

$S_2S_3S_4 = 107^\circ$ and $S_2S_3S_4/S_3S_4S_5 = 106^\circ$. The slight differences between these values and those reported earlier² for the orthorhombic structure, are within the experimental errors.

The triclinic and orthorhombic crystals both have a layer structure, and show a corresponding perfect cleavage along the *c* plane. The thickness of the layers are, $d_{001} = 10.78 \text{ \AA}$ and half the orthorhombic *c* axis, *viz.*, 10.89 \AA , respectively. Within the probable errors of the structure determinations, the atomic arrangement *within* the layers is the same in the two crystals. The orthorhombic space group requires a mirror plane of symmetry to pass through the barium ion and the middle sulphur atom of the pentathionate chain. Although not crystallographically required, a mirror plane of symmetry is actually present in the layers of the triclinic crystals, and is depicted through broken lines in Fig. 1. The plane is normal to, and passes through, the *b* axis at $z = 0$, $y = \frac{1}{2}$ and $\frac{3}{2}$, as in the orthorhombic crystals, and through the same atoms. The orthorhombic and triclinic modifications differ only in the arrangement of the layers relative to each other.

A detailed account of the structure will be published later.

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Plant Growth Regulators I.

1- and 2-Naphthylmethylarsonic Acids

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In order that a substance may exhibit auxin activity it must, among other things, have an unsaturated ring system and an acidic side chain. Hitherto mostly synthetic plant hormones with a carboxyl group have been investigated. Following a suggestion by Professor A. Fredga the author has started an investigation on

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aromatic arsonic acids which, if physiologically active, will be of interest stereochemically and in interpreting the growth regulating mechanism.

The 1-naphthylmethylarsonic acid (I) and the 2-naphthylmethylarsonic acid (II) were prepared according to the general procedure outlined by Quick and Adams¹. The yields were very low but can certainly be increased. All analyses for arsenic were performed by the method described by Ramberg and Sjöström² and the titrimetric determinations in accordance with a method by King and Rutterford³.

The biological activity is being investigated by Dr. Börje Åberg, who has kindly reported some preliminary results. Both acids show in different tests a conspicuous anti-auxin effect⁴.

Experimental. 1-Naphthylmethylarsonic acid was prepared from 1-naphthylmethylchloride following the method given for benzylarsonic acid by Quick and Adams¹. Colourless needles. M. p. $142-144^\circ$ (decomposition). Calc. for $C_{11}H_{11}O_3As$ (266.1): C 49.6; H 4.17; As 28.2; equiv. wt. 133.1. Found: C 49.9; H 4.13; As 28.1; equiv. wt. 132.9.

2-Naphthylmethylarsonic acid was prepared in the same way from 2-naphthylmethyl bromide. Colourless plates. M. p. $159-161^\circ$ (decomposition). Found: C 50.0; H 3.99; As 28.0; equiv. wt. 133.8. Calc. for $C_{11}H_{11}O_3As$ (266.1): C 49.6; H 4.17; As 28.2; equiv. wt. 133.1.

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Halogenated Guaiacoxylalkylcarboxylic Acids of Plant Physiological Interest

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If the ether linkage in aryloxyalkylcarboxylic acids (I) is replaced by S, NH or CH_2 the plant growth-regulating activity is decreased^{1,2}. This type of

Table 1. Halogenated guaiacoxylalkylcarboxylic acids.

Compound	Yield (%)		Recrystallized from	M. p. (°C)	Eq. wt.	
	crude	pure			calc.	found
<i>Phenoxyacetic acids:</i> 2-Methoxy-4-chloro-	91	47	2 × 20% formic acid, 2 × toluene.	138 —140.0	216.6	217.1
» -5- »	66	43	20 % formic acid, toluene.	141.5—143.3	216.6	217.0
» -4,5-dichloro-	90	69	50 % formic acid, toluene.	156 —157.0	251.1	253.0
» -4-bromo-	97	51	40 % formic acid, toluene.	133 —134.8	261.1	262.0
» -5- »	89	70	50 % formic acid, toluene.	142 —143.8	261.1	261.1
<i>α-Phenoxypropionic acids:</i> 2-Methoxy-4-chloro-	97	48	30 % formic acid, toluene.	103 —105.0	230.7	230.6
» -4,5-dichloro-	100	86	50 % formic acid, toluene-petr. ether.	123.5—124.0	265.1	265.4
» -4-bromo-	86	59	50 % formic acid, petroleum (85—110°)	111 —112.8	275.1	274.8
» -5- »	96	78	30 % formic acid, petroleum (85—110°)	102.5—103.5	275.1	275.4

should melt at 161° which however seems rather improbable as the 4-chloro isomer melts at 36°. It is possible that the melting point of the literature refers to the K-salt as was the case with "4-chloroguaiacol" when first reported^{9,10}. In order to settle this question the direct chlorination of guaiacol will be further investigated.

Experimental. 4,5-Dichloroguaiacol. Sulphurylchloride (148.5 g, 1.1 mole) was slowly added (2 hours) to guaiacol (62 g, 1.0 mole). The mixture was allowed to stand for 3 hours when it solidified. The crude product was washed with petroleum ether and recrystallized from petroleum (b. p. 60—85°) yielding 81 g (84 %) 4,5-dichloroguaiacol, m. p. 62—70°. Further recrystallizations from the same solvent yielded 46 g (47 %), m. p. 71.5—73.0° (lit. 71—72°).

Guaiacoxylalkylcarboxylic acids. Sodium (1.15 g, 0.05 g-atom) was dissolved in abs. ethanol (40 ml). The appropriate phenol (0.05 mole) and ethyl chloroacetate (6.1 g, 0.05 mole) or ethyl α-bromopropionate (9.1 g, 0.05 mole) were added and the solution refluxed for 3 hours. Hydrolysis was performed by refluxing for 1 hour with 2 N NaOH (40 ml). The solution was acidified with 2 N HCl when the organic acid separated, in most cases as an oil

which crystallized within 1 hour. The crude product was recrystallized as seen from Table 1.

Melting points. All melting points were determined with a hot stage microscope (Table 1). A contact preparation¹¹ of 2-methoxy-5-chlorophenoxyacetic acid and 2-methoxy-*iso*-chlorophenoxyacetic acid was studied with the same apparatus. The components are not isomorphous and the lowest melting point of the system, 116°, is thus an eutectic.

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