ABSTRACTS

Oils and Fats

Edited by
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Antioxygens of fats and oils. VII. Actions of terpene hydrocarbon, alcohols, aldehydes, ketones, acids and phenol derivatives on the oxidation of semidrying oil. Mitsuo Nakamura. *J. Soc. Chem. Ind., Japan* 36, Suppl. binding 286-8(1933); cf. C. A. 26, 2610.—Soybean oil was used as the semidrying oil for the oxidation expts. Terpene alcs. of the olefin series, aromatic alcs. and aromatic terpene alcs. showed weak antioxygenic activities. The ethers of monohydric phenols such as anethole, Ph_2O and yara-yara were proöxygenic, while thymol was strongly antioxygenic. The derivs. of dihydric phenols which have a hydroxy and an alkyl ether group together with a propenyl or an allyl radical retarded oxidation. Safrole acted as an antioxygen, while isosafrole accelerated oxidation. Camphor was inactive, as were aromatic ketones. Aromatic acids having the carboxyl radical directly attached to the benzene ring showed weak proöxygenic properties, as with BzOH and salicylic acid, while $PhCH_2CO_2H$ was inactive. **VIII. Action of terpene hydrocarbon, alcohols, aldehydes, ketones, acids and phenol derivatives on the oxidation of nondrying oil.** *Ibid.* 288-9.—The nondrying Tsubaki oil was used with the same org. compds. in oxidation tests. The terpene alcs. of the olefin series were without influence. Aromatic terpene alcs. and aromatic alcs. were inactive. Ph_2O had no effect, while anethole acted as a proöxygen; thymol was strongly antioxygenic. the derivs. of dihydric phenols such as safrole, isosafrole, isoeugenol and *cis*-isosafroeugenol retarded oxidation. Among the aromatic aldehydes, BzH and heliotropin were strongly proöxygenic. Camphor was inactive, whereas aromatic ketones, such as acetophenone, benzophenone and α-ionone were all accelerators of oxidation. The aromatic acids had no effect on oxidation. **IX. Inversion of oxidative catalyst due to the species of fatty oils.** *Ibid.* 289-92.—While certain compds. retard oxidation in earlier stages and accelerate it in a later period, others act contrariwise. This "inversion of catalysis" was studied in connection with oxidative catalysts and different species of fatty oils. A table is given showing the action of various org. compds. on the oxidation of linseed, soy-bean and Tsubaki oils. In the case of strongly oxidative catalysts the inversion of the catalyst due to the species of fatty oil could not be observed, while the opposite was true with the weak ones. Weak oxidative catalysts either antioxygenic or proöxygenic for drying or semidrying oil are inactive toward nondrying oil. The oxidative catalysts for fatty oils are the same as for the coloring matter of fatty oils. The catalysts themselves may become oxidized and give rise to other compds. which may affect the oxidation of fatty oils, so that the reactions involved in the autoxidation of fatty oils contg. oxidative catalysts are, as a rule, very complex. **X-XI. Inversion of oxidative catalyst due to the species of fatty oils.** (2-3). *Ibid.* 335-7.—The oxidative actions of the following org. compds. are tabulated for their effect on Tsubaki, olive, rape-seed, cottonseed, soy-bean, linseed and perilla oils: pyrocatechol, *o*-nitrophenol, α-naphthylamine, thymol, vanillin, hydroquinone, α-naphthol, β-naphthylamine, *p*-nitroaniline, pyrogallol, β-naphthol, eugenol, yara-yara. The compds. strongly antioxygenic toward linseed oil, which include all but vanillin, β-naphthol, yara-yara and *p*-nitroaniline, are also antioxygenic for other fatty oils. The other compds. exhibit inversion of catalytic action and shorten the induction period of each fatty oil. The inversion is closely related to the I nos. of fatty oils; the lower the no. the more rapid the inversion. E. SCHERUBEL.

Antioxygens of fats and oils. XII. Action of β-naphthol on the oxidation of soy-bean oil. Mitsuo Nakamura. *J. Soc. Chem. Ind., Japan* 36, Suppl. binding 408-10(1933); cf. preceding abstr.—β-naphthol acts as a proöxygen toward soy-bean oil throughout the oxidation in concns. of 0.05-0.2%, but above 0.6% it acts first as a proöxygen and then changes to an antioxygen. The rate of inversion depends upon the concn. of β-naphthol and also upon the velocity of oxidation of the oil. K. K.

