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Physico-chemical properties of terebic acid, MBTCA, diaterpenylic acid acetate and pinanediol as relevant α-pinene oxidation products

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Content:

1. Synthesis of investigated compounds:

1.1 General information

MBTCA was synthesized following the two-stage process strategy reported by Kostenidou et al.[1] A first was the Michael addition of ethyl isobutyrate (CAS Registry No. 97-62-1, Sigma-Aldrich, 99%) to diethyl fumarate (CAS Registry No. 623-91-6, Sigma-Aldrich, 98%) under basic conditions, while a second stage was the hydrolysis using hydrochloric acid (CAS Registry No. 7647-01-0, POCH, 35-38%). The synthesis of DTAA covers three steps process. A first stage was Grignard reaction of a methyl cyclopent-3-ene-1-carboxylate (CAS Registry No. 58101-60-3, Sigma-Aldrich, 95%) with a methylmagnesium bromide (3 M solution in diethyl ether, CAS Registry No. 75-16-1, Sigma-Aldrich). The second stage was reaction of alcohol with acetic anhydride (CAS Registry No. 108-24-7, Sigma-Adrich, ≥ 98%), whereas a last stage was a $RuCl_3 \times H2O$ (CAS Registry No. 14898-67-0, Sigma-Aldrich, ≥99.98%) oxidative double bond cleavage lead to the final product. Terebic acid was synthesized in two-step process. A first stage was Grignard reaction of a diethyl acetylsuccinate (CAS Registry No. 1115-30-6, Sigma-Aldrich 95%) with a methylmagnesium bromide and the second stage was hydrochloric acid hydrolysis. The (1S,2S,3R,5S)-(+)-pinanediol (PD, CAS Registry No. 18680-27-8, 99%) was obtained from Sigma Aldrich and used without further purification as crystals. Other chemicals used were as follows: lithium diisopropylamide (1 M solution in THF/hexane, CAS Registry No. 4111-54-0, Sigma-Adrich), sodium sulfate (CAS Registry No. 7757-82-6, Sigma-Aldrich, ≥ 99%), sodium periodate (CAS Registry No. 7790-28-5, Sigma-Aldrich, ≥ 99.8%), triethylamine (CAS Registry No. 121-44-8, Siga-Aldrich, ≥ 99.5%), 4-dimethylaminopyridine (CAS Registry No. 1122-58-3, Sigma-Aldrich, ≥ 99%), sodium hydrogencarbonate (CAS Registry No. 144-55-8, Sigma-Aldrich, ≥ 99.7%), pentane (CAS Registry No. 109-66-0, POCH, ≥ 99.9%), methylene chloride (CAS Registry No. 75-09-2, POCH, ≥ 99.9%), diethyl ether (CAS Registry No. 60-29-7, POCH, ≥ 99.9%), anhydrous tetrahydrofuran (CAS Registry No. 109-99-9, Sigma-Aldrich, 99.9%, inhibitor-free), carbon tetrachloride (CAS Registry No. 56-23-5, Sigma-Aldrich, ≥ 99.5%), acetonitrile (CAS Registry No. 75-05-8, POCH, ≥ 99.9%). Reaction mixtures were analyzed by TLC (Merck silica gel 60 F254) and visualized with cerium molybdate stain (Hanessian's stain) or UV light. Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AV 400 spectrometer in CDCl3 (CAS Registry No. 865-49-6, Sigma-Aldrich, 99.98% atom D) or D2O (CAS Registry No. 7789-20-0, Sigma-Aldrich, 99.9% atom D) or solution. ^{1}H and ^{13}C chemical shifts are given in ppm relative to

TMS. The electrospray ionization high-resolution mass spectra (ESI-HR) were recorded with a Q-TOF-2 (Waters Manchester, UK) mass spectrometer equipped with an electrospray ion source. Infrared spectra were recorded with a Jasco FTIR-6200 spectrometer. The solubilities of MBTCA, DTAA, TER and PD were determined in water, which was twice distilled, degassed, deionized and filtered with MiliporeElix 3.

Table S1. Investigated compounds: name, abbreviation, structure, molar mass, yield, HRMS and NMR analysis.

