suggested eq 5 as the correct expression for the rate of reaction. The k_B value was given by the intercept and the k_B' value from the slope. Various checks have been made at different amine and base concentrations, and in each case the observed rate constants agreed well with those calculated from the reported specific rates.

Acknowledgment. This work was supported by CNR, Rome.

Registry No. 1, 14618-10-1; 2, 929-59-9; 3, 68960-97-4; 4, 76927-70-3; 17a, 31255-11-5; 17b, 70110-27-9; 17c, 76927-71-4; *n*-butylamine, 109-73-9; 1,2-diaminoethane, 107-15-3; 1,3-diaminopropane, 109-76-2; 1,4-diaminobutane, 110-60-1; 1,8-diaminooctane, 373-44-4; *N*-*n*-butyl-2-hydroxy-5-nitro-α-toluenesulfonamide, 76927-72-5; 1,8-dichloro-3,6-dioxaoctane, 112-26-5; 1,14-dichloro-3,6,9,12-tetraoxatetradecane, 5197-65-9; 1,20-dichloro-3,6,9,12,15,18-hexaoxaeicosane, 56930-39-3; potassium phthalimide, 1074-82-4; benzonitrile, 100-47-0; *N*,*N*-dimethylacetamide, 127-19-5; dimethyl sulfoxide, 67-68-5; triphenylphosphine oxide, 791-28-6; hexamethylphosphortriamide, 680-31-9.

Fragmentation of Aryl Alkyl Sulfides. A Simple, One-Pot Synthesis of Polymercaptobenzenes from Polychlorobenzenes

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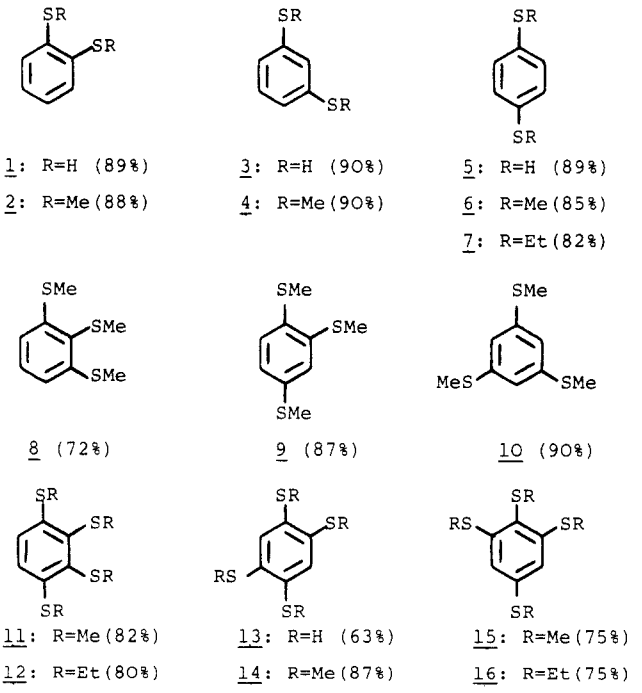
Received December 12, 1980

A simple procedure is described which allows one to prepare polymercaptobenzenes starting from chlorobenzenes. The reactions of all the possible chlorobenzenes with Me_2CHSNa in HMPA give the corresponding (isopropylthio)benzenes which can be cleaved by adding sodium to the reaction mixtures to give the arenethiolates in good yields. In some cases the polymercaptobenzenes were isolated after treatment with acid; in other cases methyl iodide was added to the reaction mixture and poly(methylthio)benzenes were obtained. It is suggested that the (isopropylthio)benzenes react with sodium to give the corresponding radical anions which fragment at the sulfur–alkyl bond to give the arenethiolates.

