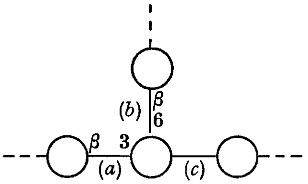
NOTES.

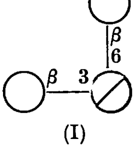
470. *Synthesis of* 3,6-*Di*-O-(β-D-*glucopyranosyl*)-D-*glucose.*

By J. R. Turvey and J. M. Evans.

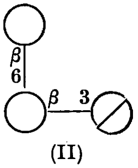
Structural analysis of laminarin[1] and yeast glucan[2] by partial acid hydrolysis and identification of the fragments produced has indicated that these polysaccharides may be unbranched. The evidence for this was based partly on the failure to isolate a trisaccharide of structure 3,6-di-*O*-(β-D-glucopyranosyl)-D-glucose (trisaccharide *Y*; I) which should be obtained if these polyglucoses possess branched structures. It must be observed, however, that this negative evidence is not conclusive and that there are alternative explanations of the absence of trisaccharide *Y* from the partial hydrolysates even if the structures are branched. A reference to the Figure makes this clear. Trisaccharide *Y* would not accumulate in the partial acid hydrolysate, (i) if either of the linkages marked (*a*) and (*b*) were, because of its position, more easily hydrolysable than other β-1,3- and β-1,6-linkages, or (ii) if the link (*c*), which might be either β-1,3 or β-1,6, were relatively more resistant. In the latter case, a branched tetrasaccharide would be produced instead of trisaccharide *Y*. We now report a chemical synthesis of trisaccharide



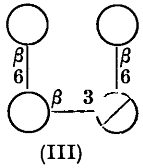
A point of branching in a glucan containing β-1,3- and β-1,6-links.



(I)
(*Trisaccharide Y*)



(II)



(III)

○ = *Glucose*; ⊘ = *reducing glucose unit.*

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[1] Peat, Whelan, and Lawley, *J.*, 1958, 724, 729.

[2] Peat, Whelan, and Edwards, *J.*, 1958, 3862.

Y and some additional information on its rate of hydrolysis, which indicates that the linkages (*a*) and (*b*) are not abnormally sensitive to acid hydrolysis. Trisaccharides similar to *Y*, *i.e.*, those with a reducing glucose unit having sugar units attached glycosidically to it at two points other than $C_{(1)}$, have been reported by Bailey *et al.*[3] and by Klemer,[4] but only limited information concerning their behaviour towards acid has been given.[3]

The Koenigs–Knorr reaction was used in this synthesis, 1,2,4,2′,3′,4′-hexa-*O*-acetyl-laminaribiose being condensed with acetobromoglucose in the usual manner.[5] Three synthetic oligosaccharides are possible products (after removal of acetyl groups), namely, the trisaccharides (I) and (II) and the tetrasaccharide (III). After removal of unchanged glucose and laminaribiose by chromatography on charcoal, the presence in the reaction mixture of two trisaccharides and one tetrasaccharide was indicated by paper chromatography. Fractionation by thick-paper chromatography gave trisaccharide *Y* in a chromatographically pure form. Partial acid-hydrolysis of *Y* gave sugars with the R_F values of laminaribiose and gentiobiose but, after reduction of the trisaccharide with sodium borohydride, only non-reducing disaccharides corresponding in R_F values to laminaribi-itol and gentiobi-itol were present in the hydrolysate. By contrast, the trisaccharide (II), which was also isolated, gave after reduction and partial hydrolysis gentiobiose and laminaribi-itol.

The hydrolysis of trisaccharide *Y* in 0·33N-sulphuric acid at 100° was followed by estimation of reducing power and by paper chromatography. In the initial stages of hydrolysis there was no rapid increase of reducing power, and gentiobiose and laminaribiose were liberated at approximately equal rates. After hydrolysis for 2 hr. under these conditions the conversion (as glucose) of trisaccharide *Y* was 40·4% compared with 35—40% for laminarin hydrolysed under the same conditions. It is concluded therefore that the linkages in this trisaccharide are not abnormally sensitive to acid and that the failure to isolate it from hydrolysates of laminarin and yeast glucan cannot be attributed to this cause.

Experimental.—The general methods of chromatography and the Koenigs–Knorr reaction were as described by Peat *et al.*[5] The analytical methods, reduction with sodium borohydride, and partial hydrolysis of oligosaccharides have also been described.[2,6]

Synthesis of trisaccharide Y. Laminaribiose (from laminarin;[1] 5 g.) was dissolved in anhydrous pyridine (100 ml.), triphenylmethyl chloride (10 g.) was added, and the solution left for 5 days at 18°. Acetic anhydride (20 ml.) was then added and the solution left for a further 2 days, then cooled to 0°. Water (1 ml.) was cautiously added and the precipitated triphenylmethanol filtered off. The filtrate was poured into iced water (2·5 l.) containing sodium acetate (10 g.) and left at 0° overnight. The precipitate was filtered off, washed with water, dissolved in acetone (100 ml.), and reprecipitated by pouring into water (500 ml.). Several such reprecipitations gave crude amorphous 1,2,4,2′,3′,4′-hexa-*O*-acetyl-6,6′-di-*O*-triphenylmethyl-laminaribiose (11·2 g.; $[\alpha]_D^{18}$ +5·9° in $CHCl_3$) which did not crystallise. Removal of triphenylmethyl groups was accomplished by dissolving the compound (10 g.) in glacial acetic acid (50 ml.) and adding 50% (w/v) hydrogen bromide in glacial acetic acid (6 ml.) as previously described.[5] Attempts to crystallise the resulting 1,2,4,2′,3′,4′-hexa-*O*-acetyl-laminaribiose failed but the crude amorphous compound had $[\alpha]_D^{18}$ +2·0° (*c* 0·24 in $CHCl_3$).

The hexa-*O*-acetyl-laminaribiose (3·8 g.) was condensed with 1-bromo-2,3,4,6-tetra-*O*-acetyl-α-D-glucose (3 g., 1·15 mol.), and the products deacetylated as previously described.[5] The mixture of sugars obtained (4·8 g.) was fractionated on a charcoal–Celite column (5 × 50 cm.), glucose and laminaribiose being removed by 10% (v/v) aqueous ethanol and the higher oligosaccharides with 50% (v/v) aqueous ethanol. After concentration of the latter solution to dryness (at 35°), examination by paper chromatography revealed two trisaccharides and a more slowly migrating sugar, possibly a tetrasaccharide. The two trisaccharides were

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[3] Bailey, Barker, Bourne, and Stacey, *Nature*, 1955, **176**, 1164; Bailey, Barker, Bourne, Grant, and Stacey, *J.*, 1958, 1895.