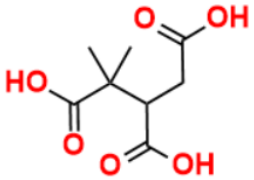
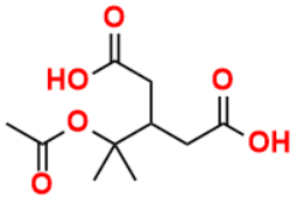
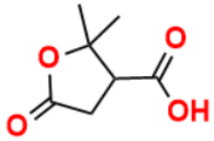
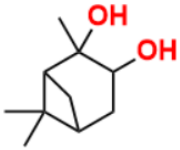
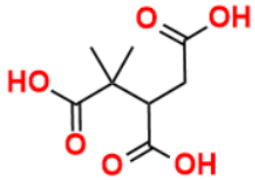
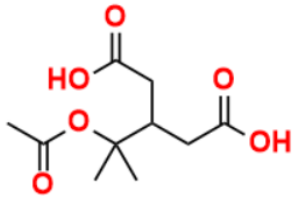
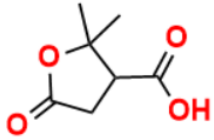
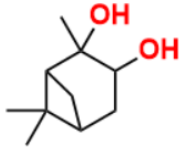
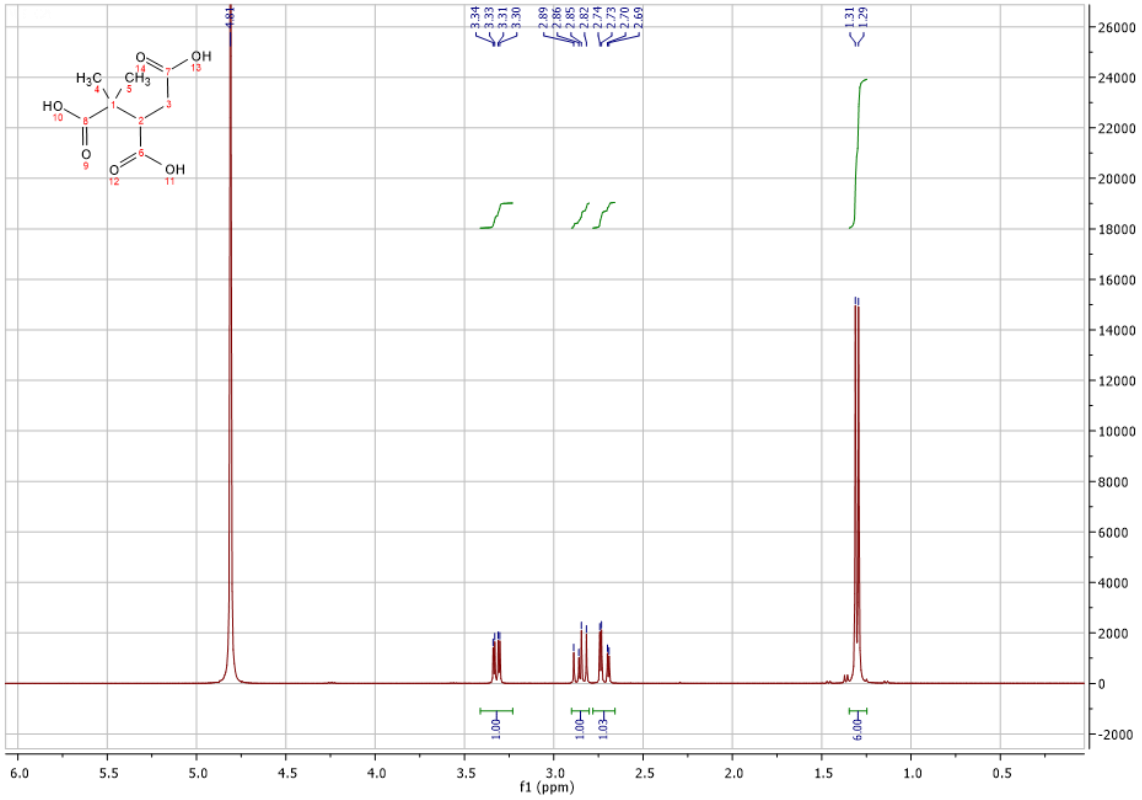
Name of compound/ Abbreviation	Source	Structural formula	M/(g·mol^{-1})	Yield	HRMS [M+H]$^+$	Density ρ^{lit} / ρ^{exp} (298.15K) / (g·cm^{-3})	NMR	Purity (%)
3-Methyl-1,2,3-butanetricarboxylic Acid/ MBTCA	Synthesis		204.18	93	Calc'd for $C_8H_{11}O_6$ [M-H]: 203.0556; Found 203.0552	-	^{1}H NMR (400 MHz, D_2O) δ 3.32 (dd, *J* = 11.3, 3.7 Hz, 1H), 2.90 – 2.80 (m, *J* = 17.1, 11.3 Hz, 1H), 2.72 (dd, *J* = 17.1, 3.7 Hz, 1H), 1.30 (d, *J* = 7.1 Hz, 6H).	≥ 99
Diaterpenylic Acid Acetate/ DTAA	Synthesis		232.23	83	Calc'd for $C_{10}H_{15}O_6$ [M-H]: 232.0546; Found 232.0901;	-	^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (t, *J* = 11.3 Hz, 1H), 2.67 (d, *J* = 14.5, 2.0 Hz, 2H), 2.28 (dd, *J* = 14.4, 11.4 Hz, 2H), 2.00 (s, 3H), 1.50 (s, 6H).	99
Terebic Acid/ TER	Synthesis		158.15	89	Calc'd for $C_7H_9O_4$ [M-H]: 157.0501; Found 157.0465;	-	^{1}H NMR (400 MHz, MeOD) δ 3.33 – 3.23 (m, 3H), 2.97 (dd, J = 17.9, 8.8 Hz, 2H), 2.74 (dd, J = 17.9, 8.8 Hz, 2H), 1.58 (s, 6H), 1.36 (s, 6H).	≥ 99
Pinanediol/ PD	Sigma-Aldrich		170.25	-	-	-	-	99

