carbon disulfide was removed to give a reddish product, which was steam-distilled to recover the unreacted material (1 g.). The steam-distillation residue was treated in the same way to give 0.1 g. of white crystals, m.p. 206°, giving no depression of the melting point when admixed with authentic 2,3,5-trimethyl-4-acetylpyrrole.

Synthesis of 2,3,5-trimethyl-4-acetylpyrrole—Acetylacetone (IV) (1.4 g.) and isonitrosomethyl ethyl ketone (III) (1.4 g.) were dissolved together in 30 cc. of glacial acetic acid, and catalytically hydrogenated using 0.1 g. of 40% palladium-charcoal, absorbed 240 cc. of hydrogen rapidly. After the catalyst was filtered off, the filtrate was distilled under a reduced pressure to remove the acetic acid, the residue was dissolved in ether, and the ether solution was washed with diluted acid and dilute alkali solution. The crystalline ether residue was recrystallized from ethyl acetate-alcohol mixture to white needles, m.p. 206°.

Summary

2,3,5-Trimethylpyrrole obtained from the Fushun shale oil gasoline was identified through 2,3,5-trimethyl-4-acetylpyrrole, m.p. 206°, prepared by the Grignard reagent and then of acetyl chloride on the pyrrole oil extracted from the neutral shale gasoline by washing it with 60% sulfuric acid.

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49. Takeo Iida* and Minoru Tanaka**: Studies on the Components of the Fushun Shale Oil. III. Nitriles from the Crude Light Oil.

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In the earlier paper[1], it was reported that the crude gasoline of the Fushun shale oil contains aliphatic nitriles (capro-, enantho-, and caprylo-nitriles) as its neutral nitrogen components to the extent of 0.5 %. Using the same procedure as that previously employed by the present authors[1], the research on the crude light oil[2] was continued and it was found that the light oil also contains caprylo-, pelargo-, capro-, hendecano- and lauro-nitriles to the total amount of about 2 %. The physical properties of these acids and their derivatives are listed in Table I.

This investigation was carried out under the continued guidance of Prof. Dr. E. Ochiai to whom the authors express their heartfelt and profound gratitude.

Experimental

Preparation of the neutral oil—Three kg. of the faint yellow crude light oil, which is freshly distilled in vacuum, was washed with 10% caustic soda, then successively with 20% and 60% sulfuric acid to remove the acid oil (5%), basic oil (4.5%), and the pyrrole oil[3] (1.5 %), and the neutral oil (82%) was obtained.

Saponification of the nitriles—The neutral oil (about 2.4 kg.) was heated with an air condenser for 12 hours at about 200°. Heating was continued until the evolution of gaseous ammonia ceased.

Separation of fatty acids—After saponification the mixture was cooled to a room temperature, and the resulting potassium soap was extracted with hot water. The aqueous extract was stirred with benzene to remove mechanically the small amount of contaminated neutral oil and then made acidic. The crude brown fatty acids were obtained.

Esterification and refining of the crude fatty acids—The crude fatty acids were boiled with 5% methanolich ydrochloric acid for 2～3 hours on a water bath converting them to the methyl esters,

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1) T. Iida, M. Tanaka: J. Pharm. Soc. Japan, 64, 162(1944).
2) This name is given to the 200～280° fraction of the crude shale oil obtained by the low-temperature carbonisation of Fushun oil shale in Manchuria.
3) Neutral oil extracted with 60 % sulfuric acid contains a large amount of pyrrole compounds.

and then distilled under a reduced pressure. Faint yellow esters (total amount, about 60 g.) were obtained. The esters were dissolved in carbon tetrachloride and the unsaturated fatty acids present in small quantities in it were removed by ozonization (inspection of the ozonides was not carried out).

Rectification—The fatty acid esters (about 57 g.) were fractionally distilled in 5° fractions, using the Klenk fractional distillation apparatus[4]. The result of the fractional distillation is shown in Fig. 1.

Confirmatory reactions—The five fractions, corresponding to the tops of the curve, were converted to the amides and 2-alkylbenzimidazoles according to the confirmatory reactions of the acids, and the results obtained are shown in Table I. The melting points of the derivatives were not depressed on admixture with the authentic specimens prepared from the pure acids, from which the presence of the normal fatty acid nitriles were confirmed.

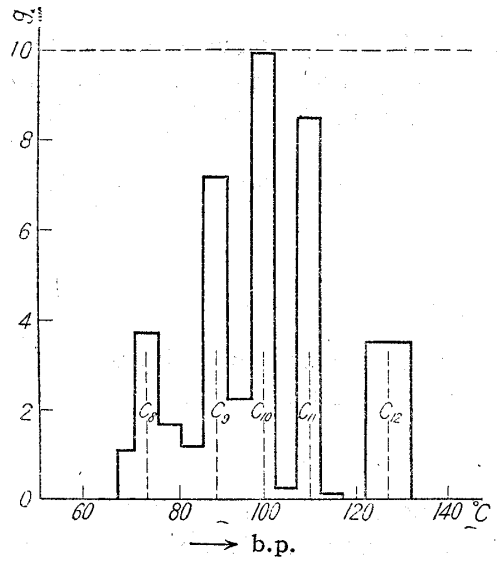

Fig. 1. Fractional Distillation Curve of Methyl Esters Separated from the Light Oil.

TABLE I

Normal fatty acids	Methyl Esters $b.p_{10}$ °C	Derivatives m.p. °C: Amides	Derivatives m.p. °C: 2-Alkylbenzimidazoles
C_8 Caprylic	72～ 77	104.5	143.5
C_9 Pelargonic	87～ 92	99.0	139.5
C_{10} Capric	97～ 92	98.0	127.0
C_{11} Undecanoic	107～112	96.5	114.5
C_{12} Lauric	126～131	98.5	—

Summary

The nitriles obtained from the crude light oil, b.p. 200～280°, of Fushun shale oil in Manchuria were studied, and caprylo-, pelargo-, capro-, hendecano-, and lauro-nitriles were identified.

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4) Z. Physiol. Chem., 224, 250 (1936).

50. Ko Arima and Ryoichi Hayatsu: Studies on Cholestapolyenes. I. Syntheses of Bicholestatriene A and 7-Dehydrocholesterol.

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There are many methods of preparing provitamin D_3 by the dehydrohalogenation of 7-halocholesteryl ester. In the present series of experiments, 7β-bromocholesteryl benzoate (I) was treated with sodium iodide and two kinds of new hydrocholesteryl benzoate possessing one tertiary hydroxyl group were obtained. These compounds were dehydrated by heating in vacuo by which provitamin D_3 was prepared with a comparatively good yield. Dehydration in glacial acetic acid was attempted but this failed to give provitamin and in its stead, yellow hydrocarbon, $C_{54}H_{82}$, was obtained in a comparatively good yield. These are described in the present paper.

Treatment of 7β-bromocholesteryl benzoate[1] (I) in a solution of anhydrous sodium iodide in dehydrated acetone at a low temperature gives 7β-iodocholesteryl benzoate[2] (II) which

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1) H. Schaltegger: Helv. Chim. Acta, 29, 285(1946).

2) H.B. Heubest: J. Chem. Soc., 1948, 1788.