Table III. Results for IIIa-c,[a] Va-c,[a] and VIa-c[a]

compd	mp, °C	yield, %	formula[b]
IIIa	70-71	93	$C_{22}H_{24}O_5$
IIIb	65-94	92	$C_{23}H_{26}O_5$
IIIc	99-100	88	$C_{22}H_{23}ClO_5$
Va	128-129	76	$C_{17}H_{16}O_3$
Vb	95-96	72	$C_{18}H_{18}O_3$
Vc	125-126	70	$C_{17}H_{15}ClO_3$
VIa	207-208	60	$C_{18}H_{22}N_6O_2$
VIb	174-175	65	$C_{19}H_{24}N_6O_2$
VIc	186-187	68	$C_{18}H_{21}ClN_6O_2$

[a] Elemental analyses (C, H, N, Cl) in agreement with theoretical values were obtained and submitted for review. [b] Compounds IIIa-c were crystallized from cyclohexane, Va-c from methanol-water mixture (3:1), and VIa-c from acetic acid.

The alkaline aqueous layer was acidified with hydrochloric acid solution and extracted with benzene. Evaporation of the solvent left an oily residue.

Reaction of Ethyl β-Aryl-γ-benzoyl-α-carbethoxybutyrates (IIIa-c) with Hydrazine Hydrate. General Procedure. A mixture of the ester III (2 g) and hydrazine hydrate (99% w/w, 3 mL) was refluxed in ethanol (25 mL) for 2 h. The reaction mixture was concentrated and diluted with water and the precipitated solid was crystallized from a suitable solvent to give the corresponding 2-(1,3-diaryl-3-hydrazonopropanyl)malonohydrazide (VI). The results are reported in Table III.

β-Aryl-γ-benzoylbutyric Acid (V). General Procedure. A mixture of the ester III (1.0 g) and 3% methanolic potassium hydroxide (25 mL) was refluxed on a boiling water bath for 1 h. The acid separated from the reaction mixture was crystallized from a suitable solvent to give the corresponding β-aryl-γ-benzoylbutyric acid IV. The results are reported in Table III.

Reaction of Diethyl Malonate with Hydrazine Hydrate. A mixture of the ester (5 g) and hydrazine hydrate (99% w/w, 3 mL) in methanol was refluxed for 2 h. The colorless needles separated from the reaction mixture on cooling were crystallized from a methanol-water mixture (3:1) to give malonohydrazide as colorless needles: mp 153-154 °C; yield 98%; mol wt (mass spectral) 132.

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Preparation and Properties of the 6-Octadecenamides

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Pure, acid-free petroselinamide (*cis*-6-octadecenamide), fp 75.13 °C, and petroselaidamide (*trans*-6-octadecenamide), fp 96.81 °C, have been prepared and characterized. The binary freezing-point diagram for the two isomers indicate the formation of an incongruently melting 1:1 molecular compound with a peritectic at 73.7 °C (53.8% petroselinamide) and a eutectic at 71.4 °C (78.0%). The X-ray diffraction patterns indicate that petroselinamide has a long-spacing value of 40.8 Å with short spacings at 4.33, 3.86, and 3.45 Å. The corresponding values for the petroselaidamide are 49.3 Å and 4.10, 3.52, and 3.08 Å.

Introduction

Petroselinic acid (*cis*-6-octadecenoic acid) and its derivatives have received considerable attention in the literature because it is the principal monounsaturated C_{18} fatty acid in the oils of the Umbelliferae family and other closely related families, some of which have been considered as possible new oilseed crops.[1] Petroselinic acid and some of its derivatives have shown biological activity which indicates the potential for utility in medical or antimicrobial areas.[2-5] One of the derivatives studied for possible industrial applications is petroselinamide.[6,7] Its trans isomer, petroselaidamide, has apparently never been reported in the literature. This paper reports on the preparation of both these isomeric amides in a highly pure form and describes some of their properties.

Table I. Binary Freezing-Point Data[a] of Petroselaidamide (A)–Petroselinamide (B)

mol % of B	temp, °C	mol % of B	temp, °C
100.00	75.1	(56.03)[c]	(73.7)[c]
89.93	73.5	50.08	76.2
80.44	72.0	40.35	81.2
(76.5)[b]	(71.5)[b]	30.67	85.6
73.70	72.2	20.64	89.8
70.10	72.4	21.15	93.1
59.98	73.4	0.00	96.8

[a] Values in parentheses are obtained by graphical extrapolation. [b] Eutectic. [c] Peritectic.

