58. *Optically Active Tetrahydrofurfuryl Alcohol.*

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dl-Tetrahydrofurfuryl alcohol, now commercially available, is easily separated into its optically pure (+)- and (−)-forms. The rotatory dispersion of the optically active alcohol is anomalous and that of a number of its derivatives is complex. The anomalous dispersion is probably caused by anisotropic absorption bands associated with either (or both) of the oxygen atoms in the molecule.

In view of the ease with which the optically active alcohol is obtained, and its interesting optical properties, it may prove a useful material in studies on optical rotatory power.

dl-TETRAHYDROFURFURYL alcohol, b. p. 177—179°, obtained by fractional distillation of the commercial liquid, is converted by the usual method into its *hydrogen phthalate,* which readily crystallises in 90% yield and is raised to its maximum melting point after one recrystallisation. Some 5% of the ester separates as an oil, which can be separated, *via* the brucine salt, into the same (+)- and (−)-*hydrogen phthalates* as are obtained from the crystalline *dl*-alcohol. It appears, therefore, that part of the *dl*-ester remains oily because it contains impurities; there is no evidence that it contains *cis*- and *trans*-isomerides derived from a hypothetical, but improbable, non-planar configuration of the tetrahydro-

furan nucleus (according to Hibbert and Allen, *J. Amer. Chem. Soc.*, 1932, **54**, 4115, the tetrahydrofuran ring is flat).

By fractional crystallisation of its brucine salt, the *dl*-hydrogen phthalate is readily separated into the (+)- and (−)-forms, the latter being obtained in better yield. From these, the (+)- and the (−)-alcohol are obtained, with no racemisation, by steam-distillation from 5N-aqueous sodium hydroxide. [We define as (+) that alcohol which is dextrorotatory at λ_{5893} and is obtained from the (+)phthalate.] Table I records the observed rotatory powers of the (−)alcohol, determined in the visible and ultra-violet spectra by Dr. C. B. Allsopp (absorption commenced at 3603 A.). Our own observations (observed and specific rotatory powers) on (+)- and (−)-alcohols in the visible spectrum are in Table II. The plot of α against λ from the data in Table I shows that the rotatory

TABLE I.

Observed Rotatory Powers of (−)*Tetrahydrofurfuryl Alcohol* ($l = 2 \cdot 0$, $t = 20°$). (Wavelengths above 4600 were observed visually, those below 4600 photographically. Absorption commenced at λ_{3603}.)

λ.	α.	λ.	α.	λ.	α.	λ.	α.	λ.	α.
6708	−4·701°	5461	−3·954°	4384	+ 4·0°	3878	+14·0°	3603	+33·0°
6438	−4·971	5086	−2·722	4282	+ 6·0	3917	+16·0	3392	+52·0
6104	−4·587	4800	−0·961	4191	+ 8·0	3872	+18·0	3340	+60·0
5893	−4·539	4603	+1·175	4108	+10·0	3767	+23·0		
5780	−4·472	4529	+2·0	4032	+12·0	3669	+28·0		

TABLE II.

Rotatory Powers of (+)- *and* (−)-*Tetrahydrofurfuryl Alcohol.*

Temp.	(+)Alcohol. 20° ($l = 2$).		(−)Alcohol. 18° ($l = 0 \cdot 5$).		20° ($l = 2$).		41° ($l = 0 \cdot 5$).		59·5° ($l = 0 \cdot 5$).	
λ.	α.	$[\alpha]$.	α.	$[\alpha]$.	α.	$[\alpha]$.	α.	$[\alpha]$.	α.	$[\alpha]$.
6438	+4·87°	+2·28°	−1·31°	−2·45°	−4·85°	−2·28°	−1·19°	−2·28°	−1·17°	−2·28°
5893	+4·64	+2·18	−1·18	−2·21	−4·65	−2·18	−1·05	−2·01	−1·03	−2·0
5780	+4·46	+2·10	−1·06	−1·99	−4·44	−2·09	−0·99	−1·89	−1·00	−1·98
5461	+3·98	+1·87	−0·98	−1·84	−3·95	−1·86	−0·89	−1·70	−0·86	−1·67
5086	+2·64	+1·24	−0·64	−1·20	−2·60	−1·22	−0·50	−0·96	−0·46	−0·89
4800	+0·78	+0·37	−0·28	−0·52	—	—	−0·10	−0·19	−0·01	−0·02
4358	−4·63	−2·18	+1·13	+2·12	+4·80	+2·25	+1·31	+2·50	+1·43	+2·78

