[CONTRIBUTION FROM THE FRUIT AND VEGETABLE CHEMISTRY LABORATORY, WESTERN UTILIZATION RESEARCH BRANCH, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Chemical Composition of Lemon Oil. I. Isolation of a Series of Substituted Coumarins[1]

BY W. L. STANLEY AND S. H. VANNIER

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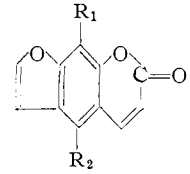
Seven substituted coumarin compounds have been isolated from domestic cold-pressed lemon oil by chromatographic separation on a column of powdered silicic acid. The identity of four of the compounds has been established, *viz.*, 5-geranoxypsoralen, 5,7-dimethoxycoumarin, 5-geranoxy-7-methoxycoumarin and byakangelicin. A fifth compound has been tentatively identified as 8-geranoxypsoralen, the geranyl group still being in doubt. The remaining two compounds were recovered in too small a quantity for analysis. However, they appear, from comparison of ultraviolet spectra, to be related to 5-geranoxypsoralen and 5-geranoxy-7-methoxycoumarin.

The presence of coumarin compounds in various citrus oils has been well established. Thus, for example, 5,7-dimethoxycoumarin, 5-methoxypsoralen, 5-hydroxypsoralen and 5-geranoxypsoralen have been isolated from oil of bergamot[2]; 5,7-dimethoxycoumarin, 5-geranoxy-7-methoxycoumarin and 5,8-dimethoxypsoralen from lime oil[3]; auraptene from orange oil[4]; and 7-hydroxycoumarin from grapefruit oil.[9] Also, 5,7-dimethoxycoumarin (limettin)[5,6] and an unidentified coumarin[7] have been reported in lemon oil.

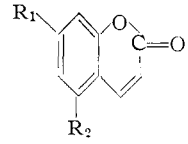
The present study was undertaken as part of a comprehensive investigation of the composition of lemon oil. By chromatography of whole cold-pressed lemon oil on a silicic acid column, seven crystalline solids were obtained. The ultraviolet spectra in neutral solution (Fig. 1)[3,8,9] and chemical properties indicated they were substituted coumarins. Furthermore, on addition of aluminum chloride and caustic soda to their cold alcoholic solution, there was no bathochromic shift in the spectral absorption. It was therefore apparent that the compounds did not contain free phenolic hydroxyl groups. All seven compounds gave a negative magnesium–hydrochloric acid test for flavones.

The spectra of II, IV and VI were closely similar to those of the 5,7-hydroxy and alkoxy coumarins (Fig. 1). Analyses of VI established the empirical formula $C_{11}H_{10}O_4$ and the presence of two methoxyl groups. The melting point, 146–147°, indicated the identity of this compound with the previously reported 5,7-dimethoxycoumarin. It was identical with material isolated from lime oil and oil of bergamot.

Compound II contained one methoxyl group. It was cleaved by mild acid treatment, indicating the presence of an allylic ether linkage. The phenol VIII thus produced was methylated with diazomethane and the product found to be identical with VI, 5,7-dimethoxycoumarin. The compound



I, R_1 = H, R_2 = $OC_{10}H_{17}$
III, R_1 = H
R_2 = OCH_2—CH = $C(CH_3)_2$(?)
V, R_1 = $OC_{10}H_{17}$; R_2 = H
VII, R_1 = OCH_2—CHOH—COH $(CH_3)_2$
R_2 = OCH_3
IX, R_1 = H; R_2 = OH
X, R_1 = H; R_2 = OCH_3
XI, R_1 = H; R_2 = $OCOCH_3$
XII, R_1 = OH; R_2 = H
XIII, R_1 = $OCOCH_3$; R_2 = H
XIV, R_1 = OCH_3; R_2 = H



II, R_1 = OCH_3; R_2 = $OC_{10}H_{17}$
IV, R_1 = OCH_3;
R_2 = OCH_2—CH = $C(CH_3)_2$(?)
VI, R_1 = R_2 = OCH_3
VIII, R_1 = OCH_3; R_2 = OH

7-methoxy-5-geranoxycoumarin was then isolated from lime oil in the manner similar to that described by Caldwell and Jones[3] and found to be identical with II.

