poxide reduction of the corresponding ketones (yields of crude product usually 80–90%); lithium aluminum hydride was used for the reduction of 2- and of 9-anthryl methyl ketone (87 and 85%), as well as of 2-chrysenyl methyl ketone (85%). The 1-anthryl methyl ketone was reduced by both reagents, but aluminum isopropoxide proved superior (70%). All the ketones were made by methods described in the literature, usually involving a Friedel and Crafts acylation of hydrocarbons, which had been purified by recommended procedures. The physical properties of all compounds and the carbon, hydrogen analyses of the new compounds are listed in Table III.[27]

Kinetic Runs.—Purified acetone[23] and boiled-out distilled water were thermostated at 25° and the necessary volumes, measured in 2-l. volumetric flasks (for instance 8 l. of acetone and 2 l. of water), were mixed in a 5 gal. Pyrex bottle. Enough of the 80 and the 90% aqueous acetone was prepared to last throughout the entire investigation. Kinetic runs below 25°, and some at 25°, were conducted in a 100-ml. volumetric flask, and 10-ml. samples were withdrawn at appropriate time intervals. Most runs at 25°, and all runs above 25°, were run in sealed tubes, prepared from 15-mm. Pyrex tubing. For these runs, an exactly weighed amount of chloride was made up to volume in a 100-ml. volumetric flask at room temperature, the mixture was cooled and eight approximately 12-ml. samples were pipetted into the ampules, sealed at ice-bath temperature and placed in the thermostat. When the tubes had reached the temperature of the thermostat, one ampule was opened and a 10-ml. sample was withdrawn and titrated for the zero titer. The contents of one sealed tube were allowed to react for at least 10 half-life times, in order to get the infinity reading. All samples, including the one for the infinity reading, were withdrawn at the reaction temperatures, which were maintained at ±0.02°. The 10-ml. samples were allowed to run into 60–80 ml. of ice-cold acetone and were titrated with a NaOH solution contained in a 5-ml. microburet graduated in hundredths; a 0.5% alcoholic lacmoid solution was used as an indicator. Initial concentrations of chloride were usually around 0.01 M, except for the less soluble 2-anthryl (0.006–0.007 M) and 2-chrysenyl (0.005 M in 80% acetone) compounds. A check with the 2-fluorenyl compound at a 0.01 and 0.005 M concentration showed that the rates were not affected by the initial concentrations. Reactions were

conducted to at least 60% completion, and usually more. Isolation runs were conducted with all compounds, except the phenyl, 1-naphthyl and 4-biphenylyl compounds, and the only products that were isolated were the corresponding carbinols, whose identity was checked by mixed melting points. The purity of the chlorides was obtained from infinity readings at 25°; all titrated for 99–100% purity except for the 1-naphthyl compound which was only 84% pure. This was undoubtedly due to some decomposition which was noticeable during vacuum distillation, but runs conducted with samples of various chloride content (60–84%) gave identical results.

Rate constants were calculated from the integrated form of the first-order rate equation. All runs were conducted at least in duplicate, all runs being listed in Table I. The average deviations within one run were 1–2%; some runs had a slight upward drift. The errors quoted for the activation energies and log A factors are probable errors obtained from least square calculations, rounded off to the values shown in Table I. The results of two typical runs are recorded in Table IV.

TABLE IV

THE HYDROLYSIS OF α-(2-FLUORENYL)-ETHYL CHLORIDE IN 80% AQUEOUS ACETONE AT 12.00° Concn., 0.01002 M			THE HYDROLYSIS OF α-(4-BIPHENYLYL) ETHYL CHLORIDE IN 80% AQUEOUS ACETONE AT 40.00° Concn., 0.01017 M		
Time, sec.	NaOH[a], ml.	$k \times 10^5$, sec.$^{-1}$	Time, sec.	NaOH[a], ml.	$k \times 10^5$, sec.$^{-1}$
0	0.501	..	0	0.306	..
1290	.855	9.58	2370	.639	4.51
2600	1.168	9.51	5970	1.100	4.63
4010	1.470	9.55	9570	1.460	4.52
5870	1.820	9.67	13170	1.790	4.56
7985	2.140	9.68	16290	2.030	4.56
10870	2.481	9.67	23970	2.494	4.57
14490	2.784	9.56	∞	3.594	..
∞	3.546	..			

