids, moisture content of ground seed also cannot be accurately determined by air oven methods because of oil deterioration.

Although oven-drying methods are not specific for water (5), data presented in Table III show that oven moisture values accurately represent the true moisture of sunflower seed. Although the KF method is relatively rapid compared to the vacuum oven-drying method, it is not recommended for routine moisture analysis because of the time required for sample preparation (2 hr). However, as proposed by Jones and Brickenkamp (5) for moisture analysis of grains, the Karl Fischer method, as presented in this paper, should be the primary reference method for the determination of moisture in sunflower seed.

## ACKNOWLEDGMENTS

Helpful suggestions and advice were provided by W. H. Morrison, III; technical assistance by Sandy Johnson.

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# *Fatty Acids: Part 25.[1]

# Chemical Transformations of $C_{18}$ Furanoid Fatty Esters

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## ABSTRACT

Synthetic and natural $C_{18}$ furanoid fatty esters were successfully converted to the corresponding furanoid alcohols, aldehydes, halides, ethers, acetates, mesylates, and chain extended by two carbon atoms in high yield to the corresponding $C_{20}$ furanoid ester homologues. Acid hydrolysis of the furanoid esters furnished dioxostearate derivatives, which were cyclized with ammonium carbonate or ammonia in titanium chloride and with phosphorus pentasulfide to pyrrole and thiophene ester derivatives, respectively.

## INTRODUCTION

In continuation of our studies of the properties of furanoid fatty acids and their derivatives, we now report the chemical transformations of the functional groups and the physical characteristics of such derivatives. Our ready source of a synthetic $C_{18}$ furanoid ester (methyl 9,12-epoxyoctadeca-9,11-dienoate, **I**) is obtained from methyl ricinoleate, giving access to the 2,5-disubstituted furan system (2). The latex of the rubber plant *(Hevea brasiliensis)* furnishes the 2,3,5-trisubstituted furanoid ester (methyl 10,13-epoxy-11-methyloctadeca-10,12-dienoate,**II**) for this study (3). The objective of this exercise was centered on the ability to effect chemical transformation of the carbomethoxy group of the furanoid esters while retaining the furan system intact, and secondly to substitute the oxygen of the furan nucleus with other elements such as nitrogen and sulfur to yield pyrrole and thiophene derivatives, respectively.

## DISCUSSION

The various chemical transformations involving the synthetic (2,5-disubstituted) and the natural (trisubstituted) $C_{18}$ furanoid esters are outlined in Scheme I.

Reduction of the ester group to the corresponding alcohol (**III**) by $LiAlH_4$ was very selective and readily accomplished in high yield, without indication of any reduction of the furanoid nucleus. The furanoid alcohol (**III**) was converted to the chloroderivative (**IV**) using thionyl chloride and to the bromoderivative (**V**) using phosphorus tribromide. The iododerivative (**VI**) was prepared by the action of sodium iodide in acetone on the furanoid chloride (**IV**). Treatment of the furanoid alcohol (**III**) with acetic anhydride gave the acetate derivative (**VII**), and reaction of the furanoid bromide (**V**) with sodium ethoxide gave the ethyl ether derivative (**VIII**) in good yield. Chain extension by two carbons using the bromo derivative (**V**) with sodio malonate resulted in the production of a $C_{20}$ furanoid ester homologue (**IX**) after decarbomethoxylation of the diester intermediate. The furanoid alcohol (**III**) was converted to the mesylate derivative (**X**) using methane sulfonyl chloride. Oxidation of the same furanoid alcohol (**III**) with chromic anhydride and pyridine complex resulted in the formation of the corresponding aldehyde derivative (**XI**). During all these transformations and reactions, the furan nucleus remained stable.

Similar reactions were conducted on the naturally occurring furanoid ester with similar success.

