product (5.6 g., 62%) was obtained by recrystallization from CCl_4; infrared (Nujol): NH at 3350, C=O at 1735 m and 1653 s, SO_2 at 1343 and 1170 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{18}N_2O_5S$: C, 49.68; H, 5.73; N, 8.92; S, 10.19. Found: C, 49.75; H, 5.71; N, 8.86; S, 10.24.

1-Acetyl-1-allyloxy-3-(*p*-tolylsulfonyl)urea was prepared similarly, m.p. 155.5–156.5°, in 29% yield.

Anal. Calcd. for $C_{21}H_{22}N_2S_2O_5$: C, 56.50; H, 4.93; N, 6.28; S, 14.35. Found: C, 56.00; H, 4.97; N, 6.43; S, 14.81.

This product decomposed to give *p*-toluenesulfonamide upon chromatography on alumina.

2-Benzyloxy-4-(*p*-tolylsulfonyl)allophonate.—A solution of 3.2 g. (0.016 mole) of N-carbethoxy-O-benzyloxyhydroxylamine[10] and 3.2 g. (0.016 mole) of *p*-toluenesulfonyl isocyanate in dry benzene was refluxed for 3 hr. The solvent was removed and 3.8 g. (60%), m.p. 97.5–99°, was obtained by recrystallization from CCl_4.

Anal. Calcd. for $C_{18}H_{20}N_2O_6S$: C, 55.10; H, 5.10; N, 7.14; S, 8.16. Found: C, 55.06; H, 5.14; N, 7.26; S, 8.25.

p-Toluenesulfonyl Isocyanate with N-Benzoyl-O-benzylhydroxylamine. Formation of Complexes. 1,3-Bis(*p*-tolylsulfonyl)urea with N-(Benzyloxy)benzamide (II) and N-(Benzyloxy)benzamide with *p*-Toluenesulfonamide (III).—A solution of 4.9 g. (0.025 mole) of *p*-toluenesulfonyl isocyanate and 2.8 g. (0.0123 mole) of N-benzoyl-O-benzylhydroxylamine in 25 ml. of benzene was refluxed for 2 hr. The solvent was evaporated, and the residue was recrystallized from acetone–petroleum ether and a product (II) (5.0 g., 67%) was isolated, m.p. 129–130°.

Anal. Calcd. for $C_{29}H_{29}N_3O_7S_2$: C, 58.59; H, 4.71; N, 7.07; S, 10.77. Found: C, 58.71; H, 4.79; N, 7.08; S, 10.73.

From the mother liquor (acetone–petroleum ether) was obtained 1.8 g. (33%) of a second solid (III), m.p. 92–94°. The infrared spectrum of III in chloroform showed NH at 3420, 3400, 3355, and 3230–3275 (broad) and CO at 1675 cm.$^{-1}$. The n.m.r. spectrum of III in $CDCl_3$ showed CH_3 δ 2.40, CH_2 5.02, ArH 7.21–7.87, 5 peaks 14H.

Anal. Calcd. for $C_{21}H_{22}N_2O_4S$: C, 63.32; H, 5.53; N, 7.04; O, 16.08. Found: C, 63.27; H, 5.50; N, 7.04; O, 16.28.

II was readily converted to III, ethyl *p*-toluenesulfonylcarbamate, *p*-toluenesulfonamide, and N-benzoyl-O-benzylhydroxylamine when recrystallization from ethanol was attempted. III was readily decomposed to *p*-toluenesulfonamide and N-benzoyl-O-benzylhydroxylamine by boiling with water, and III could be formed by refluxing equimolar quantities of *p*-toluenesulfonamide and N-benzoyl-O-benzylhydroxylamine in ethanol.

(11) L. W. Jones and E. E. Flerk, *J. Am. Chem. Soc.*, **50**, 2023 (1928).