[4] Klemer, *Chem. Ber.*, 1956, **89**, 2583; 1959, **92**, 218.

[5] Peat, Whelan, and Evans, *J.*, 1960, 175.

[6] Peat, Whelan, and Roberts, *J.*, 1957, 3916.

separated by two chromatographic fractionations on thick filter paper, with butan-1-ol–acetic acid–water (4 : 1 : 5 by vol.) as solvent. A chromatographically pure specimen of the more slowly migrating sugar, trisaccharide *Y* (170 mg.), was obtained. The second trisaccharide (II) (94 mg.) was chromatographically identical with authentic 3-*O*-β-gentiobiosylglucose.

For the results of partial hydrolysis of the trisaccharides and of the alcohols prepared by their reduction with sodium borohydride, see above.

Hydrolysis of trisaccharide Y. The trisaccharide (170 mg.) was dissolved in water (15 ml.), and the concentration determined by complete acid-hydrolysis to glucose. A portion of this solution was used for measurement of specific optical rotation. The value observed (+14·4°) is in contrast to the values for 3-*O*-β-gentiobiosylglucose and 6-*O*-β-laminaribiosylglucose (−3·2° and −6·0° respectively) but is in agreement with the value (+14°) calculated from the known molar rotations of laminaribiose and gentiobiose. Comparison of the reducing power of the trisaccharide to Somogyi's alkaline copper reagent [7] with that of glucose indicated an apparent molecular weight of 520.

Portions (1 ml. each) of the solution were hydrolysed in a total volume of 10 ml. of 0·33N-sulphuric acid at 100° for varying times. The reducing power (as glucose) of each portion, was measured after cooling, and the percentage conversion calculated. The values obtained after 0·5, 1, 2, and 4 hr. were 11·5, 26·6, 40·4, and 51·7% respectively. Each portion was also examined by paper chromatography. In the early stages of hydrolysis, gentiobiose and laminaribiose were produced at comparable rates, but in the later stages laminaribiose disappeared before gentiobiose.

We thank Professor S. Peat, F.R.S., for his advice and the Department of Scientific and Industrial Research for a grant (to J. M. E.).

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[*Received, July 24th,* 1959.]

[7] Somogyi, *J. Biol. Chem.*, 1945, **160**, 61.

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471. *Isolation of Conessine from* Holarrhena mitis *R.Br.*

By V. P. BHAVANANDAN and G. P. WANNIGAMA.

Holarrhena mitis R.Br. is a rather tall slender tree with white smooth bark and is endemic to Ceylon.[1,2] The bark juice of this plant is used by native physicians in Ceylon as a remedy for dysentery and fevers. From this bark we have isolated conessine, and obtained evidence for the occurrence of the *N*-demethylated conessines. In general, we followed the procedures adopted by Haworth, McKenna, and Nazar-Singh [3] for *H. antidysenterica* and Pyman [4] for *H. congolensis.*

Experimental.—The dry ground bark (7545 g.) was mixed with lime (1245 g.) and extracted (Soxhlet) for 24 hr. with methanol (12 l.). The extract was concentrated to a thick brown syrup, which was dissolved in chloroform and shaken with dilute hydrochloric acid, the acid extract then being basified with ammonia. The liberated bases, isolated with ether, were mixed with hot 25% ethanolic oxalic acid. On cooling, conessine hydrogen oxalate separated as prisms, m. p. 260° (2·5 g.) (Found: C, 62·7; H, 7·9; N, 5·1. Calc. for $C_{28}H_{44}O_8N_2$: C, 62·7; H, 8·2; N, 5·2%).

The ethanolic mother-liquor was concentrated, diluted with water, and made alkaline with ammonia. The recovered bases, isolated with ether, were *N*-methylated with formaldehyde and formic acid.[5] The methylated bases were treated with hot 25% ethanolic oxalic acid; conessine hydrogen oxalate (10 g.) separated as prisms, m. p. and mixed m. p. 260°.

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[1] Trimen, " A Handbook to the Flora of Ceylon," Dulau & Co., London, 1895, Part III, p. 131.
[2] Kirtikar and B. D. Basu, " Indian Medicinal Plants," L. M. Basu, Allahabad, India, 1935, Vol. II, p. 1573.
[3] Haworth, McKenna, and Nazar-Singh, *J.*, 1949, 831.
[4] Pyman, *J.*, 1919, 163.
[5] Siddiqui, *J. Indian Chem. Soc.*, 1934, **11**, 283.

An aqueous solution of the total conessine hydrogen oxalate was basified with potassium carbonate and the product extracted with light petroleum (b. p. 60—80°). Evaporation of the dried (Na_2SO_4) extract gave an oil which crystallised on addition of dry acetone. Recrystallised from acetone, conessine separated out as plates, m. p. and mixed m. p. 125° (6·5 g.) (Found: C, 80·9; H, 11·4; N, 8·0. Calc. for $C_{24}H_{40}N_2$: C, 80·9; H, 11·2; N, 7·9%), $[\alpha]_D^{31}$ +23·8° (*c* 3·86 in EtOH).

X-Ray powder photographs of the conessine obtained and of authentic conessine were very similar. They were taken with a 9 cm. powder camera with Cu-$K\alpha$ radiation.

The authors thank Professor E. L. Fonseka for his kind encouragement, Professor R. D. Haworth, F.R.S., for a sample of authentic conessine, and Dr. C. A. Beevers of the University of Edinburgh for the *X*-ray powder photographs. Microanalyses were performed by Dr. K. W. Zimmermann of the C.S.I.R.O. Microanalytical Laboratory, Melbourne, Australia.

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[*Received, November 9th.* 1959.]

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472. *Organic Complex-forming Agents for Metals. Part IV.* Some New Heterocyclic "Complexones."*

By P. Biddle, E. S. Lane, and J. L. Willans.

As only a few compounds containing the *NN*-diacetic acid grouping adjacent to a heterocyclic tertiary nitrogen atom have been described, the synthesis of some representative compounds based on the benzimidazole, thiazole, and benzothiazole ring systems was carried out. 2-Amino- and 2-amino-6-methyl-benzothiazole, and 2-amino-thiazole and -benzimidazole, with hot alkaline sodium chloroacetate solution, gave compounds containing two $CH_2 \cdot CO_2H$ groups per molecule. It has been tacitly assumed that in all these cases the grouping introduced is the *NN*-diacetic acid grouping. It must be pointed out, however, that the heterocyclic amines used are tautomeric (*e.g.*, 2-aminobenzothiazole $\rightleftharpoons$ 2,3-dihydro-2-iminobenzothiazole) and thus the possibility that reaction with sodium chloroacetate could occur with the imino-form cannot be precluded. It is noteworthy that only two $CH_2 \cdot CO_2H$ groups could be introduced into the 2-aminobenzimidazole molecule. Although Irving and Weber[1] prepared 1-benzimidazolylacetic acid from benzimidazole and sodium chloroacetate, they too were unable to introduce more than two $CH_2 \cdot CO_2H$ groups into 2-aminomethylbenzimidazole with this reagent, the 1-position remaining unsubstituted.

