3-Hydroxy-(9-*p*-hydroxyphenyl)-10-ethylphenanthrene (II).—To 8.5 g. of the ketone (XVI) above dissolved in 170 ml. of hot acetic acid, 85 ml. of 48% hydrobromic acid was added and the solution refluxed for 72 hours under an atmosphere of nitrogen. At the end of this period, the mixture was poured into water and extracted with methylene chloride. The extract was washed with water and sodium bicarbonate solution, dried and concentrated. The residue was recrystallized several times from ethanol–water to yield 4.3 g. (51%) of small irregular light yellow plates of analytical purity. This material melted at 194.5–195.5°, but in the region 125–145° there appeared to be sintering and evolution of a volatile constituent. This was presumably due to the loss of solvent from the solvated crystals, for when the air-dried material above was dried to constant weight in vacuum, 13% of its original weight was lost.[21]

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.12; H, 6.09.

A sample of the air-dried solvated material gave analytical results in good agreement with the assumption that the solvate contained one mole of ethanol per mole.

Anal. Calcd. for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71. Found: C, 80.13; H, 6.92.

The solvate obtained when the dihydroxy compound (II) crystallizes from pyridine–water melts at 148–150°. Analysis of an air-dried sample indicates that one mole of pyridine is combined with one mole of the dihydroxy compound (II).

Anal. Calcd. for $C_{27}H_{23}O_2N$: C, 82.41; H, 5.89; N, 3.56. Found: C, 82.47; H, 6.04; N, 3.60.

The dimethyl ether of II was prepared in sodium hydroxide solution by the action of methyl sulfate. It crystallized from acetic acid–ethanol as small flat colorless needles, m.p. 163.5–164.5°. In hot acetic acid, the product gives a pink color which disappears on cooling or on addition of ethanol.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.14; H, 6.67.

The dibenzoate of II, prepared by the Schotten–Baumann procedure yielded transparent plates from acetic acid, m.p. 214–215°.

Anal. Calcd. for $C_{36}H_{26}O_4$: C, 82.74; H, 5.02. Found: C, 82.68; H, 4.93.

One gram of the dibenzoate was hydrolyzed by refluxing it for three hours in a mixture containing 10 ml. of purified dioxane and 15 ml. of 20% potassium hydroxide solution. The dihydroxy compound (II) was precipitated by the action of carbon dioxide and recrystallized from ethanol–water, m.p. 193.5–195.5° alone or when mixed with the analytical sample obtained from the cyclization product.

5-Methoxy-2-acetobiphenyl[22] **(IX).**—A Grignard reagent was prepared from 28 ml. of methyl iodide and most of the ether removed. To the concentrated Grignard reagent, 31.3 g. of 5-methoxy-2-cyanobiphenyl (IV) was added in 100 ml. of dry thiophene-free benzene. The remainder of the ether was removed and the mixture refluxed with stirring for 16 hours. At the end of this period, 250 ml. of 2 *N* hydrochloric acid was added and the mixture heated for one hour with stirring on the steam-bath in order to hydrolyze the imine to the ketone. During this period, the benzene was allowed to distil. The organic residue was taken up in methylene chloride and the solution washed with water and sodium bicarbonate solution. Concentration of the solution and fractionation of the residue under reduced pressure yielded the ketone (IX) as a light yellow oil, 23.2 g. (68%), b.p. 165–170° (2 mm.), which crystallized on standing, m.p. 67–72°. Recrystallization from ethanol gave colorless prisms, m.p. 73.5–74.5°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.91; H, 6.35.

The 2,4-dinitrophenylhydrazone crystallized from ethanol as small red-orange needles, m.p. 203–204°.

Anal. Calcd. for $C_{21}H_{18}O_5N_4$: C, 62.06; H, 4.46. Found: C, 61.78; H, 4.43.

Attempted Willgerodt Reaction on 5-Methoxy-2-acetobiphenyl.—The ketone (6.8 g.) was subjected to the action of sulfur and morpholine according to the general procedure of Schwenk and Bloch.[23] On working up the product in the recommended manner, 2.4 g. of a viscous red acidic oil was obtained. This material would not crystallize even when triturated with cyclohexane and seeded with a sample of the expected acid obtained by hydrolysis of 2-phenyl-4-methoxybenzyl cyanide (X).