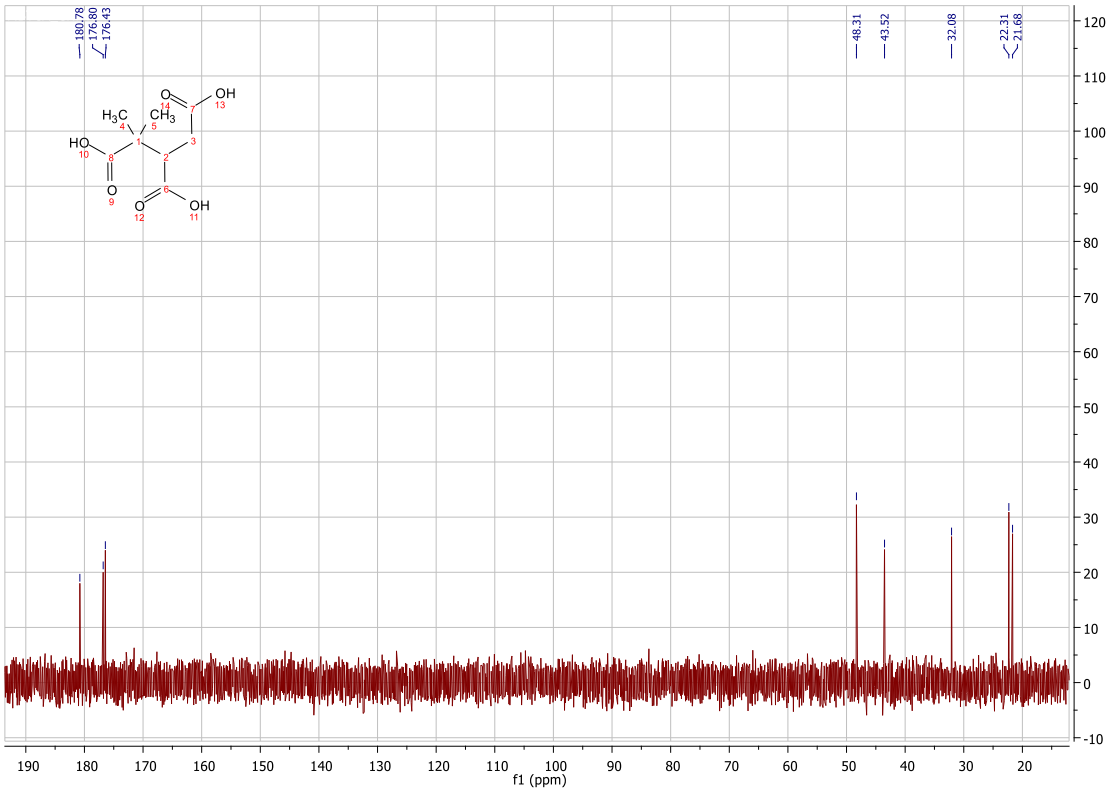
Table S2. Investigated compounds: IR, ^{13}C NMR analytical data.