(Alkylthio)benzenes can be easily obtained from the reaction of alkanethiolate anions with polynitro-[1] or halogenonitrobenzenes.[1,2] More conveniently, the same compounds can be prepared from polychlorobenzenes. We have recently reported that the reactions of Me_2CHSNa with di-,[3] tri-, tetra-, penta-, and hexachlorobenzene, in hexamethylphosphoramide, give rise to the complete replacement of chlorine, leading to the corresponding (isopropylthio)benzenes.[4] Similar reactions can be also effected by EtSNa and MeSNa. These reactions, however, require careful control of the reaction conditions because the initially formed (ethylthio)- and (methylthio)benzenes further react with the thiolates to give the products of monodealkylation.[4,5] These dealkylation reactions can find useful applications. We have recently reported a convenient synthesis of aromatic thiols from unactivated aryl halides by reaction with excess sodium methanethiolates; in this case the initially formed methyl aryl sulfides are dealkylated by the excess of MeSNa to give good yields of the aromatic thiols.[6]

It is reported in the literature that (alkylthio)benzenes can be cleaved by alkali metals in liquid ammonia,[7] in methylamine[8] or in ether[9] to give aromatic thiols. We report in this paper a very simple and efficient one-pot synthesis of mercaptobenzenes starting from the readily available corresponding chlorobenzenes and using the (isopropylthio)benzenes as intermediate products.

Chart I



Results

The general procedure employed consists of the reaction of chlorobenzenes with Me_2CHSNa in HMPA; the reaction mixtures, containing the (isopropylthio)benzenes,[3,4] are then directly treated, at 100 °C, with excess sodium.

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(2) J. R. Beck and J. A. Yahner, *J. Org. Chem.*, 43, 2048 (1978).
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(5) M. E. Peach and E. S. Rayner, *J. Fluorine Chem.*, 13, 447 (1979).
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(8) W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Am. Chem. Soc.*, 82, 2872 (1960); W. E. Truce and J. J. Breiter, *ibid.*, 84, 1621 (1962).
(9) J. V. Schooten, J. Knotnerus, H. Boer, and P. M. Duinker, *Recl. Trav. Chim. Pays-Bas*, 77, 935 (1958).

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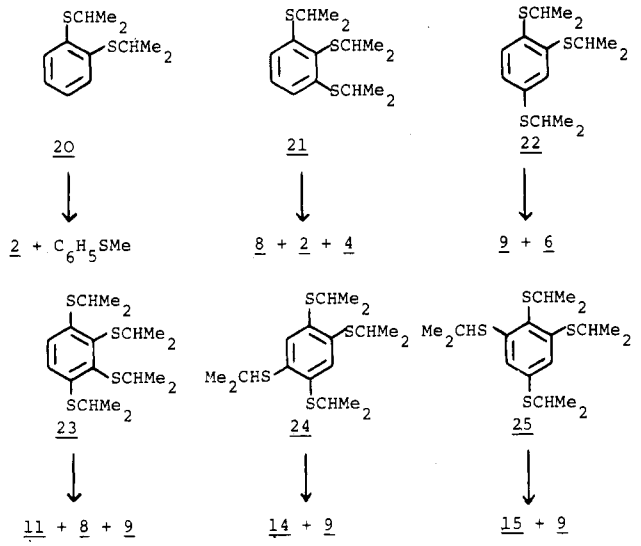
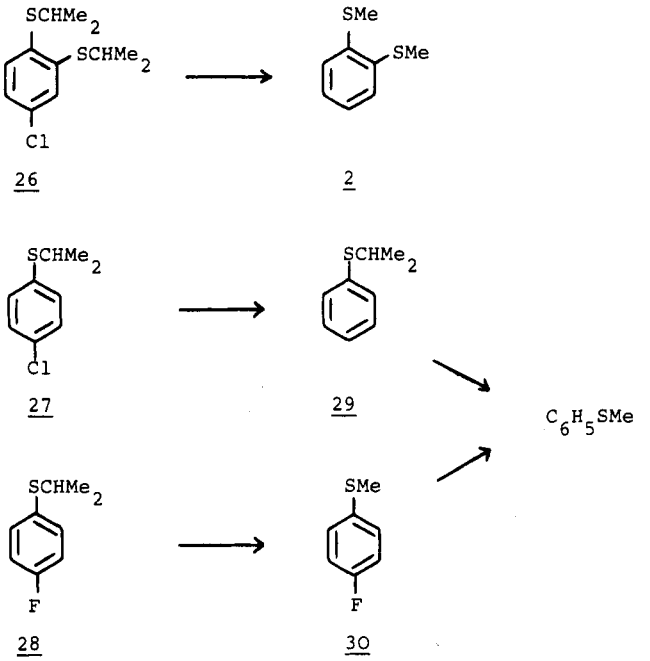
Scheme I