High-pressure hydrogenation of fatty oils. IV. Production of solid unsaponifiable matters by means of pyrogenic hydrogenation of fatty acids. V. Production of solid unsaponifiable matters by high-temperature hydrogenation of fatty oils. Yoshio Tanaka, Ryonosuke Kobayaski and Yoshio Fukushima. *J. Soc. Chem. Ind., Japan* 36, Suppl. binding 311-12, 312-13(1933); of cf. C. A. 27, 3097.—By the hydrogenation of palmitic acid at a temp. of 300° to 400° with high pressure and Ni Cu hydroxides as catalyst, a product contg. a large amt. of solid unsapon. matter is obtained, the compn. of which shows it to be palmitone. By hydrogenating soy-bean oil below 180° stearin is produced which decomposes into glycerol and stearic acid at a temp. of 300°. Stearone, distearylcarbinol, and pentatriacontane are formed from the stearic acid at temps. above 300°. The unsaponifiable solid products from palmitic and stearic acids have high m. ps. and may be used as substitutes for carnauba wax.

E. SCHERUBEL.

Detection of hardened whale oil in tallow. *The Industrial Chemist,* Vol. IX, No. 104, page 293, September, 1933.—Formerly, the presence of nickel was a satisfactory indication of hardened oils; modern improvements in manufacture of these products have been made so that the nickel content can either be reduced to such a degree that the refinements of spectroscopic analysis are needed (Kaufmann and Keller, *Chem. Umschau,* 1930, 37, 49), or else completely eliminated. This test has therefore lost much of its value.

Wittka (*Chem. Umschau,* 1927, 34, 295) points out that the unsaponifiable matter in beef tallow rarely exceeds 0.3 per cent whilst other animal and all vegetable oils (with the exception of castor) contain a much greater proportion (0.75 to 1.3 per cent) which is practically unaffected by the process of hardening.

The presence of much behenic acid (high melting point) is characteristic of hardened fish and rape oil. Davidsohn (*Metallborse,* 1930, 20, 1798 and 1854) considers that the method most generally useful is that of Grun for determining iso-oleic acid in the separated solid fatty acid by the iodine number; a value exceeding 5 is regarded as indicative of the presence of hardened oils. The method used is described by Davidsohn and Streichhan (*Seifensider-Ztg.,* 1926, 53, 551) and briefly is as follows:

Liberate the fatty acids from 2—5 gm. of the fat, dissolve in hot 96 per cent alcohol, and treat with a hot 96 per cent alcoholic solution of 1.5 gm. lead acetate. Cool overnight and ascertain the presence of an excess of lead solution by adding some dilute sulphuric acid. Filter and wash with alcohol until the filtrate remains clear when water is added. Return the precipitate into a flask with 100 c.c. alcohol, add 0.5 c.c. glacial acetic acid, and boil. Cool to 15° C., wash, crystallize the lead soaps with alcohol, and return again to the flask, washing with ether. Decompose the lead soaps with dilute nitric acid and extract the fatty acids with ether. Decompose their iodine number by the Hanus method. Tallow will show an iodine number of 0.5, while hardened oils will show an iodine number round about 33.5 caused by the formation of solid iso-oleic during hardening. Attempts to shorten this method have proved unsatisfactory.

PATENTS

Food fats. *Chemical Abstracts,* Vol. 27, No. 18, page 4600, September 20, 1933.—Swift & Co. British 389,389, March 16, 1933. Shortening agents, e.g., hog lard, hydrogenated hog lard, hydrogenated vegetable oils, etc., are improved in creaming qualities, etc., by rapidly supercooling the melted shortening to such an extent that the heat of crystallization does not quite raise the temperature to the normal congealing point, withdrawing from the cooling apparatus before any appreciable crystallization takes place and permitting to crystallize.

Modified train oils. Deutsche Hydrierwerke A.-G. Brit. 388,630, Mar. 2, 1933. Fatty substances, miscible with H_2O and with mineral and fatty oils and useful in the leather industry as a substitute for degras, are obtained from liquid train oils, composed largely of unsatd. alkyl esters, by converting the latter into satd. esters by the addn. of OH groups. Bottle-nosed-whale. sperm and physeter oils may be converted by (1) mixing with concd. H_2SO_4 at low temp., allowing to stand, stirring into excess H_2O and heating with direct steam, (2) treatment with permonosulfuric acid or HClO or (3) adding and subsequently splitting off halogen or H halide.

Separating mixtures of stearin and olein. Ernst A. Mauersberger. Brit. 391,306, Apr. 27, 1933. The mixts. are resolved by dissolving in O-free solvents, *e.g.,* benzine, C_6H_6, PhMe, chlorinated hydrocarbons and mixts. thereof, incorporating H_2O as a colloidal soln. or emulsion, cooling to crystallize the stearin and filtering or otherwise sepg. Examples are given. Cf. *C. A.* 27, 3100.

Separating solvents from oils and fats. Wilhelm Gensecke (to American Lurgi Corp.). U. S. 1,918,638, July 18. The solvent is vaporized and the vapors are condensed by direct contact with a cooling liquid not miscible with the solvent used (*e.g.,* solvent vapors such as benzine may be contacted with water) and the condensed solvent is sepd. from the cooling liquid; the temp. of the cooling liquid is lowered by surface cooling and it is returned to the condensing operation. An arrangement of app. is described.

COURTESY CHEMICAL ABSTRACTS