The acid-catalyzed ring-opening reaction of the furanoid

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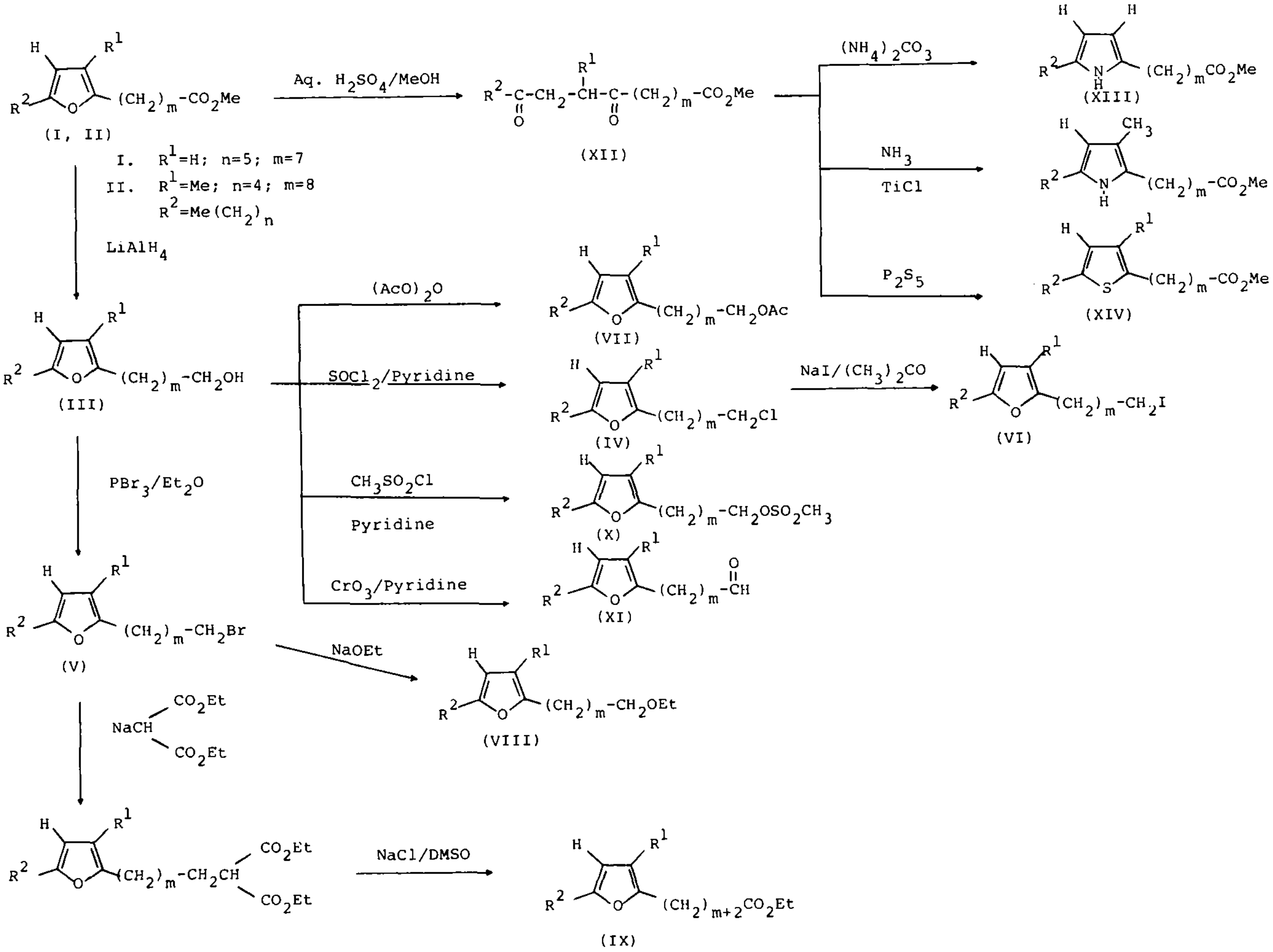
[1] For Part 24, see reference 1.



SCHEME 1. Transformation reactions of furanoid esters.

esters (**I** and **II**) was carried out with 10% aqueous sulfuric acid in methanol to yield the corresponding dimethylene interrupted dioxostearates (**XII**). Treatment of the latter with ammonium carbonate and phosphorus pentasulfide produced the corresponding pyrrole (**XIII**) and thiophene (**XIV**) derivative, respectively. However, in the case of pyrrole formation of the dioxo derivative obtained from the natural trisubstituted furanoid ester (**II**), ammonium carbonate was replaced by ammonia and titanium chloride. It appeared that the presence of a methyl group at C-11 of the chain contributed either a steric or a positive inductive effect, which caused a decrease in the reactivity of the methyl-dioxo derivative towards ammonium carbonate during pyrrole formation. In all of the above transformations of the furan system to other heterocycles, the ester function remained intact.

