hydrochloric acid, yielding 4.0 g. (81% of the theoretical amount) of N-(p-methoxybenzyl)-5-carboxy-2-pyridone. This was recrystallized twice from an ethanol–water mixture and once from water to give white, needle-like crystals melting at 198–199°.

N-(β-Phenylethyl)-6-carboxy-2-pyridone.—One gram (0.0072 mole) of 6-carboxy-2-pyridone and 1.8 g. (0.015 mole) of β-phenylethylamine were dissolved in 50 ml. of glacial acetic acid and refluxed 50 hours. The solvent was removed under reduced pressure on a steam-bath and the residue treated with 150 ml. of 5% hydrochloric acid. The crude N-(β-phenylethyl)-6-carboxy-2-pyridone was purified by dissolving in 5% sodium bicarbonate and reprecipitating with acid. Recrystallization from 50% aqueous ethanol gave 0.65 g. (37%) of product, m.p. 192–193°.

Methyl Coumalate–Benzylamine Addition Product.—Six grams (0.038 mole) of methyl coumalate and 10 g. (0.093 mole) of benzylamine were dissolved in 40 ml. of methanol. After 1.5 hours at room temperature a precipitate began to form. After 15 hours this precipitate was collected, washed and dried to give 5.73 g. (52% of the theoretical amount) of the addition product (VI?). After recrystallization from water the product melts at 108–109°. The compound shows absorption maxima at 287 mμ (ϵ 4.18) and 326 mμ (ϵ 4.39). It is converted by alkali in 20% yield to N-benzyl-5-carboxy-2-pyridone identical with that obtained by the above procedure as determined by the method of mixed melting points.

Anal. Calcd. for $C_{14}H_{15}O_4N$: N, 5.36. Found: N, 5.30, 5.34.

Ultraviolet absorption measurements were made in alcohol solution with a Beckman DU spectrophotometer using 1-cm. quartz cells.

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Configuration of 3-Substituted 1-Chloropropenes

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The configuration of the 1,3-dichloropropenes remained ambiguous even though considerable work had been done in an attempt to establish the structure of the two isomeric forms by means of relative reactivities[3] or by means of physical data,[4] until Hatch and Perry[5] succeeded in chemically transforming each isomer into a compound whose configuration had been established previously. Later work[6] on relative reactivities substantiated the chemical work of Hatch and Perry.[5] A further aid in the establishment of structure of the 1,3-dichloropropenes was encountered in the preparation of compounds in the 1-naphthalene series to be used in plant-growth regulator investigations.[7]

When the 1-naphthylmagnesium bromide reacted with 1,3-dichloropropene, 3-(1-naphthyl)-1-chloro-1-propene was obtained as a product[8] but no mention was made of the possibility of *cis–trans* isomerism. Harris[9] pointed out that two isomers were obtained in this reaction, a white solid melting at 50° and a pale yellow liquid boiling at 155–160° (6–7 mm.). He concluded that he had the *cis*- and *trans*-isomers of 3-(1-naphthyl)-1-chloro-1-propene and, from dipole moment studies conducted by Lander and Svirbely,[10] tentatively assigned the following configurations; solid isomer *trans*, liquid isomer *cis*. However, he made no effort to start with *cis*-1,3-dichloropropene and correlate that product with the corresponding naphthyl product.

The work of Hatch and Perry[5] established the isomeric forms of 1,3-dichloropropene as follows: low boiling isomer I, *cis*-configuration; high boiling isomer II, *trans*-configuration. Starting with pure *cis*-1,3-dichloropropene (I) and converting it to the 3-(1-naphthyl)-1-chloro-1-propene by way of the Grignard reaction, we obtained a white solid III as a product, while the *trans*-isomer (II) gave a liquid product (IV). This seemed at variance with the work of Harris[9] for the assignment of configuration to the 3-(1-naphthyl)-1-chloro-1-propenes. For this reason, dipole moment measurements on all these isomeric compounds were repeated (Table I) and, although possibly not of a conclusive nature, they show a correlation of the *cis-trans*-1,3-dichloropropenes with the isomeric 3-(1-naphthyl)-1-chloro-1-propenes.