Experimental Procedures

Pure samples of petroselinic acid (fp 29.6 °C) and petroselaidic acid (fp 52.7 °C), prepared as previously described,[8] were converted to the amides by the formamide procedure of Roe, Scanlon, and Swern.[9] The amides were freed of residual acid by a method previously described,[10] involving the passage of a cyclohexane solution of the crude amide through a gently heated column of Alorco activated alumina, followed by repeated recrystallization of the recovered amide from acetone to a constant freezing point. Anal. Calcd for petroselinamide: N, 4.98. Found: N, 4.94, 4.97; fp 75.13 °C. Calcd for petrose-

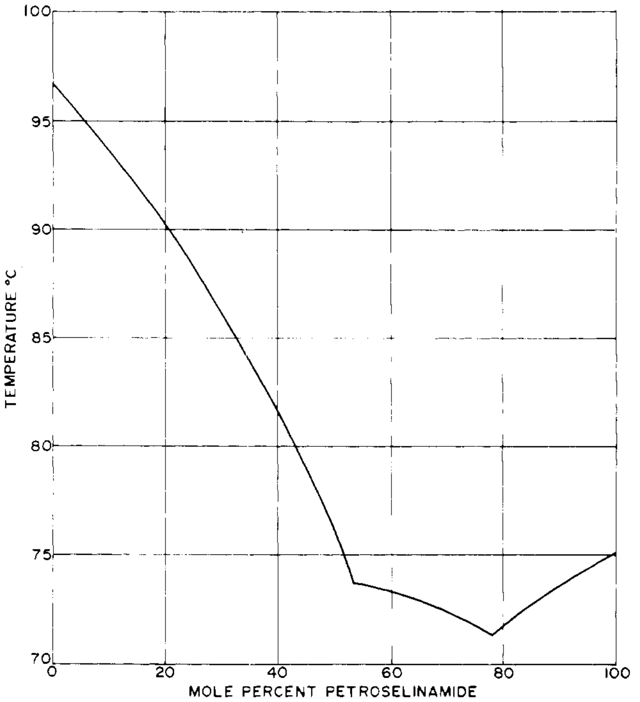

Figure 1. Binary freezing-point diagram for petroselaidamide with petroselinamide.

laidamide: N, 4.98. Found: N, 4.97, 4.98; fp 96.81 °C.

Freezing points were determined by the static method.[11] For each composition, weighed amounts of the two amides were sealed in a glass tube. A glass bead was included to ensure efficient stirring as the sample tubes were turned end over end in a constant-temperature water bath. Two temperatures a few tenths of a degree apart were found, one at which the last crystals disappeared and the other at which a few crystals remained undissolved after prolonged agitation. The freezing point was taken as the mean of these two temperatures, corrected for both thermometer calibration and emergent stem.

The X-ray long- and short-spacing measurements were made by the powder method of O'Connor et al.[12] A General Electric XRD-5 diffractometer was used to obtain X-ray diffractions by the direct-measurement technique with a chart recorder. The instrument was equipped with a copper target X-ray tube and a 0.0007 in. thick nickel filter. Divergence and antiscattering slits were used. The X-rays were generated at 30 kVp and 15 mA from 0 to 12.5°, 2θ, and 36 kVp and 16 mA from 12.5 to 50°, 2θ.

Results and Discussion

The freezing-point data for the binary system are summarized in Table I and represented in Figure 1. The two isomeric amides form an incongruently melting 1:1 molecular compound with a peritectic at 73.7 °C (53.8% petroselinamide) and a eutectic at 71.4 °C (78.0%). Thus, the binary freezing-point behavior of the *cis*- and *trans*-6-octadecenamides parallels that of the *cis*- and *trans*-9-octadecenamides.[10] Both binary systems exhibit the formation of a 1:1 molecular compound with an incongruent melting point and a eutectic.

The X-ray diffraction patterns indicate that the petroselinamide has a long-spacing value of 40.8 Å and short spacings at 4.33, 3.86, and 3.45 Å. The corresponding values for the petroselaidamide are 49.3 and 4.10, 3.52, and 3.08 Å.

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Synthesis of Isomeric Methyl- and Dimethyl-Substituted 4-Benzylidene-2-phenyloxazolin-5-ones and Ring-Opened Derivatives

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4-Benzylidene-2-phenyloxazolin-5-one and 15 mono- and dimethylated isomers as well as their ring-opened methyl ester and acid derivatives have been synthesized. Absorption spectroscopy indicates insignificant changes in the chromophore due to the methyl groups.

Because of the implication of cyclic species resembling oxazolinones in enzymatic reactions[1-3] and because oxazolinones themselves are able to acylate various enzymes,[4,5] recent attention has been given to the resonance Raman[6,7] and absorption spectroscopy[5-7] of these molecules. Due to work indicating significant changes in reactivity of various methyl isomers of furylacrylic and thienylacrylic acid acyl enzymes of α-chymotrypsin,[8] it was considered worthwhile to synthesize isomeric methylated oxazolinones for structure–activity relationship studies. It was also of interest to determine if any perturbation of the structure of these intense chromophores would result from the substitution of methyl groups for hydrogen.

The characteristic absorption spectrum of the (*Z*)-4-benzylidene bond[5,8] indicates that all of the oxazolinones synthesized were of the *Z* configuration. The λ_{max} and ϵ values

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