## RESULTS AND METHODS

Column and thin layer chromatography (TLC) were carried out by the standard procedures. Details of spectroscopic methods are described in Part 5 (4). Mass spectra were run at 70 eV and the data are presented in the order: m/z, source of fragment, intensity relative to base peak = 100.

In view of the fact that both furanoid esters (**I**, **II**) or their derivatives were subjected to similar reaction conditions, except in the transformation leading to the pyrrole derivatives, a general experimental procedure will be described for both substrates. Yields and physical properties of the derivatives are given in Tables I-VI. The purity of each product was checked by thin layer chromatographic analysis on silicic acid (alumina TLC in the case of pyrrole and thiophene derivatives) using mixtures of diethyl ether in petroleum ether.

### $C_{18}$ Furanoid Alcohol (III)

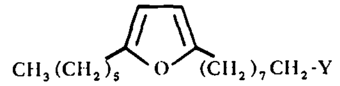
A solution of furanoid ester (**I** or **II**, 2 g) in dry diethyl ether (100 mL) was added in drops to a suspension of $LiAlH_4$ (2.2 g) in dry diethyl ether (200 mL) and the mixture refluxed for 3 hr. Moist diethyl ether (200 mL) was added followed by dilute $H_2SO_4$ (0.05 M, 20 mL). The ether extract was washed with water (50 mL), aqueous sodium bicarbonate (10%, 50 mL) and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent gave pure furanoid alcohol (**III**).

### $C_{18}$ Furanoid Chloride (IV)

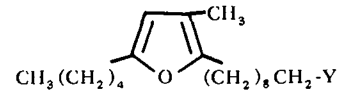
Freshly distilled thionyl chloride (3 mL) was added to a mixture of furanoid alcohol (**III**, 200 mg), dry pyridine (2 mL) and diethyl ether (60 mL). The reaction mixture was kept at 0-5 C for 3 hr. Ice water (50 mL) was added and the ether layer separated. Evaporation of the solvent furnished crude furanoid chloride which was percolated through a Silica Gel G (10 g) column using petroleum ether (60-80 C) as eluent. Evaporation of the solvent gave pure furanoid chloride (**IV**).

TABLE I

**Yields and Chromatographic Properties of Furanoid Derivatives**



| Substituent (Y) | Yield (%) | Chromatographic properties | |
|---|---|---|---|
| | | TLC ($R_f$) ($SiO_2$) | $GLC_{OV\text{-}101}$(ECL) |
| OH | 95 | 0.27[a] | 17.4 |
| Cl | 60 | 0.80[b] | 17.8 |
| Br | 47 | 0.80[b] | 18.4 |
| I | 95 | 0.80[b] | 19.0 |
| OAc | 97 | 0.63[a] | 18.4 |
| OEt | 90 | 0.58[a] | 17.6 |
| $CH_2CO_2Et$ | 37[d] | 0.90[c] | – |
| $CH_2CO_2Me$ | – | 0.90[c] | 20.1 |
| $OSO_2Me$ | 50 | 0.30[a] | – |
| Aldehyde (CHO) | 69 | 0.45[a] | – |

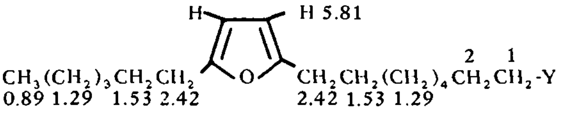


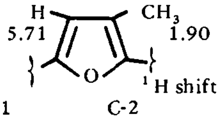
| Substituent (Y) | Yield (%) | TLC ($R_f$) ($SiO_2$) | $GLC_{OV\text{-}101}$(ECL) |
|---|---|---|---|
| OH | 90 | 0.27[a] | 18.0 |
| Cl | 65 | 0.80[b] | 18.5 |
| Br | 43 | 0.80[b] | 19.0 |
| I | 97 | 0.80[b] | 19.6 |
| OAc | 95 | 0.65[a] | 19.0 |
| OEt | 87 | 0.60[a] | 18.1 |
| $CH_2CO_2Et$ | 35[d] | 0.90[c] | – |
| $CH_2CO_2Me$ | – | 0.90[c] | 20.7 |
| $OSO_2Me$ | 55 | 0.30[a] | – |
| Aldehyde (CHO) | 68 | 0.45[a] | – |

[a] Developer: diethyl ether/petroleum ether (1:5, v/v).
[b] Developer: pure petroleum ether.
[c] Developer: diethyl ether/petroleum ether (1:10, v/v).
[d] Overall yield based on furanoid ester.