Monothiophenyl Malonate

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Monothiophenyl malonate is a useful intermediate in the synthesis of malonyl coenzyme A, but although two methods of its preparation have been reported[1,2] the product has in each case been an oil. By a modification of the method of Trams and Brady[1] we have isolated the product as an analytically pure crystalline solid.

Experimental Section[3]

To a mixture of 4.17 g. (40 mmoles) of malonic acid and 30 ml. of dimethylformamide was added at 0–5°, 2.2 g. (20 mmoles) of benzenethiol[4] all at once; a dark blue solution resulted. A solution of 9.1 g. (44 mmoles) of dicyclohexylcarbodiimide in 50 ml. of dimethylformamide was placed in an addition funnel and added dropwise to the magnetically stirred solution at 0–5°. Addition was completed in 30–45 min. The mixture was then stirred for 2–3 hr. at 0–5°. During the addition and subsequent stirring the color changed from blue to yellow. The mixture was added to 600 ml. of ice water, stirred for several minutes, and collected on a sintered-glass funnel. The yellow solid, which consisted mainly of dicyclohexylurea, was washed with 150 ml. of ice water and 200 ml. of ether. The two phases of the filtrate were separated and the aqueous phase was extracted with 200 ml. of ether. The ethereal extracts were combined and washed with 100 ml. of 0.01 *M* HCl and 200 ml. of ice water. This solution was then dried ($MgSO_4$, Darco) for 0.5 hr. The solvent was removed by a rotary evaporator at room temperature and reduced pressure. The residual golden brown oil was dissolved in 10 ml. of toluene and diluted with 40 ml. of petroleum ether (b.p. 30–60°). The nearly colorless crystals which separated were collected and recrystallized from the same solvent. The yield was 0.5–0.7 g. (13–18%), m.p. 72–73°, ultraviolet absorption $\epsilon_{237}^{CH_3CN}$ 4200. A 10% $CHCl_3$ solution in a 0.1-mm. NaCl cell absorbed strongly in the infrared at 1740 cm.$^{-1}$.

Anal. Calcd. for $C_9H_8O_4S$: C, 55.09; H, 4.11; S, 16.34. Found: C, 55.07; H, 4.09; S, 16.44.

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(2) R. Bressler and S. J. Wakil, *J. Biol. Chem.*, **236**, 1643 (1961).

(3) The melting point was determined in a capillary by means of a calibrated, electrically heated block. Ultraviolet and infrared spectra were measured, respectively, by Beckman DU and Perkin-Elmer 137-B spectrophotometers. Elemental analyses were carried out by Clark Microanalytical Laboratory, Urbana, Ill.

(4) Benzenethiol frequently causes severe dermatitis. Rubber gloves should be worn and all operations should be conducted in an efficient hood.

The Reaction of Chloramine with Mercaptopyridine and Mercaptopyrimidine Derivatives

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The reaction of chloramine with heterocyclic mercaptans has, in every instance that was investigated, resulted exclusively in the sulfenamido derivative. The resulting compounds are of considerable interest because of the known biological and agricultural application of the closely related aminopyridine analogs[1,2] and the extremely potent germicidal action of 2-mercaptopyridine N-oxide.[3]

Experimental Section

All the melting points were taken in capillary tubes and were corrected (ASTM specification thermometers). The molecular weights were obtained by use of a Mecrolab Osmometer, Model 302. Sucrose and benzil were employed as standards.

2-Sulfenamidopyridine.—An aqueous solution of chloramine was prepared by the slow addition of 90 ml. of iced 1.84 *M* NaOCl solution to 278 ml. of 1.84 *M* NH_3 solution previously cooled to −5°. To the resulting chloramine solution, an aqueous solution of the sodium salt of 2-mercaptopyridine was added slowly taking care that the temperature did not exceed 5°. The sodium salt was prepared by dissolving 16.5 g. (0.15 mole) of 2-mercaptopyridine in 75 ml. of 2 *M* NaOH solution. The product precipitated immediately on addition of the sodium salt to the chloramine solution. The crude product was filtered, dried under vacuum to remove excess water, and recrystallized from a petroleum ether–isopropyl alcohol mixture. This resulted in 10.5 g. (55% yield) of a white crystalline product, m.p. 79–80°.

