

The acid-base titration method previously described ("Experimental") was used for determining the solubility of HCl reported in Table II. The solubility of HCl in *n*-butanol at 45°C was obtained to check the accuracy of the method: 0.66 mole of HCl per mole of *n*-butanol, which is the same as the value reported by Gerrard (7). The solubility of HCl expressed as mole of HCl per mole of ROH is very nearly the same in the temperature range of 80–140°C also. Ionin et al. (8) and Gerrard et al. (5–7) have shown similar behavior only up to a temperature of 60°C.

ACKNOWLEDGMENT

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ORGANIC SECTION

Ternary Liquid Equilibrium Systems Ethanol–Water–Methyl Isobutyl Carbinol and Acetic Acid–Water–Ethyl Butyrate

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Phase equilibrium data for the ternary liquid-liquid systems ethanol–water–methyl isobutyl carbinol and acetic acid–water–ethyl butyrate were determined at three temperatures adopting the method of Othmer, White, and Trugger and a new method which is a simple modification of the same. There is fair agreement between the data obtained by both methods. The tie-line data were correlated by the methods of Hand and Othmer and Tobias. The effect of temperature on distribution is slight. In the system ethanol–water–methyl isobutyl carbinol, the solute is in greater weight fraction in the solvent phase, and in the system acetic acid–water–ethyl butyrate, the solute is present in greater weight fraction in the aqueous phase.

The aim of the present investigation is to determine the phase-equilibrium data for the systems ethanol–water–methyl isobutyl carbinol and acetic acid–water–ethyl butyrate at three different temperatures and atmospheric pressure using a method which is a simple modification of the method of Othmer et al. (3) for determining the weight fraction of the components in each of the phases in heterogeneous ternary liquid-liquid systems. The proposed method, despite its limitations, is useful for such systems where the determination of the tie-line data is limited by the accuracy of the analytical methods. The phase-equilibrium data at 28°C for the system acetic acid–water–ethyl butyrate were reported earlier by Ramana Rao and Dakshinamurty (4).

MATERIALS

Absolute alcohol was used. Methyl isobutyl carbinol from the British Drug House was fractionated; the fraction boiling

between 131.5° and 132°C was collected and used (density at 30° = 0.8003 g/cc and refractive index at 30°C = 1.4090 for sodium D line). Acetic acid from the British Drug House, analar grade of 99.8% purity, having a density at 30°C of 1.0365 and a refractive index at 30°C of 1.3680 was used. Ethyl butyrate (Naarden Co., density at 30°C = 0.8685 and refractive index at 30°C = 1.3880) with negligible free acidity was used.

PROCEDURE

Weighed mixtures having a constant ratio of x_c/x_w , x_w/x_s , or x_s/x_c and increasing amounts of the third component were placed in a borosilicate glass test tube (20 cc) with a ground glass joint, and fitted with a thermometer. The test tube was slowly heated or cooled in a water bath and the temperature, corresponding to the appearance or disappearance of turbidity, was noted. The end points were reproducible to $\pm 0.5^\circ\text{C}$ either on heating or cooling. Thus, the phase-equilibrium

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points of several mixtures of different temperatures (5–60°C) were obtained. Graphs were drawn between temperature and percentage of the third component (Figure 1) for the system ethanol–water–methyl isobutyl carbinol, with a constant ratio of x_c/x_w , and so forth, as parameters. A similar procedure was adopted for the other system. From these graphs phase-equilibrium points for the required isotherms were interpolated and thus the three isotherms were plotted in each case.

For the determination of the tie lines, a known mixture was taken into a separating funnel and kept for 6 hr in a thermostated bath at the required temperature ($\pm 0.1^\circ\text{C}$) with frequent shaking. At the end of the period the separating funnel was taken out and the layers were separated immediately and weighed. Also, the refractive indices of the two phases were determined by means of an Abbe refractometer. The tie lines were located by drawing lines through the known mixture points by trial and error using the mixture rule. The saturation isotherm and tie-line data were determined at 30°C for the