Name of compound/ Abbreviation	Source	Structural formula	IR	NMR
3-Methyl-1,2,3-butanetricarboxylic Acid/ MBTCA	Synthesis		IR (CH_2Cl_2): 2981, 2876, 1711, 164, 1439, 1405, 1263, 1208, 1173, 899, 843, 598 cm^{-1}	^{13}C NMR (101 MHz, D_2O) δ = 180.8, 176.8, 176.4, 48.3, 43.5, 32.1, 22.3, 21.7
Diaterpenylic Acid Acetate/ DTAA	Synthesis		IR (CH_2Cl_2): 3000, 2725, 1718, 1692, 1732, 1250, 1025 cm^{-1}	^{13}C NMR (101 MHz, $CDCl_3$) δ = 179.7, 167.0, 82.8, 42.0, 35.4, 23.3, 22.3
Terebic Acid/ TER	Synthesis		IR (CH_2Cl_2): 3000, 2925, 1720, 1717, 1732, 1150, 1000, 985 cm^{-1}	^{13}C NMR (101 MHz, MeOD) δ = 175.7, 171.8, 84.7, 49.9, 31.5, 27.1, 22.1
Pinanediol/ PD	Sigma-Aldrich		-	-

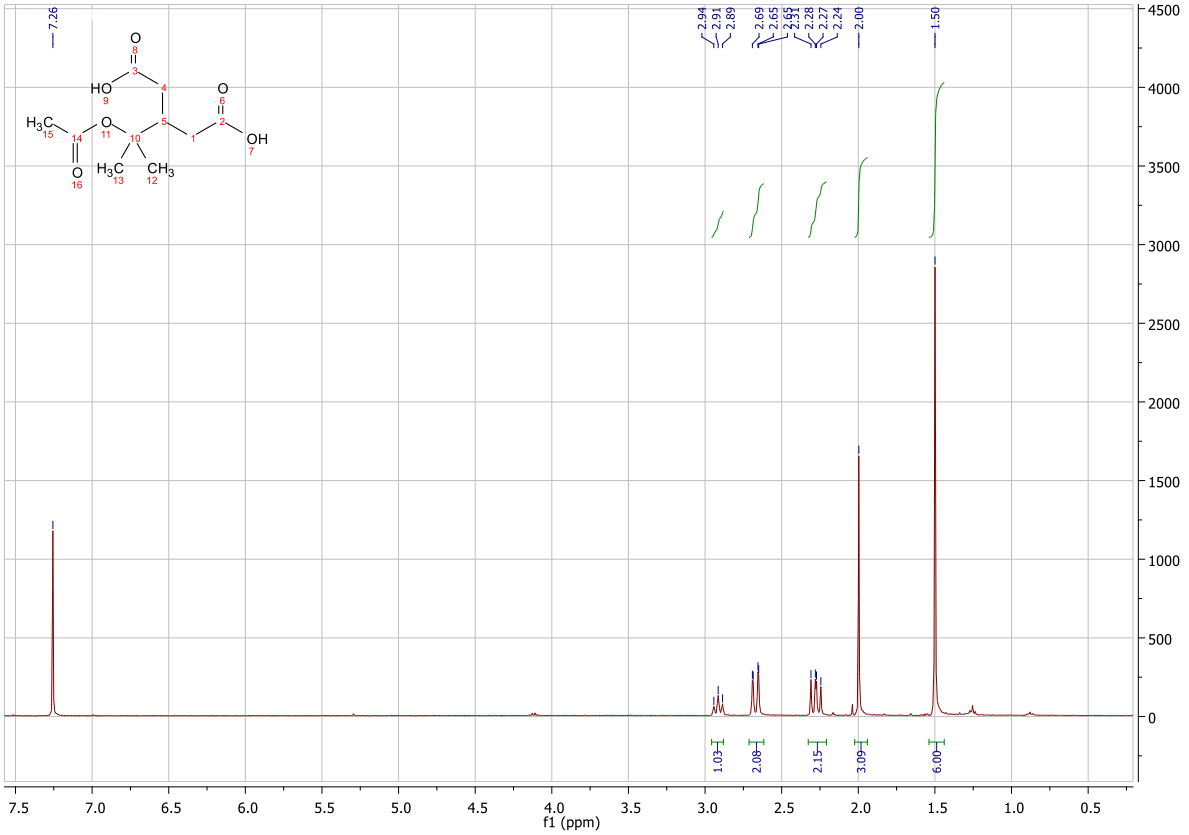
2. Copies of ^{1}H and ^{13}C NMR spectra of isolated compounds:

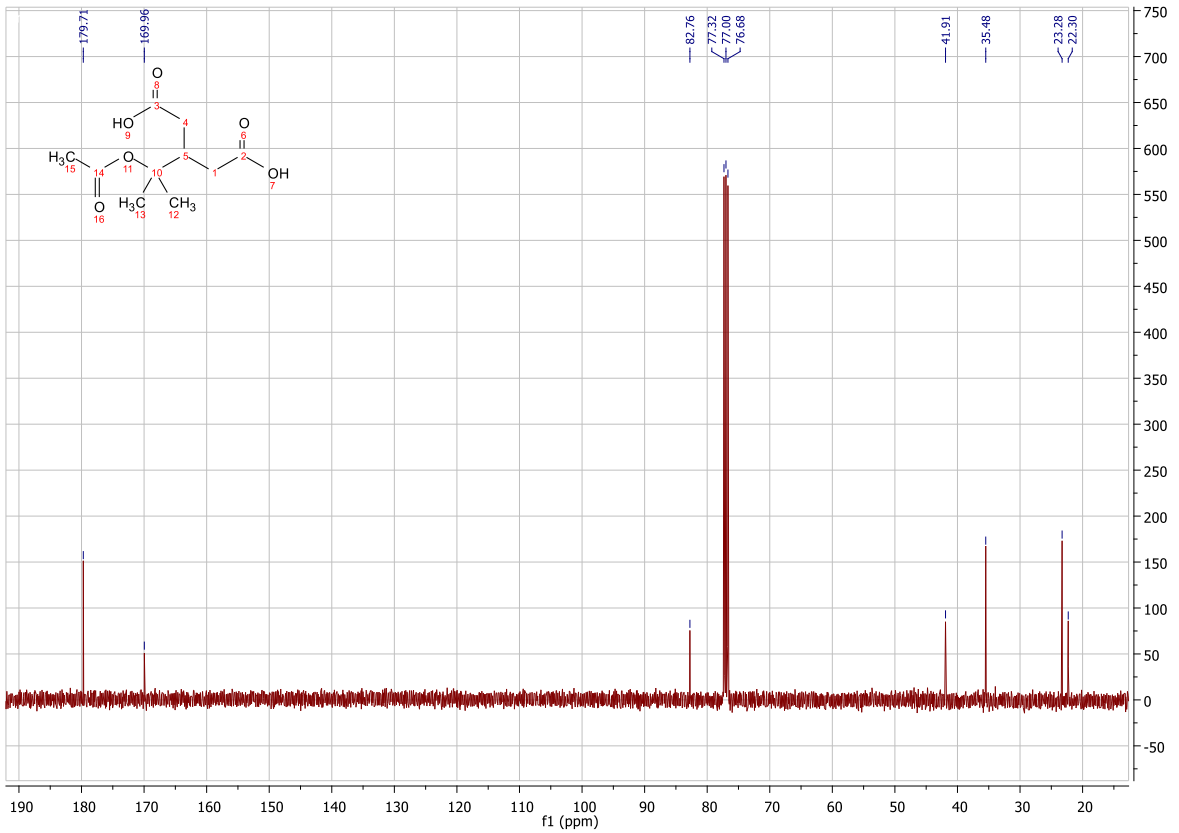
Spectrum S1. MBTCA acid



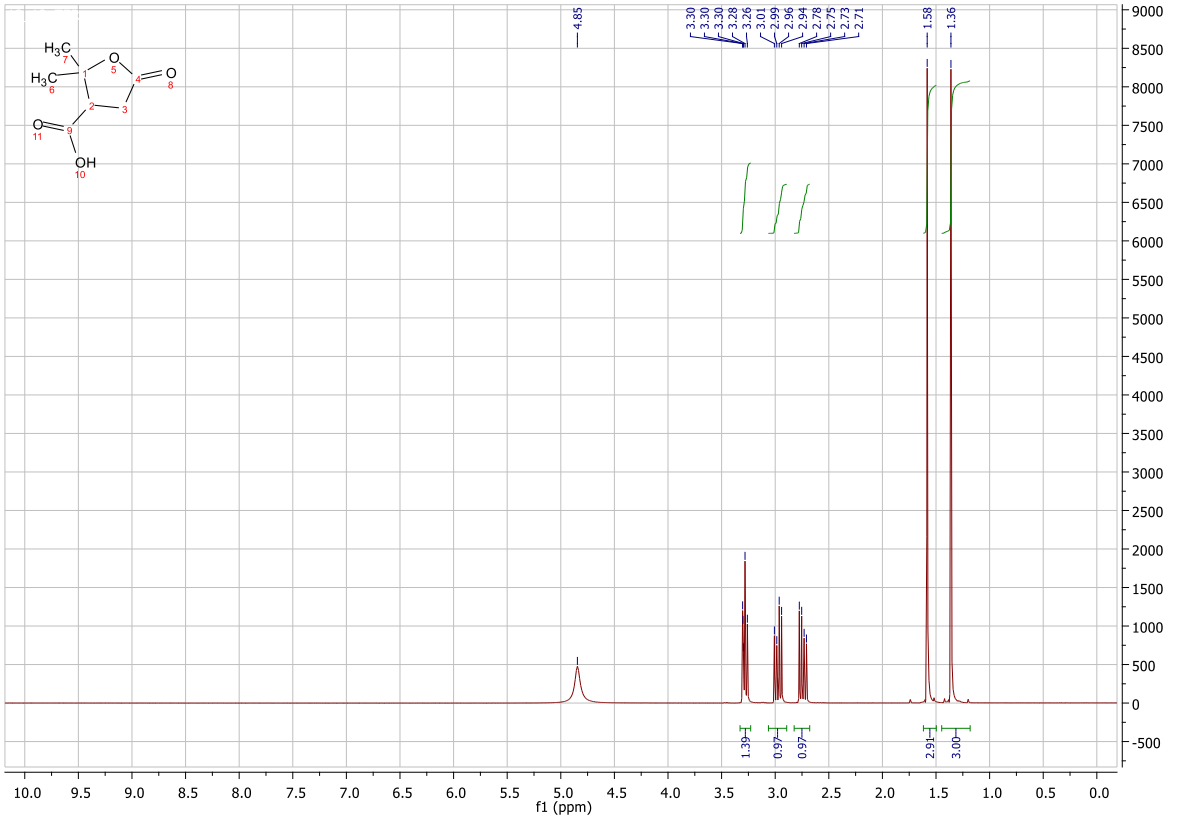


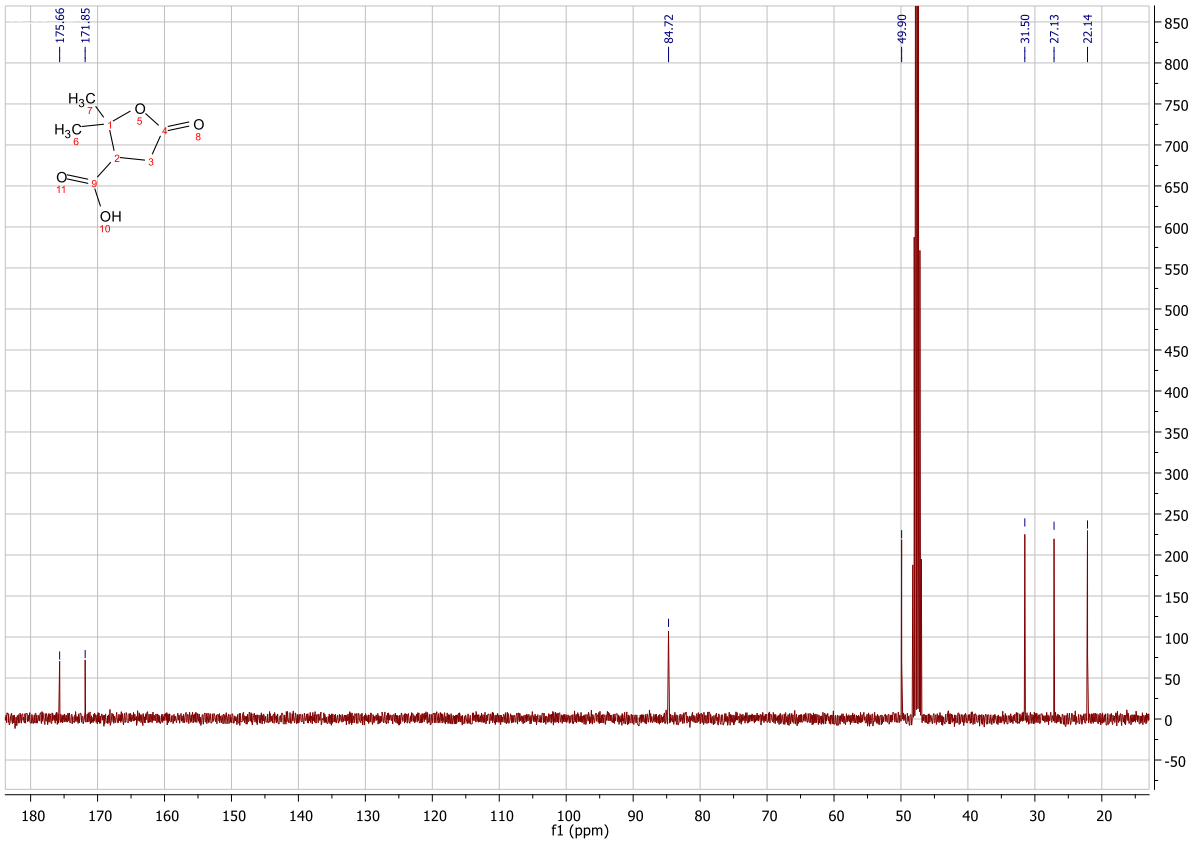
Spectrum S2. Diaterpenylic acid acetate





Spectrum S3. Terebic acid





3. The Bates-Schwarzenbach method