(21) The per cent. yield quoted above was based upon the estimated vacuum-dried weight of product.

(22) This is a modification of the procedure used by Mr. H. K. Porter of this Laboratory in the preparation of 5-methoxy-2-propiobiphenyl.

(23) E. Schwenk and E. Bloch, THIS JOURNAL, **64**, 3051 (1942).

DURHAM, N. C.
LEIDEN, THE NETHERLANDS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Molecular Structure of the Galactogen from Beef Lung[1]

BY M. L. WOLFROM, GORDON SUTHERLAND AND MAX SCHLAMOWITZ[2]

RECEIVED MARCH 12, 1952

The galactogen of beef lung, designated pneumogalactan, has been further purified and shown to contain no significant amount of L-galactose. As isolated, the polysaccharide is alkali-sensitive and contains one titratable acid function, probably carboxyl, per 35–40 anhydrohexose units. This allows it to move as an anion, essentially but not quite homogeneously, under electrophoresis. A search for its hydrolytic enzyme was made without significant result. Its acetate and methyl ether are described. Hydrolysis of the latter yielded the 2,4-, 2,3,4- and 2,3,4,6- methyl ethers of D-galactose identified by paper chromatograms and by chromatographic separation of their crystalline anilides. Periodate oxidation of the polysaccharide indicated an oxidant consumption of 4 moles per anhydrotrisaccharide unit with the formation of 2 moles of formic acid. Pneumogalactan therefore consists of a main chain of D-galactopyranose units linked 1 → 6. To every other unit of this backbone structure is attached one D-galactopyranose entity in the 1 → 3 position.

In some commercial processes for the preparation of heparin from beef lung, a by-product polysaccharide is obtained which has been characterized as a galactan (galactogen).[3] This substance is of interest as representing the first galactan isolated from mammalian tissue and we propose for it the name pneumogalactan. We report herein a different method of purification which resulted in a product that on acid hydrolysis indicated a content of D-galactose of 100 ± 2%. Therefore no significant amount of L-galactose is present in the polymer. An examination of the crystalline hydrolyzate material for the possible presence of D,L-galactose was made but none was found. Contrary to our previous report,[3] the presently better purified preparation exhibited a negative test with the alkaline

(1) The data herein recorded supersede those reported by M. L. Wolfrom and F. A. H. Rice, *Abstracts Papers Am. Chem. Soc.*, **113**, 3Q (1948).

(2) Postdoctoral Research Fellow of the National Institutes of Health, United States Public Health Service.

(3) M. L. Wolfrom, D. I. Weisblat, J. V. Karabinos and O. Keller, *Arch. Biochem.*, **14**, 1 (1947).

copper reagent of May[4] and was alkali-sensitive, thus differing in behavior from snail galactogen.[4] It did not gel with borax. When passed through ion exchange resins the product exhibited a small but definite acidity (Fig. 1) and an increased viscosity. That this acidity was an integral part of

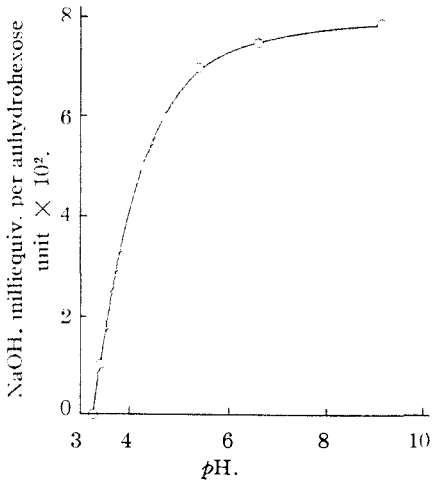


Fig. 1.—Potentiometric titration at 25° of pneumogalactan (452 mg.) in 1.13% aqueous solution with 0.1 *N* NaOH; corrected for blank; initial *p*H 3.25; acidity from neutral point, 0.028 equiv. per $C_6H_{10}O_5$ unit.

the molecule was established by the electrophoretic anionic mobility (Fig. 2) of the preparation. Figure 2 demonstrates that the preparation is mainly, but not quite, electrophoretically homogeneous. A phosphate acid ester as the sole cause of this acidity would appear to be excluded by the low phosphorus content and by the fact that the nature of the curve of Fig. 1 would indicate that most (*ca.* 90%) of the acidity is such as would be satisfied by the carboxyl group of a uronic acid. On this basis, the acid function would occur once in every 35–40 hexose units. Such a constituent could be an integral part of the natural product or it could represent oxidative alteration effected in its isolation.