In an attempt to extend the reaction to benzoxazole, cyanogen bromide was caused to react with *o*-aminophenol, 2-amino-4-nitrophenol, and 2-aminoresorcinol forming, respectively, 2-amino-, 2-amino-5-nitro-, and 2-amino-4-hydroxy-benzoxazole. On treatment with sodium chloroacetate these compounds decomposed with evolution of ammonia, demonstrating the instability of the benzoxazole ring system to alkaline reagents.

All these new "complexones" form complexes with metals in the expected fashion. The benzothiazole derivatives are of particular interest in that they precipitate copper at low pH values (3—4), deposition becoming complete as the pH is raised. Precipitation of copper by this class of amino-acid was unexpected, except possibly in pH ranges where the hydroxide could exist. Nickel, on the other hand, forms complexes with these reagents and remains in solution.

Experimental.—*Cyanogen bromide.* In the following reactions slightly less than a molecular proportion of cyanogen was used in order to ensure its complete removal from the reaction mixture so as to facilitate working-up.

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* Part III, *J.*, 1956, 4670.

[1] Irving and Weber, *J.*, 1959, 2296.

2-*Aminobenzoxazole.* Cyanogen bromide (10·0 g., 0·095 mole) was added in separate portions to a cooled, stirred solution of *o*-aminophenol (10·9 g., 0·1 mole) in alcohol (50 ml.) during ½ hr. After 1 hour's stirring, the mixture was filtered and the filtrate diluted with water (100 ml.), treated with charcoal, and neutralized with aqueous sodium hydroxide. Colourless crystals of the base were deposited (2·5 g.; m. p. 130—131°) (Found: C, 62·9; H, 4·3; N, 21·0. Calc. for $C_7H_6ON_2$: C, 62·7; H, 4·5; N, 20·9%). Skraup[2] gives m. p. 129—130°.

2-*Amino*-5-*nitrobenzoxazole.* Sodium 2-amino-4-nitrophenoxide (17·6 g., 0·1 mole) was agitated with water (50 ml.), and cyanogen bromide (10·0 g., 0·095 mole) added in separate portions. After 1 hour's stirring a dark brown product was filtered off. This was redissolved in dilute hydrochloric acid, and the solution was filtered and made basic with aqueous sodium hydroxide. The basic *product* was precipitated as a yellow solid, m. p. 294° (decomp.) (Found: C, 47·0; H, 2·7; N, 23·65. $C_7H_5O_3N_3$ requires C, 46·9; H, 2·8; N, 23·5%).

2-*Amino*-4-*hydroxybenzoxazole.* 2-Aminoresorcinol hydrochloride (22·0 g., 0·137 mole) in water (50 ml.) was neutralized with sodium hydrogen carbonate, cyanogen bromide (13·0 g., 0·123 mole) was added dropwise to the stirred slurry, and the mixture left for 2 days and then filtered. The filtrate was neutralized and the colourless precipitate filtered off. The *base* (10·2 g.) was recrystallized from water and had m. p. 183—184° (Found: C, 55·3; H, 3·9; N, 18·75. $C_7H_6O_2N_2$ requires C, 56·0; H, 4·0; N, 18·7%). A solution of this compound in acetone gave a red colour with uranyl nitrate solution.

2-*Aminobenzimidazole.* *o*-Phenylenediamine (43·2 g., 0·4 mole) was stirred with water (400 ml.) in an ice-bath, and cyanogen bromide (35·5 g., 0·333 mole) added dropwise during ½ hr. The mixture was stirred for 3 hr., filtered, and made basic with aqueous sodium hydroxide, the base being precipitated and filtered off; it had m. p. 229—230° (from aqueous acetone) (Found) N, 31·5. Calc. for $C_7H_7N_3$: N, 31·6%). Pierron[3] gives m. p. 222°. The *benzoyl derivative*, prepared by using benzoyl chloride and aqueous alkali, had m. p. 241·5—242° (Found: C, 70·7; H, 4·5; N, 17·4. $C_{14}H_{11}ON_3$ requires C, 71·0; H, 4·65; N, 17·7%).

2-*Aminobenzothiazole.* 2-Aminothiophenol and cyanogen bromide reacted almost quantitatively under the above conditions, to give 2-aminobenzothiazole, m. p. 129—130°, not depressed on mixing with an authentic sample.

Reaction of aminoheterocyclic compounds with chloroacetic acid. The following general procedure was used: Chloroacetic acid (0·6 mole) was dissolved in a solution of sodium hydroxide (0·6 mole) in water (75 ml.). The amino-compound (0·1 mole) was added and the mixture raised to the b. p. with stirring. A solution of sodium hydroxide (0·6 mole) in water (75 ml.) was added dropwise to keep the mixture alkaline to phenolphthalein. When no further reaction occurred the mixture was cooled and filtered and the filtrate made acid with hydrochloric acid. The "complexones" separated from this solution and were recrystallized from water. Thus were obtained:

2-*Di*(*carboxymethyl*)*aminothiazole* (39% yield from 2-aminothiazole), m. p. 210—215° (decomp.) [Found: C, 35·85; H, 4·45; N, 11·5; S, 13·6%; *M* (by titration), 236. $C_7H_8O_4N_2S,H_2O$ requires C, 36·0; H, 4·3; N, 12·0; S, 13·7%; *M*, 234]; 2-*di*(*carboxymethyl*)-*aminobenzothiazole* (64·5% yield from 2-aminobenzothiazole), very sparingly soluble in water, m. p. 230—240° (decomp.) [Found: C, 49·6; H, 3·8; N, 10·85; S, 12·35; *M* (by titration), 270. $C_{11}H_{10}O_4N_2S$ requires C, 49·65; H, 3·8; N, 10·5; S, 12·0%; *M*, 266]; 2-*di*(*carboxymethyl*)*amino*-6-*methylbenzothiazole* (40·1% yield from 2-amino-6-methylbenzothiazole, m. p. 244—245° (decomp.) [Found: C, 48·0; H, 4·35; N, 10·2; S, 11·5, *M* (by titration), 301. $C_{12}H_{12}N_2SO_4,H_2O$ requires C, 48·3; H, 4·7; N, 9·4; S, 10·7%; *M*, 298]; 2-*di*(*carboxymethyl*)-*aminobenzimidazole* (78·1% yield from 2-aminobenzimidazole), m. p. 262° (decomp.), gave a low nitrogen value on analysis [Found: C, 49·7; H, 4·6; N, 11·5% *M* (by titration), 260. $C_{11}H_{11}O_4N_3,H_2O$ requires C, 49·5; H, 4·9; N, 15·7%; *M*, 259].