Scheme II



Aromatic thiolates are thus formed according to reactions 1 and 2. Aromatic thiols can be obtained by treatment

$$ArCl + Me_2CHSNa \rightarrow ArSCHMe_2 + NaCl \quad (1)$$

$$ArSCHMe_2 + Na \rightarrow ArSNa + Me_2CH\cdot \quad (2)$$

with acid, or the thiolates can be directly used for further reactions. In order to make the separation and identification of the reaction products easier, methyl iodide was added to the final reaction mixtures and (methylthio)benzenes were obtained.

The mercaptobenzenes and the (alkylthio)benzenes prepared in this way are reported in Chart I; reaction yields, based on isolated products after column chromatography, are indicated in parentheses. In some cases the reaction mixtures were also treated with ethyl iodide, and the poly(ethylthio)benzenes **12**, **16**, and **18** were obtained. In the case of *p*-dichlorobenzene the reaction mixture was treated with ethyl acetate, and *p*-bis(ethylthio)benzene (**7**) was obtained; this represents a further example of the ease with which thiolates can effect the *O*-alkyl cleavage of alkyl esters[10] (eq 3).

$$p\text{-}C_6H_4(SNa)_2 + 2MeCO_2Et \rightarrow 2MeCO_2Na + \underset{\mathbf{7}}{p\text{-}C_6H_4(SEt)_2} \quad (3)$$

When the reaction was carried out on hexachlorobenzene, hexakis(isopropylthio)benzene reacted with sodium and MeI to give hexakis(methylthio)benzene (**19**, 60%) together with a considerable amount of pentakis(methylthio)benzene **17**, 30%), indicating that in this case the cleavage of one aryl–sulfur bond also occurs to a considerable extent. A similar behavior was observed also in other cases. Thus, the (isopropylthio)benzenes **20–25** were cleanly obtained from the reactions of Me_2CHSNa with the corresponding chlorobenzenes;[3,4] however, after the reactions with Na and MeI, the expected products **2**, **8**, **9**, **11**, **14**, and **15**, respectively, were accompanied by small amounts of less substituted (methylthio)benzenes as indicated in Scheme I. The identities of these byproducts were established by their GLC retention times and by their melting points and NMR spectra after separation by column chromatography. In the reaction carried out on C_6HCl_5, $C_6H(SMe)_5$ was formed togehter with small amounts of other compounds; these could not be fully identified, but their GLC retention times corresponded to those of the isomeric tetrakis(methylthio)benzenes.

These dealkylation reactions are not limited to the isopropylthio derivatives, other (alkylthio)benzenes being equally well transformed, by reaction with sodium in HMPA, into the benzenethiolates. Thus, for instance, when **6** is employed as the starting product, compound **7** can be obtained after treatment with EtI; similarly, pentakis(ethylthio)benzene (**18**), by reaction with sodium and MeI, is transformed into the pentakis(methylthio)benzene (**17**).

Some halogeno(alkylthio)benzenes were also treated with Na in HMPA in order to compare the easiness of the cleavage of the carbon–halogen bonds with that of the sulfur–alkyl bond. The reaction mixtures were then treated with MeI. The treatment of 4-chloro-1,2-bis(isopropylthio)benzene (**26**) and of 4-chloro- (**27**) and 4-fluoro(isopropylthio)benzene (**28**) with excess sodium gave rise to the products deriving from reductive dehalogenation and dealkylation, **2** and C_6H_5SMe, respectively (Scheme II). If, however, an insufficient quantity of sodium is employed, **27** gave (isopropylthio)benzene (**29**), and **28** gave the 4-fluoro(methylthio)benzene (**30**); some unreacted **27** and **28** were obviously also present in these experiments.