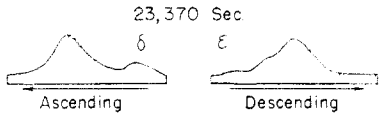


Fig. 2.—Electrophoretic patterns of pneumogalactan, 1.5% in phosphate buffer, *p*H 8.0, μ 0.20, 0°, 4.15 v./cm. Mobility of major component (average from ascending and descending patterns) -2.35×10^{-5} cm.² sec.$^{-1}$; mobility of minor component (from descending pattern) -0.75×10^{-5} cm.² sec.$^{-1}$.

A search was made for an enzyme effective in degrading this substrate. An unidentified soil bacillus was isolated that utilized the pneumogalactan. The data of Fig. 3 would suggest an adaptive behavior on the part of the bacillus. An extract of sprouted alfalfa seed exhibited weak hydrolytic properties. Otherwise, these efforts were fruitless.

The alkali sensitivity of pneumogalactan rendered its methylation difficult. An acetate was prepared but its solubilities were not suitable for em-

(4) F. May, *Z. Biol.*, **96**, 277 (1934).

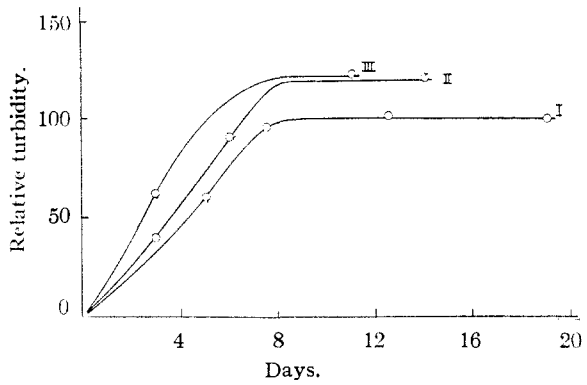


Fig. 3.—Growth curves for soil Gram negative coccobacillus in pneumogalactan–salt mixture liquid medium at 30°: I, 1st transfer; II, 2nd transfer; III, 3rd transfer.

ployment in the Haworth alkaline methyl sulfate etherification.[5] Success was obtained by application of the Menzies thallium alkoxide alkylation[6] as adapted by Hirst and Jones.[7] Essentially complete methylation was then effected by repeated application of the Purdie[8] procedure. The resultant trimethyl ether of pneumogalactan was subjected to successive methanolysis and hydrolysis and the hydrolyzate was analyzed by paper chromatographic methods. There was found approximately equal amounts of 2,4-di-O-methyl-D-galactose, 2,3,4-tri-O-methyl-D-galactose and 2,3,4,6-tetra-O-methyl-D-galactose, identification being effected by comparison with authentic preparations of these derivatives. Final verification was then effected by conversion of the hydrolyzate to the crystalline anilides and resolution of the mixture by chromatography on Magnesol. Periodate oxidation (Fig. 4) of pneumogalactan under controlled