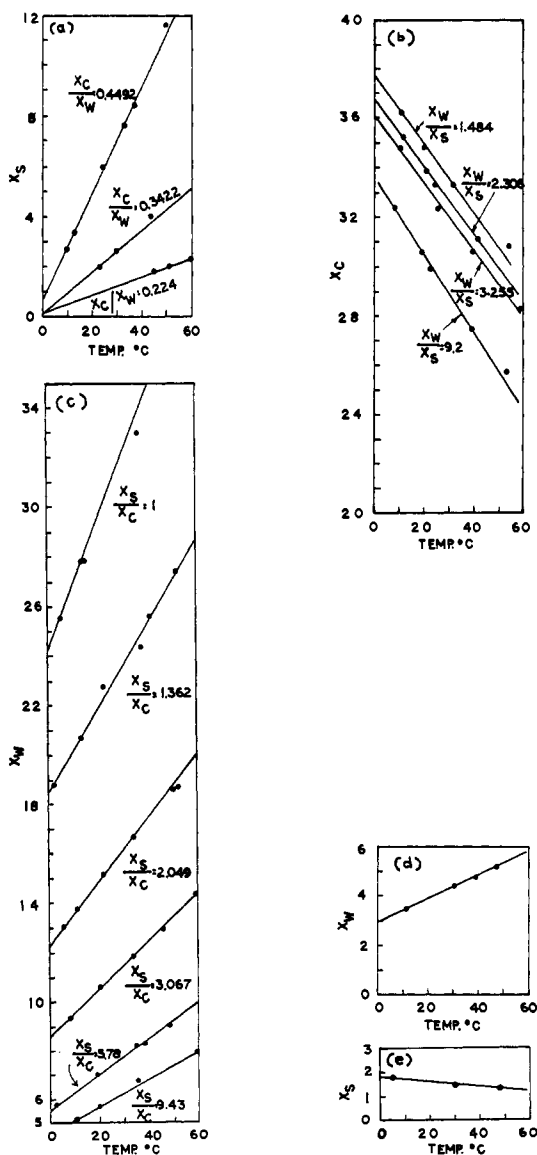


Figure 1. x_s , x_c , x_w vs. temperature with x_c/x_w , x_w/x_s , x_s/x_c as parameters

- x_s vs. temperature x_c/x_w as parameter
- x_c vs. temperature x_w/x_s as parameter
- x_w vs. temperature x_s/x_c as parameter
- x_w in solvent vs. temperature
- x_s in water vs. temperature

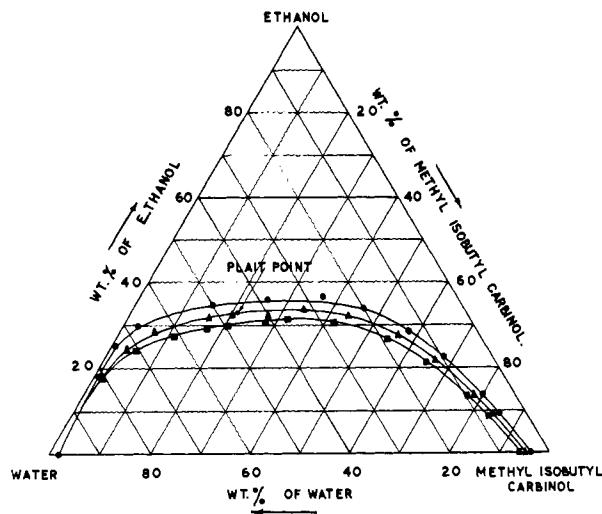


Figure 2. Phase equilibrium diagram for system ethanol–water–methyl isobutyl carbinol

● 10°C. ▲ 30°C. ■ 50°C.