Discussion

The results described in this paper demonstrate that the procedure now described represents a very efficient and simple method for the synthesis of mercaptobenzenes; very likely this method can be applied also to other aromatic systems. The dealkylations of the (isopropylthio)benzenes and the reactions of the thiolates thus obtained with methyl or ethyl iodide have also some synthetic importance. In this way, in fact, poly(methylthio)- and poly(ethylthio)benzenes can be obtained in high yields; this procedure overcomes the difficulties encountered when the synthesis of these products is carried out by the direct reactions of MeSNa or EtSNa with the polychlorobenzenes[4,5] (see the beginning of the paper) or with the halogenonitrobenzenes.[1]

It seems reasonable to assume that the interaction of the (isopropylthio)benzenes with sodium consists of an electron-transfer from which the radical anions of the thio-

(10) J. C. Sheehan and G. Doyle Daves, Jr., *J. Org. Chem.*, **29**, 2006 (1964); P. A. Bartlett and W. S. Johnson, *Tetrahedron Lett.*, 4459 (1970); G. I. Feutrill and R. N. Mirrington, *Aust. J. Chem.*, **25**, 1731 (1972).

Scheme III

$$ArSR + Na \rightarrow [ArSR]^{-}\cdot Na^{+} \quad (\mathbf{31})$$

$$\mathbf{31} \rightarrow RS^{-}Na^{+} + Ar\cdot \rightarrow ArH \quad (4)$$

$$\mathbf{31} \rightarrow ArS^{-}Na^{+} + R\cdot \quad (\mathbf{32}) \quad (5)$$

ethers, **31**, are formed (Scheme III). As it has also been suggested by Bunnett and Creary,[11] radical anions **31** are considered to be the reactive intermediates through which the fragmentation of the aryl alkyl thioethers occurs. Two possible routes can in principle be open to these radical anions. Fragmentation can involve the aryl–sulfur bond to give the alkanethiolate and an aryl radical (which then abstracts an hydrogen atom) (eq 4) or the alkyl–sulfur bond to give the arenethiolate and an alkyl radical (eq 5). In previous work only this second behavior has been observed[7-9,11] in the case of aryl alkyl sulfides; the cleavage of the aryl–sulfur bond, however, can easily occur with diaryl sulfides.[7-9,11] In the present work both processes (eq 4 and 5) have been observed; the alkyl–sulfur bond cleavage, however, is preferred. The factors controlling the preferred direction of cleavage in the radical anions **31** (eq 5) and in those of unsymmetrically substituted diaryl sulfides have been examined and discussed by Truce[8] and Bunnett[11] and need not to be repeated here. It remains instead to explain why in some of the (isopropylthio)benzenes investigated the fragmentation of **31** involves also the aryl–sulfur bond (eq 4). The results obtained seem to indicate that this occurs simply for steric reasons. As indicated in Scheme I, this process is not observed with 1,3- or 1,4-bis(isopropylthio)benzenes and 1,3,5-tris(isopropylthio)benzene. The aryl–sulfur cleavage occurs whenever at least two alkylthio groups are in the ortho position and becomes important in the crowded $C_6(SCHMe_2)_6$. Thus, the steric relief which the molecules can obtain by the expulsion of an Me_2CHS group is probably responsible for this otherwise unfavorable reaction.

At which step this fragmentation occurs is difficult to say and experimentally complicated to demonstrate; on the basis of the previous discussion, however, it can be supposed that the cleavage of the aryl–sulfur bond takes place in one of the first steps, if not the beginning of the entire process.

What is rather surprising is the fact that the fragmentation does not stop after that the first isopropyl radical has been expelled; on the contrary, the reaction proceeds until all the possible isopropylthio groups have suffered fragmentation. One would expect that once an arenethiolate like **32** has been formed, the electron transfer should become difficult and even prohibitive as the number of fragmentations increases. As a tentative explanation, which, however, has not at present any experimental support, we suggest that, in the reaction medium employed, the arenethiolates are not present as free anions but remain strongly associated with the sodium cation; this would avoid the delocalization of negative charge into the aromatic ring.