TABLE II

**$^1H$ NMR Chemical Shifts of Furanoid Derivatives (δ)**





| Substituent (Y) | $^1H$ shifts at position (δ) C-1 | C-2 | Y |
|---|---|---|---|
| OH | 3.61 | 1.50 | 1.80 |
| Cl | 3.59 | 1.60 | – |
| Br | 3.37 | 1.5-1.8 | – |
| I | 3.14 | 1.5-1.8 | – |
| $OCOCH_3$ | 4.04 | 1.30 | 2.60 |
| $OCH_2CH_3$ | 3.42 | 1.60 | 3.42(-C$\underline{H}_2$-) 1.27(-C$\underline{H}_3$) |
| $CH_2COOCH_3$ | 1.50 | 1.29 | 2.2(-C$\underline{H}_2$-) 3.69(-C$\underline{H}_3$) |
| $OSO_2CH_3$ | 4.21 | 1.60 | 2.98 |
| C-1=Aldehyde ($\overset{O}{\overset{\parallel}{C}}H$) | 9.75 | 2.55 | |

## $C_{18}$ Furanoid Bromide (V)

Phosphorus tribromide (12 mL) was added dropwise to a mixture of furanoid alcohol (**III**, 1 g), diethyl ether (60 mL) and pyridine (1 mL) at 20 C. The reaction mixture was left at room temperature for 18 hr. The ether layer was decanted and the precipitate extracted with a portion of diethyl ether (30 mL). The ether extracts were combined and washed with water (2 × 50 mL) and dried over $Na_2SO_4$. The crude furanoid bromide was percolated through a Silica Gel G (20 g) column using petroleum ether (60-80 C) as eluent. Evaporation of the solvent gave pure furanoid bromide (**V**).

## $C_{18}$ Furanoid Iodide (VI)

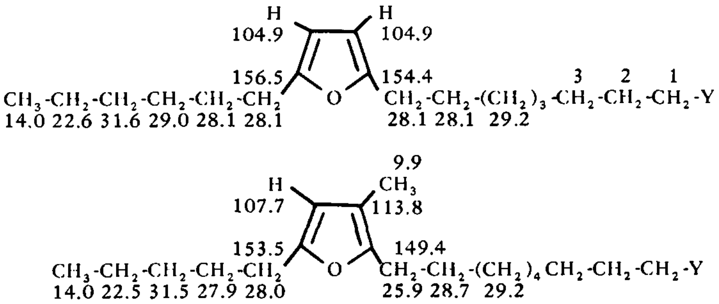
A mixture of furanoid chloride (**IV**, 100 mg), sodium iodide (170 mg) and dry acetone (40 mL) was refluxed for 16 hr. The reaction mixture was diluted with water (100 mL) and extracted with petroleum ether (60-80 C). The petroleum extract was dried over $Na_2SO_4$ and evaporation of the solvent gave pure furanoid iodide (**VI**).

## $C_{18}$ Furanoid Acetate (VII)

A mixture of furanoid alcohol (**III**, 100 mg), acetic anhy-

TABLE III

$^{13}C$ NMR Chemical Shifts of Furanoid Derivatives (ppm)



| Substituent (Y) | $^{13}C$ shifts at position C-1 | C-2 | C-3 | Y |
|---|---|---|---|---|
| -OH | 62.9 | 32.8 | 25.8 | – |
| -O-CO-$CH_3$ | 64.7 | 25.9 | 29.2 | 171.1 (CO) 20.9 ($CH_3$) |
| -Cl | 45.1 | 32.7 | 26.8 | – |
| -Br | 33.6 | 32.8 | 28.7 | – |
| -I | 16.7 | 33.6 | 30.5 | – |
| -O-$CH_2CH_3$ | 70.8 | 25.0 | 29.2 | 66.0 (-$CH_2$-) 15.3($CH_3$) |
| $\overset{\overset{O}{\|}}{C_1}$=-CH | 201.7 | 43.1 | 21.3 | – |

dride (6.5 mL) and pyridine (1.5 mL) was stirred at ambient temperature for 18 hr. The excess reagent was removed under high vacuum and the product percolated through a Silica Gel G (10 g) column using diethyl ether/hexane (1:9, v/v, 200 mL) as eluent. Evaporation of the eluate gave pure furanoid acetate (**VII**).