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, DIDCOT, BERKS.

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Skraup, *Annalen*, 1919, **419**.
Pierron, *Ann. Chim. Phys.*, 1908, **15**, 145.

473. *Method for obtaining the Rate Coefficient and Final Concentration of a First-order Reaction.*

By E. S. SWINBOURNE.

WHEN carrying out kinetic studies it is frequently difficult or impracticable to measure the concentration of reactant at the start of a reaction or after equilibrium has been attained. Guggenheim[1] outlined a useful method for computing the reaction rate coefficient for a first-order process when the initial concentration is unknown and Hartley's method,[2] although tedious, may be used for the same purpose.

The final and (in some cases) the initial concentrations in a first-order process may be estimated from the extremely simple extrapolation procedure outlined below. The treatment is for a gas reaction obeying the law,

$$(p_\infty - p) = (p_\infty - p_0) \exp(-kt)$$

although its adaptation to any first-order process is obvious.

If pressure readings $p_1, p_2, \ldots. p_n$ are made at times $t_1, t_2 \ldots t_n$, and a second series $p_1', p_2', \ldots\ldots p_n'$ is made at the corresponding times $t_1 + T, t_2 + T, \ldots. t_n + T$ (where T is constant) then

$$(p_\infty - p_n) = (p_\infty - p_0) \exp(-kt_n)$$

and

$$(p_\infty - p_n') = (p_\infty - p_0) \exp[-k(t_n + T)]$$

Dividing of one these two equations by the other and rearranging them, we have

$$p_n = p_\infty (1 - \exp kT) + p_n' \exp(kT)$$

A straight line is therefore obtained when the pressure readings in the first series are plotted against the corresponding pressure readings in the second series, and an estimate of the reaction rate coefficient may be evaluated from the logarithm of the slope of the line. For $t = \infty$, $p_n = p_n' = p_\infty$. Therefore p_∞ is the point on the line at which p_n and p_n' have equal value. If the time of commencement of the reaction is known it is possible to extrapolate back along the curve and find the corresponding initial pressure.

The method has been successfully applied to the pressure–time data for the pyrolysis of cyclohexyl chloride[3] and cyclopentyl chloride,[4] and good agreement was found between the values of k so estimated and as determined by Guggenheim's procedure. Its application to the tabulated data is shown in the accompanying diagram.

t (min.)	p (cm.)			t (min.)	p (cm.)	t (min.)	p (cm.)
(0)	(15·1)		p_0	10	$24{\cdot}2_5$	18	$27{\cdot}2_5$
2	$17{\cdot}7_2$	p_1	↑	12	$25{\cdot}2_4$	20	$27{\cdot}6_9$
4	$19{\cdot}8_3$	↓	p_0'	14	$26{\cdot}0_5$	22	$28{\cdot}0_5$
6	$21{\cdot}5_9$	p_1'		16	$26{\cdot}7_1$	24	$28{\cdot}3_6$
8	$23{\cdot}0_5$						

In the graph, $T = 4$ min., and extrapolation gives $p_\infty = 30{\cdot}0$ cm. The reaction being assumed to commence at time $t = 0$, extrapolation back along the curve gives $p_0 = 15{\cdot}1$ cm. From the slope, k has been estimated as $1{\cdot}63 \times 10^{-3}$ sec.$^{-1}$ compared with $1{\cdot}65 \times 10^{-3}$ sec.$^{-1}$ computed by Guggenheim's method (same T calculations by the method of averages.[5]

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[1] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

[2] Hartley, *Biometrika*, 1948, **35**, 32.

[3] Swinbourne, *Austral. J. Chem.*, 1958, **11**, 314.

[4] Swinbourne, unpublished work.

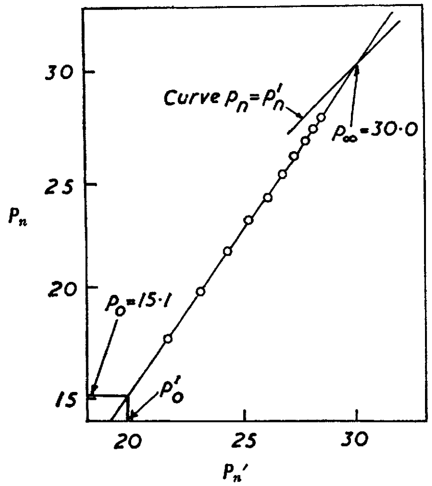
[5] Livingston in "Technique of Organic Chemistry," Interscience Publ. Inc., New York, 1953, Vol. VIII, p. 190, ed. Friess and Weissberger.

The features of the method may be critically assessed as follows:

(1) The original pressure data are used directly without the necessity of first taking logarithms, differences, etc. Plots are therefore quickly and easily made, and a number of graphs using different values of T may be conveniently compared on the one diagram.

(2) Readings taken towards the end of the reaction are " telescoped " on the graph and thus weighted less than those near the beginning which give a more accurate indication of the rate.

(3) Values of k, p_∞, and pressure at zero time (which is often close to the theoretical initial pressure, p_0) may be readily determined from the one straight-line graph. In order to obtain reliable estimates of k and p_∞, the data should normally be recorded over a period of time greater than the half-life ($t_{\frac{1}{2}}$) and preferably greater than two half-lives (this will depend upon the accuracy of the recorded values); T should be of the order of $0{\cdot}5t_{\frac{1}{2}}$ to $t_{\frac{1}{2}}$. For the accurate estimation of slope, a numerical method (*e.g.*, the method of averages) is to be preferred.



(4) The method is relatively insensitive to deviations from the strict first-order law, so it is advisable to have an independent check of the conformity of the reaction to this law.

(5) In comparison with the other two procedures previously mentioned, the present method has the advantages of simplicity and versatility. It appears to have the same order of reliability as Guggenheim's procedure for the estimate of k from a given set of data. The method due to Hartley is the most formally correct but, in view of the accuracy of measurement and the assumptions normally involved in chemical kinetic studies, it is doubtful whether it has any practical advantage over the other procedures (particularly in view of the more complex nature of the computations involved).

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University College, London, W.C.1. [*Received, October* 30*th*, 1959.]

474. *Echinocystic Acid in* Fouquieria peninsularis.

By F. Giral and L. Rodriguez Hahn.

Seven species of genus *Fouquieria* (Fouquieriaceae) have been found in Mexico. *F. peninsularis*, Nash, is known in Baja California (mainly in the Southern Territory) as " palo de Adan " (Adam's stick) or " cirio " (candle). Its bark produces foam with water and is used for washing. We have isolated from it a sapogenin which was identified as echinocystic acid by mixed melting points with the authentic sapogenin and its derivatives.