[a] 0.02803 N.

(27) We are indebted to Miss N. Pearson, who prepared most of the ketones and the known carbinols during her tenure of a fellowship at Bryn Mawr College.

(28) J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924).

On Some cis-Forms of Phenylundecapentaenal

BY CH. GANSSER AND L. ZECHMEISTER

All-trans-11-phenyl-2,4,6,8,10-undecapentaenal (I) can be rearranged to give four cis isomers, termed I–IV. The pertinent experimental conditions, relative thermo- and photostabilities and certain interconversions are described. Some connected spectroscopic phenomena are discussed and tentative configurational assignments are made.

While the stereoisomerization of some α,ω-diphenylpolyenes,[1] $C_6H_5(CH{=}CH)_nC_6H_5$, and symmetrical azines,[2] $C_6H_5(CH{=}CH)_nCH{=}N{-}N{=}$ $=CH(CH{=}CH)_nC_6H_5$, was studied earlier, cis forms of phenylpolyene aldehydes, $C_6H_5(CH{=} {=}CH)_nCHO$, containing a rather high number of conjugated double bonds in an unbranched chain, do not seem to be known.

All-trans-11-phenylundecapentaenal ($n = 5$) was first obtained by Kuhn and Wallenfels,[3] then by Schmitt[4] who used a modified procedure. Theoretically, the molecules of this unsymmetrically built compound may assume 32 spatial configurations, the all-trans form included.[1e] We find

(1) (a) Diphenylbutadienes: F. Straus, Ann., **342**, 190 (1905); C. Kelber and A. Schwarz, Ber., **45**, 1946 (1912); E. Ott and R. Schröter, ibid., **60**, 624 (1927); A. Sandoval and L. Zechmeister, THIS JOURNAL, **69**, 553 (1947); J. H. Pinckard, B. Wille and L. Zechmeister, ibid., **70**, 1938 (1948). (b) Diphenylhexatrienes: K. Lunde and L. Zechmeister, ibid., **76**, 2308 (1954). (c) Diphenyloctatetraenes: L. Zechmeister and A. L. LeRosen, ibid., **64**, 2755 (1942); L. Zechmeister and J. H. Pinckard, ibid., **76**, 4144 (1954). (d) Biphenylene derivatives: E. F. Magoon and L. Zechmeister, ibid., **77**, 5642 (1955). (e) Survey articles: L. Zechmeister, Chem. Revs., **34**, 267 (1944); Experientia, **10**, 1 (1954).

(2) J. Dale and L. Zechmeister, THIS JOURNAL, **75**, 2379 (1953).

(3) R. Kuhn and K. Wallenfels, Ber., **70**, 1331 (1937).

(4) J. Schmitt, Ann., **547**, 270 (1941).

that when the all-*trans* aldehyde is submitted to some thermic or photochemical treatments, upon subsequent chromatographic resolution of the stereoisomeric mixture, four *cis* zones appear, all located below the *trans* zone. They were termed *cis*es I–IV, in the sequence of decreasing adsorption affinities. As will be indicated in the Experimental Part, this resolution is successful only on a specially prepared adsorbent, because of the rather difficult separation of the isomers and the sensitivity of the aldehyde group.[5]

In all experiments, regardless of the method, the main product of the *trans* → *cis* rearrangement was

