acid is attributed to the complex formation between oxalic acid and chromium(VI) which prevents the formation of energetically unfavourable chromium(IV) species (*loc. cit.*) and allows the direct one step reduction involving 3 electrons.

TABLE I

Dependence of rate constant (k) on [Oxalic acid]

$[MeOH] = 0\ 5\ M$
$[H_3PO_4] = 1\ M$
$[Cr(VI)] = 2{\cdot}33 \times 10^{-3}\ M$
Temp. = 40° C.

Oxalic acid $M \times 10^4$	Rate constant $k \times 10^6\ sec^{-1}$
..	9·8
1·0	10·9
2·0	12·0
4·0	14·3
6·0	15·5
8·0	18·7
10·0	20·5

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SYNTHESIS AND ANTIMICROBIAL SCREENING OF AMINO-1, 2-BENZISOXAZOLES AND SULPHANILAMIDO-1, 2 BENZISOXAZOLES

AMINO-1, 2-benzisoxazoles (II) have been synthesised by the reduction of nitro-1, 2-benzisoxazoles (I). Some of these amino-1, 2-benzisoxazoles have been converted into their sulphanilamido derivatives (IV). The antimicrobial activity of these compounds has been evaluated. Amino-1, 2-benzisoxazoles (II) have shown promising activity against *M. tuberculosis*, *in vitro*. The IR spectra of these compounds have been recorded. The mass spectrum of 5-amino-3-ethyl-7-methyl-1-, 2-benzisoxazole has also been represented.

In our recent publications[1–5] we have reported the synthesis and physiological activity of 1, 2-benzisoxazole derivatives. Some derivatives of 1, 2-benzisoxazole newly synthesised by us, showed antitubercular[2], antifungal[4,5] and antibacterial[5] activity. Amino and sylphanilamido derivatives are known for their physiological activity. Amino-1, 2-benzisoxazoles and their sulphanilamido derivatives are, therefore, synthesised and tested for their antimicrobial activity.

The nitro-1, 2-benzisoxazoles (I) prepared as reported by us earlier[3], on reduction with stannous chloride and HCl yielded amino-1, 2-benzisoxazoles (II). Sulphanilamido derivatives (IV, R=H) of some amino-1, 2-benzisoxazoles (II) were prepared by the condensation of amino compounds with *p*-acetamidobenzene sulphonyl chloride in presence of dry pyridine and subsequently hydrolysing N^4-acetyl-sulphanilamido-1, 2-benzisoxazoles (III, $R=COCH_3$) with 50% HCl. The physical data of these compounds are given in Table I.

Infrared spectra.—The infrared spectra of the compounds II, III and IV showed characteristic bands for primary amino group, N^4-acetylsulphanilamido group and sulphanilamido group respectively.

Mass spectra.—A mass spectrum of 5-amino-3-ethyl-7-methyl-1, 2-benziosxazole (IIe) is scanned as a representative of this series. The mass spectrum showed prominent peaks at *m/e* (M^+, 63%); 175 (*a*, 38%); 148 (*c*, 10%); 93 (*d*, 100%) and 65 (*e*, 32%). The fragmentation pattern of this compound is represented in Chart 1.