Finally, the reactions of the halogeno(isopropylthio)benzenes deserve some comments. Whenever excess sodium is employed, products are obtained in which reductive dehalogenation and fragmentation of the alkyl–sulfur bond have both occurred (See Scheme II). This was already observed in the case of the 1,2,4-tris(isopropylthio)dichlorobenzene, which, on treatment with sodium and methyl iodide, gave 1,2,4-tris(methylthio)benzene (**9**).[4] From the experiments carried out with the *p*-chloro- (**27**) and *p*-fluoro(isopropylthio)benzene (**28**) with difect sodium, it can be said that the carbon–chlorine bond is cleaved more easily than the alkyl–sulfur bond. The carbon–fluorine bond, on the contrary, can be broken with greater difficulty. These results can have some synthetic applications and support the proposal that radical anions are the reactive intermediates in these fragmentation reactions. In fact, from the extensive work of Bunnett on $S_{RN}1$ reactions (in which radical anions are involved as intermediates in the propagation step) it is well-known that in the radical anions of halogenobenzenes carbon–fluorine bonds are more difficult to break than carbon–chlorine bonds.[12]

Experimental Section[13]

All the chlorobenzenes employed in this work were commercial products. Commercial HMPA was used without further purification. *p*-Fluorophenyl isopropyl sulfide,[3] *p*-chlorophenyl isopropyl sulfide,[3] and 4-chloro-1,2-bis(isopropylthio)benzene[1] were prepared as described in the literature.

All the reactions were carried out according to the following general procedure. The (isopropylthio)benzenes were prepared from the reactions of Me_2CHSNa with the corresponding chlorobenzenes (0.01 mol) in HMPA under the conditions already described in our previous works.[3,4]

The progress of the reactions can be easily monitored by TLC. When the transformation is complete (a single product is observed by TLC in every case) the reaction mixture is warmed up at 100 °C. Small pieces of sodium (1.3 atoms for each $SCHMe_2$ group present in the molecule) are then added, and the mixture is stirred until all the sodium was dissolved. The cooled reaction mixtures are then treated with hydrochloric acid, methyl iodide, or ethyl iodide (or $MeCO_2Et$) and, in the last two cases, poured on water. Extraction with ether followed by the usual workup gave a residue which was analyzed by GLC. The various components could be easily separated by column chromatography using mixtures of ethyl ether and petroleum ether as eluant.

In the case of the reactions of **27** and **28** the final mixtures were analyzed by GLC only.

The products obtained in this work are presented in Chart I, in which reaction yields are also reported in parentheses. The physical and NMR data of compounds **6**, **7**, **9**, **15**, and **16** were identical with those already described in our previous work.[1,4] Physical and NMR data for the remaining compounds reported in Chart I are given below.

1,2-Dimercaptobenzene (1): bp 85–87 °C (4 mm) [lit.[7] bp 102 °C (6.5 mm)]; NMR (60 MHz) δ 7.3–6.8 (m, 2 H), 3.6 (s, 1 H).

1,2-Bis(methylthio)benzene (2): bp 92–96 °C (4 mm) [lit.[14] bp 70–80 °C (1 mm)]; NMR (60 MHz) δ 7.2–7.0 (m, 2 H), 2.4 (s, 3 H); sulfone, mp 227–228 °C (lit.[15] mp 225 °C).

1,3-Dimercaptobenzene (3): bp 125–127 °C (18 mm) [lit.[16] bp 123 °C (17 mm)]; NMR (60 MHz) δ 7.2–6.8 (m, 2 H), 3.35 (s, 1 H).

1,3-Bis(methylthio)benzene (4): bp 150–152 °C (18 mm) [lit.[16] bp 149 °C (17 mm)]; NMR (60 MHz) δ 7.1–6.8 (m, 2 H), 2.4 (s, 3 H); sulfone, mp 194–196 °C (lit.[17] mp 196 °C).