TABLE I

RATIO OF STEREOISOMERS OBTAINED BY TREATMENT OF ALL-*trans*-PHENYLUNDECAPENTAENAL AND OF ITS *cis*-II AND III FORMS

Treatment	Ratio, all-*trans*: cis-I:cis-II:cis-III (in the recovered substance)	Irreversible loss (% of starting material)[g]
(A) Starting material, all-*trans*:		
(Mostly 15 mg. substance were dissolved in 15 ml. of benzene. The ratios are based on observed extinction of the iodine catalyzed eluates of the respective zones.)		
Refluxing in darkness (30 min.)[a]	100:0:0:0	7
Standing in diffuse daylight (2 hr.)[b]	61:3:32:4	5
Insolation (2 hr.)[c]	62:6:25:7	25
Irradiation (2 hr.)[d]	58:6:32:4	10
Iodine catalysis, in light (30 min.)[e]	84:1:5:10	6
Melting crystals (90 sec.)[f]	72:1:27:0	31
(B) Starting material, *cis*-II:		
(Mostly 0.5 mg. substance in 5 ml. of benzene)		
Refluxing in darkness (30 min.)[a]	1:0:99:0	2
Standing in diffuse light (2.5 mg. in 50 ml.) (2 hr.)[b]	47:3:45:5	10
Insolation (2 hr.)[c]	61:5:27:7	39
Irradiation (2 hr.)[d]	54:2:39:5	22
Iodine catalysis, in light (30 min.)[e]	82:3:5:10	15
Melting crystals (90 sec.)[f]	69:3:28:0	40
(C) Starting material, *cis*-III:		
Refluxing in darkness (1 mg. in 50 ml.) (30 min.)[a]	10:trace:1:89	4
Standing in darkness (1 mg. in 5 ml.). (75 min.)[a]	0.5:trace:0:99.5	1
Insolation (5 mg. in 5 ml.) (20 sec.)[c]	9:0:4:87 (and traces of *cis*-IV)	1
Iodine catalysis, in light (4 min.)[e]	48:1:13:38	1

[a] A slow stream of nitrogen is recommended. [b] Intense diffuse light in the open (shade). [c] Intense morning sunshine (summer); end temp., 35°. [d] Three Photoflood bulbs from 10 cm. distance; end temp., 35–40°. [e] At 60 cm. distance from the light source. [f] 1–2 mg. substance in an evacuated capillary tube at about 190°, then cooled in iced water, extracted, and chromatographed. [g] These figures are based on the loss in extinction of iodine-catalyzed mixtures obtained from aliquots before and after the treatment but preceding chromatographic resolution.

(5) Cf. J. F. Thomas and G. Branch, THIS JOURNAL, 75, 4793 (1953).

cis-II, while IV appeared only in traces. The *cis*es II and III have been obtained as crystals but I and IV only as chromatographically homogeneous solutions. Each *cis* form yielded, upon iodine catalysis, (in part) the all-*trans* compound that was chromatographically inseparable from, and spectroscopically identical[6] with, the synthetic product.

With reference to relative stabilities the following observations were made (Tables I–II).

TABLE II

RATIOS OF STEREOISOMERIC PHENYLUNDECAPENTAENALS OBTAINED UPON EXPOSURE TO WEAK DIFFUSE LIGHT[a] AT 20–25° FOR 4 MIN. (2.5 MG. IN 5 ML. BENZENE)

The ratios are based on observed extinctions of the iodine catalyzed eluates of the respective zones.

Isomer treated	Ratio, all-*trans*:cis-I: cis-II:cis-III (in recovered substance)	Irreversible loss (% of starting material)[b]
all-*trans*	95:1:3:1	1
cis-II	12:traces:76:12	1
cis-III	48:1:13:38	1

[a] Light intensity corresponding to f/5.6–1/100 sec.; (10 ASA) (Metraphot photometer). [b] Cf. footnote g to Table I.

When benzene solutions were refluxed in darkness for 0.5 hr., the all-*trans* compound remained sterically unaltered, while, respectively, 1 and 10% of the *cis* forms II and III were converted into the all-*trans* form.[7]

Like the diphenylbutadienes, the stereoisomeric phenylundecapentaenals show marked stereolability when exposed to intense scattered daylight. Under the conditions defined in Table I, roughly half of the all-*trans* and *cis*-II molecules were thus rearranged, while the *cis*-III configuration practically disappeared. Upon short exposure to weak daylight the data given in Table II were obtained. Likewise, in direct intense sunshine the photolability of the *cis*-III configuration surpasses that of the other isomers.

Under the usual conditions of the iodine catalysis (in light, in quartz cells) the rearrangement rates in this set are not significantly higher than in the absence of the catalyst (cf. the similar behavior of C=N bonds in azines).[2]

The spectral curves of the individual isomers, taken in the visible and ultraviolet regions,[8] appear in Figs. 1–3. The Figs. 1 and 2 also demonstrate the strong dependence of the fine structure on the solvent. Furthermore, while *trans* → *cis* rearrangements depressed the extinction values at λ_{max} con-

(6) However, for some reason, our *trans* ex *cis* preparations showed a moderate band at 5.8 μ that was missing or present with much lower intensity in the spectra of synthetic all-*trans* samples.