Echinocystic acid was first found, as saponin, in the root of *Equinocystis fabacea*, a Cucurbitacea from California,[1] and it has not been found in any other saponin. Recently [2] it has been found as free sapogenin in the seeds of various *Strophanthus* species together with the cardiac glucosides.

Experimental.—The botanical classification of "palo de Adan" was made by Dr. F. Miranda (Institute of Biology of the University of Mexico).

Extraction and purification. The dried and ground bark (received as splits from La Paz, Baja California) was percolated with ethanol containing 5% of benzene. The extracts were concentrated to a syrup which was hydrolysed with ethanol (400 ml.), water (400 ml.), and hydrochloric acid (40 ml.) for 4 hr. under reflux. The solution was diluted with water (4 l.), and the resin obtained filtered off, dried (10% yield), and extracted with boiling isopropyl ether (6 l.). The ethereal extract was decolorised with charcoal and evaporated to give crude echinocystic acid, m. p. 295—300° (0·85—2·58% yield). Crystallisation from methanol, acetone, or propan-2-ol gave the pure acid, m. p. 309—310°, $[\alpha]_D^{20}$ +35·1° (*c* 2·0 in dioxan) [Found: C, 76·1; H, 10·3%; *M*, (Rast) 533, (titration) 496. Calc. for $C_{30}H_{48}O_4$: C, 76·2; H, 10·2%; *M*, 473]. It gave a positive reaction with tetranitromethane, and did not contain a carbonyl group.

With boiling acetic anhydride (24 ml.; 1 hr.) the acid gave the diacetate (from ethyl acetate), m. p. 274—276°, $[\alpha]_D^{20}$ −11·0° (*c* 2·0 in dioxan) (Found: C, 73·6; H, 9·8. Calc. for $C_{34}H_{52}O_6$: C, 73·3; H, 9·4%). With ethereal diazomethane it gave the methyl ester (from methanol), m. p. 210—212°, $[\alpha]_D^{20}$ +27·6° (*c* 2·0 in alcohol) (Found: C, 75·6; H, 10·2. Calc. for $C_{31}H_{50}O_4$: C, 76·5; H, 10·3%). The methyl ester diacetate, prepared from the diacetate, had m. p. 200—201°, $[\alpha]_D^{20}$ −9·0° (*c* 2·0 in ethanol) (Found: C, 72·9; H, 9·5. Calc. for $C_{35}H_{54}O_6$: C, 73·6; H, 9·5%).

The microanalysis were by Dr. A. Bernhardt, Mulheim/Ruhr (Germany).

The authentic samples of echinocystic acid and its derivatives were generously provided by Professor C. R. Noller.

Laboratorios Farquinal, Industria Nacional Quimico Farmaceutica,
Mexico, D.F.
[*Received, December 7th,* 1959.]

[1] Bergsteinsson and Noller, *J. Amer. Chem. Soc.*, 1934, **56**, 1403.

[2] Barton, Mohr, Reichstein, and Schindler, *Helv. Chim. Acta*, 1956, **39**, 413.

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475. *The Tetrafluoroiodates.*

By G. B. Hargreaves and R. D. Peacock.

Although hexafluoroiodates, formed by the action of iodine pentafluoride on alkali fluorides, have been known for several years,[1] no attempts appear to have been made to prepare tervalent iodine complexes analogous to the tetrafluorobromates $MBrF_4$. During recent work it was noticed that a solution of alkali iodide in iodine pentafluoride, which has been treated with cold fluorine until the iodine colour just disappears, has mild reducing properties, *e.g.* it can reduce [2] MoF_6 to quinquevalent MoF_6^-. Since the iodide ion does

[1] Emeléus and Sharpe, *J.*, 1949, 2206.

[2] Hargreaves and Peacock, *J.*, 1958, 4390.

not exist in iodine pentafluoride solution it follows that a colourless reducing agent is present which can only be another complex fluoroiodate. We have confirmed this deduction by observing the behaviour of mixtures of potassium iodide and potassium fluoride dissolved in iodine pentafluoride. As expected, in the presence of sufficient potassium fluoride the initial iodine colour caused by the action of the iodine pentafluoride on the potassium iodide present soon disappears, especially on warming of the mixture.

Solid tetrafluoroiodates MIF_4 (M = K,Rb, and Cs) and solvated compounds MIF_4,IF_5 (M = Cs and Me_4N) are obtained by the action of iodine pentafluoride on the alkali iodides in cold, dilute solution (Table). They are white powders, decomposed by moist air and by water. It is clear that the stability of each series of salts is markedly dependent on the size of the cation, and parallels that of other polyhalides such as the tetrachloroiodates. The Debye *X*-ray powder photographs, like those given by the hexafluoroiodates, are not sufficiently good to indicate the symmetry or the unit-cell size, but their complexity suggests that the tetrafluoroiodates are not isostructural with the corresponding tetrafluorobromates.[3]

Starting material	Product from hot solution	Product from cold solution
NaI	NaF	NaF
KI	KIF_6 (>150°)	KIF_4 (<70°)
RbI	$RbIF_6$ (>150°)	$RbIF_4$ (70°)
CsI	$CsIF_6$ (>150°)	CsI_2F_9 (60°) $\xrightarrow[100^\circ]{\textit{in vacuo}}$ $CsIF_4$ (>120°)
Me_4NI	$Me_4NI_2F_9$	$Me_4NI_2F_9$ (slow decomp. at 140°)

(Temperatures in parentheses indicate limit of thermal stability.)

Experimental.—Tetrafluoroiodates(III). A large excess of iodine pentafluoride, prepared from the elements and purified by trap-to-trap distillation in a vacuum, was allowed to interact with finely powdered, freshly dried alkali iodide in the cold. Iodine was immediately liberated, and when all the solid had dissolved the excess of solvent was pumped off and the residual solid carefully warmed to about 50° in a vacuum to remove iodine. Tetrafluoroiodates were then obtained as follows: *potassium salt* (Found: F, 33·0; I, 45·3. KIF_4 requires F, 31·4; I, 48·4%), which slowly decomposed even at room temperature with loss of iodine; *rubidium salt* (Found: I, 43·3; F, 26·2%; RbI equivalent, 309. $RbIF_4$ requires I, 44·6; F, 26·3%; RbI equivalent, 288); solvated *cæsium salt* (Found: I, 46·6; F, 30·7. CsI_2F_9 requires I, 46·3; F, 30·7%); and solvated *tetramethylammonium salt* (Found: I, 52·2; F, 33·9. $Me_4NI_2F_9$ requires I, 50·9; F, 34·3%). When the solvated cæsium *salt* was heated in a vacuum at 100° *cæsium tetrafluoroiodate* was produced (Found: I, 37·9; F, 24·8. $CsIF_4$ requires I, 38·7; F, 22·6%). The tetramethylammonium salt solvate did not give a definite compound when heated; samples contained 51·8% and 53·4% of iodine after being heated in a vacuum at 80° and 140°, respectively. At 220° iodine pentafluoride was evolved but the " Pyrex " vessel was attacked.