Compound IV was not isolated in amounts sufficient for elemental analysis. However, its ultraviolet spectrum suggested that it was also a 5,7-dialkoxycoumarin. Its R_f value, intermediate between that of II and VI, suggested that it is possibly a lower isoprene homolog of II, *viz.*, 5-γ,γ-dimethylallyloxy-7-methoxycoumarin. Such an allyl ether group is present in brayleyanin.[10]

The ultraviolet spectra of I and III were similar to the spectrum reported for 5-methoxypsoralen[9] (Fig. 1). Compound I did not contain a methoxyl group and was hydrolyzed readily with acids to give a phenol IX. This phenol gave a product X which was identical with authentic 5-methoxypsoralen.[11] Consideration of these data supported the identity of I with 5-geranoxypsoralen. This identity was confirmed by direct comparison of I

(1) Presented in part before the Symposium on Chemistry in the Citrus Fruit Industry at the Miami Meeting of the American Chemical Society, April, 1957.

(2) E. Späth and P. Kainrath, *Ber.*, **70B**, 2272 (1937).

(3) A. G. Caldwell and E. R. H. Jones, *J. Chem. Soc.*, 540 (1945).

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(9) D. G. Crosby, Doctoral Thesis, 1954, Calif. Inst. of Technology.

(10) L. Anet, G. K. Hughes and E. Ritchie, *Austral. J. Sci.*, **A2**, 508 (1949).

(11) Samples of 5-methoxypsoralen and 8-γ,γ-dimethylallyloxypsoralen were kindly supplied by Dr. T. Soine, Univ. of Minnesota.

with authentic 5-geranoxypsoralen isolated from oil of bergamot.[2,11]

An insufficient amount of III was isolated for analytical study. From chromatographic behavior and similarity of ultraviolet spectra with that of I, it may be a lower homolog of I.

Compound V was isomeric with I. It did not contain a methoxyl group. Acid hydrolysis of V gave a phenol XII, the acetate of which XIII had an ultraviolet spectrum closely similar to that of psoralen[9] (Fig. 2). Since Nakabayshi[12] has shown that the spectra of the acetates of phenolic coumarins resemble the spectrum of coumarin, it was apparent that V was probably a mono-ether of psoralen. This was confirmed by preparation of the mono-ether XIV of the phenol XII. Direct comparison of this methyl ether with 8-methoxypsoralen[13] showed them to be identical. Compound V is, therefore, an 8-alkoxypsoralen. The C_{10} allylic alkoxy group, by analogy with other compounds, is probably geranyl, but this has not been proved.

Compound VII, m.p. 119–123°, had an ultraviolet spectrum (Fig. 1) similar to that reported for 5,8-dimethoxypsoralen.[9] It was optically active, having an $[\alpha]^{25}D$ 25.61°, and did not migrate on chromatostrips with hydrophobic solvents. Noguchi[14] reported that the 5,8-diether of psoralen (byakangelicin) melts at 125°, forms a monohydrate melting at 117–118° and has an $[\alpha]^{25}D$ 24.62. Subsequently, direct comparison of VII with an authentic sample of byakangelicin[15] indicated they were identical.