dispersion is anomalous, since the curve passes through a maximum and a reversal of sign. This is not unexpected, since anisotropic absorption bands due to either oxygen atom may contribute partial rotations to the observed rotatory powers. In support of this may be cited the following cases. In amyl alcohol (2-methyl-1-butanol), as in tetrahydrofurfuryl alcohol, a methylene group is interposed between the hydroxyl group and the asymmetric carbon atom. The high dispersion of amyl alcohol (Lowry, " Optical Rotatory Power," 1935, p. 266) compared with that of the secondary alcohols suggests that its dispersion is not really simple. Similarly, the interposition of a methylene group between the carboxyl group and the asymmetric carbon atom converts the simple dispersion of *iso*-valeric acid and its esters into the complex dispersion of β-methylvaleric acid and its esters (Levene *et al.*, *J. Chem. Physics*, 1933, **1**, 662, 667). With regard to the ethereal oxygen atom, it may be observed that the *n*-alkyl ethers of (+)-γ-nonanol show complex dispersion, whereas dispersion of (+)-γ-nonanol itself is simple (Kenyon and Barnes, *J.*, 1924, **125**, 1395).

When the rotatory powers of (−)tetrahydrofurfuryl alcohol are observed in a series of aqueous solutions of increasing dilution (Tables I and III, the curve for the highest concentration being that of the homogeneous alcohol), the results can be plotted as a family of curves in which the points of inflection, maxima, and changes of sign move progressively towards shorter wave-lengths as the dilution is increased. A similar series of curves is given by aqueous solutions of tartaric acid (Lowry and Austin, *Phil. Trans.*, 1922, *A*, **122**, 249). A somewhat similar series of curves is also given by the rotatory powers of 5%

TABLE III.

Specific Rotatory Powers of (—)*Tetrahydrofurfuryl Alcohol in Aqueous Solutions*
($l = 2\cdot0$; $t = 17\cdot0°$).

λ.	$c = 80\cdot0$.	70·0.	60·0.	50·0.	40·0.	20·0.	10·0.	5·0.
6438	−3·16°	−4·37°	−5·63°	−7·52°	−8·70°	−11·68°	−12·85°	−14·0°
5893	3·34	4·86	6·37	8·61	10·03	13·57	15·10	16·15
5780	3·36	4·91	6·54	8·90	10·47	14·18	16·75	—
5461	3·30	5·13	6·93	9·62	11·23	15·55	17·15	17·7
5086	2·98	5·19	7·37	10·48	12·35	17·40	19·35	20·6
4800	2·48	5·17	7·49	11·09	13·12	18·85	20·80	22·4
4358	0·65	4·12	7·21	11·25	14·07	20·94	24·85	26·9

solutions of (—)tetrahydrofurfuryl alcohol in the *n*-aliphatic alcohols from methyl to *n*-amyl (Table IV), though the relative positions of the rotatory powers in *n*-propyl and *n*-amyl alcohols are transposed.

TABLE IV.

Specific Rotatory Powers of (—)*Tetrahydrofurfuryl Alcohol in Solution in* n-*Alcohols*
($l = 2\cdot0$; $t = 20°$).