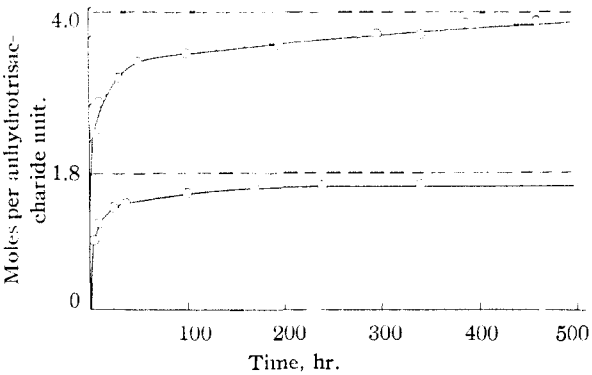


Fig. 4.—Periodate oxidation of pneumogalactan (*c* 0.019) in 0.0232 *M* sodium metaperiodate at 4–6° for first 336 hr. and at 28° thereafter; reaction mixture maintained in the dark; formic acid (lower curve) by acidity to methyl red-methylene blue indicator; initial *p*H adjusted to 6.0; corrected for blanks; periodate uptake (upper curve) unchanged in reaction mixtures buffered to *p*H 4.6; *p*H of unadjusted reaction mixture at 28° was 5.15 changing to 3.1 after 336 hr.

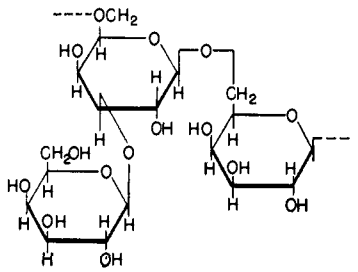
(5) W. N. Haworth, E. L. Hirst and H. A. Thomas, *J. Chem. Soc.*, 821 (1931).

(6) Christina M. Fear and R. C. Menzies, *ibid.*, 937 (1926).

(7) E. L. Hirst and J. K. N. Jones, *ibid.*, 496 (1938).

(8) T. Purdie and W. Pitkeathly, *ibid.*, **75**, 153 (1899); T. Purdie and J. C. Irvine, *ibid.*, **83**, 1021 (1903).

conditions indicated an oxidant consumption of 4 moles per anhydrotrisaccharide unit with the production of 2 moles of formic acid. There is thus uniquely established the following repeating unit for pneumogalactan, wherein the configurations of the glycosidic linkages are not equivocally established but are shown as β-D.



The above structure differs from the possibilities presented, but not in all cases uniquely defined, for the galactans[9] from the snail *Helix pomatia*, the mold *Penicillium charlesii* G. Smith, marine algae, and the seeds of *Lupinus albus*.[10] It establishes the occurrence of 1,3-glycosidic linkages in a polysaccharide of mammalian origin.

Experimental[11]

Pneumogalactan.—The crude galactan from beef lung[12] was purified somewhat differently than described previously.[3] An amount of 30 g. of the crude material, dissolved in 1000 ml. of water, was treated for 5 min. at 60–80° with 3 g. of decolorizing carbon (Darco G-60) and filtered hot through paper. The filtrate was cooled to room temperature and 2 vol. of 95% ethanol was added with stirring over a period of 45 min. The precipitated material was removed by centrifugation and the process was repeated. The centrifugate was dissolved in 900 ml. of water and dialyzed for 90 hr. against water, employing a cellophane membrane.[13] The filtered dialyzate was brought to a volume of 1200 ml., a 10-ml. solution of 740 mg. of ammonium acetate was added, and precipitation effected as before. The centrifugate was washed with 95% ethanol and finally with abs. ethanol; yield 14.7 g.

An amount of 3.0 g. of the above product, dissolved in 100 ml. of water, was passed through a 15 × 1 (i.d.) cm. column of mono-bed MB-3 ion exchange resin.[14] The eluant was treated at 90° with 200 mg. of decolorizing carbon (Darco G-60) and again passed through a mono-bed column (8 × 1 cm., diam.). To the eluant and washings (138 ml.) ethanol was added slowly under stirring to make a 60% ethanol concentration. The precipitated solid was removed by centrifugation and washed with 100 ml. of 65% ethanol. The product was dissolved in 84 ml. of water and precipitated as above with 226 ml. of abs. ethanol to make a 73% ethanol concentration. The precipitated solid was removed by centrifugation, washed successively with 95% and abs. ethanol and dried at room temperature under reduced pressure (for analysis, at 80° over P_2O_5 *in vacuo* for 24 hr.); yield 2.2 g., $[\alpha]^{29}D$ +19° (*c* 3, water). Visual observation showed that deionization produced a marked increase in the viscosity of the polymer solution.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.44; H, 6.22. Found: C, 44.28; H, 6.29; S, absent; P, trace; N, 0.25.