Experimental

Chromatographic Fractionation of Lemon Oil.—A 300-g. sample of domestic cold-pressed lemon oil was added to a column of silicic acid 8 cm. in diameter and 25 cm. long prepared from a slurry in hexane.[16] When the oil had penetrated the column, hexane was added and the eluted solvent leaving the column was collected in a fraction cutter (about 20 ml. per tube). Every fifth tube from the fraction cutter was tested for unsaturation with chromatostrips[17] developed with 15% ethyl acetate in hexane and sprayed with a fluorescein–bromine test reagent.[18] When it was observed by this test that the mixture of unsaturated hydrocarbons (chiefly limonene) had passed through the column, a solution of 1% ethyl acetate in hexane was added, followed by gradually increasing amounts of ethyl acetate in hexane, and finally by a solution of 10% ethanol in ethyl acetate. After removal of the terpene hydrocarbons, the fractions were tested by development on chromatostrips containing small amounts of luminescent mineral phosphors. The developed strips were examined under ultraviolet light (maximum emission at 253 mμ) for fluorescent compounds and for compounds capable of absorbing the rays of the exciting illumination. These latter compounds appeared as purple shadows on a yellow background. Compounds II, IV and VI fluoresced a brilliant blue, and I, III, V and VII appeared as purple spots. The strips were also tested for carbonyl

(12) T. Nakabayashi, T. Tokoroyama, H. Miyazaki and S. Isono, *J. Pharm. Soc. Japan*, **73**, 669 (1953); *C. A.*, **47**, 10348e (1953).

(13) A sample of 8-methoxypsoralen was kindly supplied by Dr. H. E. Parker of the Paul D. Elder Co. who obtained it from the Egyptian Ammi Majus plant.

(14) T. Noguchi and M. Kawanami, *J. Pharm. Soc. Japan*, **59**, 755 (1939); *C. A.*, **34**, 2346 (1940).

(15) Samples of byakangelicin and byakangelicol were kindly supplied by Dr. D. G. Crosby of Carbide and Carbon Chemicals Co., who obtained his material from Dr. Noguchi.

(16) J. M. Miller and J. G. Kirchner, *Anal. Chem.*, **24**, 1480 (1952).

(17) J. M. Miller and J. G. Kirchner, *ibid.*, **26**, 2002 (1954).

(18) J. G. Kirchner, J. M. Miller and G. J. Keller, *ibid.*, **23**, 420 (1951).

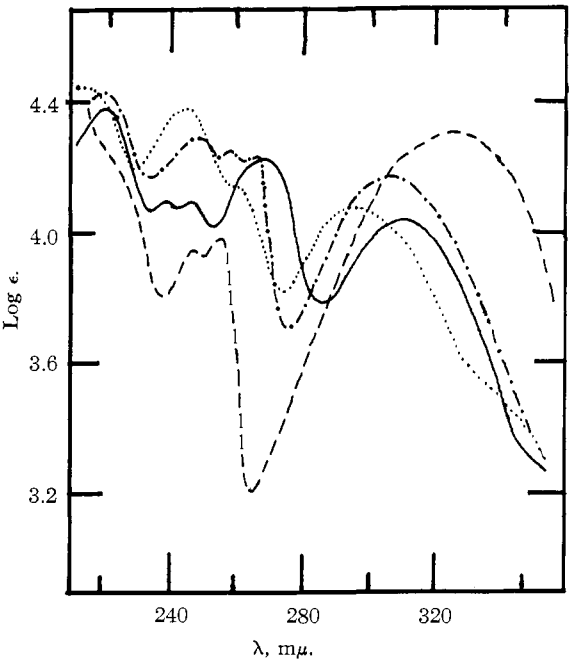

Fig. 1.—Ultraviolet spectra of coumarin compounds from lemon oil: –.–.–.–.–.–.–, 5-geranoxypsoralen (I) in absolute ethanol. Also characteristic for 5-geranoxypsoralen from oil of bergamot, 5-methoxypsoralen from oil of bergamot and synthetic from I, and unknown compound III. – – – – – – –, 5-geranoxy-7-methoxycoumarin (II) in absolute ethanol. Also characteristic for 5,7-dimethoxycoumarin (VI) and unknown IV. . . . . , 8-Geranoxypsoralen (V) in absolute ethanol. Also characteristic for 8-methoxypsoralen[13] and 8-γ,γ-dimethylallyloxypsoralen.[11] ————, Byakangelicin (VII). Also characteristic for 5,8-dimethoxypsoralen,[9] byakangelicol[14] and 5,8-dimethoxypsoralen from lime oil.