### $C_{18}$ Furanoid Ether (VIII)

A mixture of furanoid bromide (**V**, 100 mg) and sodium ethoxide (1 M, 50 mL) was refluxed for 10 hr. The reaction mixture was neutralized with dilute HCl (2 M) and extracted with $Et_2O$. Evaporation of the solvent gave pure furanoid ethyl ether (**VIII**).

### 2-Carbon Chain Extension of $C_{18}$ Furanoid Bromide (V)

A mixture of furanoid bromide (**V**, 150 mg), sodium iodide (150 mg) and sodio diethyl malonate (prepared from sodium (0.1 g), diethyl malonate (0.84 g) and anhydrous ethanol (8 mL)) was refluxed for 16 hr. Water (40 mL) was added and the product isolated in the usual way with diethyl ether. The recovered product was refluxed in dimethyl sulfoxide (4 mL), water (0.3 mL) and sodium chloride (0.35 g) for 18 hr. Water (20 mL) was added and the reaction mixture extracted with diethyl ether. Evaporation of the solvent furnished crude ethyl $C_{20}$ furanoid ester, which was percolated through a Silica Gel G (10 g) column using petroleum ether/diethyl ether (9:1, v/v, 150 mL) as eluent. The ethyl ester was saponified and the free acid esterified using boron trifluoride methanol complex to give pure methyl $C_{20}$ furanoid ester (**IX**).

### $C_{18}$ Furanoid Mesylate (X)

Furanoid alcohol (**III**, 50 mg) was dissolved in dry pyridine (2 mL) and stirred for 3 hr with methane sulfonyl chloride (0.5 mL) at room temperature under nitrogen. The reaction mixture was acidified with dil HCl (2 M) and the product was extracted with diethyl ether. The ether extract was washed with water, aqueous sodium bicarbonate (10%) and dried over anhydrous $Na_2SO_4$. The crude mesylate was further purified by Silica Gel G (20 g) column chromatography using benzene/diethyl ether (9:1, v/v) as eluent.

### $C_{18}$ Furanoid Aldehyde (XI)

To a stirred solution of pyridine (2.4 mL) in methylene chloride (37.5 mL) was added chromic anhydride (1.5 g) in small portions at 20 C. When the mixture turned to a dark red solution, furanoid alcohol (**III**, 0.7 g) in methylene chloride (5 mL) was added in small portions. After 1 hr, the excess methylene chloride was removed under reduced pressure and the residue was extracted with diethyl ether (3 x 20 mL). The ether layer was washed with aqueous NaOH (10%), HCl (10%) and finally with saturated sodium bicarbonate solution. The ether extract was dried over $Na_2SO_4$. The crude aldehyde was percolated through Silica Gel G (20 g) column using petroleum ether/diethyl ether (96:4, v/v). Evaporation of the solvent gave pure furanoid aldehyhyde (**XI**).

### Preparation of $C_{18}$ Pyrrole Ester Derivatives (XIII)

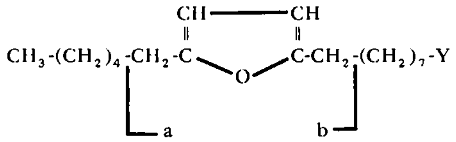
Acid hydrolysis of the methyl furanoid esters to give the corresponding dioxo derivatives (**XII**) was described earlier (5).

In the case of the nonmethyl-substituted dioxostearate (where $R^1$ = H), the latter (100 mg) was heated with ammonium carbonate (450 mg) at 100 C for 3 hr. The product (**XIII**) was isolated with diethyl ether and purified by preparative alumina TLC (using 15% diethyl ether in petroleum ether as developer).