The amorphous, colorless solid was essentially quantitatively (96%) precipitable with ethanol (trace of ammonium acetate added) immediately after solution at room temperature in 30% KOH but after heating under nitrogen for 2 hr. the recovery was *ca.* 10%. The galactan gave no precipitate with the May[4] alkaline copper reagent and did not gel with borax.[15]

A 3% solution of the galactan in 0.39 *N* H_2SO_4 was hydrolyzed under reflux (98°). Polarimetric data indicated a first order reaction, $k = 0.37 \pm 0.03$, with no apparent trend in the observed variations. The final rotation was $[\alpha]^{27}D$ +71° (basis D-galactose) which rose to +75° on treatment with the above-described mono-bed ion exchange resin. The accepted value for D-galactose is $[\alpha]^{27}D$ +78°. The acid hydrolyzate of the galactan was investigated by crystallization methods for the possible presence of D,L-galactose. None was found but two types of crystals were obtained which were established as the anomeric forms of D-galactose by comparison with authentic specimens.

O-Triacetylpneumogalactan.—Freshly precipitated pneumogalactan (0.500 g.) was acetylated with pyridine (11 ml.) and acetic anhydride (15 ml.) for 16 hr. at room temperature followed by 10 min. at 105–110°. The product was isolated by pouring the reaction mixture into water; yield 0.720 g. (80%), m.p. 187–190°, $[\alpha]^{24}D$ −28.4° (*c* 6.8, chloroform). The amorphous, colorless solid was soluble in chloroform and pyridine but was insoluble in acetone, alcohol, ether and water.

Anal. Calcd. for $C_6H_7O_5(CH_3CO)_3$: CH_3CO, 44.8. Found[16]: CH_3CO, 43.

Biologic Breakdown of Pneumogalactan.—An increase of 12% in reducing power (determined by the method of Nelson[17] using the Shaffer–Somogyi reagent 60[18] was obtained on digesting the purified material with a galactosidase preparation from sprouted alfalfa seed[19] employed as a 2.5% extract of the defatted tissue at *p*H 4.4 (citrate–phosphate buffer). This preparation showed strong hydrolyzing activity on a preparation of mixed methyl α- and β-D-galactopyranosides. Negative results with the galactan were obtained with: extracts of lung, liver, kidney, duodenum, spleen, pancreas, guar bean, brewers yeast; with crude preparations of the enzymes emulsin, α-amylase, β-amylase, maltdiastase; and the commercial enzyme preparations Clarase-300, Rohm and Haas AP-19, Rohm and Haas Pectinol-100D and Rhozyme S; likewise with a purified β-D-galactosidase kindly tested by Dr. S. A. Kuby of the Institute for Enzyme Research of The University of Wisconsin at Madison.

An unidentified soil microörganism was capable of utilizing the purified galactan for growth. Repeated transfers followed by streaking on agar and culturing a single colony yielded a Gram negative cocco-bacillus. A sterile, lyophilized preparation of this organism has been made and stored. The data of Fig. 3 suggest that the process may be an adaptive one.

Tri-O-methylpneumogalactan.—Modifications of the general technique of Hirst and Jones[7] were employed. A thallous hydroxide solution was prepared by heating 3.3 g. of barium hydroxide octahydrate with 5.0 g. of thallous sulfate in 50 ml. of water for 30 min. All operations were performed in subdued light or in light-guarded vessels. The filtered solution was cooled to 0–5° (ice-bath) and added at this temperature under nitrogen to a stirred and cooled (0–5°) solution of 500 mg. of purified pneumogalactan in 30 ml. of water. The mixture was maintained for 1 hr. at 0–5° and then at room temperature for 30 min. A precipitate was removed by decantation. A further quantity of thallous salt was obtainable by adding acetone to the decantate (250 ml. final total volume) followed by centrifugation. Thallium may be recovered from the supernatant by carbonation. The combined precipitates of thallium salts were then refluxed with 25–30 ml. of methyl iodide for 6 hr. and the methyl iodide was subsequently removed under reduced pressure. The resultant solid mixture was treated with 30 ml. of water and the resultant suspension was again

(9) *Cf.* ref. 3 for literature citations.