Cæsium iodide was allowed to interact with a small excess of iodine pentafluoride. A white deposit, mixed with purple iodine crystals, was obtained. When the solvent had been removed in a vacuum the residue gave correct analytical figures for *cæsium hexafluoroiodate* (Found: I, 32·0. $CsIF_6$ requires I, 33·9%).

Hexafluoroiodates(V). Alkali iodides were treated as before with excess of iodine pentafluoride, and the solutions were boiled for a few minutes. They were then rapidly cooled and the iodine pentafluoride was pumped off. None of the residual solids, when treated with water, yielded free iodine (Found: I, 45·7; F, 40·2. Calc. for KIF_6: I, 45·3; F, 40·7%. Found: I, 38·3; F, 35·5. $RbIF_6$ requires I, 38·3; F, 35·5%. Found: I, 33·0; F, 30·0. $CsIF_6$ requires I, 33·9; F, 30·5%).

We thank Imperial Chemical Industries Limited, General Chemicals Division, Widnes, for the use of a fluorine cell, and the Department of Scientific and Industrial Research for a maintenance grant (to G. B. H.).

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EDGBASTON, BIRMINGHAM, 15.

[*Received, December 11th,* 1959.]

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[3] Sly and Marsh, *Acta Cryst.*, 1957, **10**, 378.

476. *Alkaloidal Constituents of* Senecio discolor, *D.C.: Retrorsine and Isatidine.*

By R. SCHOENTAL.

IN a collaborative investigation with Professor G. Bras, Mona, and Dr. P. György, Philadelphia, aimed at the identification of the specific factors responsible for " veno-occlusive " disease of the liver in children in Jamaica,[1] about 8 lb. of dried leaves of *Senecio discolor*, D.C. (a plant which may be used for the preparation of " bush-teas " [2]) were received from Professor A. D. Skelding, Department of Botany, Mona.

The main alkaloid isolated from the plant proved to be retrorsine and to be present mostly in the form of its *N*-oxide.

Experimental.—The crushed leaves were extracted with ethanol by percolation at room temperature, the extract was concentrated *in vacuo*, and the residue extracted with dilute hydrochloric acid. The filtered clear solution gave an opacity with the Mayer reagent, and a much stronger precipitation with the silicotungstic reagent. The latter reacts with pyrrolizidine alkaloids and with their *N*-oxides, but the Mayer test is given only by the alkaloids. It was thus evident that *N*-oxides predominate. This was confirmed by the isolation of only a small quantity of alkaloid by direct extraction of the basified extract with chloroform. The aqueous extract was therefore reduced with zinc and hydrochloric acid by Koekemoer and Warren's procedure [3] before extraction of the alkaloids. The yield of crude alkaloids was about 1·5 g., but this probably represented only part of the actual content of the plant, decomposition being indicated by darkening during the reduction. On paper chromatography the alkaloids gave a major spot corresponding to retrorsine. They were chromatographed on alumina with chloroform and then with methanol. On concentration, the chloroform eluate gave crystals which, recrystallised from alcohol, and then from acetone, afforded retrorsine as prisms,[4] m. p. and mixed m. p. 216—217° (decomp.) (depressed on admixture with seneciphylline) (Found: C, 61·9; H, 7·3; N, 4·2. Calc. for $C_{18}H_{25}O_6N$: C, 61·5; H, 7·2; N, 4·0%), having the correct infrared absorption spectrum (in KCl).

The methanolic eluate gave a brown oil on concentration. No attempt was made to identify minor alkaloids from the mother-liquors, as the presence of retrorsine and isatidine would account for the lesions seen in rats that were given the crude products of chloroform or butanol extracts from the plant material. The liver lesions were indistinguishable from those due to retrorsine [5] or isatidine.[6]

I thank Professor A. D. Skelding for the plant material, Professor F. L. Warren, Natal, for the gift of retrorsine, Dr. R. H. F. Manske for the gift of seneciphylline, and Dr. R. K. Callow, F.R.S., for the infrared absorption spectra and their evaluation. Microanalyses were by Mrs. B. Jarrett.

TOXICOLOGY RESEARCH UNIT, M.R.C. LABORATORIES,
WOODMANSTERNE ROAD, CARSHALTON, SURREY.
[*Received, December 21st*, 1959.]

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[1] Bras, Jelliffe, and Stuart, *Arch. Path.*, 1954, **57**, 285.
[2] Asprey and Thornton, *West Indian Med. J.*, 1955, **4**, 76.
[3] Koekemoer and Warren, *J.*, 1951, 66.
[4] Christie, Kropman, Leisegang, and Warren, *J.*, 1949, 1700.
[5] Davidson, *J. Path. Bact.*, 1935, **40**, 285; Schoental and Magee, *J. Path. Bact.*, 1959, **78**, 471.
[6] Schoental, *Voeding*, 1955, **16**, 268.

477. *Chemistry of New Zealand* Melicope *Species. Part VIII.** *Constituents of the Bark of* Melicope mantellii *Buch.*

By R. C. CAMBIE.

Melicope mantellii BUCH. has been considered by botanists at various times to be a distinct species,[1] a variety of *M. ternata* [2] or a hybrid of *M. ternata* and *M. simplex*.[3] In earlier parts of this series [4,5] it was shown that, besides meliternatin and ternatin, the bark of *M. ternata* contains meliternin, wharangin, and xanthoxyletin, while the bark of *M. simplex* contains melisimplexin, melisimplin, evodionol, and alloevodionol 7-methyl ether. As the barks of these species contain some constituents not common to both it was considered that chemical examination of the bark of *M. mantellii* might aid the botanical identification. Accordingly, the bark was extracted and worked up as in the previous investigations and has led to the isolation of the same constituents as are present in *M. ternata*.

Although paper-chromatographic investigation indicated that the constituents were distributed in light petroleum, ether, and ethyl acetate extracts, the bulk of flavonoid material was contained in the ether extract. Meliternatin, the principal constituent, was isolated by dilution of a concentrated hydrochloric acid extract and separated from small amounts of meliternin by fractional crystallisation. Ternatin occurred in the fraction soluble in sodium hydroxide while xanthoxyletin crystallised from the neutral fraction. These compounds were all identified by direct comparison with authentic samples. Although no authentic sample of wharangin from *M. ternata* remained for direct comparison, a small amount of a flavonoid compound was isolated from a fraction soluble in sodium carbonate, whose properties agreed well with those previously recorded for wharangin.[4] From a sodium hydrogen carbonate extract, cinnamic acid, a constituent not detected in the previous investigation of *M. ternata*, was isolated. There was no evidence for the presence of melisimplexin or melisimplin when fractions and authentic samples were examined by co-chromatography. These results support the view that *M. mantellii* is probably a variety of *M. ternata*.