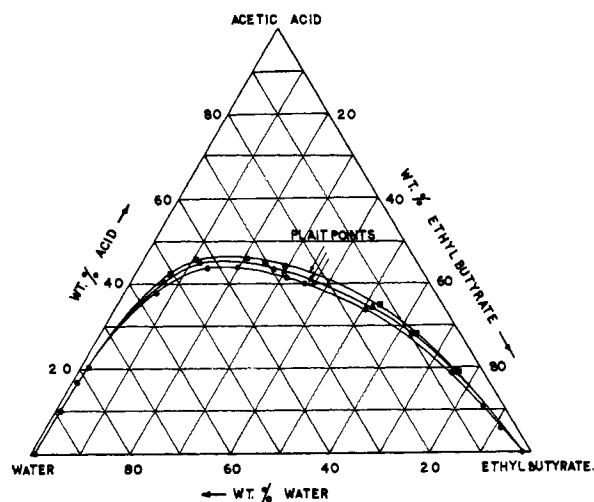


Figure 3. Phase equilibrium diagrams for system acetic acid–water–ethyl butyrate

● 50°C. ▲ 28°C. ■ 10°C

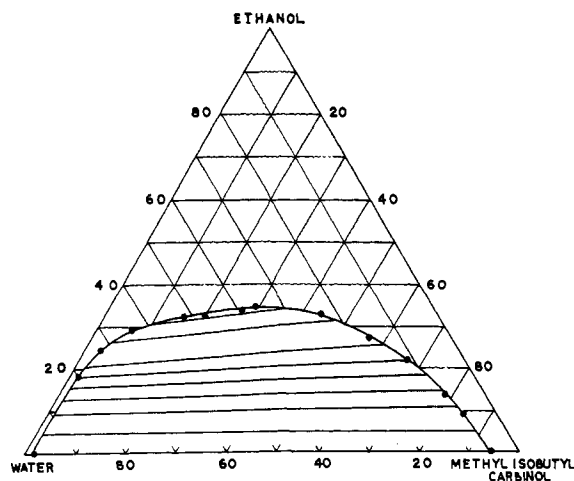


Figure 4. Phase equilibrium diagram at 30°C for system ethanol–water–methyl isobutyl carbinol

— Curve indicates Othmer's method
 ● Proposed method

system ethanol-water-methyl isobutyl carbinol and at 10°, 28°, and 50°C for the system acetic acid-water-ethyl butyrate

adopting the method of Othmer et al. (3), using refractive index and titration of the acid against standard sodium hydroxide as the method of analysis, respectively.

The saturation isotherms at 10°, 30°, and 50°C and at 10°, 28°, and 50°C for both systems are plotted in Figures 2 and 3, and the data of the isotherms are presented in Tables I and II, respectively. The saturation isotherm at 30°C by both methods for the system ethanol-water-methyl isobutyl carbinol is plotted in Figure 4 for comparison. The distribu-

Table I. Phase-Equilibrium Data

System ethanol-water-methyl isobutyl carbinol

Solute	10°C		30°C			50°C		
	Solvent	Water	Solute	Solvent	Water	Solute	Solvent	Water
0.0	1.7	98.3	0.0	1.5	98.5	0.0	1.3	98.7
18.1	0.5	81.4	18.0	1.2	80.8	17.9	2.0	80.1
25.4	0.6	74.0	24.8	2.6	72.6	24.3	4.6	71.1
30.2	2.6	67.2	28.9	6.9	64.2	27.5	11.2	61.3
34.7	15.4	49.9	32.0	16.0	52.0	29.4	16.6	54.0
35.4	19.5	45.1	32.6	20.4	47.0	29.9	21.2	48.9
36.1	35.7	38.2	33.4	26.8	39.8	30.7	27.9	41.4
36.7	36.7	26.6	34.2	34.2	31.6	31.7	31.7	36.6
33.8	46.1	20.1	32.3	44.1	23.6	30.8	42.0	27.2
28.4	58.2	13.4	27.5	56.5	16.0	26.7	54.8	18.5
22.3	68.3	9.4	21.8	66.8	11.4	21.3	65.3	13.4
13.8	79.9	6.3	13.6	78.6	7.8	13.4	77.3	9.3
9.1	85.8	5.1	9.0	84.8	6.2	8.9	83.8	7.3
0.0	96.7	3.3	0.0	95.7	4.3	0.0	4.7	5.3
			33.3 ^a	20.8 ^a	45.9 ^a			

^a Plait point.

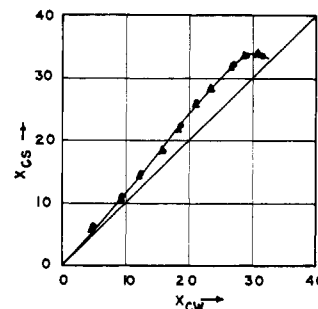


Figure 5. Distribution data at 30°C for system ethanol-water-methyl isobutyl carbinol