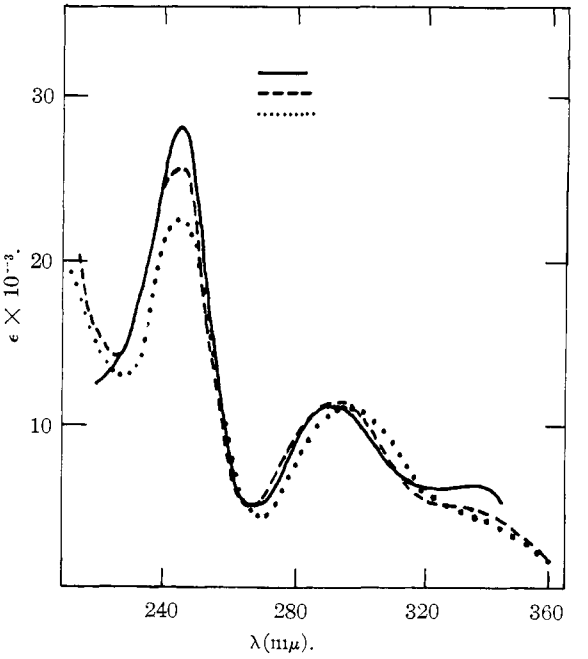

Fig. 2.—Ultraviolet absorption spectra in absolute ethanol: ————, psoralen; – – – – – – –, 8-acetoxypsoralen; . . . . . , 5-acetoxypsoralen.

compound by spraying with acidified 2,4-dinitrophenylhydrazine in ethanol and *o*-dianisidine in glacial acetic acid. The 1,037 individual fractions were reduced to 25 composites by combining tubes containing material that behaved under ultraviolet light and reacted with test reagents in the same manner and had similar R_f values. The composites were reduced to 3–5 ml. (with the exception of composite 1 which contained limonene and other hydrocarbons and represented about 85% of the original oil) by flashing off solvent under vacuum in a stream of nitrogen. The composites were stored at 5° and those depositing crystals were then filtered and the crystalline products purified by recrystallization. Table I summarizes the recoveries of crystalline coumarins and the R_f values for these compounds on silicic acid coated chromatostrips. The total amount of coumarins recovered from lemon oils by this technique averages approximately 0.38% by weight. Melting points were determined on the Kofler block.

TABLE I

DATA ON COUMARIN COMPOUNDS FROM LEMON OIL

Compd. from lemon oil	Recovery, mg./100 g. oil	R_f value[a]	Compd. from lemon oil	Recovery, mg./100 g. oil	R_f value[a]
I	90	0.68	V	59.3	0.40
II	116	.64	VI	53.2	.25
III	2.5	.57	VII	9.0	.00
IV	3.0	.50			

[a] R_f values determined on silicic acid chromatostrips[15] by capillary ascent with 25% ethyl acetate in hexane (v./v.).

Isolation of 5-Geranoxypsoralen (I).—The product crystallizing from composite 10 at refrigerator temperatures (5°) was washed on a filter with cold petroleum ether and recrystallized from petroleum ether to yield the analytical sample (long needles) of 5-geranoxypsoralen, m.p. 53.5–54.5°.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.5; H, 6.55; MeO–, 0.0. Found: C, 74.5; H, 7.14; MeO–, 0.26.

5-Hydroxypsoralen (IX).—Two drops of sulfuric acid was added with stirring to a solution of 5-geranoxypsoralen (0.490 g.) in glacial acetic acid (5 ml.). A tan precipitate formed in a few minutes and the reagent solution turned light brown. The reaction mixture was stirred at room temperature for 1 hr., cooled to about 10° and filtered with suction. The melting point of the crude material (0.278 g.) was approximately 270°. A series of solvents was tried in attempts to recrystallize the phenol, but only amorphous nodules were produced. Minute shiny platelets were obtained from ethanol but with poor recovery.