Experimental.—Analyses are by Dr. A. D. Campbell, University of Otago, New Zealand. Infrared spectra were measured as potassium bromide discs. Descending paper chromatography of flavonoid constituents was carried out on Whatman's No. 1 paper with the system 1% ammonia solution–dioxan–light petroleum (1 : 1 : 1; upper phase). The positions of spots were shown by ammonia vapour, and by spraying with Dragendorff's reagent, and then with 5% aqueous ferric chloride. Melisimplexin and melisimplin have R_f 0·73 and 0·83, respectively.

Extraction. The dried and ground bark (2·02 kg.), from a specimen of *M. mantellii* Buch. cultivated in the Auckland Domain, was exhaustively extracted (Soxhlet) with methanol, and the solvent removed *in vacuo*. The residual tar was dissolved in the minimum amount of methanol and intimately mixed with Celite. The dried and powdered mass was then successively extracted (Soxhlet) with light petroleum, ether, ethyl acetate, and acetone, each for 24 hr. The concentrates from the first three extracts were fractionated between saturated aqueous sodium hydrogen carbonate, 10% aqueous sodium carbonate, and 10% aqueous sodium hydroxide and then extracted with concentrated hydrochloric acid. The highly coloured acid extracts were immediately diluted with a ten-fold excess of water whereupon completely alkylated flavonols were precipitated. An amorphous colourless solid from the neutral fraction of the light petroleum extract contained a mixture of long-chain aliphatic alcohols (infrared spectrum) which were not further investigated.

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* Part VII, Briggs and Locker, *J.*, 1951, 3136.

[1] Buchanan, *Trans. New Zealand Inst.*, 1871, **3**, 212.

[2] Kirk, " The Forest Flora of New Zealand," Government printer, New Zealand, 1889, p. 118; Cheeseman, " Manual of the New Zealand Flora," Government printer, New Zealand, 2nd Edn., 1925, p. 539.

[3] Cockayne, *The New Phytologist*, 1923, **22**, 115; Allan, *Genetica*, 1925, **7**, 288.

[4] Briggs and Locker, *J.*, 1949, 2157.

[5] Briggs and Locker, *J.*, 1950, 2376; 1951, 3131.

Meliternatin. Fractional crystallisation of the acid-soluble fraction of the ether extract from aqueous dioxan and then from ethanol gave, as the major product, meliternatin (181 mg.), m. p. and mixed m. p. 201—201·5°, R_f 0·42 (Found: C, 61·6; H, 3·9; OMe, 17·0. Calc. for $C_{19}H_{14}O_8$: C, 61·6; H, 3·8; 2OMe, 16·8%) (identical infrared spectrum).

Meliternin. The more soluble material from the fractional crystallisation above gave meliternin (16 mg.), m. p. and mixed m. p. 184—185°, R_F 0·17 (identical infrared spectrum).

Ternatin. Crystallisation from aqueous ethanol of the residue from the sodium hydroxide soluble fraction of the ether extract gave ternatin (24 mg.), m. p. and mixed m. p. 209—210°, R_F 0·63 (identical infrared spectrum).

Wharangin. Slow crystallisation from methanol of the residue from the sodium carbonate soluble fraction of the light petroleum extract gave wharangin (3 mg.), m. p. 274—276° (lit.,[4] m. p. 277—278°), R_f 0·09. The properties were identical with those previously recorded. Infrared spectrum: 3448 (OH), 3333 (OH), 2941 (C–H), 2874 (C–H), 1650 (conjugated CO) cm.$^{-1}$.

Xanthoxyletin. The neutral fraction from the ether extract was washed well with water, and solvent was removed from the dried solution. The residue in the presence of ethanol slowly deposited xanthoxyletin (58 mg.), m. p. and mixed m. p. 134—135° (identical infrared spectrum).

Cinnamic acid. The gum from the sodium hydrogen carbonate fraction of the ether extract was extracted with hot water. Concentration of the extract gave plates of cinnamic acid (20 mg.), m. p. and mixed m. p. 132—132·5° (Found: C, 72·8; H, 5·8. Calc. for $C_9H_8O_2$: C, 73·0; H, 5·4%).

The author thanks Dr. R. C. Cooper, Auckland Institute and Museum, for identification and assistance in collection of the specimen, Mr. J. A. McPherson, Auckland City Council Parks Department, for a generous gift of the bark, Mr. B. Anderson of this Department for R_f measurements and Professor L. H. Briggs for continued interest in this work. Assistance is gratefully acknowledged from the Research Grants Committee of the University of New Zealand.

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[*Received, December 23rd,* 1959.]

478. *The Heats of Combustion of Butanal and Heptanal.*

By G. R. Nicholson.

The standard heats of combustion of butanal and heptanal have been determined, and their heats of formation calculated. There is a previous estimated value [1] for the heat of formation of butanal, and Kharasch [2] quotes a value for the heat of combustion of heptanal based on early measurements by Louguinine (1880).

Samples of the two aldehydes were supplied by Imperial Chemical Industries Limited, Heavy Organic Chemicals Division. Preparation of pure aldehydes presents considerable difficulty. It was stated that the butanal sample contained (% by weight) water 0·21 and butyric acid 0·94, whilst the heptanal sample contained water 0·04 and heptanoic acid 1·25. In corrections of the combustion results for the acid impurities, Kharasch's values [2] for their heats of combustion (524·3 and 986·1 kcal./mole for butyric and heptanoic acid, respectively) were used. There are no more recent reliable values for these acids, but errors of, say, ±3 kcal./mole would be insignificant in this application.

Experimental.—A Griffin–Sutton bomb [3] of capacity 240 c.c., in an isothermal calorimeter of Dickinson type,[4] was used, the apparatus having previously been calibrated by combustion of benzoic acid (B.D.H. thermochemical standard). Calorimeter temperatures were measured with a platinum resistance thermometer of Meyers's type,[5] which had been constructed and calibrated at fixed points in this laboratory, in conjunction with a Smith's no. 3 type bridge.[6]

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[1] Parks, Kennedy, Gates, Mosley, Moore, and Renquist, *J. Amer. Chem. Soc.*, 1956, **78**, 56.
[2] Kharasch, *Bur. Stand. J. Res.*, 1929, **2**, 359.
[3] Carlton-Sutton, *J. Sci. Instr.*, 1933, **10**, 286.
[4] Dickinson, *Bull. Bur. Stand.*, 1915, **11**, 189.
[5] Meyers, *Bur. Stand. J. Res.*, 1932, **9**, 807.
[6] Smith, *Phil. Mag.*, 1912, **24**, 541.