(7) No reliable data are available for *cis*-I, since this isomer undergoes, while being rechromatographed, a partial structural alteration, whereby a beige-colored new zone appears on the column, much above the *cis*-I zone. The adsorption affinity of this pigment surpasses that of all-*trans*-phenylundecapentaenal; λ_{max} in benzene at 421 mμ, *versus* 425 mμ for all-*trans*-phenyltridecahexaenal.[5] Considering these observations, the spectral data listed in the Experimental Part and represented for this isomer in Fig. 4 are given with some reservation.

(8) Considering the photosensitivity of our substances, the unchanged steric homogeneity of the solutions was checked chromatographically each time after ultraviolet or infrared spectra had been taken. Qualitative curves of (probably not chromatographed) all-*trans*-phenylundecapentaenal samples had been given earlier by Thomas and Branch.[5] Quantitative spectrum of the all-*trans-p*-methoxy derivative; D. Marshall and M. C. Whiting, J. Chem. Soc., 4082 (1956).
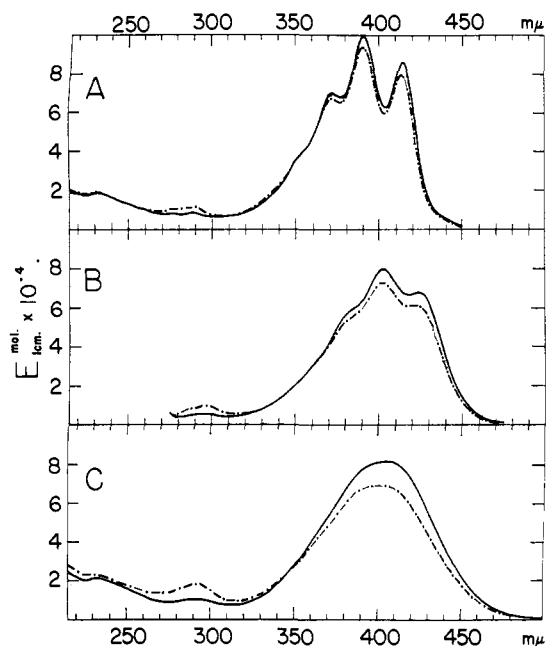
Fig. 1.—Molecular extinction curves of all-*trans*-phenyl-undecapentaenal: ————, fresh solution, and —·—·—·, mixture of the stereoisomers after iodine catalysis: A, in hexane; B, in benzene; and C, in methanol.
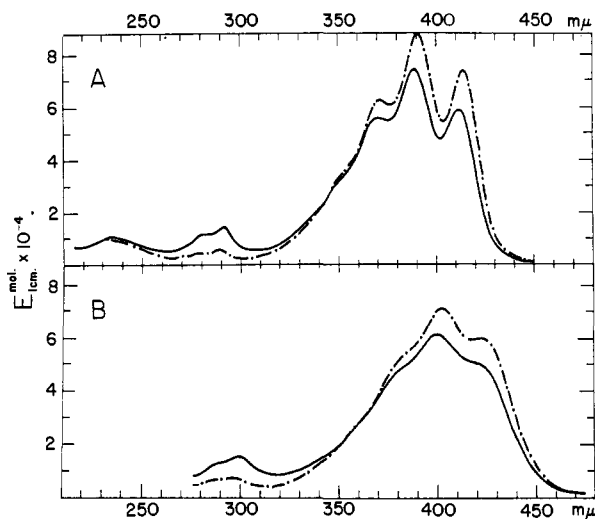

Fig. 2.—Molecular extinction curves of *cis*-II-phenyl-undecapentaenal: ————, fresh solution; and —·—·—·, mixture of stereoisomers after iodine catalysis: A, in hexane; and B, in benzene.

siderably, the position of the latter on the wave length scale was shifted by a few millimicrons only (Table III). In the *cis*-peak region the all-*trans*, *cis*-I and *cis*-IV curves are flat, while those of II and III do show some peaks. The shape of the latter is comparable with that of some *cis*-peaks observed in the lycopene[14] and methylbixin[9] sets.