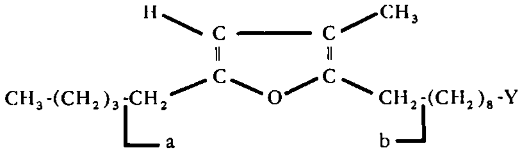
For methyl-substituted dioxostearate (where $R^1$ = Me),

**TABLE IV**

**Mass Spectral Fragmentation of Furanoid Derivatives**



| Substituent (Y) | Ion fragment | | | Others |
|---|---|---|---|---|
| | $M^+$ | a | b | |
| OH | 280(25) | 209(31) | 165(100) | 281(M+1, 5)<br>166(b+1, 15) |
| Cl | 300(11)<br>298(28) | 229(21)<br>227(50) | 165(100) | 179(b+4, 13)<br>166(b+1, 14) |
| Br | 344(18)<br>342(17) | 273(34)<br>271(34) | 165(100) | 179(b+14, 9)<br>166(b+1, 20)<br>95(14) |
| I | 390(32) | 319(32) | 165(100) | 166(b+1, 17)<br>95(29) |
| $OCOCH_3$ | 322(37) | 251(25) | 165(100) | 179(b+14, 11)<br>166(b+1, 16)<br>95(30) |
| $OCH_2CH_3$ | 308(20) | 237(15) | 165(100) | 179(b+14, 19)<br>166(b+1, 19)<br>95(27) |
| $CH_2COOC_2H_5$ | 350(68) | 279(24) | 165(100) | 179(b+14, 20)<br>166(b+1, 28)<br>95(42) |
| $CH_2COOCH_3$ | 336(32) | 265(22) | 165(100) | 179(b+14, 20)<br>166(b+1, 14) |
| $OSO_2CH_3$ | 358(42) | 287(27) | 165(100) | 359(M+1, 16)<br>288(a+1, 13)<br>166(b+1, 26)<br>95(45) |
| *COH | 278(29) | 207(25) | 165(100) | 279(M+1, 10)<br>179(b+14, 2)<br>166(b+1, 2)<br>95(43) |



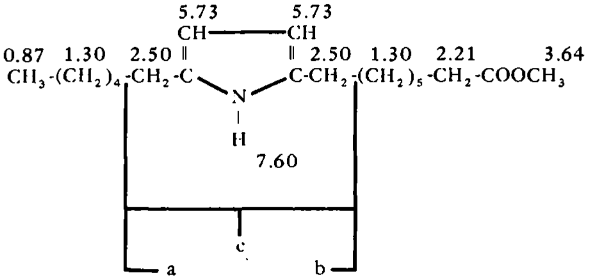
| Substituent (Y) | $M^+$ | a | b | Others |
|---|---|---|---|---|
| OH | 294(28) | 237(11) | 165(100) | 166(b+1, 13)<br>108(25)<br>83(10) |
| Cl | 314(27)<br>312(10) | 257(10)<br>255(27) | 165(100) | 166(b+1, 14)<br>83(28) |
| Br | 358(24)<br>356(30) | 301(17)<br>299(18) | 165(100) | 179(b+14, 12)<br>166(b+1, 30)<br>108(30)<br>83(13) |
| I | 404(60) | 347(38) | 165(100) | 166(b+1, 22)<br>83(9) |
| $OCOCH_3$ | 336(40) | 279(12) | 165(100) | 166(b+1, 18)<br>108(7)<br>83(8) |
| $OCH_2CH_3$ | 332(12) | 265(5) | 165(100) | 83(21) |
| $CH_2COOC_2H_5$ | 364(35) | 307(53) | 165(100) | 179(b+14, 10)<br>166(b+1, 30) |
| $CH_2COOCH_3$ | 350(30) | 293(48) | 165(100) | 166(b+1, 18) |
| $OSO_2CH_3$ | 372(40) | 315(30) | 165(100) | 373(M+1, 10)<br>316(a+1, 12)<br>166(b+1, 25)<br>95(40) |
| *COH | 292(30) | 235(28) | 165(100) | 293(M+1, 5)<br>179(b+14, 5)<br>166(b+1, 4)<br>95(35) |

*Aldehyde derivative is one methylene less.