The other compounds were made with appropriate modifications of the general method described above. The results are listed in Table I.

(1) H. E. Thompson, C. P. Swanson, and A. G. Norman, *Botan. Gaz.*, **107**, 476 (1946).

(2) F. Leonard, F. A. Barkley, E. V. Brown, F. E. Anderson, and D. M. Green, *Antibiot. Chemotherapy*, **6**, 261 (1956).

(3) W. A. Lott and E. Shaw, *J. Am. Chem. Soc.*, **71**, 71 (1949).

TABLE I
ANALYTICAL RESULTS FOR HETEROCYCLIC SULFENAMIDES

Compd.[a]	Yield, %	M.p., °C.	Formula	Mol. wt. Calcd.	Mol. wt. Found	Calcd., % C	H	N	S	Found, % C	H	N	S
2-Pyridinesulfenamide	55	79–80	$C_5H_6N_2S$	126	122	47.6	4.8	22.2	25.4	47.7	5.2	22.1	25.3
4-Methyl-2-pyridinesulfenamide	46	79–80	$C_6H_8N_2S$	140	145	51.4	5.7	20.0	22.9	51.2	5.8	20.1	22.7
2-Pyrimidinesulfenamide	40	110–112	$C_4H_5N_3S$	127	133	37.8	3.9	33.1	25.2	37.7	3.8	33.6	25.0
4-Methyl-2-pyrimidinesulfenamide	42	114–116	$C_5H_7N_3S$	141	149	42.6	5.0	29.8	22.7	42.7	5.0	30.2	22.5
Sodium 2-sulfenamido-6-methylpyrimidine-4-olate monohydrate	58	280–285	$C_5H_8N_3NaO_2S$	...	...	30.5	4.0	21.3	16.2	30.4	3.5	20.9	16.5
2-(Pyridyl 1-oxide)sulfenamide	40	146–148	$C_5H_6N_2OS$	142	136	42.3	4.2	19.7	22.5	42.2	4.6	20.0	22.5

[a] All of the compounds were recrystallized from benzene–petroleum ether (b.p. 65–110°) except 2-pyridinesulfenamide (isopropy alcohol–petroleum ether), sodium 2-sulfenamido-6-methylpyrimidin-4-olate monohydrate (water), and 2-(pyridyl 1-oxide)sulfenamide (methanol.)

Potential Inhibitors of Cancerous Growth. V. Substituted Benzylidene Derivatives of D-Ribose as Synthetic Intermediates

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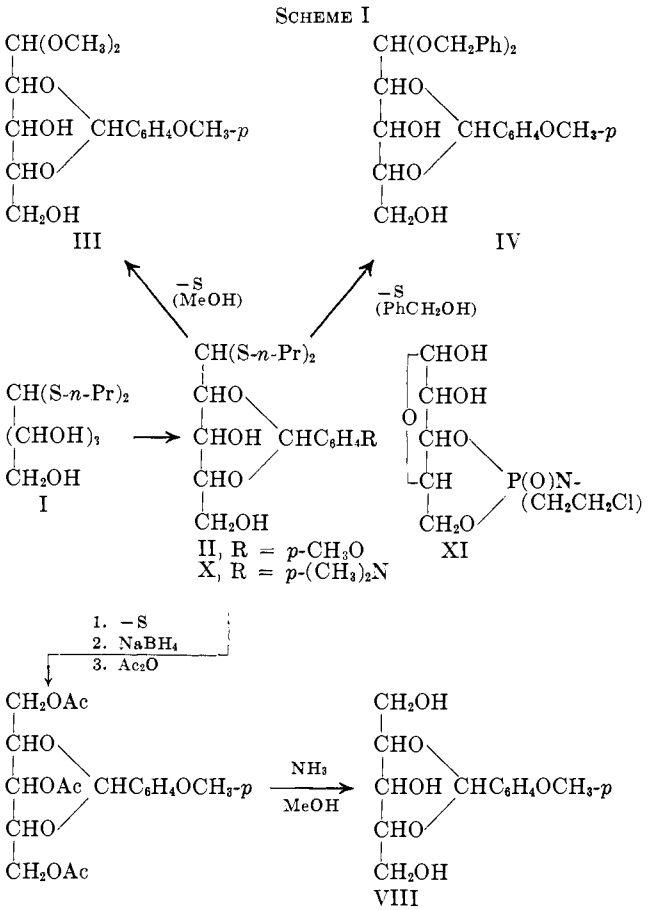
The selection of ribose as a "carrier" molecule in the design[1] of anticancer compounds with enhanced specific action (XI) is suggested by its role in cellular nucleic acid synthesis. Ribose compounds selectively phosphorylated[2] on positions 3 and 5 may be anticipated to be particularly favorable with respect to biological reactivation in actively growing cancer cells. In this respect, the anisylidene group has been found to be suitable for the selective protection of hydroxyls on positions 2 and 4 in the course of these syntheses.