Solvent.	MeOH.	EtOH.	Pr^{a}OH.	Am^{a}OH.	Solvent.	MeOH.	EtOH.	Pr^{a}OH.	Am^{a}OH.
$c = 5\cdot20$.		5·06.	4·98.	5·06.	$c = 5\cdot20$.		5·06.	4·98.	5·06.
λ.					λ.				
6438	− 8·8°	−1·68°	+1·50°	−0·49°	5086	−11·6°	+1·01°	+4·21°	+2·57°
5893	− 9·5	−1·38	+1·80	+0·30	4800	−12·6	—	+5·01	+3·66
5780	− 9·7	—	+2·31	+1·19	4358	−13·1	+5·14	+9·53	+7·12
5461	−10·2	±0	+3·21	+1·58					

A curve of anomalous dispersion, such as is shown by the present alcohol, would be expected to conform to a two-term Drude equation (as Hunter, Thesis, London, 1922, points out, the rotatory powers of organic compounds are not usually of sufficient magnitude to show the effect of a third term). However, we have not been able to derive such an equation to fit the results recorded in Table I.

Table II shows the variation of rotatory dispersion of the (—)alcohol with change of temperature. The variation of the dispersion ratio with temperature is small : it changes only from 1·15 to 1·66 between 18° and 59·5°, and is in contrast to the cases of, *e.g.*, tartaric acid and its esters (for the ethyl ester the dispersion ratio changes from 0·27 to 0·8 between 20° and 64°). This is in agreement with the suggestion that the anomalous dispersion of tetrahydrofurfuryl alcohol is not due to the existence of labile structures such as have been postulated to explain the anomalous dispersion of tartaric acid and its esters, but is a fixed property of the alcohol molecule, *i.e.*, is derived from the two oxygen atoms in the molecule.

Table V records the rotatory powers of the (—)alcohol in a number of other solvents. These, as would be expected, also show evidence of complexity. In two cases reversals

TABLE V.

Specific Rotatory Powers of (—)*Tetrahydrofurfuryl Alcohol in Various Solvents* (l, 2·0; t, 20°).

Solvent.	6N-HCl.	5N-NaOH.	MeNO$_2$.	CHCl$_3$.	C$_5$H$_5$N.	Dioxan.	C$_6$H$_6$.	CS$_2$.	Et$_2$O.	Pr$^\beta$OH.
$c = 5\cdot00$.	5·09.	5·14.	5·34.	5·10.	5·22.	5·48.	5·32.	5·60.	5·11.	
λ.										
6438	−18·10°	−8·83°	−14·8°	−15·85°	−15·9°	−7·2°	−6·2°	−6·1°	−4·5°	+3·21°
5893	22·3	9·23	17·5	17·1	17·1	7·2	6·1	5·2	3·9	4·55
5780	23·7	—	—	18·0	—	—	—	—	—	4·72
5461	25·7	10·70	19·7	18·9	18·6	7·2	6·1	4·1	3·3	5·74
5086	28·8	—	—	22·5	—	—	—	—	—	8·06
4800	31·3	—	—	23·9	—	—	—	—	—	10·29
4358	38·8	12·80	26·2	27·1	26·7	7·2	2·3	+1·5	+0·9	14·18

of sign occur, and in all cases the dispersion constants $\alpha_{4358}/\alpha_{5461}$ are far removed from the value 1·65 approximately characteristic of the simple dispersion of the *sec.*-carbinols, or the calculated value of 1·57 for simple dispersion. The results in 1 : 4-dioxan solution

are remarkable, the rotatory power in this case being independent of wave-length, in the visible spectrum. Complex dispersion is also shown by a number of derivatives of the alcohol. The hydrogen phthalate in a variety of solvents (Table VI), and the *p*-toluene-sulphonate, p-*xenylurethane*, and p-*nitrobenzoate* (Table VII), in respect of dispersion con-

TABLE VI.

Specific Rotatory Powers of (—)*Tetrahydrofurfuryl Hydrogen Phthalate in Various Solvents* (l = 2·0; t = 17—20°).