As demonstrated in Fig. 4 the infrared spectra show a significant influence of the spatial configuration mainly in two regions: (a) in the 7.5–9.0 μ re-

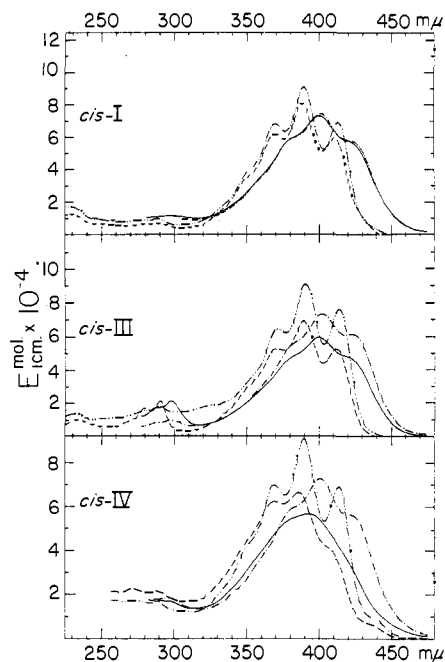(9) L. Zechmeister and R. B. Escue, This Journal, **66**, 322 (1944).

Fig. 3.—Molecular extinction curves of some *cis*-phenyl-undecapentaenals: fresh solutions: — — — —, in hexane; ————, in benzene; mixture of stereoisomers after iodine catalysis: —·· —··, in hexane; and —·—·—·, in benzene.

gion that had been found by Lunde, *et al.*,[10] to be stereochemically sensitive in diphenylpolyene sets, without the possibility of a clear interpretation; and (b) in the 10.0–10.6 μ region where the presence of a conjugated *cis-trans* diene group[11,12]
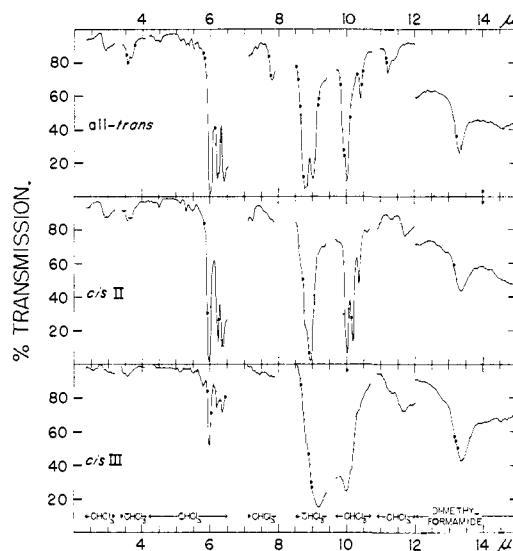

Fig. 4.—Infrared spectra of some stereoisomeric phenyl-undecapentaenals: from 2.0–12.0 μ in chloroform, and 12.0–15.0 μ in dimethylformamide (1 mm. cells). Concentrations: all-*trans* and *cis*-II, 0.7%; *cis*-III, 0.07% (microcell).

(10) K. Lunde and L. Zechmeister. *Acta Chem. Scand.*, **8**, 1421 (1954).

(11) J. E. Jackson, R. F. Paschke, W. Talberg, H. M. Boyd and D. H. Wheeler, *J. Am. Oil Soc.*, **29**, 229 (1952).

(12) W. D. Celmer and I. A. Solomons, This Journal, **75**, 3430 (1953).

TABLE III

SOME SPECTRAL CHARACTERISTICS OF STEREOISOMERIC
PHENYLUNDECAPENTAENALS IN HEXANE SOLUTION

Steric form	Fine structure	Main band — Position of λ_{max} (mμ)	Diff. from all-*trans* form at λ_{max} (mμ)	——— cis-Peak ———
all-*trans*	Very extensive	392	0	none
cis-I	Extensive	389	3	none
cis-II	Extensive	390	2	moderate⎫ peak at
cis-III	Extensive	390	2	moderate⎰ 290 mμ
cis-IV	Very moderate	387	5	none

causes a splitting of the main band (located at 10.02 μ in the case of our all-*trans* compound). This doublet formation became strongly manifest in the curve of cis-II-undecapentaenal (new band at 10.19 μ), although only a small shoulder appeared in the cis-III curve, at 10.13 μ.
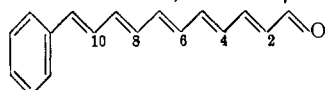
all-*trans*-phenylundecapentaenal

Considering the available experimental data, only tentative configurational assignments can be made at the present time (cf. ref. 13 and 14). The condensation product must represent the all-*trans* compound (cf. the formula) showing the greatest stability, the deepest color, the highest extinction values and by far the highest melting point. On the basis of observations made in comparable stereoisomeric sets, it is very probable that the cises I–III represent mono*cis* forms.