TABLE I

DIPOLE MOMENTS OF 1,3-DICHLOROPROPENE AND 3-(1-NAPHTHYL)-1-CHLORO-1-PROPENE ISOMERS

Compounds	Debye units			Configuration
1,3-Dichloropropene				
104° isomer (I)	1.92 (4a)	..	1.85[11]	*cis*
112° isomer (II)	1.73 (4a)	..	1.74[11]	*trans*
3-(1-Naphthyl)-1-chloro-1-propene				
Solid isomer (III)	..	1.27(9,10)	1.60[11]	*cis*
Liquid isomer (IV)	..	1.47(9,10)	1.39[11]	*trans*

The infrared spectra of these compounds (Fig. 1) also are interpreted to indicate that the solid isomer of 3-(1-naphthyl)-1-chloropropene is the *trans* form, at variance with the work of Harris.[9] To aid in the interpretations, the curves of *cis*- and *trans*-3-chloropropenoic acid are shown also. The configuration correlations applying to simple ethylenic groups did not seem applicable because of the effect of an adjacent halogen atom in all cases, and of the complexity from aromatic unsaturation in some. However, a band near 7.5 μ consistently was of prominent intensity in all the isomers assigned the *cis*-configuration, and this was either absent or very weak in all the remaining (*trans*) isomers. Because other nearby spectral patterns correspond to a recognizable extent in the respective isomers,

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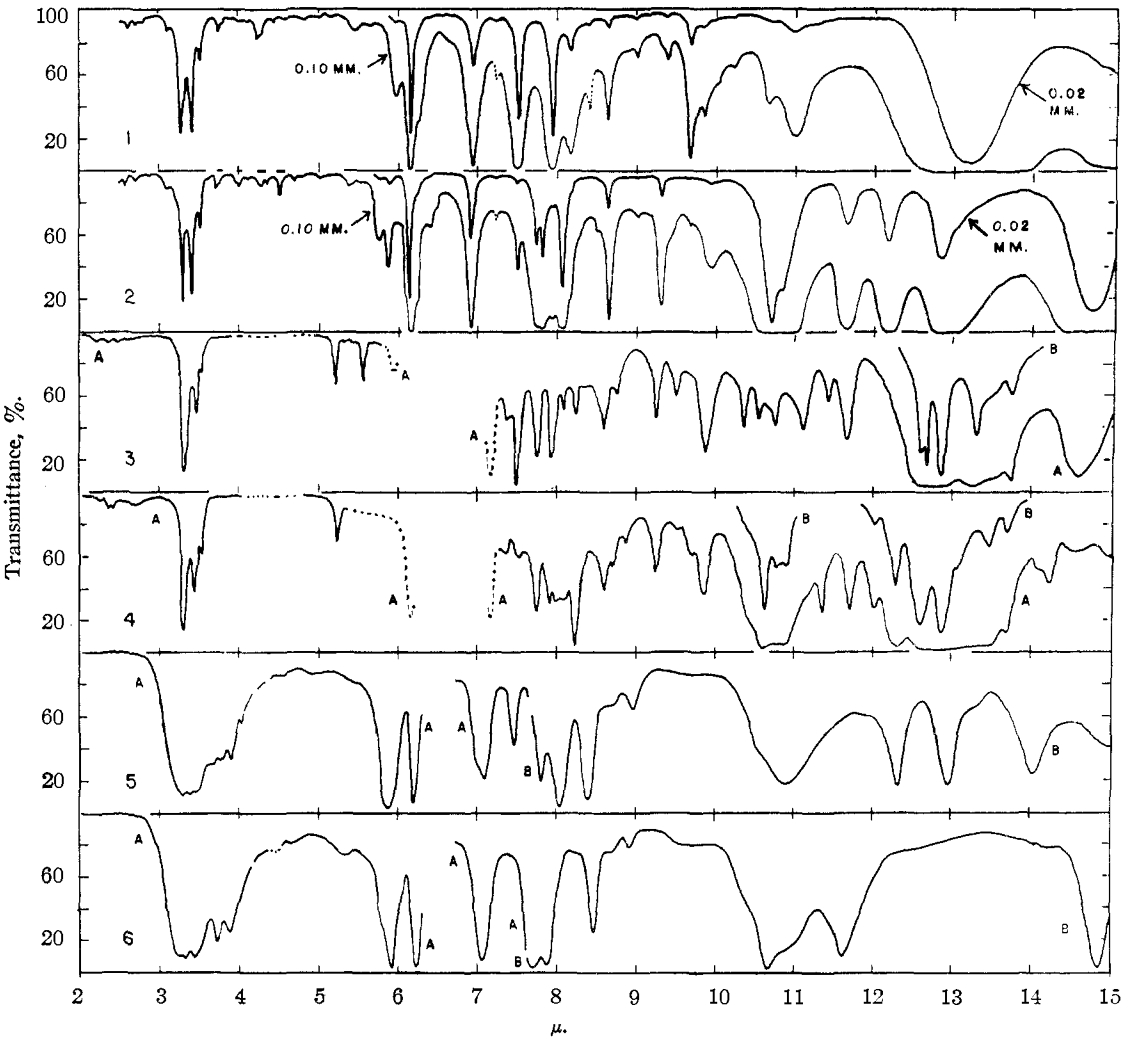