Preparation of 5-Methoxypsoralen (X).—A solution of the crude 5-hydroxypsoralen (0.040 g.), dimethyl sulfate (1 ml.) and anhydrous potassium carbonate in acetone (dried over anhydrous potassium carbonate) (20 ml.) was refluxed 3 hr. and allowed to cool. About 50 ml. of water was added in increments and the fine needles which formed were filtered off and taken up in ethanol, whereupon frond-like clusters of thin platelets were obtained (0.011 g.), m.p. 185–192°. A mixture of the product with 5-methoxypsoralen from bergamot oil (m.p. 186.5–188°) had m.p. 186–187°, with authentic material from wild parsnip, m.p. 186–187°.[11]

5-Acetoxypsoralen (XI).—The acetate was prepared from 5-hydroxypsoralen with an excess of acetic anhydride and freshly fused sodium acetate. Fine colorless needles were obtained from methanol, m.p. 177–179°.

Anal. Calcd. for $C_{13}H_8O_5$: C, 63.9; H, 3.30. Found: C, 64.0; H, 3.30.

Isolation of 5-Geranoxy-7-methoxycoumarin (II).—During the removal of solvent from composite 12, white crystals were deposited. The crystals redissolved when the concentrate was warmed but again appeared at room temperature. On recrystallization from petroleum ether–ethyl acetate fine colorless needles (0.348 g.) were obtained, m.p. 86–87°. The melting point of a mixture of II with 5-geranoxy-7-methoxycoumarin isolated from lime oil was not depressed. By comparison of infrared spectra the two compounds were judged to be identical.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.15; H, 7.35; 1 MeO–, 9.4. Found: C, 72.7; H, 7.33; MeO–, 9.5.

7-Methoxy-5-hydroxycoumarin (VIII).—A sample of 7-methoxy-5-geranoxycoumarin (0.519 g.) was dissolved in glacial acetic acid (5 ml.), allowed to react with two drops of concentrated sulfuric acid with stirring for 1.5 hr. The product phenol (0.228 g.), m.p. 227–228°, gave, with ferric chloride, a yellow-green solution darkening with time, and with 1% sodium nitrate in concentrated sulfuric acid a bright yellow solution which turned orange-red when the solution was made alkaline with sodium hydroxide.

Preparation of 5,7-Dimethoxycoumarin.—To a methanol solution of 7-methoxy-5-hydroxycoumarin (0.065 g.) was added an ethereal solution of diazomethane. Recrystallized from acetone–hexane the product had m.p. 145–146°. The mixed melting point with compound VI (5,7-dimethoxycoumarin) was not depressed. Their infrared spectra were identical.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89; 2 MeO–, 30.10. Found: C, 63.5; H, 5.11; MeO–, 29.5.

Isolation of Compound III.—Composite 14 obtained from fractions 360 to 365 was concentrated under vacuum to about 1 ml. On standing overnight at about 5° the concentrate deposited crystals (7.5 mg.) which, on recrystallization from hexane–ethyl acetate (colorless blades), melted at 94–96°.

Isolation of Compound IV.—Composite 16 from fractions 380 to 405 was reduced to about 2 ml. under vacuum. On standing overnight at 5°, the concentrate deposited crystals (9 mg.). This material was recrystallized from hexane–ethyl acetate, yielding nodules, m.p. 90–92°.

Isolation of 8-Geranoxypsoralen (V).—Composite 17, made up of fractions 406 to 475, was reduced to about 5 ml. by flashing off solvent under vacuum in a stream of nitrogen. The concentrate was allowed to stand overnight at 5° whereupon a copious deposit of crystals was obtained (0.178 g.). Recrystallized from hexane–ethyl acetate this material (long blades) melted at 59–60°.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.5; H, 6.55; MeO–, 0.0. Found: C, 74.7; H, 6.75; MeO–, 0.32.