The cis-I isomer, because of its strongest adsorption affinity among the cis forms and the absence of a cis-peak in its spectral curve, may well possess the 2-cis configuration, and hence an essentially straight molecular shape. In the case of cises II and III the 2-cis position is excluded because of the presence of marked cis-peaks, and the centrally located 6-position is excluded because of the moderate height of these peaks as compared with the maximum values observed in the diphenyloctatetraene and diphenylhexatriene sets. Consequently, we assign the 8-mono*cis* configuration to cis-II and the 4-mono*cis* configuration to cis-III (or perhaps vice versa). The minor isomer IV seems to be a di*cis* compound, although, considering the flatness of its spectral curve in the cis-peak region and the small extent of fine structure in the main band, the sterically "hindered" 10-mono*cis* configuration cannot be excluded.[14,1b,c] Either of these assignments would explain the very weak adsorption affinity.

Acknowledgment.—We are indebted to Dr. Eugene F. Magoon for valuable discussions.

Experimental

Materials and Methods.—As adsorbent zinc carbonate (Merck Reagent Gr., precip.) was used. On zinc carbonate Harshaw (Techn. Gr.) and a number of other adsorbents, the stereoisomeric mixtures could not be resolved. The adsorbent was activated by heating, with occasional shaking, in large erlenmeyer flasks, in a drying oven at 120° for 3.5 hr.

The powder should remain colorless and appear violet in ultraviolet light; it should be kept in sealed bottles and shaken before use. Overactivation results in too low migration rates on the chromatographic column. All operations should be carried out in quasi-darkness and the chromatographic tubes should be wrapped in black cloth, otherwise the orange colored zones might turn pink on the side facing the window. Benzene (Reagent Gr.) was used as the developer and ethanol as the eluent. Washing of benzene solutions was effected according to LeRosen.[15] Evaporations were carried out in vacuo, at near-room temperature. Melting points (cor.) were taken in a Fisher–Johns apparatus. For microanalyses we are indebted to Dr. A. Elek (Los Angeles, Calif.).

All photometric treatments refer to Pyrex volumetric flasks. A Photoflood bulb (Gen. Electric, No. 1) with attached Corning light filter No. 5840 served as the ultraviolet light source; and for irradiations the same bulb was used without the filter. Iodine catalyses ($I_2 = 2\%$ of the substance) were carried out in the light of two 120-cm. Mazda lamps (3500°, 40 watt, white and yellowish) at 60 cm. distance. Instruments: Beckman spectrophotometer model DU (quartz cells); Cary recording ultraviolet spectrophotometer model 11 M (quartz cells); and Perkin–Elmer infrared double beam spectrophotometer model 21 (NaCl prism). The extinction coefficients given represent averages of at least two independent experiments. When direct weighing of the substance was impossible, the mol. extinction coefficient of the iodine-equilibrium mixture was used in the calculations as determined by iodine-catalyzing a weighed all-*trans* sample.

All-*trans*-phenylundecapentaenal was prepared by condensing cinnamaldehyde with crotonaldehyde[4] and was freed from its 7-phenylheptatrienal content by extraction with 70% ethanol.[16] After recrystallization from acetone the aldehyde was purified chromatographically (instead of the usual sublimation) as follows. A benzene solution of 17 mg. substance was developed on a 27 × 4.4 cm. column for about 90 min.[17] Above the orange-yellow main zone several other colored zones appeared, evidently containing some higher condensation products (these had been eliminated by Kuhn and Wallenfels[3] by fractional crystallization). The main zone was cut out; its eluate was washed with water, the benzene solution dried with sodium sulfate, evaporated to a few milliliters and crystallized by cautious, dropwise addition, with stirring, of hexane. Brownish-orange prisms with pointed ends, m.p. 185–186°, yield 12 mg. $E_{1cm.}^{mol.}$ 9.98 × 10^4 at λ_{max} 392 mμ (in hexane); 7.98 × 10^4 at λ_{max} 403 mμ (in benzene); 8.2 × 10^4 at λ_{max} 406 mμ (in methanol).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.93; H, 6.83. Found: C, 87.13; H, 7.22.

