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NAPHTHENIC ACIDS DERIVED FROM NISHIYAMA PETROLEUM

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Introduction

In a previous paper[1] the authors described the properties and composition of the mixture of naphthenic acids derived from a "neutral oil" distillate of Akita-Kurokawa petroleum. Our attention has been drawn to the fact that the specific gravities of the naphthenic acids derived from Akita-Kurokawa oil are much higher than those given in the literature for similar products of other origin. In subsequent work[2] acids having high specific gravities have similarly been found in the naphthenic acids derived from Echigo-Niitsu oil.

The object of this paper is to describe an investigation of the naphthenic acids derived from a "neutral oil" distillate (33.2 Bé.) from Echigo-Nishiyama oil.

Experimental Part

The crude petroleum acids employed were obtained by acidifying the waste lye produced in the refining of a "neutral oil" distillate from Echigo-Nishiyama crude oil; acid value, 143.5; water, 20.0%; organic acid substance, 57.6%.

The crude acids were shaken with one and a half volumes of petroleum ether containing a small amount of alcohol. The petroleum ether solution thus obtained, containing the naphthenic acids, was distilled under 9 mm. pressure. The distillate was converted into the potassium soaps and extracted with petroleum ether. This soap solution, on acidification, gave the crude naphthenic acids as a pale yellow oil of faint odor; d_4^{15}, 0.9768; n_D^{15}, 1.4770; acid value, 249.7.

For further purification, the crude naphthenic acids were converted into the methyl esters by treating them with an excess of methyl alcohol and dry hydrogen chloride. The methyl esters were obtained as a pale yellow liquid of fruity odor; d_4^{15}, 0.9446; n_D^{15}, 1.4651; 80% distilled at 130–180° (8.9–9.0 mm.).

The mixture of pure naphthenic acids was obtained by saponification of the methyl esters with alcoholic potassium hydroxide and by subsequent acidification with dil. hydrochloric acid. It was a light yellow, viscous oil; d_4^{15}, 0.9741; n_D^{15}, 1.4762; neutralization value, 248.0; about 80% distilled at 170–210° (8.9–9.0 mm.).

Comparing the pure naphthenic acids of Echigo-Nishiyama origin with those of Akita-Kurokawa origin, it is significant that the range of distillation temperatures of the main portions and the neutralization values of the corresponding fractions are in close agreement, but the specific gravities and the refractive indices of the fractions of the former are remarkably lower than those of the fractions of the latter, showing that the naphthenic acids from these different sources contain different isomers.

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[1] Tanaka and Nagai, THIS JOURNAL, **45**, 754 (1923).

[2] Tanaka, Nagai and Ishida, *J. Faculty Eng. Tokyo Imp. Univ.*, **16**, 11 (1924).

About 4500 g. of the mixture of methyl esters was fractionally distilled at 8.9–9.0 mm. pressure, using the modified type of Claisen flask described in the previous paper. By means of a series of 25 systematic fractional distillations, the mixture of methyl esters was separated into four main fractions which proved to be the methyl esters of dodeca-, trideca-, tetradeca- and pentadecanaphthenic acids. All were colorless liquids with fruity odor.

Table I

Properties of the Methyl Esters

			$C_{11}H_{21}COOCH_3$	$C_{12}H_{23}COOCH_3$	$C_{13}H_{25}COOCH_3$	$C_{14}H_{27}COOCH_3$
d_4^{15}			0.9412	0.9443	0.9491	0.9501
n_D^{15}			1.4579	1.4612	1.4647	1.4672
B. p. (8.9–9.0 mm.), °C.			127–129	136–138	145.5–147.5	155–157
B. p. (760 mm.), °C.			265–266	277–278	289–290	300–301
Anal.:	Calcd.	C	73.5	74.3	74.9	75.5
		H	11.4	11.6	11.8	11.9
	Found	C	73.4	74.2	74.8	75.4
		H	11.4	11.7	11.7	12.0
Mol. wt.:	Calcd.		212.3	226.3	240.3	254.3
	Found		213.3	230.9	244.2	257.3
Sap. value:	Calcd.		264.3	247.9	233.5	220.6
	Found		265.9	244.3	236.5	221.0
Mol. refract.:	Calcd.		61.52	65.78	69.95	74.31
	Found		61.20	65.30	69.92	74.54