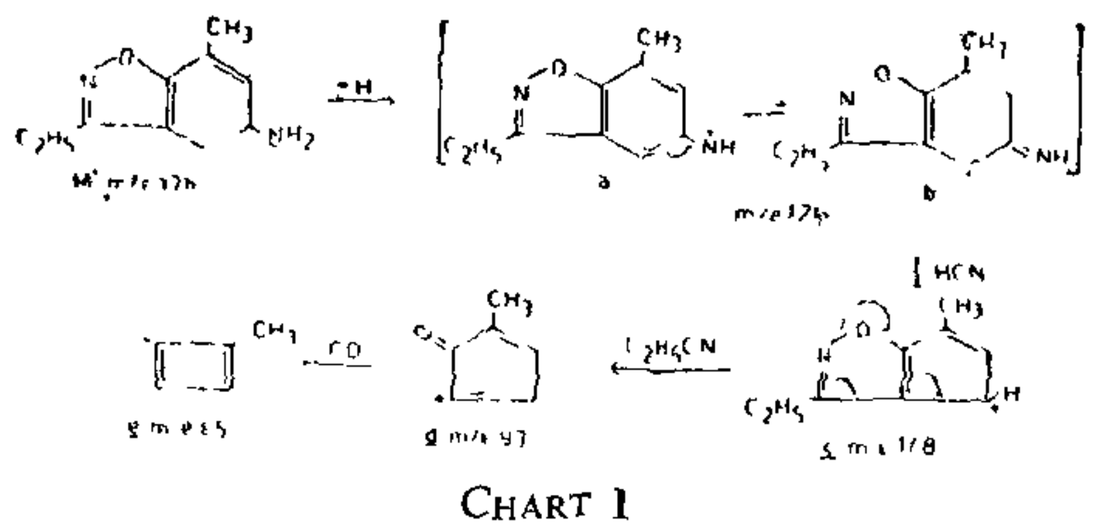

CHART 1

Antimicrobial activity

Antitubercular activity.—*In vitro* screening for antitubercular property of the compounds was carried out against human virulent "*Microbacterium tuberculosis*" (H_{37} Rv) by the method of Doub and Youmans[6]. The minimum concentration of the compounds (mentioned in μg/ml) which completely inhibited the growth of the test organism are recorded (Table I). For comparison the activity under similar conditions for Streptomycin is 1 μg/ml.

TABLE I

*Physical data and antitubercular activity (in μg/ml) of amino-***1, 2***-benzisoxazoles (II), N⁴-acetylsulphanilamido-***1, 2***-benzisoxazoles (III) and sulphsanilamido-***1, 2***-bezisoxazoles (IV)*

	R_1	R_2	R_3	m.p, °C	Yield %	Antitubercular activity (in μg/ml)
			Amino-1, 2-benzisoxazoles (II)			
a	CH_3	CH_3	NH_2	91[c]	45	0·1
b	CH_3	NH_2	CH_3	130[c]	78	2·0
c	CH_3	Cl	NH_2	106[d]	40	100·0
d	CH_3	NH_2	Cl	179[e]	55	0·2
e	C_2H_5	NH_2	H	61[g]	50	0·5
*f**	C_2H_5	CH_3	NH_2HCl	231[a]	45	0·2
g	C_2H_5	NH_2	CH_3	102[e]	70	2·0
i	C_2H_5	Cl	NH_3	57[e]	46	10·0
			N⁴-Acetylsulphanilamido-1, 2-benzisoxazloles (III)			
a	CH_3	CH_3	ASA	142[f]	60	..
b	CH_3	ASA	CH_3	251[a]	95	Inactive
c	CH_3	Cl	ASA	228[f]	85	..
d	CH_3	ASA	Cl	248[f]	96	..
e	C_2H_5	ASA	CH_3	223[e]	84	..
			Sulphanilamido-1, 2-benzisoxazoles (IV)			
a	CH_3	CH_3	SA	225[b]	69	100
b	CH_3	SA	CH_3	203[a]	54	Inactive
c	CH_3	Cl	SA	176[a]	60	Inactive
d	CH_3	SA	Cl	223[a]	65	Inactive
e	CH_3	SA	CH_3	132[b]	55	Inactive

All compounds showed satisfactory C, H and and N analyses.

* Free amine was isolated as an oily product. Its hydrochloride melted at 231°.

ASA = N⁴-Acetylsuplhanilamido; SA = Sulphanilamido; *a* = Crystallised from ethanol; *b* = Crystallised from 60% ethanol; *c* = Crystallised from 50% ethnal; *d* = Crystallised from 40% ethanol; *e* = Crystallised from 20% ethanol; *f* = Crystallied from acetic acid and *g* = Crystallised from petroleum ether (40-60 °C).

Almost all amino-1, 2-benzisoxazoles have shown significant activity against *M. tuberculosis*.

Antifungal activity,—In vitro antifungal screening of these compounds was carried out against plant pathogenic fungi, *viz.*, *Helminthosporium apattarnae* and *Pestalotia annonicola* by dry weight method[5].

Among the tested compounds only 7-amino-5-chloro-3-methyl-1, 2-benzisoxazole and 5-amino-3-ethyl-1, 2-benzisoxazole showed complete inhibitior of growth of *H. apattarnae* at 50 ppm. The former compound also showed 50% inhibition of *P. annonicola* at the same concentration.