1,4-Dimercaptobenzene (5): mp 97–99 °C (lit.[7] mp 97.5–98.5 °C); NMR (60 MHz) δ 7.0 (s, 2 H), 3.4 (s, 1 H).

1,2,3-Tris(methylthio)benzene (8): mp 110–111 °C (lit.[2] mp 111–113 °C); NMR (60 MHz) δ 7.4–6.7 (m, 1 H), 2.4 (s, 2 H), 2.35 (s, 1 H).

(11) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **40**, 3740 (1975).

(12) J. F. Bunnett, *Acc. Chem. Res.*, 11, 413 (1978).

(13) NMR spectra were recorded ($CDCl_3$ solutions) at 60 MHz on a JEOL C60HL or at 90 MHz on a Varian EM 390 instrument. GLC analyses were performed on a Hewlett-Packard 5830 chromatograph with a 20-in., 10% UCW 982 column. Satisfactory elemental analyses were obtained for all new compounds.

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(15) W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, **1821** (1926).

(16) T. Zincke and O. Kruger, *Ber. Dtsch. Chem. Ges.*, **45**, 3468 (1912).

(17) R. F. Twist and S. Smiles, *J. Chem. Soc.*, 1248 (1925).

1,3,5-Tris(methylthio)benzene (10): mp 63–65 °C (lit.[5] mp 61–63 °C); NMR (60 MHz) δ 6.85 (s, 1 H), 2.45 (s, 3 H).

1,2,3,4-Tetrakis(methylthio)benzene (11): mp 108–109 °C (lit.[5] mp 104–106 °C); NMR (60 MHz) δ 7.05 (s, 1 H), 2.45 (s, 3 H), 2.4 (s, 3 H).

1,2,3,4-Tetrakis(ethylthio)benzene (12): oil; NMR (90 MHz) δ 7.15 (s, 1 H), 3.0 (q, 2 H), 2.9 (q, 2 H), 1.4 (t, 3 H, J = 7.5 Hz), 1.25 (t, 3 H, J = 7.5 Hz); mass spectrum, m/e (relative intensity) 320 (20.7, M + 2), 318 (100, M), 289 (25.8, M - C_2H_5), 260 (25.8, M - C_4H_{10}), 245 (36, M - C_5H_{13}), 230 (15.5, M - C_6H_{16}).

1,2,4,5-Tetramercaptobenzene (13): mp 138–141 °C (lit.[18] mp 139–141 °C); NMR (60 MHz) δ 7.25 (s, 1 H), 3.6 (s, 2 H).

1,2,4,5-Tetrakis(methylthio)benzene (14): mp 128–130 °C (lit.[14] mp 125–126 °C); NMR (60 MHz) δ 7.1 (s, 1 H), 2.45 (s, 6 H).

Pentakis(methylthio)benzene (17): mp 103–106 °C (lit.[2] mp 103–105 °C); NMR (90 MHz) δ 6.8 (s, 1 H), 2.55 (s, 3 H), 2.5 (s, 6 H), 2.45 (s, 6 H).

Pentakis(ethylthio)benzene (18): mp 64–65 °C; NMR (90 MHz) δ 6.9 (s, 1 H), 3.1 (q, 2 H), 2.95 (q, 8 H), 1.45 (t, 6 H, J = 7.5 Hz), 1.25 (t, 9 H, J = 7.5 Hz); mass spectrum, m/e (relative intensity) 380 (25, M + 2), 378 (100, M), 349 (20, M - C_2H_5), 320 (36, M - C_4H_{10}), 305 (21.3, M - C_5H_{13}), 290 (9.3, M - C_6H_{16}).

Hexakis(methylthio)benzene (19): mp 87–88 °C (lit.[2] mp 88–90 °C); NMR (60 MHz) δ 2.5 (s).