(10) E. L. Hirst, J. K. N. Jones and W. O. Walder, *J. Chem. Soc.*, 1225 (1947).

(11) Preliminary experimental work was performed in this Laboratory by Dr. Rex Montgomery.

(12) We are indebted to Hoffmann-La Roche, Inc., Nutley, New Jersey, for this material.

(13) A 23/32 Nojax casing, a product of The Visking Corp., Chicago, Illinois.

(14) A product of the Resinous Products Division of the Rohm and Haas Co., Philadelphia, Pennsylvania.

(15) R. Hart, *Ind. Eng. Chem., Anal. Ed.*, **2**, 329 (1930).

(16) R. W. Kerr, "Chemistry and Industry of Starch," Academic Press, Inc., New York, N. Y., 2nd ed., 1950, p. 683.

(17) N. Nelson, *J. Biol. Chem.*, **153**, 375 (1944).

(18) P. A. Shaffer and M. Somogyi, *ibid.*, **100**, 708 (1933).

(19) S. Veibel in J. B. Sumner and K. Myrbäck (editors), "The Enzymes," Vol. I, Part 1, Academic Press, Inc., New York, N. Y., 1950, p. 624.

methylated with thallous hydroxide and methyl iodide as described above. The second solid mixture was treated with water and the canary yellow thallous iodide was removed by centrifugation and washed with water. The solids obtained on solvent removal under reduced pressure from the aqueous solution and washings were then suspended in 15–20 ml. of methyl iodide and refluxed for 6 hr. with 28 g. of silver oxide.[8] The silver residues were removed by filtration and washed successively with hot chloroform, methanol and acetone. The solids obtained on solvent removal under reduced pressure from the combined methyl iodide solution and extracts were submitted to three more such methylations. The final methylated product was completely soluble in methyl iodide and chloroform and the latter solvent was employed as the sole extracting agent in the last methylation. The final combined methyl iodide solution and the chloroform extracts were freed of silver ion by treatment with hydrogen sulfide and the methylated product was obtained on solvent removal under reduced pressure as a frothed, light yellow solid; yield 260 mg., $[\alpha]^{26}D$ −54° (*c* 0.8, chloroform).

Anal. Calcd. for $C_6H_7O_5(OCH_3)_3$: OCH_3, 45.5. Found: OCH_3, 44.

Identification of the Products of Methanolysis and Hydrolysis of Tri-O-methylpneumogalactan.—Tri-O-methylpneumogalactan (100 mg.) was dissolved in 20 ml. of anhydrous methanol containing 1% hydrogen chloride and heated in a sealed tube at 98° for 15 hr. The cooled tube was then opened, 20 ml. of water added, the methanol removed by boiling and the resultant aqueous acid solution was heated at 98° for 3 hr. Chloride ion was removed from the cooled hydrolyzate with silver carbonate and any silver ion with hydrogen sulfide. Solvent was removed under reduced pressure to yield a sirup.

Portions of the above sirup were subjected to descending paper chromatography,[20] following the general technique of Hirst, Hough and Jones,[21] employing butanol–water development and Tollens reagent as indicator. Three spots of approximately the same order of size and intensity were found and were identified as 2,4-di-O-methyl-D-galactose, 2,3,4-tri-O-methyl-D-galactose and 2,3,4,6-tetra-O-methyl-D-galactose by comparison with concurrently run authentic specimens.[22]