Solvent.	$CHCl_3$.	C_6H_6.	HOAc.	Dioxan.	C_5H_5N.	EtOH.	Et_2O.
	c = 5·04.	5·02.	5·04.	5·44.	5·16.	5·01.	5·28.
λ.							
6438	−25·3°	−20·0°	−16·4°	−10·93°	—	−6·6°	−3·3°
5893	31·8	27·0	20·7	13·14	−10·16°	7·3	4·1
5780	33·4	28·8	21·4	14·24	10·35	7·5	4·5
5461	38·0	31·8	23·7	14·98	10·8	7·9	4·6
5086	43·6	37·5	28·7	18·93	—	9·1	5·7
4800	53·7	53·5	33·3	20·95	—	10·1	6·1
4358	68·0	55·6	42·2	26·47	16·35	11·6	6·3

TABLE VII.

Rotatory Powers of Other Derivatives of (—)*Tetrahydrofurfuryl Alcohol* (t = 20·0°).

Derivative.	*p*-Toluenesulphonate.		*p*-Xenyl-urethane.	*p*-Nitro-benzoate..	Benzoate.	Acetate.
Solvent.	None.*	CS_2.	$CHCl_3$.	$CHCl_3$.	None.	None.
	c = —	9·13.	4·87.	5·04.	—	—
	l = 0·25.	2·0.	2·0.	2·0.	0·5.	0·5.
λ.						
6438	−12·08°	−1·26°	−21·7°	—	13·0°	−15·3°
5893	13·88	0·93	27·1	−31·6°	15·5	17·9
5780	14·32	0·81	30·0	32·6	16·3	18·8
5461	15·82	0·66	33·5	36·5	18·0	20·8
5086	18·92	0·33	38·4	—	20·8	23·6
4800	21·08	1·48	42·4	—	23·4	26·2
4358	23·28	3·67	—	65·5	28·2	31·1

* This column gives observed rotatory powers; all the other columns give specific rotatory powers.

stant and curvature of the plot of $1/\alpha$ against λ^2, are obviously complex. The benzoate and acetate have dispersion constants which could correspond to simple dispersion, and the plots of $1/\alpha$ against λ^2 for these esters can only be represented as straight lines, the divergences being random and probably due to experimental error. We think it likely, however, that this apparent simplicity would not be maintained if the dispersion curve were followed into the ultra-violet spectrum.

EXPERIMENTAL.

Commercial tetrahydrofurfuryl alcohol was redistilled, and the fraction of b. p. 177—179°, $n_D^{16°}$ 1·4529, collected. Its phenylurethane has m. p. 62° (Wienhaus, *Ber.*, 1920, **53**, 1656, gives m. p. 61°); its p-*xenylurethane*, short needles, m. p. 104—106° from ether and light petroleum (Found : N, 5·1. $C_{18}H_{19}O_3H$ requires N, 4·7%); and its *p*-toluenesulphonate, m. p. 39—40° (Barger, Robinson, and Smith, J., 1937, 720, give m. p. 38·7—39·1°).

dl-*Tetrahydrofurfuryl Hydrogen Phthalate.*—A mixture of the alcohol (102 g.), phthalic anhydride (148 g.), and pyridine (100 g.) was heated for 2 hours on the steam-bath, and the product worked up in the usual way. The resulting hydrogen phthalic ester was obtained as an oil (233 g.), which after several days set—not quite completely—to a compact mass of irregular rhombs, m. p. 44—46°. From ether–light petroleum it crystallised slowly in hard, glassy rhombs, m. p. 62—64° (Found, by titration with NaOH : M, 249. $C_{13}H_{14}O_5$ requires M, 250). On saponification it yielded dl-tetrahydrofurfuryl alcohol with $n_D^{16°}$ 1·4515.

l-*Tetrahydrofurfuryl Hydrogen Phthalate.*—Brucine (438 g.) was dissolved in a hot solution of the dl-ester (278 g.) in acetone (1500 c.c.). The salt which separated on cooling, in rosettes of short needles (about 350 g.), was removed by filtration and decomposed with dilute hydrochloric acid. The liberated l-*ester*, which usually had $[\alpha]_{5893}$—20° (ca.) in chloroform solution,

was recrystallised three or four times from ether–light petroleum until its rotatory power was constant; it formed large glassy rhombs, m. p. 82—83·5° (Found, by titration with NaOH : M, 247). Rotatory powers are in Table VI.