Soda-glass ampoules were completely filled with samples of the two aldehydes by means of a hypodermic syringe, and then sealed. Filling was done in a glove-box in an atmosphere of nitrogen since aldehydes react fairly quickly with atmospheric oxygen. The ampoules contained 0·6—0·8 g. of sample. Sample weights were corrected for buoyancy, densities of 0·811 g./c.c. for butanal [7] and 0·850 g./c.c. for heptanal [8] being used, and the stated water contents were subtracted. Sealed ampoules were pressure-tested at 30 atm. (equal to the initial oxygen pressure in the bomb), and those surviving were used for combustion. To promote breaking, the ampoules were smeared locally with 0·01—0·02 g. of petroleum jelly which was ignited by means of a platinum wire and cotton-thread fuse. Corrections to the gross heat evolved were made for the heats of combustion of the cotton and petroleum jelly (previously determined), the joule heat in the platinum wire, and the heat produced in the formation of nitric acid in the bomb from residual nitrogen in the oxygen.

Corrections were also made for small quantities (up to 0·8 mg.) of residual carbon found fused in the remains of the ampoules after combustion. The gaseous products of combustion were tested for carbon monoxide by using a " Pallado-Sulphite " Detector (Siebe, Gorman and Co. Ltd.) and corrections made for up to 0·003% by volume of carbon monoxide.

In the case of butanal ten satisfactory combustions gave a mean heat of combustion for the sample (less water) of 8·1894 ± 0·0047 kcal./g. (1 cal. = 4·1840 absolute joules), referred to the usual standard conditions (isothermal combustion of the liquid at 25° and a constant pressure of 1 atm.) with CO_2(g) and H_2O(l) as products of combustion. The estimated error was calculated by combining the combustion error (twice the standard error of the mean) and the benzoic acid calibration error. Correction for butyric acid then gave the heat of combustion, for butanal alone, as 8·2106 ± 0·0047 kcal./g., or $-\Delta H_c°(l) = 592{\cdot}05 \pm 0{\cdot}34$ kcal./mole (*M*, 72·108). This leads to a heat of formation $\Delta H_f°(l) = -57{\cdot}43$ kcal./mole by using appropriate heats of formation [9] of CO_2(g) and H_2O(l). Parks *et al.*[1] have estimated the value $\Delta H_f°(l) = -58{\cdot}94$ kcal./mole from that for butan-1-ol on the assumption that the heat of hydrogenation of butanal is the same as that of acetaldehyde.

In the case of heptanal, six satisfactory combustions gave a mean heat of combustion for the sample (less water) of 9·2801 ± 0·0078 kcal./g. referred to standard conditions as above. Correction for heptanoic acid then gave the heat of combustion, for heptanal alone, as 9·3017 ± 0·0078 kcal./g. or $-\Delta H_c°(l) = 1062{\cdot}1 \pm 0{\cdot}9$ kcal./mole (*M*, 114·189). This is equivalent to $\Delta H_f°(l) = -74{\cdot}5$ kcal./mole. Kharasch [2] gives 1062·4 kcal./mole for the heat of combustion derived from Louguinine's results (1880). This value, however, should have the Washburn correction to standard states applied, and should also be corrected for temperature, molecular weight, and the energy unit to bring it up to date. If this is done the value becomes about 1061·7 kcal./mole, but this takes no account of possible impurity of Louguinine's sample of heptanal.

Imperial Chemical Industries Limited, Dyestuffs Division,
Hexagon House, Blackley, Manchester, 9. [*Received, January 28th,* 1960.]

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[7] Imperial Chemical Industries Limited, Heavy Organic Chemicals Division, personal communication.

[8] " Handbook of Chemistry and Physics," Chemical Rubber Publ. Co., Cleveland, Ohio, 37th edn., 1955.

[9] " Selected Values of Chemical Thermodynamic Properties," U.S. Dept. Commerce, Nat. Bur. Standards, Washington, D.C., 1952.

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479. *The Heat of Combustion of* 3,5,5-*Trimethylhexanol.*

By G. R. Nicholson.

The standard heat of combustion of 3,5,5-trimethylhexanol has been determined, and its heat of formation calculated. There are no previous published values for this compound.

A sample of the alcohol was supplied by Imperial Chemical Industries Limited, Heavy Organic Chemicals Division. It was stated to contain 0·16% by weight of water and less than 0·0003 equiv. of acid; no other impurities were detected by chromatographic analysis.

Experimental.—The method of measurement was as previously described [1] except that a Mahler–Cook bomb of capacity 540 c.c. was used. Ampoules for combustion contained 1·1—1·3 g. of sample. Sample weights were corrected for buoyancy by using a density [2] of 0·826 g./c.c., and the stated water content was subtracted.

It proved difficult to obtain complete combustion, but ultimately five satisfactory measurements were obtained. Corrections were made for residual carbon found fused into the ampoules after combustion (up to 2·9 mg.), but no carbon monoxide was detected by the method previously described [1] (lower limit of sensitivity about 0·0005% by volume in the gaseous products of combustion). The mean heat of combustion for the sample (less water) was 9·8465 ± 0·0050 kcal./g. (1 cal. = 4·1840 absolute joules) referred to the usual standard conditions (isothermal combustion of the liquid at 25° and a constant pressure of 1 atm.), with CO_2(g) and H_2O(l) as products of combustion. The estimated error was calculated as before.[1] The acid impurity was taken to be 0·0003 mole of the corresponding carboxylic acid per mole of alcohol; this is equivalent to 0·03% by weight. For such a small impurity the heat of combustion of the acid need not be known precisely, and the value 1295 kcal./mole was estimated from values given by Kharasch [3] for lower aliphatic carboxylic acids. Correction for acid then gave the heat of combustion, for 3,5,5-trimethylhexanol alone, as 9·8470 ± 0·0050 kcal./g. or $-\Delta H_c{}^\circ(l) = 1420{\cdot}5 \pm 0{\cdot}7$ kcal./mole (*M*, 144·259). This leads to a heat of formation $\Delta H^\circ{}_f(l) = -109{\cdot}2$ kcal./mole by using appropriate heats of formation of CO_2(g) and H_2O(l).[4]

IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9.

[*Received, January 28th,* 1960.]

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[1] Nicholson, preceding paper.

[2] Imperial Chemical Industries Limited, Heavy Organic Chemicals Division, personal communication.

[3] Kharasch, *Bur. Stand. J. Res.*, 1929, **2**, 359.

[4] " Selected Values of Chemical Thermodynamic Properties," U.S. Dept. Commerce, Nat. Bur. Standards, Washington, D.C., 1952.