Table S3. Values of an acidity functions $p(a_H\gamma_{Cl})$ and ionic strength (I) for buffers.

Compound	Buffer / pH	T / K	$p(a_H\gamma_{Cl})$	I
DTAA	3.8	298.15	3.867	0.01
		303.15	3.868	
		308.15	3.871	

Figure S1. Measurements of p*K*a (absorbance vs. wavelength): experimental points for {DTAA (1) + water (2)} at T = 298.15 K mixtures: (- · -) 0.2 M NaOH; (- - -) 0.2 M HCl; (· · ·) buffer pH = 3.8.

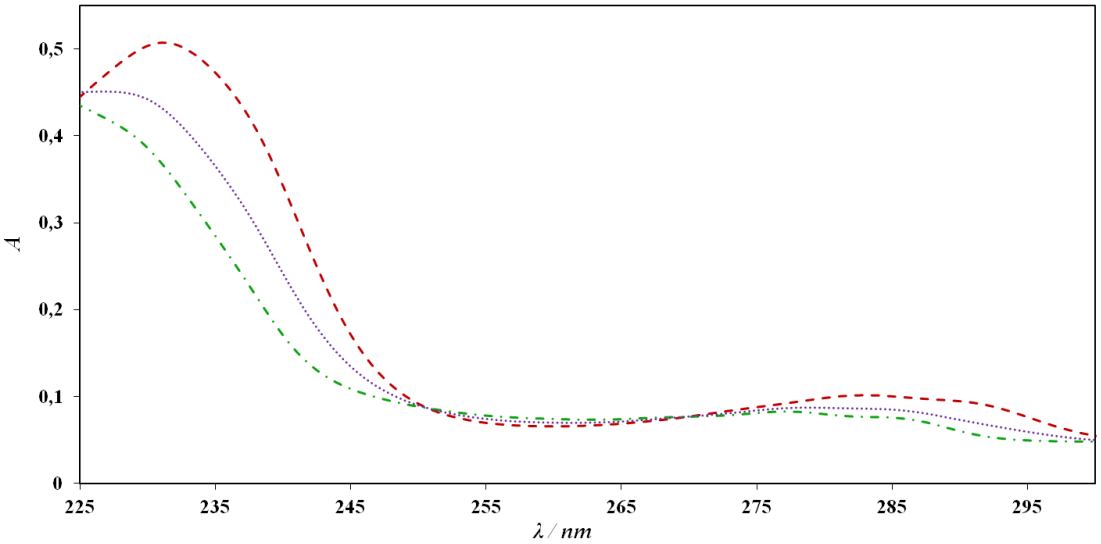


Figure S2. Measurements of p*K*a (absorbance vs. wavelength): experimental points for {DTAA (1) + water (2)} at T = 303.15 K mixtures: (- · -) 0.2 M NaOH; (- - -) 0.2 M HCl; (· · ·) buffer pH = 3.8.

