TABLE I

PHYSICAL PROPERTIES, YIELDS AND ANALYSES OF 2-ALKYLBICYCLOHEXYLS

Bicyclohexyl hydrocarbon	M.p., °C.	B.p., °C. at 760 mm.	$n^{20}\text{D}$	d^{20}, g./ml.	ΔH_f, kcal./mole	Est. purity, mole %	Heat of comb.,[c] kcal./mole	Relative yield, %	Carbon, %		Hydrogen, %		Viscosity, centistokes[d]			
									Calcd.	Found	Calcd.	Found	32° F.	100° F.	140° F.	210° F.
2-Methyl[a]	−26.43	249.87	1.4791	0.88447	4.4	98.9	1855	41	86.58	86.65	13.42	13.35	8.84	3.11	2.08	1.22
2-Methyl[b]	−10.27	255.00	1.4836	.89450	4.6	99.2	1870	59	86.58	86.58	13.42	13.41	12.85	4.20	2.69	1.51
2-Ethyl[a]	Glass	266.23	1.4827	.89065	...	..	1995	34	86.51	86.60	13.49	13.48	16.33	4.20	2.58	1.40
2-Ethyl[b]	−0.35	269.54	1.4851	.89624	5.4	99.9	2015	66	86.51	86.46	13.49	13.47	18.53	4.75	2.89	1.54
2-Propyl[a]	Glass	279.40	1.4807	.88527	...	..	2145	35	86.46	86.44	13.54	13.56	28.32	5.38	3.05	1.56
2-Propyl[b]	0.25	282.22	1.4838	.89205	5.7	99.8	2160	65	86.46	86.47	13.54	13.56	34.08	6.20	3.46	1.71
2-Isopropyl[a]	Glass	277.18	1.4843	.89305	...	..	2140	49	86.46	86.45	13.54	13.54	46.82	6.94	3.75	1.80
2-Isopropyl[b]	−9.13	283.06	1.4901	.90365	5.7	99.9	2165	51	86.46	86.50	13.54	13.53	29.12	6.54	3.78	1.91
2-Butyl[a]	Glass	294.15	1.4799	.88227	...	..	2300	40	86.40	86.42	13.60	13.48	42.37	6.74	3.64	1.76
2-Butyl[b]	−6.51	296.56	1.4827	.88819	6.5	..	2300	60	86.40	86.44	13.60	13.48	51.18	7.65	4.05	1.91

[a] Low-boiling isomer. [b] High-boiling isomer. [c] ASTM procedure: D240-39. [d] ASTM procedure: D445-46T.

synthesis of 2-methylbicyclohexyl and 2-ethylbicyclohexyl from cyclohexylidenecyclohexanone has been reported,[2] but no reference is made to the existence of geometrical isomerism in these hydrocarbons.

The general application of von Auwers' rule[3] has been shown to be susceptible to error[4,5] as indicated by the recent change in the name of the *cis* and *trans* isomers of 1,3-dimethylcyclohexane. Consequently, since the pertinent thermodynamic properties have not been investigated, no specific assignment of *cis* and *trans* configurations can be made, and the products isolated are referred to simply as the low- and high-boiling isomers.

The high-boiling isomer of each isomeric pair and the low-boiling isomer of 2-methylbicyclohexyl could be successfully crystallized. An estimation of their purities on the basis of their time–temperature melting curves and heats of fusion is shown in Table I. Because of the short length of the equilibrium portion of the melting curve for the high-boiling isomer of 2-butylbicyclohexyl, the estimation of purity of this compound was not deemed valid and is not recorded.

For the low-boiling isomers which could not be crystallized, fractions were combined on the basis of constant refractive index and density values. A systematic evaluation of purity could not be made for these isomers, but the distinct plateaus of refractive index and density values indicated purities of the same order of magnitude as those recorded for the compounds obtained in the crystalline state.

All of the physical properties were determined by methods previously described,[1] and the estimated mole % purities were determined according to the method of Glasgow, Streiff and Rossini.[6]

Experimental[7]

Materials and Procedure.—The 2-alkylbiphenyls used in this investigation had physical properties similar to those previously reported.[1] The quantity of each hydrocarbon hydrogenated varied according to the amount available for such use. Hydrogenations were carried out in a 3-liter bomb at 1500–2000 p.s.i. and 190–210°. A volume of methylcyclohexane equal to that of the hydrocarbon was used as solvent, and 10–12% by weight of UOP nickel was used as catalyst except for the hydrogenation of 2-butylbiphenyl. Small amounts of halogen-containing olefin were present in this material; consequently 18–20% by weight of UOP nickel was used in this case.