An amount of 90 mg. of the above hydrolyzate was heated for 6 hr. in a sealed tube at 98° with 1 ml. of aniline (freshly distilled under reduced pressure) and 5 ml. of abs. ethanol. The cooled tube was opened and the sirup obtained on solvent removal was dissolved in benzene (thiophene-free) and chromatographed on a 150 × 35 (i.d.) mm. column of Magnesol[23]–Celite[23] (5:1 by wt.) employing 350 ml. of benzene as developer. The three widely separated zones, located by the alkaline permanganate indicator[23] on the extruded column, were sectioned and eluted with ethanol. Crystallization was effected with the same solvent. From the top zone there was obtained 2,4-di-O-methyl-D-galactose anilide of m.p. 214–217° (cor.); from the middle zone 2,3,4-tri-O-methyl-D-galactose anilide of m.p. 167–168° (cor.); and from the bottom zone 2,3,4,6-tetra-O-methyl-D-galactose anilide of m.p. 192–194° (cor.), $[\alpha]^{24}D$ −64° → +36° (*c* 0.5, acetone). Mixed melting points with authentic samples[22] were undepressed in each case. Melting points were taken on the Fisher–Johns apparatus. Accepted[24] values are, respectively: 216°,[25] 167°,[25] 169°,[26] 192°,[25,27] and −77° → +38°.[28]

(20) Acknowledgment is made to Dr. G. N. Kowkabany of this Laboratory for advice and assistance in the techniques of paper chromatography.

(21) E. L. Hirst, L. Hough and J. K. N. Jones, *J. Chem. Soc.*, 928 (1949).

(22) We are indebted to Professors D. J. Bell (Cambridge), E. L. Hirst (Edinburgh), F. Smith (Minnesota), and M. Stacey (Birmingham) for kindly furnishing this material.

(23) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

(24) D. J. Bell, *Advances in Carbohydrate Chem.*, **6**, 11 (1951).

(25) F. Smith, *J. Chem. Soc.*, 1724 (1939).

(26) D. McCreath and F. Smith, *ibid.*, 387 (1939).

(27) W. N. Haworth and Grace C. Leitch, *ibid.*, **113**, 198 (1918).

(28) J. C. Irvine and D. McNicoll, *ibid.*, **97**, 1454 (1910).

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Reactions of Fatty Materials with Oxygen. XII. New Method for Concentrating Long-chain Peroxides[2,3]

BY JOSEPH E. COLEMAN, H. B. KNIGHT AND DANIEL SWERN

RECEIVED APRIL 25, 1952

Published procedures for the concentration of peroxides from autoxidized methyl oleate are generally small-scale procedures, they are tedious and time-consuming, and yields are low and difficult to duplicate. By precipitation of the non-peroxidic portion of methyl oleate autoxidation mixtures (containing 4–37% peroxides) as urea complexes, concentrates containing 70–90% peroxides have been isolated from the filtrates in 50–95% yields. The three isolation techniques developed are applicable on a large laboratory scale, no specialized equipment or chemicals are required, temperatures in the range of room temperature to the boiling point of methanol are employed, and the procedures are readily duplicated. Preliminary study indicates that the new techniques are applicable to the concentration of peroxides from autoxidized methyl elaidate and polyunsaturated acids.

Concentrating long-chain peroxides is one of the most important and difficult problems in studies on the autoxidation of fats and compounds derived from them. Although a few procedures have been published[4–8] to accomplish this, with the exception of the recent work on methyl linoleate hydroperoxide[8a] the techniques are generally tedious, they are small-scale operations, frequently yields are low, and the degree of concentration is usually not high. In concentrating peroxides formed during autoxidation of methyl oleate, some difficulty has been experienced in duplicating published procedures.

In view of these inadequacies and the importance of the peroxides from autoxidized methyl oleate in reaction mechanism and other investigations being

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) For paper XI, see *J. Am. Oil Chemists' Soc.*, **29**, 44 (1952).

(3) Presented in part at the Meeting-in-Miniature of the Philadelphia Section of the American Chemical Society, January 18, 1951, and at the Spring Meeting of the American Chemical Society, Boston, Massachusetts, April 5, 1951.

(4) E. H. Farmer and D. A. Sutton, *J. Chem. Soc.*, 119 (1943).

(5) S. Bergström, *Arkiv Kemi, Mineral. Geol.*, **21A**, No. 14, 1 (1945).

(6) J. L. Bolland and H. P. Koch, *J. Chem. Soc.*, 445 (1945).

(7) C. E. Swift, F. G. Dollear and R. T. O'Connor, *Oil and Soap*, **23**, 355 (1946).

(8) L. R. Dugan, Jr., B. W. Beadle and A. S. Henick, *J. Am. Oil Chemists' Soc.*, **25**, 153 (1948).

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