Experimental

All melting points are uncorrected. The IR spectra (nujol) were recorded on Beckman IR-20 spectrophotometer. The mass spectrum was recorded on a Varian Mat CH-7 spectrometer.

7-Amino-3, 5-dimethyl-1, 2-benzisoxazole (II a).—Stannous chloride (14 g) was dissolved in conc. HCl (20 ml) by heating. To this clear solution, powdered 3, 5-dimethyl-7-nitro-1, 2-benzisoxazole (2 g) was added. The reaction mixture was then refluxed for 2 hrs. The crystalline amine hydrochloride was then dissolved in water, neutralised with dilute solution of ammonia and the precipitated free amine was extracted with ether. The amine was isolated by the evaporation of ether and crystallised from 50% alcohol. It melted at 91°. Yield 45%.

Similarly all other amines (II *b–i*) were prepared from the corresponding nitro compounds. The physical data of these amines are given in Table I.

7-(N⁴-Acetylsulphanilamido)-3, 5-dimethyl-1, 2-benzisoxazole (III a).—A mixture of 7-amino-3, 5-dimethyl-1, 2-benzisoxazole (0·01 mol), freshly prepared *p*-acetamidobenzene sulphonyl chloride (0·012 mol) and dry pyridine (10 ml) was heated on a water-bath for half an hour and kept at room temperature for 48 hours. It was then poured over crushed ice containing H_2SO_4. The precipitated solid was filtered, washed with water and crystallised from acetic acid. m.p. 242°. Yield 60%.

All other N⁴-acetylsulphanilamido compounds (III *b–e*) were also prepared as above.

3, 5-Dimethyl-7-sulphanilamido-1, 2-benzisoxazole (IV a).— 7-(N⁴-Acetylsulphanilamido)-3, 5-dimethyl-1, 2-benzisoxazole (2 g) was refluxed with 50% hydrochloric acid (25 ml) and ethanol (10 ml) for 1 hr. The reaction mixture was filtered hot and diluted with ice-water. It was then neutralised with sodium bicarbonate solution and the resulting solid was filtered, washed with water and crystallised from 60% ethanol *M.P. 225°. Yield 69%.*

The same procedure was used for the preparation of all other sulphanilamido-1 ,2-benzisoxazoles (IV *b–e*).

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A STAINING TECHNIQUE FOR MICROSCOPIC IDENTIFICATION OF BOEHMITE (GAMMA—ALOOH)

BOEHMITE (gamma—ALOOH) usually occurs in nature in a very fine-grained form. It is a common constituent of most of the bauxite deposits. It is more abundant in the Karst bauxites and the pisolitic varieties of lateritic bauxites than in the massive bauxites[1]. While the other two important allitic minerals of bauxites, namely gibbsite and diaspore are usually well crystallised and lend themselves readily to optical methods of identification, boehmite owing to its sub-microscopic character often poses problems during routine petrographic examination of bauxites. A staining technique has been developed for rapid identification of boehmite both in thin section and grain mounts.

The staining method reported here is actually a modification of the staining tests employed for identification of clay minerals[2]. During the detailed petrological studies of the bauxite samples from the East Coast of India, it was found that besides the clay minerals, boehmite also picks-up the aniline dyes used for staining clay minerals. Since there is a considerable difference in the refractive indices of boehmite and the common clay minerals, it is not difficult to differentiate them in spite of their poorly crystallised nature.

Reagents

Solvenrs : *Nitrobenzene, Methylene iodide.*
Dyes : Safranine–Y, Malachite green, Crystal violet.

Nitrobenzene and methylene iodide are mixed in suitable proportions such that the resulting solution has a refractive index of about 1·62. The staining solutions are prepared in separate glass containers by dissolving about 50 mg of the dyes in about 25 ml of the nitrobenzene-methylene iodide solution. The staining solutions will last for several weeks if they are refrigerated.

The thin section to be stained is left uncovered after grinding it to about 30 microns thickness. The surface of the section is washed free of Canada balsam using xylol. A few drops of 1 : 1 HCl are smeared on the surface of the thin section and