Fig. 1.—Infrared curves of substituted *cis*- and *trans*-chloropropenes. Curves 1 and 2 were obtained with a Perkin-Elmer instrument Model 21; curves 3–6 with Model 12-C: 1, 1,3-dichloropropene (I), b.p. 104.5°, n^{20}_{D} 1.4670, interpreted to be the *cis*-form, liquid state; 2, 1,3-dichloropropene (II), b.p. 110–111°, n^{20}_{D} 1.4740, interpreted to be the *trans*-form, liquid state; 3, 3-(1-naphthyl)-1-chloro-1-propene (III) solid isomer, m.p. 50–51°, interpreted to be the *cis*-form, 0.55-mm. cell, A-10% in CS_2, B-1% in CS_2; 4, 3-(1-naphthyl)-1-chloro-1-propene (IV), liquid isomer, interpreted to be the *trans*-form, 0.55-mm. cell, A-10% in CS_2, B-1% in CS_2; 5, 3-chloropropenoic acid (V), m.p. 63–64°, *cis*-form, 0.55-mm. cell, A-2% in CCl_4, B-2% in CS_2; 6, 3-chloropropenoic acid (VI), m.p. 84–85°, *trans*-form, 0.55-mm. cell, A-2% in CCl_4, B-2% in CS_2.

this 7.5 μ band stands out as an additional band, which indicates a mode of origin prominent in only one (*cis*) of the isomeric forms. At wave lengths this short, bands of such intensity characteristically have stable positions representing identical portions of varied molecules, and are unlikely to appear randomly from other causes. The group in common for which it seems characteristic, when weak or absent in the opposite isomer, is the *cis*-form of Cl–CH=CH–C. A consideration of the spectra of other halogenated ethylenic substances indicated that neither of the two hydrogen atoms should be substituted if strict consistency with these examples is to be expected, though the nearby region seems promising as a source of similar correlations.

Spectral correlation of I and III, and correspondingly of II and IV, seems to exclude any possibility of abnormal reaction with the Grignard reagent, thus confirming the conclusion reached by Kirrmann[12] that the reaction occurs in the normal way, with the reactive chloride attached to the single-bonded carbon atom.

Experimental

1,3-Dichloropropenes.—Commercial samples of the mixed isomers were distilled at a slow rate at atmospheric pressure and the *cis*- and *trans*-isomers boiling at 104.5–105.0° (I) and 110–111° (II), respectively, were collected.

3-(1-Naphthyl)-1-chloro-1-propenes.—The method of Bert and Dorier[8] was used to prepare the *cis*- and *trans*-isomers. *cis*-1,3-Dichloropropene (I) was treated with 1-naphthylmagnesium bromide to give a solid isomer (III) (*cis*) in 48% yield, m.p. 50–51°, b.p. 132–134° (1.4–1.7 mm.). From II a liquid isomer (IV) (*trans*) was obtained in 38% yield, b.p. 137–145° (2.5 mm.).

3-Chloropropenoic Acids.—The *cis* (V) and *trans* (VI) isomers, m.p. 63–64° and 84–85°, respectively (lit. 63–

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(12) A. Kirrmann, Pacaud and H. Dosque, *Bull. soc. chim.*, [5] 1 860 (1934); A. Kirrmann, *ibid.*, [4] 47, 834 (1930).

64°, 85.5–86°[13]), were prepared by the method of Backer and Beute[13] from 2-propynoic acid.

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[14] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

The Detection of 3-Indoleacetic Acid in Cauliflower Heads. Chromatographic Behavior of Some Indole Compounds[1,2]

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Introduction

In 1949 Wittwer[3] ascertained that both plant growth inhibitors and growth stimulators occurred in the ether extract of cauliflower heads with a predominance of the growth inhibitor. Luckwill[4] made the same observation in other plant tissue and also found two "auxins" and one inhibitor present in young broccoli leaves. Bennet-Clark and Ball[5] postulated a possible mechanism of action between growth inhibitors and growth stimulators in plants.