The quantities of material hydrogenated were as follows: 2590 g. (15.4 moles) of 2-methylbiphenyl; 1925 g. (10.6 moles) of 2-ethylbiphenyl; 1100 g. (5.6 moles) of 2-propylbiphenyl; 950 g. (4.8 moles) of 2-isopropylbiphenyl; and 1015 g. (4.8 moles) of 2-butylbiphenyl. Yields of completely hydrogenated product were essentially quantitative, although the rate of hydrogenation was much lower for the 2-butylbiphenyl than for any of the other hydrocarbons (23 hours compared to an average of 5 hours for each of the others), because of the presence of halogen impurity.

Purification.—Separation and purification of the five isomeric mixtures was effected by passage of the hydrogenation products through silica gel columns followed by careful fractionation at reduced pressure through six-foot Podbielniak distillation columns.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS
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[2] C. E. Garland and E. E. Reid, THIS JOURNAL, **47**, 2333 (1925).

[3] K. von Auwers, *Ann.*, **420**, 92 (1920).

[4] K. S. Pitzer and C. W. Beckett, THIS JOURNAL, **69**, 978 (1947).

[5] F. D. Rossini and K. S. Pitzer, *Science*, **105**, 647 (1947).

[6] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

[7] Macroanalyses by Mr. A. B. McKeown, heats of combustion by Mr. A. M. Busch, viscosities by Mr. W. J. Yankauskas, and other physical properties by Mr. J. F. Thompson of this Laboratory.

Paper Chromatography in the Separation of Estradiol-17α from Estradiol-17β and of Equilin from Equilenin

BY ERICH HEFTMANN

It has recently been shown that paper chromatography may be used for the identification of mixtures of estrone, estradiol-17β ("α"-estradiol) and estriol.[1] The same method is applicable to the binary mixtures of estradiol-17α and estradiol-17β and of equilin and equilenin with only a minor change in the developing solvent. The separation of the 17-epimers of estradiol and of dihydroequilenin by partition chromatography on Celite has also been accomplished by Haenni.[2]

Experimental

Conditions for the preparation of the *p*-nitrobenzeneazodimethoxyaniline derivatives of the estrogens and for the development of the chromatogram are exactly as previously described,[1] except that equilin and equilenin couple more readily without heating than the other estrogens studied and that the development with the modified solvent mixture takes only 1.25 hours. The new solvent mixture is prepared by equilibration of 200 cc. of petroleum ether (boiling range 35–60°), 100 cc. of toluene, 10 cc. of ethanol and 90 cc. of distilled water. The R_f values of estrogen derivatives in the new solvent mixture and in the solvent mixture previously described are given in Table I.

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[1] E. Heftmann, *Science*, **111**, 571 (1950).

[2] Unpublished work, mentioned in J. Carol, E. O. Haenni and D. Bates, *J. Biol. Chem.*, **185**, 267 (1950).

TABLE I

COLOR AND LOCATION OF SPOTS IN THE PAPER CHROMATOGRAM OF ESTROGENS

Compounds	Color of spots	*Rf* values in New solvent	*Rf* values in Old solvent[1]
Estradiol-17α[3]	Purple	0.32	0.96
Estradiol-17β	Purple	.09	.82
Estradiol-17α + estradiol-17β	Purple	.35 + 0.08	.96 + 0.83
Equilin	Purple	.49	.96
Equilenin[3]	Blue	.05	.80
Equilin + equilenin	Purple + blue	.45 + 0.05	.97 + 0.81
Estrone	Purple	.29	.96
Estriol	Purple	.00	.10

Discussion.—Paper partition chromatography is capable of resolving such closely related pairs as the epimeric estradiols and the equine estrogens equilin and equilenin, which differ only in the degree of saturation in ring B. The new solvent improves the separation of estradiol-17β from estrone and removes the latter farther from the yellow solvent front, but the estriol spot is not moved. This makes the identification of estriol difficult if other immobile pigments are present, as in urine. By using both the new and the old solvent mixtures in a two-dimensional chromatogram this difficulty can be avoided and the resolution further increased.

(3) Provided by Ayerst, McKenna and Harrison, Ltd., through the courtesy of Dr. Gordon Grant.

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Specific Gravities of Ferrous Sulfate Solutions

BY HARRIS HOLTZMAN AND LEONARD MAY

In view of the variable degree of hydration of commercial grade ferrous sulfate heptahydrate crystals known as copperas, it is necessary that each individual lot be tested before use. The compositions of different lots of copperas may run as low as $FeSO_4 \cdot 3\text{-}4H_2O$ instead of $FeSO_4 \cdot 7H_2O$.