New crystalline anisylidene D-ribose derivatives (II–IV) that may be used in the synthesis of new anticancer compounds have been obtained (see Scheme I).

The structural proof of II was based on evidence obtained by means of acetylation and reduction studies. Demercaptalation of 3,5-di-*O*-acetyl-2,4-*O*-anisylidene-D-ribose di-*n*-propyl dithioacetal (V) in aqueous acetone in the usual manner produced an oil which was reduced with sodium borohydride, and the product then was acetylated to yield an optically inactive crystalline product VII. Upon deacetylation of this product, another optically inactive crystalline product VIII was obtained. These results may be construed as evidence of a symmetrical structure of the molecule.[3] It was therefore inferred that VII was 1,3,5-tri-*O*-acetyl-2,4-*O*-anisylideneribitol, which in turn required VIII to be 2,4-*O*-anisylideneribitol.

SCHEME I



Experimental Section

All reagents and solvents were of ordinary grade quality. When required, solvents were purified and dried according to standard methods.[4] All evaporations, unless when stated otherwise, were conducted in a rotary flash evaporator at water aspirator pressure. Melting points were determined on a Kofler apparatus and are uncorrected. Infrared spectra of the compounds prepared were obtained on a Unicam SP. 200 recording spectrophotometer, using a 3% solution in $CHCl_3$ in a 0.1-mm. NaCl cell. Ultraviolet spectra were obtained on a Beckman DK2 recording ultraviolet spectrophotometer. Elementary analyses were done by the Microanalytical Section, National Chemical Research Laboratory, C.S.I.R., Pretoria.

2,4-*O*-Anisylidene-D-ribose Di-*n*-propyl Dithioacetal (II).—Anisaldehyde (4.36 ml., 36 mmoles) was added to a solution of D-ribose di-*n*-propyl dithioacetal (8.53 g., 30 mmoles) in 20 ml. of dioxane and the solution was cooled to 5–10° in an ice bath. To this solution was added a mixture of 29 ml. of concentrated HCl (sp. gr. 1.16) and 16 ml. of water, previously cooled to 5–10°, and the mixture was shaken vigorously with intermittant cooling. Within 1 min. a precipitate formed. After 4 min. ice water (10 ml.) was added and the mixture was shaken for another min. The product was then filtered rapidly and washed with ice water (50 ml.). The precipitate was taken up in 500 ml. of ethyl acetate and successively washed with cold saturated $NaHCO_3$ and water. After drying (Na_2SO_4), the ethyl acetate was evaporated under reduced pressure to yield 11.0 g. of a crystal-

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(3) H. Zinner and H. Schmandke, *Chem. Ber.*, **94**, 1304 (1961).

(4) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., New York, N. Y., 1957.