These esters were saponified with 2 *N* alcoholic potassium hydroxide solution and extracted with petroleum ether (b. p., 40°) to remove the traces of unsaponified esters. The soap solutions were acidified, whereupon the corresponding naphthenic acids separated. These acids were washed with water, dried over calcium chloride and heated to 70° in a vacuum to expel traces of the solvent. The naphthenic acids isolated, namely, dodecanaphthenic, $C_{12}H_{22}O_2$, tridecanaphthenic, $C_{13}H_{24}O_2$, tetradecanaphthenic, $C_{14}H_{26}O_2$, and pentadecanaphthenic, $C_{15}H_{28}O_2$, were colorless, odorless liquids having no iodine number.

Table II

Properties of the Free Acids

		$C_{12}H_{22}O_2$	$C_{13}H_{24}O_2$	$C_{14}H_{26}O_2$	$C_{15}H_{28}O_2$
d_4^{15}		0.9712	0.9736	0.9762	0.9776
n_D^{15}		1.4697	1.4727	1.4759	1.4784
B. p. (8.9–9.0 mm.), °C.		168–170	177–179	186–188	194–196
Neutr. value:	Calcd.	283.0	264.0	247.9	233.4
	Found	279.4	267.3	248.6	232.0
Mol. refract.:	Calcd.	56.95	61.56	66.16	70.80
	Found	56.92	61.13	65.49	69.63

It is significant that the specific gravities of the constituents of the naphthenic acids derived from Nishiyama petroleum are much lower than those given for the corresponding acids of Kurokawa origin, showing that the respective acids are isomers.

It is well known that Kurokawa and Niitsu oils have rather high specific gravities and have very dissimilar properties from those of Nishiyama oil. The identification of the naphthenic acids of low specific gravities in Nishiyama oil and of the isomers of high specific gravities in Kurokawa oil is of great interest in view of the geological formation of these petroleums. It seems probable that Kurokawa and Niitsu petroleums have been subjected to volcanic action and that consequently the isomeric change of naphthenic acids has occurred through the possible influence of heat and pressure.

Summary

A mixture of pure naphthenic acids was obtained from the waste lye produced in the refining of a "neutral oil" distillate (33.2 Bé.) from Echigo-Nishiyama oil and the corresponding free naphthenic acids, namely, dodecanaphthenic, tridecanaphthenic, tetradecanaphthenic and pentadecanaphthenic and their methyl esters have been isolated. It is noted that the specific gravities of the acids are much lower than those given for the corresponding acids of Akita-Kurokawa origin, indicating that the respective acids are isomers.

It is also pointed out that the presence of these isomers of the naphthenic acids is of great interest in view of the geological formation of petroleums.

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[Contribution from the Chemical Laboratory of the University of Florida]

THE PREPARATION AND PROPERTIES OF 1-BENZOYLAMINO-2-METHYLANTHRAQUINONE[1]

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The amino-anthraquinones have received considerable attention because they serve as the starting point in the synthesis of many anthraquinone derivatives, some of which are valuable vat dyes. It is known that the replacement of an amino hydrogen atom by an alphyl or aryl group causes greater depth of color, but none of the compounds so formed has affinity for textile fibers. On the other hand, the introduction of an acyl group is accompanied by a decrease in the depth of color, and the product may be a vat dye.[2]

Very little work has been done with the substitution products of the methylamino-anthraquinones. Roemer and Link prepared the mono-

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[1] This paper incorporates a thesis presented to the Faculty of the University of Florida by J. Lowry Bray in partial fulfilment of the requirements for the degree of Master of Science.

[2] Barnett, "Anthracene and Anthraquinone," D. Van Nostrand Co., **1921**, p. 8.