▲ Analytical method. ○ Proposed method

Table II. Phase-Equilibrium Data

System acetic acid-ethyl butyrate-water

10°C			28°C			50°C		
Solute	Solvent	Water	Solute	Solvent	Water	Solute	Solvent	Water
10.1	0.9	89.0	10.1	0.9	89.0	10.1	0.9	89.0
16.8	1.0	82.2	16.8	1.0	82.2	16.8	1.0	82.2
20.5	1.6	77.9	20.5	1.6	77.9	24.2	1.6	74.2
25.0	1.8	73.2	24.0	1.8	74.2	28.2	2.2	69.6
30.0	2.6	67.4	28.8	2.4	68.8	32.2	2.2	65.6
35.1	3.8	61.1	32.0	3.0	65.0	34.8	4.2	61.0
37.6	4.6	57.8	36.0	4.0	60.0	37.0	5.4	57.6
39.2	5.2	55.6	38.2	4.9	56.9	40.7	8.6	50.7
42.2	6.6	51.2	41.2	6.6	52.2	44.4	13.4	42.2
44.8	8.8	46.4	43.8	9.4	46.8	44.4	17.7	37.9
46.2	12.0	41.8	45.0	13.0	42.0	44.2	19.2	36.6
46.4	18.9	34.7	44.6	22.0	33.4	40.6	33.6	25.8
44.2	29.6	26.2	40.6	36.6	22.8	37.4	42.2	20.4
40.8	39.4	19.8	36.4	46.8	16.8	34.8	48.0	17.2
31.4	58.4	10.2	31.8	55.6	12.6	27.0	63.0	10.0
21.8	72.6	5.6	24.6	67.0	8.4	18.4	75.8	5.8
12.2	84.2	3.6	12.6	83.2	4.2	8.4	88.6	3.0
42.8 ^a	33.9 ^a	23.3 ^a	41.2 ^a	35.2 ^a	23.6 ^a	39.9 ^a	36.2 ^a	23.9 ^a
Tie-Line Data. Water Layer								
7.25	0.85	91.9	8.46	0.95	90.59	8.28	0.90	90.82
13.4	1.00	85.6	14.54	1.15	84.31	13.53	1.00	85.47
18.63	1.10	80.27	23.45	1.75	74.80	22.31	1.40	76.29
27.74	2.20	70.06	30.83	2.80	66.37	26.90	1.95	71.15
29.58	2.60	67.82	34.18	3.45	62.37	30.53	2.50	66.97
33.05	3.30	63.65	36.45	4.15	59.40	32.84	3.40	63.76
36.37	4.20	59.43	39.77	5.80	54.43	35.66	4.60	59.74
38.47	4.90	56.63	43.19	8.50	48.31	38.61	6.60	54.79
40.14	5.60	54.26						
Solvent Layer								
2.97	94.95	2.08	3.55	94.45	2.00	3.34	94.80	1.86
5.44	91.95	2.61	6.41	90.80	2.79	5.93	91.70	2.37
8.35	88.60	3.05	12.07	83.90	4.03	11.09	85.15	3.76
15.04	81.00	3.96	17.66	76.75	5.59	14.31	81.10	4.59
17.69	77.80	4.51	20.26	73.15	6.59	16.48	78.30	5.22
19.90	75.05	5.05	22.97	69.30	7.73	18.81	75.20	5.99
22.80	71.30	5.90	26.61	64.10	9.29	21.24	71.65	7.11
24.98	68.30	6.72	33.01	53.45	13.54	25.87	64.70	9.43
27.14	65.15	7.71						

^a Plait point.

tion data obtained by both methods are plotted in Figures 5 and 6 for comparison, and the data are presented in Tables II and III, respectively. The refractive index of the saturation isotherm at 30°C for the system ethanol-water-methyl isobutyl carbinol is shown plotted in Figure 7. The accuracy of the refractive index method of analysis is $\pm 0.5\%$ and the proposed method is $\pm 2\%$.

RESULTS AND DISCUSSION

The tie-line data at 30°C for the system ethanol-water-methyl isobutyl carbinol and at 10°, 28°, and 50°C for the other system are satisfactorily correlated by the methods of Othmer and Tobias (2) and Hand (1). The constants and exponents of the equations for the two systems are given in Table IV. The plait points at 30°C and at 10°, 28°, and 50°C

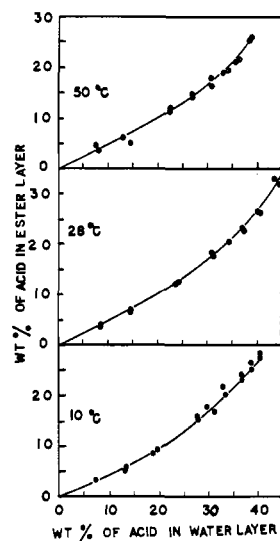


Figure 6. Distribution diagrams at 10°, 28°, and 50°C for system acetic acid-water-ethyl butyrate