By chromatographing as described crude all-*trans*-phenylundecapentaenal samples on a much weaker, unactivated adsorbent, such as zinc carbonate Harshaw (Techn. Gr.), the presence of some higher condensation products could be demonstrated in a simple way. (The figures on the left designate thickness of zones, in mm.; the parentheses refer to fluorescence in ultraviolet light; and the spectral data to λ_{max} in benzene):

30   three minor pink zones and interzones
30   pink (dull red): 15-phenylpentadecaheptaenal,[3] *444*, 470 mμ
25   empty interzone
40   beige (weak dull red): 13-phenyltridecahexaenal[5] (?), 423 mμ
10   empty interzone
50   orange-yellow (golden-yellow): 11-phenylundecapentaenal, 403 mμ (96% of the recovered pigment)
90   empty section

(13) L. Pauling, Fortschr. Chem. organ. Naturstoffe, **3**, 203 (1939).

(14) L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár and L. Pauling, THIS JOURNAL, **65**, 1940 (1943).

(15) A. L. LeRosen, Ind. Eng. Chem., Anal. Ed., **14**, 165 (1942).

(16) M. Korach and W. Bergmann, J. Org. Chem., **14**, 1118 (1949).

(17) A chromatographic treatment of relatively more substance on a longer column (e.g., 100 mg.; 40 × 4.4 cm.) should be avoided, because of structural changes causing dark-violet colorations of the zones. Such all-*trans*-zones yielded crimson, rod-like crystals, m.p. 197–200°, λ_{max} at 421 mμ in benzene, versus 210–213° and 425 mμ observed for phenyltridecahexaenal). Likewise, some chemical processes (liberation of aldehydes) took place when benzene or hexane solutions of some polyene aldehyde anils, $C_6H_5(CH=CH)_nCH=N\cdot C_4H_5$ ($n = 2$, 3 or 5) were developed on zinc carbonate, calcium carbonate, neutral alumina or even sugar. For this reason a planned stereochemical study of the anils was unsuccessful.

cis-I-Phenylundecapentaenal was obtained from the chromatogram described in the next Section. Since it could not be rechromatographed unchanged, the following data were determined upon iodine catalysis. $E_{1\ cm.}^{mol.}$ 8.08 × 10^4 at λ_{max} 389 mμ (in hexane); 7.30 × 10^4 at λ_{max} 401 mμ (in benzene).

cis-II-Phenylundecapentaenal.—Seventeen milligrams of pure all-*trans* crystals was dissolved in 15 ml. of benzene on a water-bath and, after cooling to 20°, exposed to intense diffuse daylight on a window sill. After 2 hr. the solution was developed on a 22 × 3.5 cm. column:

20	orange-yellow (golden-yellow): unchanged all-*trans*
5	pale yellow (dull dark brown): *cis*-I
5	empty interzone
23	yellow (golden light yellow): *cis*-II
7	pale yellow (dull brown): *cis*-III
160	empty section

The eluate of the 23-mm. zone was transferred to benzene, dried, concentrated and rechromatographed as described on a 18 × 2 cm. column. The developing process was continued until a narrow but clear interzone appeared between the *cis*-II and *cis*-III zones. The benzene solution obtained from the former was evaporated completely, the crystalline residue dissolved at 25° in the minimum amount of benzene and crystallized by cautious addition of hexane; yield 4 mg. (in all, 20 mg. were prepared). Fine, orange-yellow needles grouped in sheaves or fan-like forms, m.p.

103–105°, or short needles, m.p. 108–110°; $E_{1\ cm.}^{mol.}$ 7.49 × 10^4 at λ_{max} 390 mμ (in hexane); 6.2 × 10^4 at λ_{max} 401 mμ (in benzene).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.93; H, 6.83. Found: C, 87.25; H, 7.39.