Routine evaluations of commercial salts such as copperas are most readily performed by use of specific gravity or Baumé tables for aqueous solutions. However, when the currently accepted tables for aqueous ferrous sulfate solutions are used,[1] we have found that the values for composition of the salt are approximately 9% in error over values as determined by oxidimetric titrations of the same solutions, lower values being obtained by the chemical analysis.

An investigation of the literature indicated that the values given in the "International Critical Tables"[1] were based almost entirely on work performed prior to 1900.[2,3,4] Except for some work at very low concentrations,[5,6] it would appear that chemical analytical procedures were not used. It is also possible that, in the very earliest work, the monohydrate ($FeSO_4 \cdot H_2O$), which breaks down only at high temperatures,[7] was mistaken for the anhydrous salt. Such a discrepancy would result in an error of 6.5% (based on $FeSO_4 \cdot 7H_2O$), or 11.8% (based on $FeSO_4$).

In view of the discrepancies encountered in our laboratory, we decided to set up a specific gravity *vs.* concentration curve based on new analytical data.

Experimental Work.—Baker C.P. ferrous sulfate heptahydrate was used for this work. Analyses were run, using 0.100 *N* $KMnO_4$ and $K_2Cr_2O_7$ solutions for oxidation of ferrous iron. Titanous chloride titrations indicated less than 0.01% ferric iron, so that direct titrations with $KMnO_4$ or $K_2Cr_2O_7$ gave the total amount of iron without significant error. The differences between permanganate and dichromate titrations were less than 1 part in 400. Specific gravity determinations using pycnometer and hydrometer were made on solutions of several concentrations, temperature being maintained at 18°.

Results.—Titrations indicated that the C.P. ferrous sulfate was 99.0% pure, as $FeSO_4 \cdot 7H_2O$.

Table I, column A gives the concentration of $FeSO_4 \cdot 7H_2O$, in g. per liter at 18°, by actual analysis. Column D gives the concentration of $FeSO_4 \cdot 7H_2O$, in g. per liter at 18°, on the basis of "I.C.T." values,[1] and column E indicates the percentage error in composition introduced by use of "I.C.T." or chemical handbook tables.

TABLE I

A $FeSO_4 \cdot 7H_2O$ g. per l. by analysis	B Specific gravity 18°/18°	C Baumé = 145 − 145/B	D $FeSO_4 \cdot 7H_2O$ g. per l. ("I.C.T." values)	E % error in "I.C.T." tables
180.5	1.099	13.0	198.0	+ 9.9
198.2	1.107	14.0	215.2	+ 8.6
215.4	1.115	15.0	232.6	+ 8.0
230.5	1.124	16.0	250.2	+ 7.8
244.2	1.133	17.0	268.9	+10.1
			Av. deviation	+ 8.9

From these results, it is evident that the values given in the literature for specific gravities of ferrous sulfate solutions are in error, particularly for ranges around 10 to 20% or higher.

(1) "International Critical Tables," Vol. III, 1929. These values have been repeated and recalculated in terms of Baumé readings in several handbooks.

(2) Klein, *Ann. Physik*, **27**, 151 (1886).

(3) Gerlach, *Dinglers Polytechnisches Journal*, **181**, 129 (1866).

(4) Gerlach, *Z. Anal. Chem.*, **8**, 245 (1869).

(5) Trotsch, *Ann. Physik*, **41**, 259 (1890).

(6) Pasea, *Proc. Roy. Soc. Can.*, **6-III**, 27 (1900); MacGregor, *Chem. News* (Nov. 7, 1890).

(7) Mellor, "Treatise on Inorganic Chemistry," Vol. 14, p. 248.

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Paper Partition Chromatography of Simple Phenols[1]

BY RALPH L. HOSSFELD

The application of paper partition chromatography to the qualitative separation of phenolic compounds has been reported.[2-5] However, the results indicated that the method did not effectively separate mixtures of simple phenols of closely

(1) University of Minnesota Agricultural Experiment Station Scientific Journal Series Paper No. 2584.

(2) R. A. Evans, W. H. Paar and W. C. Evans, *Nature*, **164**, No. 4172, 675 (1949).

(3) E. C. Bate-Smith and R. G. Weltall, *Biochim. Biophys. Acta*, **4**, 427 (1950).

(4) A. E. Bradfield and E. C. Bate-Smith, *ibid.*, **4**, 441 (1950).

(5) G. Lindstedt, *Acta Chem. Scand.*, **4**, 448 (1950).