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Registry No. 1, 17534-15-5; 2, 2388-68-3; 3, 626-04-0; 4, 2388-69-4; 5, 624-39-5; 6, 699-20-7; 7, 17661-83-5; 8, 65516-81-6; 9, 2570-41-4; 10, 2388-71-8; 11, 70648-36-1; 12, 77520-28-6; 13, 20133-21-5; 14, 1846-35-1; 15, 70416-04-5; 16, 70416-05-6; 17, 65516-74-7; 18, 77520-29-7; 19, 58468-22-7; 20, 70398-84-4; 21, 74542-66-8; 22, 70415-95-1; 23, 74542-68-0; 24, 74542-69-1; 25, 70416-07-8; 26, 70416-15-8; 27, 7205-62-1; 28, 702-13-6; 29, 3019-20-3; 30, 371-15-3; 1,2-dichlorobenzene, 95-50-1; 1,3-dichlorobenzene, 541-73-1; 1,4-dichlorobenzene, 106-46-7; 1,2,3-trichlorobenzene, 87-61-6; 1,2,4-trichlorobenzene, 120-82-1; 1,3,5-trichlorobenzene, 108-70-3; 1,2,3,4-tetrachlorobenzene, 634-66-2; 1,2,3,5-tetrachlorobenzene, 634-90-2; 1,2,4,5-tetrachlorobenzene, 95-94-3; pentachlorobenzene, 608-93-5; hexachlorobenzene, 118-74-1; Me_2CHSNa, 20607-43-6; C_6H_5SMe, 100-68-5.

New Flavonoid and Coumarin Derivatives of *Uvaria afzelii*

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Received January 14, 1981

Three new compounds, 2'-hydroxydemethoxymatteucinol (6), 2-hydroxy-7,8-dehydrograndiflorone (7), and uvafzelic acid (9) have been identified in extracts of *Uvaria afzelii*. Their structures were determined mainly from interpretation of the ^{13}C NMR spectral data. 7 was unstable and was rapidly converted to emorydone (8). Four other known compounds, coumarin (3), syncarpic acid (4), demethoxymatteucinol (5), and emorydone (8), were also identified along with the previously reported constituents, vafzelin (1) and uvafzelin (2). The stabilities of 1, 7, and 8 under neutral, acidic, and basic conditions were studied by HPLC.

The genus *Uvaria* continues to be an interesting source of biologically active constitutents,[1] and this has prompted us to examine other species of this genus. Extracts of *U. afzelii* Scot Elliot (Annonaceae) showed significant antimicrobial activity against gram-positive and acid-fast bacteria although no antitumor or cytotoxic activity was noted. Fractionation of the ethanolic extract using an ethyl acetate–water partition resulted in concentration of the antimicrobial activity in the ethyl acetate soluble fraction. Chromatography of the ethyl acetate soluble fraction over silicic acid yielded a number of fractions from which a number of novel compounds were isolated. We recently reported on the identification of two of these constituents, vafzelin (1) and uvafzelin (2), by single-crystal X-ray diffraction experiments.[2] We now report the identification of the known compounds coumarin (3), syncarpic acid (4), demethoxymatteucinol (5), and emorydone (8) and three new compounds, 2'-hydroxydemethoxymatteucinol (6), 2-hydroxy-7,8-dehydrograndiflorone (7), and uvafzelic acid (9).

Coumarin (3) and syncarpic acid (4) were readily identified from spectral data and their identities confirmed by direct comparison with authentic samples. Demethoxymatteucinol (5) had spectral data consistent with a flavanone with methyl groups at C-6 and C-8 (^1H and ^{13}C NMR). Its identity was confirmed by a direct comparison with an authentic sample.

An optically active crystalline substance (6) with a molecular formula of $C_{17}H_{16}O_5$ had UV and IR data similar to those of 5. The ^1H NMR spectrum of 6 displayed the characteristic ABX pattern of flavanones (H-2 and H-3) and two aromatic methyl signals (Me at C-6 and C-8). There were three D_2O-exchangeable signals and a four-proton multiplet in the aromatic region (δ 6.73–7.60),

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