cis-III-Phenylundecapentaenal.—The 7-mm. zone of the above chromatogram was treated as described for *cis*-II and combined with seven similar zones originating from parallel experiments. After rechromatographing (column, 22 × 3.5 cm.) the benzene solution (50 ml.) was evaporated to 1 ml. at 10° (oil pump, receiver in acetone–Dry Ice). Upon cautious addition of hexane at 20°, this concentrate deposited crystals. Recrystallization in the same manner yielded 3 mg. of small, sturdy, yellow spears. The sample sintered at about 103° and melted at 176–178°, *i.e.*, somewhat below the m.p. of the all-*trans* isomer; evidently, this determination was disturbed by spatial changes in the fused state. The following values were obtained upon iodine catalysis: $E_{1\ cm.}^{mol.}$ 6.91 × 10^4 at λ_{max} 390 mμ (in hexane); 5.90 × 10^4 at λ_{max} 401 mμ (in benzene).

cis-IV-Phenylundecapentaenal was formed, when a solution of 5 mg. of *cis*-III in 5 ml. of benzene was exposed to sunshine (*cf.* Table IC). In the chromatogram, the thin, pale yellow *cis*-IV zone was located just below *cis*-III. After rechromatographing, the following data were obtained by the iodine catalysis method: $E_{1\ cm.}^{mol.}$ 6.64 × 10^4 at λ_{max} 387 mμ (in hexane); 5.67 × 10^4 at λ_{max} 394 mμ (in benzene).

Pasadena, Calif.

Structure of Corn Hull Hemicellulose. Part VI. The Synthesis of 5-O-β-D-Galactopyranosyl-L-arabinose[1,2]

By Irwin J. Goldstein, F. Smith and H. C. Srivastava

The synthesis of 5-O-β-D-galactopyranosyl-L-arabinose is described.

In a previous paper[3] of this series there was discussed the isolation and characterization of 5-O-β-D-galactopyranosyl-L-arabinofuranose, a disaccharide formed amongst others when corn hull hemicellulose[4] is subjected to graded hydrolysis with dilute mineral acid.[3]

The formulation of the disaccharide as 5-O-β-D-galactopyranosyl-L-arabinose was based upon these observations: Acid hydrolysis showed the presence of galactose and arabinose, while hydrolysis of the phenylosazone of the disaccharide gave galactose, but no arabinose. Hydrolysis of the fully methylated disaccharide furnished 2,3,4,6-tetra-O-methyl-D-galactopyranose and 2,3-di-O-methyl-L-arabinose. The decision to assign a β-configuration to the galactose residue and a furanose conformation to the arabinose moiety was based upon the rules of isorotation.[3,5]

This communication is concerned with the synthesis of 5-O-β-D-galactopyranosyl-L-arabinose in order to confirm the structure assigned to the disaccharide from the corn hull hemicellulose. The synthesis was accomplished as follows: interaction of ethyl 2,3-di-O-acetyl-α-L-arabinofuranoside with 2,3,4,6-tetra-O-acetyl-α-D-galactosyl bromide in the presence of silver oxide gave a sirup which, when deacetylated and subjected to controlled hydrolysis, afforded 5-O-β-D-galactopyranosyl-L-arabinofuranose. This was purified by chromatography on a carbon:Celite column[6] taking care to avoid washing with water to remove monosaccharides, since this leads to imperfect separations.[7] In this manner two isomeric galactose–arabinose disaccharides were obtained. Methylation of the one whose rotation corresponded to that of the galactose–arabinose disaccharide isolated from the corn hull hemicellulose, first with methyl sulfate and 40% potassium hydroxide solution in the absence of air, and then with methyl iodide and silver oxide, gave methyl 5-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-2,3-di-O-methyl-L-arabinofuranoside, a non-reducing sirup which showed $[\alpha]^{24}D$ −45° in methanol. Acid hydrolysis of the latter followed by paper chromatographic analysis afforded two cleavage products, namely, 2,3,4,6-

(1) Paper No. 3730 Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota.

(2) This research was done under contract with the United States Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract was supervised by the Northern Utilization Research Branch of the Agricultural Research Service.

(3) H. C. Srivastava and F. Smith, This Journal, 79, 982 (1956).

(4) M. J. Wolf, M. M. MacMasters, J. H. Cannon, E. C. Rosewall and C. E. Rist, *Cereal Chem.*, 30, 451 (1953).

(5) C. S. Hudson, This Journal, 31, 66 (1909); F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," Circular C-440 of the National Bureau of Standards, 1942, p. 411.

(6) R. L. Whistler and D. F. Durso, *ibid.*, 72, 677 (1950).

(7) F. Smith and H. C. Srivastava, *ibid.*, 78, 1404 (1956).