This fractional crystallisation of $l + dl$-hydrogen phthalic ester is the more efficient method of resolution, for the original brucine salt, after being recrystallised four times from acetone or methyl acetate, yields a hydrogen phthalate of only approximately 92% optical purity.

d-*Tetrahydrofurfuryl Hydrogen Phthalate.*—The more soluble fractions of brucine salt contained in the filtrates yielded on decomposition with hydrochloric acid $d + dl$-hydrogen phthalic ester (with $[\alpha]_{5893} + 24°$ in chloroform), from which, after several crystallisations from ether and light petroleum, optically pure d-*tetrahydrofurfuryl hydrogen phthalate* was readily obtained as glassy rhombs, m. p. 82—83·5° (Found, by titration with NaOH : M, 252).

When ethereal solutions of equal amounts of the d- and the l-hydrogen phthalic ester were mixed and allowed to evaporate, glassy rhombs of the dl-ester, m. p. 62—64°, separated.

l-Tetrahydrofurfuryl alcohol was obtained in almost theoretical yield when the l-hydrogen phthalate was dissolved in sodium hydroxide ($5N$; 2·2 mols.), and the solution steam-distilled. The aqueous distillate was saturated with potassium carbonate and extracted several times with ether. l-Tetrahydrofurfuryl alcohol has b. p. 74·5°/14 mm., $n_D^{20°}$ 1·4529; $d_4^{17·5°}$ 1·064, $d_4^{33·5°}$ 1·051, $d_4^{47·5°}$ 1·038, $d_4^{61·5°}$ 1·027. Wienhaus (*loc. cit.*) gives $d_0^{20°}$ 1·054 for the dl-alcohol.

Its rotatory powers in the homogeneous state at different temperatures and in various solutions at room temperature are recorded in Tables I—V. A portion was reconverted into its hydrogen phthalate; this had $[\alpha]_{5893} - 32·8°$ (l, 2; c, 5·160 in chloroform), showing that no racemisation occurred during the saponification.

d-Tetrahydrofurfuryl alcohol, obtained in a similar manner from the d-hydrogen phthalate, had b. p. 79°/20 mm., $n_D^{17·0°}$ 1·4531; its rotatory powers are recorded in Table II.

l-*Tetrahydrofurfuryl* p-*nitrobenzoate* (Table VII), prepared by Einhorn's method, separated from ether and light petroleum in long, slender, flat, almost colourless needles, m. p. 36—37° (Found : N, 5·7. $C_{12}H_{13}O_5N$ requires N, 5·6%). The corresponding dl-compound, flat needles, had m. p. 48—49°. The acetate, prepared by Einhorn's method, had b. p. 90°/20 mm., $n_D^{20°}$ 1·4371, and the benzoate, b. p. 173°/20 mm., $n_D^{19·5°}$ 1·5242. Rotatory powers of both these esters are in Table VII. [For the corresponding dl-acetate, Zanetti (*J. Amer. Chem. Soc.*, 1928, **50**, 1821) gives b. p. 194—195°, $d_0^{20°}$ 1·061; and for the dl-benzoate b. p. 300—302°, $d_0^{20°}$ 1·137, but he does not give the refractive indices.]

l-Tetrahydrofurfuryl p-toluenesulphonate (Table VII) formed massive crystalline plates, m. p. 25°.

dl-Tetrahydrofurfuryl hydrogen phthalate (5 g.) was dissolved in anhydrous formic acid (8 g.) and heated on the steam-bath during several hours, and then left at room temperature for several months, but was recovered completely unchanged. Attempts to prepare the formate by reaction of the alcohol with formic-acetic anhydride were unsuccessful, dark viscous products being formed, possibly by opening of the tetrahydrofuran ring (compare Robinson and Smith, J., 1936, 195).