Preparation of 8-Hydroxypsoralen (XII).—A sample of 8-geranoxypsoralen (V) (0.275 g.) was dissolved in glacial acetic acid (4 ml.), and a drop of concentrated sulfuric acid was added with stirring. A precipitate began to appear within five minutes. Stirring was continued at room temperature for 1 hr. whereupon the solution was cooled to about 10°, the solid was filtered off and washed on the filter with a small amount of ethyl acetate followed by cold ethyl ether (product (0.115 g.).

Preparation of 8-Methoxypsoralen (XIV).—The methyl ether XIV of the phenol XII was prepared by the addition of an ethereal solution of diazomethane to a methanol solution of the phenol. Recrystallized from hexane–acetone solution the product (long hollow needles) had m.p. 145–146°. The melting point of a mixture with an authentic sample of 8-methoxypsoralen was not depressed.[13] A comparison of the infrared spectra of the two compounds indicated that they were identical.

Anal. Calcd. for $C_{12}H_8O_4$: C, 66.7; H, 3.73. Found: C, 66.5; H, 3.87.

Preparation of 8-Acetoxypsoralen (XIII).—A mixture of the 8-hydroxypsoralen (XII) (0.019 g.), acetic anhydride (1.0 ml.) and freshly fused sodium acetate (0.01 g.) was heated in a water-bath for 1 hr. The mixture was allowed to cool and water was gradually added with shaking until the acetic anhydride had hydrolyzed. The pale yellow solid that appeared was filtered off and dried *in vacuo* (0.014 g.). Recrystallized from methanol the pale yellow prisms melted at 177–180°.

Recovery of 5,7-Dimethoxycoumarin (VI).—Fractions 500 to 605 were composited (composite 18) and reduced under vacuum to about 6 ml. During concentration a crystalline solid appeared. The residue mixture was warmed, enough warm ethyl acetate added to dissolve the crystals and the clear solution was allowed to crystallize at room temperature. The product (0.160 g.) recrystallized from ethyl acetate had m.p. 146–147°.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89; 2 MeO–, 30.10. Found: C, 64.0; H, 5.00; MeO–, 29.9.

Recovery of Byakangelicin (VII).—During the final development of the chromatogram with a solution of 10% (v./v.) ethanol in ethyl acetate, material appeared in the chromatostrip tests which indicated the possible presence of a coumarin. Fractions 937 to 1037 were composited

(composite 25) and concentrated to about 3 ml. under vacuum. After storage at 5° a pale yellow crystalline product formed which was filtered off (0.027 g.). The material recrystallized from ethanol melted at 119 to 123° and had an $[\alpha]^{25}D$ of 25.61 in pyridine. A negative Molisch test for sugars and glycosides was obtained. In alcoholic solution the compound gave no coloration when warmed with a chip of magnesium turnings and concentrated hydrochloric acid (a negative test for flavones). The mixed melting point of VII with an authentic sample of byakangelicin[15] was not depressed, and a comparison of the infrared spectra of the two compounds indicated they were identical.

Anal. Calcd. for $C_{17}H_{18}O_7$: C, 61.1; H, 5.43; 1 MeO–, 9.3. Found: C, 61.6; H, 5.59; MeO–, 8.9.

Acknowledgments.—The authors wish to thank Leonard Jurd and R. W. Horowitz of this Laboratory and T. A. Geissman of the University of California in Los Angeles for their helpful suggestions. They are also indebted to Fred Stitt and Glen Bailey, Western Utilization Research Branch, U.S.D.A., Albany, California, for measurements and interpretation of infrared spectra and to L. M. White of the same laboratory for analytical determinations.

