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

mental 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,  $d_{001} = 10.78$  Å and half the orthorhombic c axis, viz., 10.89 Å, 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,  $y = \frac{1}{4}$  and  $\frac{3}{4}$ , 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 SVEN-OLOV LAWESSON

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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

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 Adams <sup>1</sup>. The yields were very low but can certainly be increased. All analyses for arsenic were performed by the method described by Ramberg and Sjöström <sup>2</sup> and the titrimetric determinations in accordance with a method by King and Rutterford <sup>3</sup>.

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 effect 4.

Experimental. 1-Naphthylmethylarsonic acid was prepared from 1-naphthylmethylchloride following the method given for benzylarsonic acid by Quick and Adams <sup>1</sup>. Colourless needles. M. p. 142—144° (decomposition). Calc. for C<sub>11</sub>H<sub>11</sub>O<sub>3</sub>As (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° (decomposition). Found: C 50.0; H 3.99; As 28.0; equiv. wt. 133.8. Calc. for C<sub>11</sub>H<sub>11</sub>O<sub>3</sub>As (266.1): C 49.6; H 4.17; As 28.2; equiv. wt.

133.1.

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## Halogenated Guaiacoxyalkylcarboxylic Acids of Plant Physiological Interest

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If the ether linkage in aryloxyalkyl-carboxylic acids (I) is replaced by S, NH or CH<sub>2</sub> the plant growth-regulating activity is decreased <sup>1,2</sup>. This type of

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linkage thus seems to be of great importance for the biological activity. However, the activity seems not to increase further if another —OCH(R)COOH side chain is introduced. The dioxyacetic acid derivatives of pyrocatechol (II) and hydroquinone (III) are inactive like phenoxyacetic acid <sup>3</sup>.

ity relations, further experiments are planned involving derivatives of vanillin, creosol, catechol and *iso*eugenol.

According to Beilstein, 2nd supplement, guaiacols should be numbered with the methoxy group in position 1 and the free hydroxy

The introduction of the second carboxylic group probably disturbs the balance between the hydrophilic and the lipophilic parts of the molecule. This H/L balance has been shown by Veldstra to be an important idea in dealing with structureactivity relations 4. If an alkoxy group without carboxyl is introduced into phenoxyacetic acid the H/L balance is only slightly changed and the effects can be more unequivocally ascribed to the ether linkage. In fact Aberg has found that m- and p-methoxyphenoxyacetic acids are weak auxins, about 100 times less active than 2,4-D, while the o-derivative is an anti-auxin 3. These results are contrary to the opinion that only halogens or alkyl groups are of importance in the study of structure-activity relations. It thus seemed important to investigate some alkoxy compounds and in this paper some halogenated guaiacoxyalkylcarboxylic acids will be described (Table 1).

A contributory cause for choosing guaiacol as starting material is that this phenol can be obtained by degradation of lignin. Except for vanillin, low molecular compounds are not prepared in a technical scale from this immense source of raw material. This is due not only to technical difficulties but also to difficulties in making use of the phenolic degradation products of lignin, e. g. guaiacol, creosol and pyrocatechol, which have been obtained from lignin in as high yield as 35 %. For this reason and also in order to study structure-activgroup in position 2. This system is inconvenient when applied to aryloxyalkylcarboxylic acids, which are usually numbered with the carboxylic acid chain in position 1. The latter system has been used here. Guaiacols named according to Beilstein's system have been placed within quotation marks.

The bromoguaiacols used as starting materials were obtained in good yields according to procedures already described in the literature 6,7. 4,5-Dichloroguaiacol was prepared according to Peratoner and Ortoleva 8. By a slight modification of their procedure the yield and purity of the product could be improved to an essential degree. "4-Chloroguaiacol" was prepared according to Jona and Pozzi?. These authors also prepared "5-chloroguaiacol" but their procedure was found to be very time-consuming and gave a very low yield. Peratoner has reported a liquid monochloroguaiacol of unknown structure obtained by the action of sulphurylchloride on guaiacol 8. The chloroguaiacoxyacetic acid of this compound has now been prepared and was found to melt at 140°, only 3° below the guaiacoxyacetic acid derived from "4-chloroguaiacol". However, these two acids form an eutectic at 116° which proves that they are not identical. As the introduction of a second chlorine atom into guaiacol by means of sulphurylchloride leads to 4,5-dichloroguaiscol the product of Peratoner must contain mainly "5-chloroguaiacol". According to the literature it

Compound	Yield (%)		Recrystallized	М. р.	Eq. wt.	
	crude	pure	from	(°C)	calc.	found
Phenoxyacetic acids:			$2 \times 20\%$ formic acid,			
2-Methoxy-4-chloro-	91	47	$2 \times \text{toluene.}$	138 —140.0	216.6	217.1
•	İ		20 % formic acid,		'	
» -5- »	66	43	toluene.	141.5—143.3	216.6	217.0
			50 % formic acid,			222
» -4,5-dichloro-	90	69	toluene.	156 —157.0	251.1	253.0
4 1	0.7	-,	40 % formic acid,	133 —134.8	061 1	0000
» -4-bromo-	97	51	toluene. 50 % formic acid,	133 -134.8	201.1	202.0
» -5- »	89	70	toluene.	142 —143.8	261.1	261.1
a-Phenoxypropionic acids:			30 % formic acid,			
2-Methoxy-4-chloro-	97	48	toluene.	103 —105.0	230.7	230.6
			50 % formic acid,			
» -4,5-dichloro-	100	86	toluene-petr. ether.	123.5—124.0	265.1	265.4
			50 % formic acid,			
» -4-bromo-	86	59	petroleum (85—110°)	111112.8	275.1	274.8
» -5- »	96	78	30 % formic acid, petroleum (85—110°)	102.5—103.5	275.1	275.4

Table 1. Halogenated guaiacoxyalkylcarboxylic acids.

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°).

Guaiacoxyalkylcarboxylic 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 a-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 preparation <sup>11</sup> of 2-methoxy-5-chlorophenoxyacetic acid and 2-methoxy-eso-chlorophenoxyacetic acid was studied with the same apparatus. The components are not isomorphic and the lowest melting point of the system, 116°, is thus an eutectic.

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