● By analysis. ○ By proposed method

Table III. Tie-Line Data at 30°C by Proposed Method

Water layer			Solvent layer		
Solute	Solvent	Water	Solute	Solvent	Water
5.0	1.4	93.6	6.1	88.4	5.5
9.6	1.4	89.0	9.8	83.8	6.4
12.6	1.4	86.0	14.6	77.4	8.0
16.0	1.3	82.7	17.9	72.7	9.4
18.6	1.4	80.0	21.9	66.6	11.5
21.1	2.9	76.0	25.9	59.7	14.4
23.4	2.4	74.2	27.9	55.7	16.4
27.0	4.3	68.7	32.1	44.9	23.0
28.9	6.9	64.2	33.4	40.6	26.0
31.1	12.4	56.5	33.6	39.6	26.8
31.4	13.6	55.0	33.4	40.6	26.0

Tie-Line Data by Refractive Index Method					
Solute	Solvent	Water	Solute	Solvent	Water
4.8	1.2	94.0	5.8	88.4	5.8
9.2	1.2	89.6	11.0	82.2	6.8
12.5	1.2	86.3	14.3	77.6	8.1
15.7	1.5	82.8	18.5	71.7	9.8
18.2	1.8	80.0	21.6	67.0	11.4
20.9	2.4	76.7	25.6	60.5	13.9
23.5	3.1	73.4	28.3	55.1	16.6
26.7	4.6	68.7	31.8	47.4	20.8
28.8	6.9	64.3	33.4	41.2	25.4
30.8	11.0	58.2	33.8	39.7	26.5
31.2	12.2	56.6	34.1	35.9	30.0

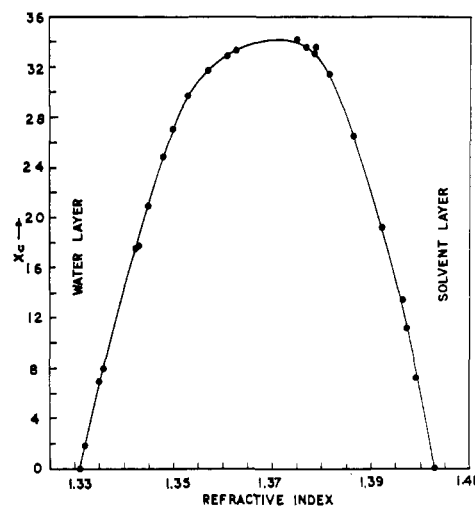


Figure 7. Refractive index calibration curve at 30°C for system ethanol-water-methyl isobutyl carbinol

Table IV. Constants and Exponents of Equations for Two Systems

Correlation	Exponents n		Constants k	
	Ethanol-water-methyl isobutyl carbinol	Acetic acid-water-ethyl butyrate	Ethanol-water-methyl isobutyl carbinol	Acetic acid-water-ethyl butyrate
Hand (1)	1.40	1.22	1.5	0.6
Othmer and Tobias (2)	1.38	1.20	3.5	0.7

for the two systems were located by the method of Treybal et al. (5), and their compositions are given in Tables I and II, respectively. From Figures 2 and 3 it is evident that the region of heterogeneity increases as the temperature is lowered from 50–10°C.

The comparison of the data of the isotherm at 30°C for the ethanol-water-methyl isobutyl carbinol system obtained by both of the methods shown in Figure 4 indicates fair agreement between the two methods. The distribution data for this system plotted in Figure 5 indicated the solute prefers the solvent phase and that there is fair agreement between the two methods, thereby confirming the accuracy of the present method. For the acetic acid-water-ethyl butyrate system a comparison of the tie-line data obtained by both the methods (Figure 6) indicates that there is fair agreement between the two. Also, Figure 6 indicates that the solute prefers the aqueous phase for all three conditions of restraint. In this system, the effect of temperature on distribution is negligible (Figure 8).