**TABLE V**

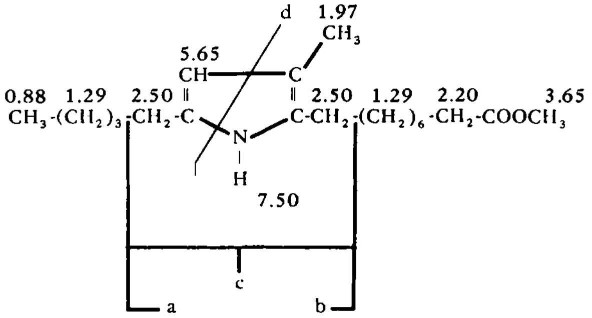
**Chromatographic and Spectroscopic Properties of Pyrrole Ester**

(a) NMR (δ):



| | |
|---|---|
| MS (70 eV): | 307 ($M^+$, 32); 276 (M-31, 8); 236 (a, 59); 178 (b+14, 4); 164 (b, 100); 94 (c+1, 11) |
| TLC R$_f$: | 0.55 ($Al_2O_3$, solvent: 10% diethyl ether in petroleum ether) |
| GLC$_{\text{OV-101}}$: | ECL = 19.4 |
| IR(cm$^{-1}$): | 3420 (νN-H); 3100 (νC-H pyrrole); 1580 (νC=C, ring); 1740 (νC=O, ester) |

(b) NMR (δ):



| | |
|---|---|
| MS (70 eV): | 321 ($M^+$, 20); 225 (d, 30); 164 (b, 100); 264 (a, 8); 108 (c+1, 8) |
| TLC R$_f$: | 0.55 ($Al_2O_3$, 10% diethyl ether in petroleum ether) |
| GLC$_{\text{OV-101}}$: | ECL = 20.4 |
| IR(cm$^{-1}$): | 3400 (νN-H); 1740 (νC=O, ester); 1580 (νC=C, ring) |

a solution of titanium chloride (6 mL) in benzene (20 mL) was added in drops to a mixture of methyl 11-methyl-10,13-dioxostearate (200 mg), benzene (25 mL) and liquid ammonia (10 mL) in a cooled flask at −10 C over a period of 2 hr. The reaction was allowed to stir at room temperature for a further 20 hr. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The product (**XIII**) was purified by preparative alumina TLC.

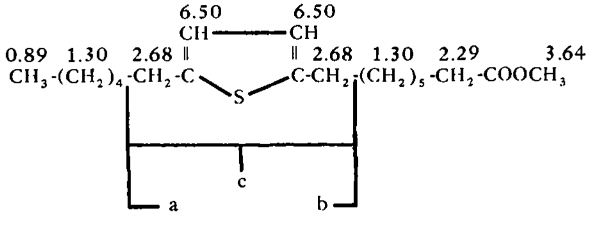
## Preparation of Thiophene Ester Derivative (XIV)

A mixture of methyl dioxostearate (100 mg) and phosphorus pentasulfide (75 mg) was heated at 110 C for 15 min. The product (**XIV**) was isolated with diethyl ether and purified by preparative alumina TLC (using 15% diethyl ether in petroleum ether as developer).

**TABLE VI**

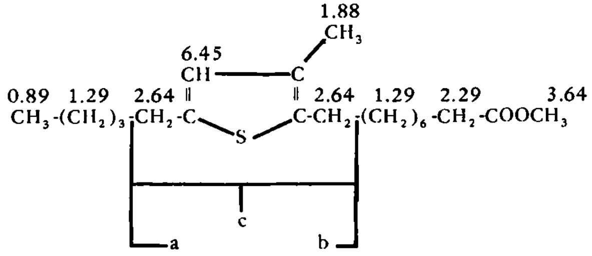
**Chromatographic and Spectroscopic Properties of Thiophene Ester**

(a) NMR (δ):



| | |
|---|---|
| MS (70 eV): | 325 (M+1, 8); 324 (M, 30); 293 (M-31, 10); 253 (a, 10); 181 (b, 100); 182 (b+1, 5); 111 (c+1, 40); 97 (c-15, 30) |
| TLC R$_f$: | 0.89 ($Al_2O_3$, solvent: 10% diethyl ether in petroleum ether) |
| GLC$_{\text{OV-1}}$: | ECL = 19.5 |
| IR(cm$^{-1}$): | 3040 (CH, thiophene), 1735 (νC=O, ester), 1560, 1580 (νC=C, ring) |

(b) NMR (δ):



| | |
|---|---|
| MS (70 eV): | 388 ($M^+$, 16); 307 (M-31, 10); 281 (a, 10); 181 (b, 100); 125 (c+1, 20) |
| TLC R$_f$: | 0.89 ($Al_2O_3$, 10% diethyl ether in petroleum ether) |
| GLC$_{\text{OV-1}}$: | ECL = 20.5 |
| IR(cm$^{-1}$): | 1740 (C=O, ester), 1560, 1585 (νC=C, ring) |

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