

TABLE 1—MOLAR EXCESS VOLUMES V_m^E FOR $x\text{C}_6\text{H}_{12} + (1-x)\text{C}_6\text{H}_6$ AT 2.98.15K AND THEIR DEVIATIONS δV_m^E FROM EQUATION 1.

x	V_m^E $\text{cm}^3\text{mol}^{-1}$	$10^4 \delta V_m^E$ $\text{cm}^3\text{mol}^{-1}$	x	V_m^E $\text{cm}^3\text{mol}^{-1}$	$10^4 \delta V_m^E$ $\text{cm}^3\text{mol}^{-1}$
0.0603*	0.1425	16	0.5190	0.6488	14
0.0879	0.1991	-8	0.5604	0.6414	1
0.1089	0.2421	-1	0.5713	0.6364	-18
0.1319*	0.2847	-19	0.6141	0.6207	7
0.1613	0.3384	-11	0.6698*	0.5825	9
0.2576	0.4838	-4	0.6856	0.5659	-18
0.3874	0.6088	8	0.8033	0.4204	-3
0.4691	0.6424	-5	0.8761	0.2923	13
0.4749	0.6468	28	0.9051*	0.2801	-8

* See Text.

TABLE 2—COMPARISON OF MOLAR EXCESS VOLUMES OF $x\text{C}_6\text{H}_{12} + (1-x)\text{C}_6\text{H}_6$ DETERMINED WITH DIFFERENT TECHNIQUES AND FITTED IN $V_m^E/\text{cm}^3\text{mol}^{-1} = x(1-x)A + B(1-2x) + C(1-2x)^2$

	a	b	c	d	e	f	g
0.1	0.2246	0.2297	0.2294	0.2297	0.2276	0.2318	0.2249
0.2	0.4030	0.4092	0.4092	0.4104	0.4049	0.4130	0.4058
0.3	0.5337	0.5390	0.5393	0.5418	0.5347	0.5458	0.5494
0.4	0.6160	0.6193	0.6197	0.6237	0.6116	0.6241	0.6230
0.5	0.6472	0.6496	0.6497	0.6551	0.6313	0.6535	0.6546
0.6	0.6271	0.6289	0.6284	0.6349	0.6207	0.6313	0.6325
0.7	0.5538	0.5558	0.5545	0.5615	0.5487	0.5563	0.5560
0.8	0.4259	0.4283	0.4264	0.4328	0.4231	0.4273	0.4248
0.9	0.2418	0.2440	0.2424	0.2465	0.2413	0.2426	0.2391

	A	B	C
a This work	2.5887	-0.1195	0.0044
b Kumaran and McGlashan ^a	2.5983	-0.0990	0.0518
c Stokes, Leven and Marsh ^a	2.5988	-0.0901	-0.08445
d Goates, Ott and Moellmer ^a	2.6206	-0.1168	0.0395
e Radojkovic', Tasic' and Djordjevic' ^a	2.565	-0.095	0.063
f Weeks and Benson ^a	2.6141	-0.0744	0.0337
g Wood and Austin ^a	2.6180	-0.0986	-0.0633

uncertainties in the experimental determinations. (0.0011 for the temperature variation of $\pm 0.005^\circ$ and 0.0002 $\text{cm}^3 \text{mol}^{-1}$ for uncertainties in the composition). V_m^E values at rounded mole fractions have been compared in Table 2 with the reported values determined by different techniques. To test the reproducibility of the results, four mole fractions marked with asterisk were studied by making fresh lot of solvents. The agreement is satisfactory. Comparison of our results with those obtained using non-dilatometric techniques reveals that no systematic conclusion or reason regarding the deviations may be drawn. Vibrating densitometer^a gives higher values for all mole fractions while a similar instrument⁴ gives lesser values for most of the range of compositions. Values determined by magnetic float are the highest of all the techniques. Our simple dilatometer which does not involve the use of any standard joint gives quite satisfactory results agreeing to the dilution dilatometric technique values.

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Chemical Investigation of the Leaves of *Rubus moluccanus* Linn. (Rosaceae)

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RUBUS moluccanus Linn. (Rosaceae) is a plant of tropical India and grows abundantly in South India. The leaves and fruits of the plant are used as a remedy for the nocturnal micturation of children¹.