Holley, *et al.*,[6] isolated from the acid fraction of an ether extract of cabbage a substance without biological activity but giving a positive test with the Tang and Bonner reagent.[7] They indicated that 3-indoleacetic acid was responsible for most of the activity along with two other unidentified biologically active substances. Jones, *et al.*,[8] identified 3-indoleacetonitrile in the neutral fraction of an ether extract of cabbage. More recently, Bennet-Clark and Kefford[9] have suggested the general occurrence of several growth regulators in the ether extract of broad bean, peas, sunflower, corn and potatoes and identified one of them as 3-indoleacetic acid.

This communication reports the identification of 3-indoleacetic acid in cauliflower heads by chromatographic techniques and the R_f values of several related indole compounds.

Experimental

Colorimetric Assay of 3-Indoleacetic Acid.—One kg. of an ethanol extract representing 20 kg. of fresh cauliflower heads (Snowball X) was diluted with one l. of water, acidified with orthophosphoric acid and extracted with ethyl acetate. This extract was shown to contain 7 mg. of 3-indoleacetic acid by the Gordon and Weber procedure.[10] However, later work, reported herein, indicated that most of the color produced in the colorimetric assay did not result from 3-indoleacetic acid but from other compounds probably containing an indole nucleus. As a consequence, an attempt to isolate 3-indoleacetic acid as the *sym*-trinitrobenzene adduct,[11] based on the presence of 7 mg. of acid, was not successful since so small an amount of adduct was obtained that purification was not satisfactory. This lack of specificity of existing colorimetric procedures for 3-indoleacetic acid has been recognized earlier[6,10] and more recently investigated in this Laboratory.[12]

Detection of 3-Indoleacetic Acid.—Thirty kg. of fresh cauliflower heads was successively extracted four times with 5-l. portions of peroxide-free ether. Upon removal of the ether *in vacuo* 30 g. of residue was obtained. One g. of this residue was dissolved in 25 ml. of ethyl acetate and extracted with a 1% solution of sodium bicarbonate until the aqueous solution remained alkaline following extraction. The combined aqueous extracts were acidified with orthophosphoric acid and then re-extracted with ethyl acetate. This extract was placed on a line on a 20 × 30 cm. sheet of Whatman No. 1 filter paper and chromatographed using a solution of 1-propanol–15 *N* ammonium hydroxide–water (60:30:10 v./v.) and employing the descending technique. The location of the indole compounds on the chromatogram was determined by spraying with a solution of 1 g. of *p*-dimethylaminobenzaldehyde, 10 ml. of concentrated hydrochloric acid and 90 ml. of ethanol. The indole compounds in general produce a red to purple coloration. The area between the R_f values of 0.60–0.90 which contained all the colored zones, as determined by developing a center strip, was eluted with acetone. A portion of the resulting material was rechromatographed as a spot using the same technique

TABLE I

R_f VALUES OF INDOLE COMPOUNDS

(R_f values × 10^2), temp., 30°

Compound	Solvent		Color of spot with *p*-dimethylaminobenzaldehyde
	1-Butanol sat. with 5% NH_4OH	1-Propanol–concd. NH_4OH–H_2O (60–30–10 v./v.)	
3-Indoleacetic acid	25	75	Purple
3-Indoleacetonitrile	85	89	Purple
3-Indoleacetaldehyde[a]	88	88	Yellow brown (streak)
3-Indoleacetohydrazide	91	69	Purple
3-Indoleacetohydroxamic acid	58	71	Yellow
3-Indoleacetamide	84	87	Blue-purple
3-Indolepropionic acid	30	77	Purple
3-Indolebutyric acid	37	84	Purple
3-Indolecarboxaldehyde	87	87	Purple
3-Indolecarboxylic acid	15	68	Pink
Ethyl 3-indoleacetate	84	89	Purple
Ethyl 3-indolecarboxylate	88	96	Yellow
2-Phenyl-3-indoleacetic acid	90	88	Yellow-purple
2-Methyl-3-indoleacetic acid	26	78	Purple
2-Methylindole	86	96	Red
Tryptophol	88	90	Purple
L-Tryptophan	23	74	Purple
Tryptamine	79	90	Purple
1-Hydroxyl-3-indoleacetic acid	22	97	Brown
N,N′-Diindolyl-3,3′-diacetic acid	24	80	Brown
Indole	95	95	Pink
Isatin	74	80	Yellow

[a] Obtained as the sodium bisulfite addition product from Dr. Reed Gray, Pineapple Research Institute, Honolulu, Hawaii.

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