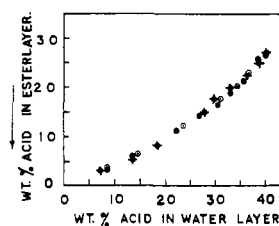


Figure 8. Distribution data at 10°, 28°, and 50°C for system acetic acid-water-ethyl butyrate

◆ 10°C. ○ 28°C. ● 50°C

The accuracy with which the tie-line data can be determined depends upon the accurate separation of the two phases. The two phases can be separated to within one or two drops (i.e., about 0.1 grams). In the present work, only 10 cc of the mixture was taken for the determination of the tie-line data and each phase was about 5 grams. Hence, the error involved is about 2%. The scope for such error is greater when the weight ratio of phases is large. However, the error can be minimized by taking a large quantity of the mixture. Further, in Figure 6, where a comparison of the distribution data was made between the two methods, for the acetic acid-water-ethyl butyrate system the deviation between the two methods in a few points may be due to the limitations of the proposed method and to the effect of hydrolysis and ester interchange. Maximum deviations are observed at high temperature and with large amounts of water. These are perhaps due to the effect of hydrolysis and ester interchange.

CONCLUSIONS

It has been demonstrated that phase-equilibrium and tie-line data could be satisfactorily determined adopting a new method as proposed by the authors. In the determination of the tie-line data the proposed method appears to be advantageous for, despite its limitations, it avoids the analytical

procedure which may be a difficult problem in the case of certain mixtures.

NOMENCLATURE

x_c = weight % of solute
 x_s = weight % of solvent
 x_w = weight % of water
 x_{cw} = weight % of solute in water layer
 x_{cs} = weight % of solute in solvent layer
 x_{ss} = weight % of solvent in solvent layer
 x_{ww} = weight % of water in water layer

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Proton Magnetic Resonance Studies of 4-Substituted Coumarins

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Proton magnetic resonance spectral studies of 4-methyl coumarins are reported. The position of the resonance signal, due to three protons of the methyl group at C₄, depends on the nature and position of the substituents in benzene ring of the coumarin ring system. A resonance peak at $\tau = 3.78-4.15$ indicates the presence of a proton at C₃ in the form $-C=C-H$. Coupling of CH₃ at C₄ exhibits allylic coupling with proton at C₃ with $J = 1.1$ Hz. Coupling constants ($J_{5,6}$) has been calculated, and its value shows ortho coupling. The resonance peak due to protons H₆ and H₅ depends on the nature of substituents in the benzene ring at C₅ and C₇. When the methyl groups at C₅ and C₇ are replaced by hydroxy groups, the resonance signal due to H₆ and H₅ splits, and these protons are rendered magnetically nonequivalent.

Although the literature is replete with studies of coumarins (6), there are surprisingly few data dealing with the nmr spectra of coumarin derivatives (1, 2). Structural studies in coumarin chemistry have been made using many instrumental techniques, and a number of difficulties have been encountered in structure elucidation of this class of compounds. The present investigation was undertaken to determine whether the application of pmr studies in the structural chemistry of coumarin derivatives would lead to some general correlations between structure and spectra in this series of heterocyclic compounds.

The coumarin derivatives involved in this study were prepared by the well-known Pechmann reaction by condensing the corresponding phenol with ethyl acetoacetate using concentrated sulfuric acid as the condensing agent. Coumarins prepared are already known (6) and their structures are well established. Purity of these compounds was checked by thin-

layer chromatography. The nmr spectra were taken at 60 MHz on a Varian A-60 nmr spectrometer in deuteriochloroform solution with the exception of 5-hydroxy-4, 7-dimethylcoumarin, which was taken in dimethyl sulfoxide. Tetramethylsilane was used as an internal standard in all cases.

For compounds I and II, resonance signals are at $\tau = 7.60$ and $\tau = 7.59$, respectively, and show the presence of a CH₃ group in the allylic form—i.e., a C=C—CH₃ linkage. Signals at $\tau = 7.43$ and $\tau = 7.45$ in compounds III and IV are also due to a CH₃ group at C₄ in the allylic form and minor shift toward lower field may be attributed to the vicinal substituent at C₅ in these compounds. Peaks at $\tau = 3.89, 3.78, 3.98$, and 4.15 , respectively, in compounds I–IV are due to protons at C₃ in the form $-C=C-H$. Protons of CH₃ at C₄ exhibit allylic coupling with the proton at C₃ with coupling constant equal to 1.1 Hz. See Table I.

In compounds I and III peaks at $\tau = 6.13$ and $\tau = 7.70$ are due to H₃CO and CH₃ (at C₇) groups, respectively.

For compound I a quartet consisting of two doublets is ob-

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