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Chemical investigation of the plant resulted in the isolation of a triterpene acid which is characterised as tormentic acid from the following chemical and spectral analyses.

The triterpene acid is isolated as its methyl ester from the acid fraction of the ethanolic extract of the air dried powdered leaves of the plant by column chromatography over neutral alumina using benzene as eluent. The methyl ester, $C_{81}H_{50}O_5$, M^+ 502, mp. 156° , $[\alpha]_D^{43} (CHCl_3)$ gives positive Libermann Burchardt test for triterpene. ν_{max}^{nujol} 3500 (OH), 1720 (COOR) cm^{-1} . The PMR spectrum (90MHz, $CDCl_3$) shows signals at 5.3 (m, 1H), 3.63 (s, 3H), 3.02 (d, 1H, $J=10Hz$), 2.90 (m, 1H), 0.78–1.85 ppm (m, 21H).

Treatment of the methyl ester with acetic anhydride and pyridine on steam bath for 6 hours furnishes a diacetyl derivative, $C_{85}H_{54}O_7$, M^+ 586, mp. $101-2^\circ$, $[\alpha]_D^{25} (CHCl_3)$, ν_{max}^{nujol} 3500 (OH), 1730, 1250 (OCOOR) cm^{-1} . PMR spectrum shows signals at 5.30 (m, 1H), 5.05 (q, 1H, $J_1=5Hz$, $J_2=5Hz$), 4.76 (d, 1H, $J=10Hz$), 2.06 (s, 3H), 1.96 ppm (s, 3H).

Alkaline hydrolysis of the methyl ester gives the free triterpene acid, $C_{80}H_{48}O_5$, mp. $272-3^\circ$, $[\alpha]_D^{20}$ (pyridine) crystallises from ethanolic chloroform in fine needles.

All these physical and spectral data are found to be in close conformity with tormentic acid previously isolated from *Potentilla tormentilla* Neck (*Rosaceae*)². Complete identity of our triterpene acid as methyl ester with methyl tormentate is established by the direct comparison with an authentic sample (mmp, tlc).

This work, probably in our knowledge, constitute the second isolation of tormentic acid.

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Studies on the Synthesis of Heterocyclic Compounds—Part-I. 1-Hydroxy-3-Substituted-4-Keto-3,4-Dihydrophthalazines

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1-HYDROXY-3-phenyl-4-keto-3,4-dihydrophthalazine is useful in the chemotherapy of tuberculosis¹. The following general methods are known for the preparation of the title compounds²⁻⁶.

(i) Isomerisation of N-arylamino-phthalimide by alcoholic sodium ethoxide.

(ii) Oxidation of 1-hydroxy-3-aryl-3,4-dihydrophthalazine-4-acetic acid by potassium permanganate.

(iii) Demethylation of *o*-methyl ethers of 1-hydroxy-3-aryl-4-keto-3,4-dihydrophthalazines by hydrobromic acid.

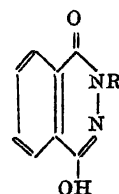
The present communication describes a new method for the synthesis of hydroxyphthalazines using polyphosphoric acid (PPA) as a condensing agent. This method has the advantage over other methods in respect of high yields with clean products.

Experimental

Synthesis of 1-hydroxy-3-substituted-4-keto-3, 4-dihydrophthalazines :

A mixture of phthalic anhydride (0.03M) and mono N-substituted hydrazine (0.03M) was heated on a sandbath with PPA (12 ml : 20 gm :: H_3PO_4 : P_2O_5) at $150^\circ (\pm 10^\circ)$ for half an hour and allowed to cool. The mass was decomposed with ice-water and the compound purified by crystallisation from acetic acid.

TABLE



No.	R	Yield	M.P. °C	Colour	References
1	H	80%	333°	Colourless	2-4
2	C_6H_5	78%	211°	Yellowish-white	5,6
3	$C_6H_4(NO_2)_2$ (2 : 4)	92%	271°	Yellowish-white	7
4	$CH_3C_6H_4$	68%	245°	Yellowish-white	8

The compounds are soluble in dilute alkali giving red colouration and insoluble in dilute mineral acid. Further work along this line is in progress.

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