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[CONTRIBUTION FROM THE RESEARCH DIVISION OF ABBOTT LABORATORIES]

The Preparation of Some Organic Diazides

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The polymethylene diazides containing five to ten carbon atoms and examples of other classes of organic diazides have been prepared through displacement of halogen or arenesulfonoxy groups by the azide ion.

A recent review[1] of the literature on organic azides lists no diazidoalkanes other than 1,2-diazidoethane.[2] We have prepared a series of eight aliphatic diazides containing five to ten carbon atoms for pharmacologic testing as hypotensive agents. Examples of the oxa and aza analogs of these diazides were also synthesized, as was α,α'-diazido-*p*-xylene. Pharmacologic studies in these laboratories have shown that some of these diazides possess marked hypotensive action in normal animals.[3]

The treatment of polymethylene dibromides with sodium azide in aqueous methanol[4] generally gave the corresponding diazides in good yield.

$$Br—(CH_2)_n—Br + 2NaN_3 \rightarrow N_3—(CH_2)_n—N_3 + 2NaBr$$

Replacing one or both primary alkyl bromide groups in the reactant by secondary groups gave progressively lower yields of product. Table I summarizes the data obtained from these diazidoalkanes. α,α'-Diazido-*p*-xylene, in which an aromatic ring joins two azidoalkyl groups, was obtained in the same manner from α,α'-dichloro-*p*-xylene and sodium azide.

The displacement of an arenesulfonoxy group by azide ion, a method recently applied to the preparation of cyclohexyl azide,[5] is an effective alternate method of synthesis. The benzenesulfonic acid or *p*-toluenesulfonic acid esters of 1,6-hexanediol and 1,7-heptanediol were thus converted to the corresponding diazidoalkanes.

$$Ar—SO_3—(CH_2)_n—O_3S—Ar + 2NaN_3 \longrightarrow N_3—(CH_2)_n—N_3 + 2ArSO_3Na$$

Because 1,7-diazidoheptane possesses greater hypotensive potency than its homologs,[3] an isoster, di-3-azidopropyl ether, was prepared by the following reactions.

$$(ClCH_2CH_2CH_2)_2O + 2NaI \longrightarrow (ICH_2CH_2CH_2)_2O$$

$$(ICH_2CH_2CH_2)_2O + 2NaN_3 \longrightarrow (N_3CH_2CH_2CH_2)_2O$$

Treatment of N-methyl- and N-phenyl-N,N-bis-(β-chloroethyl)-amines with sodium azide gave the corresponding amino diazides, one of which was converted to a diazide quaternary ammonium salt.

$$RN(CH_2CH_2Cl)_2 + 2NaN_3 \longrightarrow RN(CH_2CH_2N_3)_2 \xrightarrow{CH_3I} [R(CH_3)N(CH_2CH_2N_3)_2]^+ I^-$$

No fires or explosions were experienced in working with these diazides. However, because of the reported sensitivity to heat of diazidoethane they were regarded as potentially explosive materials and handled accordingly.

Acknowledgment.—We are grateful to Mr. E. F. Shelberg and staff of the Microchemical Department for the analyses reported here.

Experimental

Dibromoalkanes.—With two exceptions these were commercially available. 1,7-Dibromoheptane and 1,8-dibromoöctane were made by the action of anhydrous hydrogen bromide[6] upon the corresponding glycols. The latter compounds were obtained by reduction of methyl or ethyl esters of pimelic and suberic acids with lithium aluminum hydride.[7] In the synthesis of diethyl pimelate from pimelonitrile using alcoholic hydrogen chloride there was obtained, along with the desired ester (75%), **ethyl pimelamate**, m.p. 76–77°, in 4% yield.

Anal. Calcd. for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48; O, 25.64. Found: C, 58.29; H, 9.16; N, 7.47; O, 25.43.

Arenesulfonic Esters.—1,6-Dibenzenesulfonoxyhexane, prepared by a procedure described for alkyl esters,[8] decomposed upon attempted distillation and was purified by crystallization from alcohol which gave crystals melting at 58–60°.

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