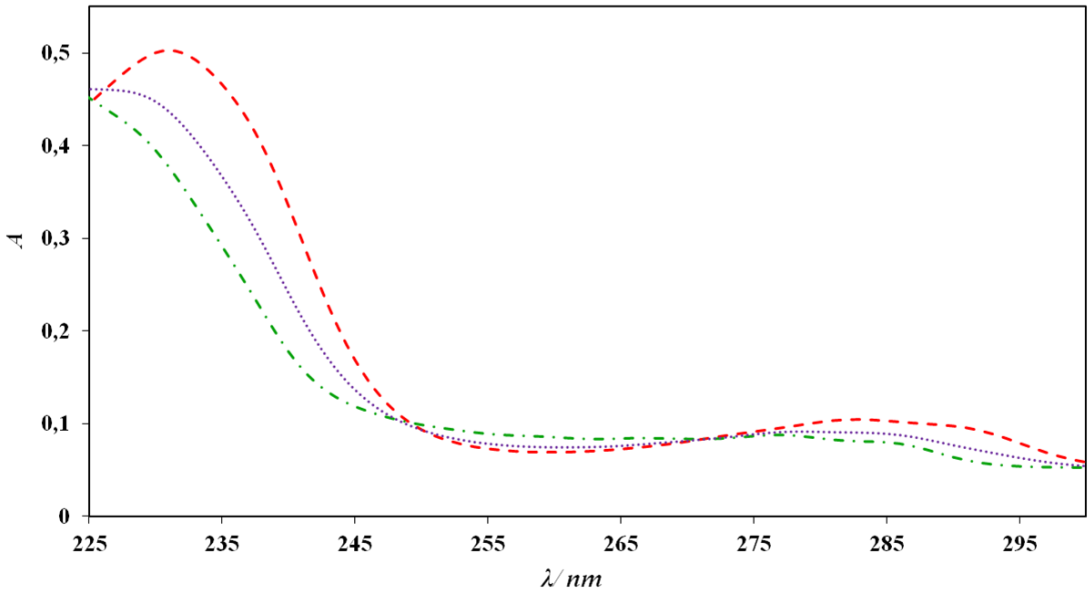
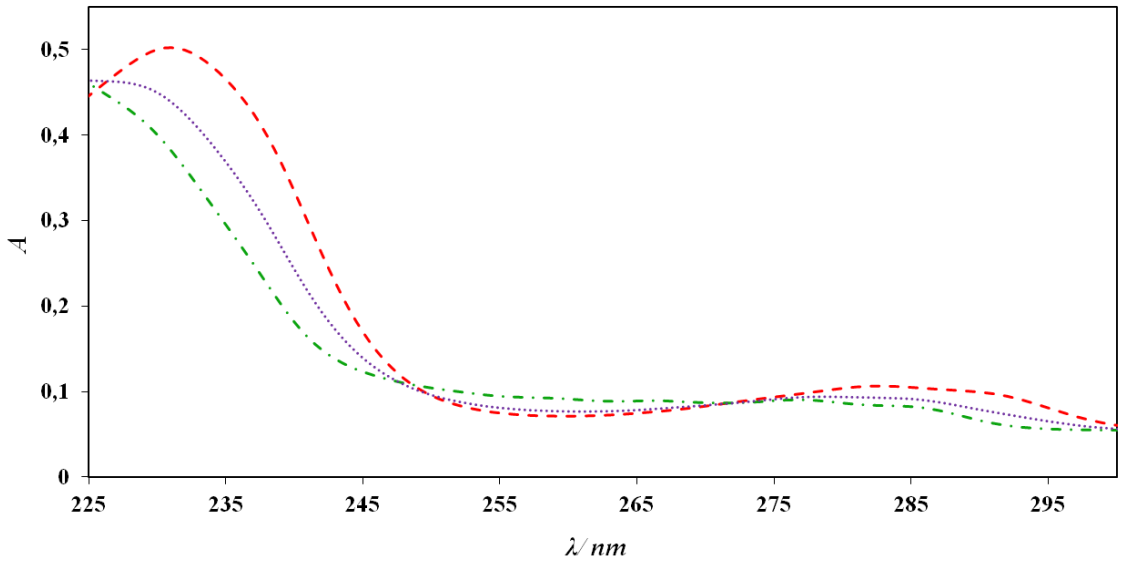


Figure S3. Measurements of p*K*a (absorbance vs. wavelength): experimental points for {DTAA (1) + water (2)} at T = 308.15 K mixtures: (- · -) 0.2 M NaOH; (- - -) 0.2 M HCl; (· · ·) buffer pH = 3.8.



4. Experimental solubility and correlation parameters

Figure S4. Experimental and calculated solubility of {MBTCA (1) + water (2)} binary systems. Solid lines have been designated by the Wilson equation for water; the dotted line represents ideal solubility.

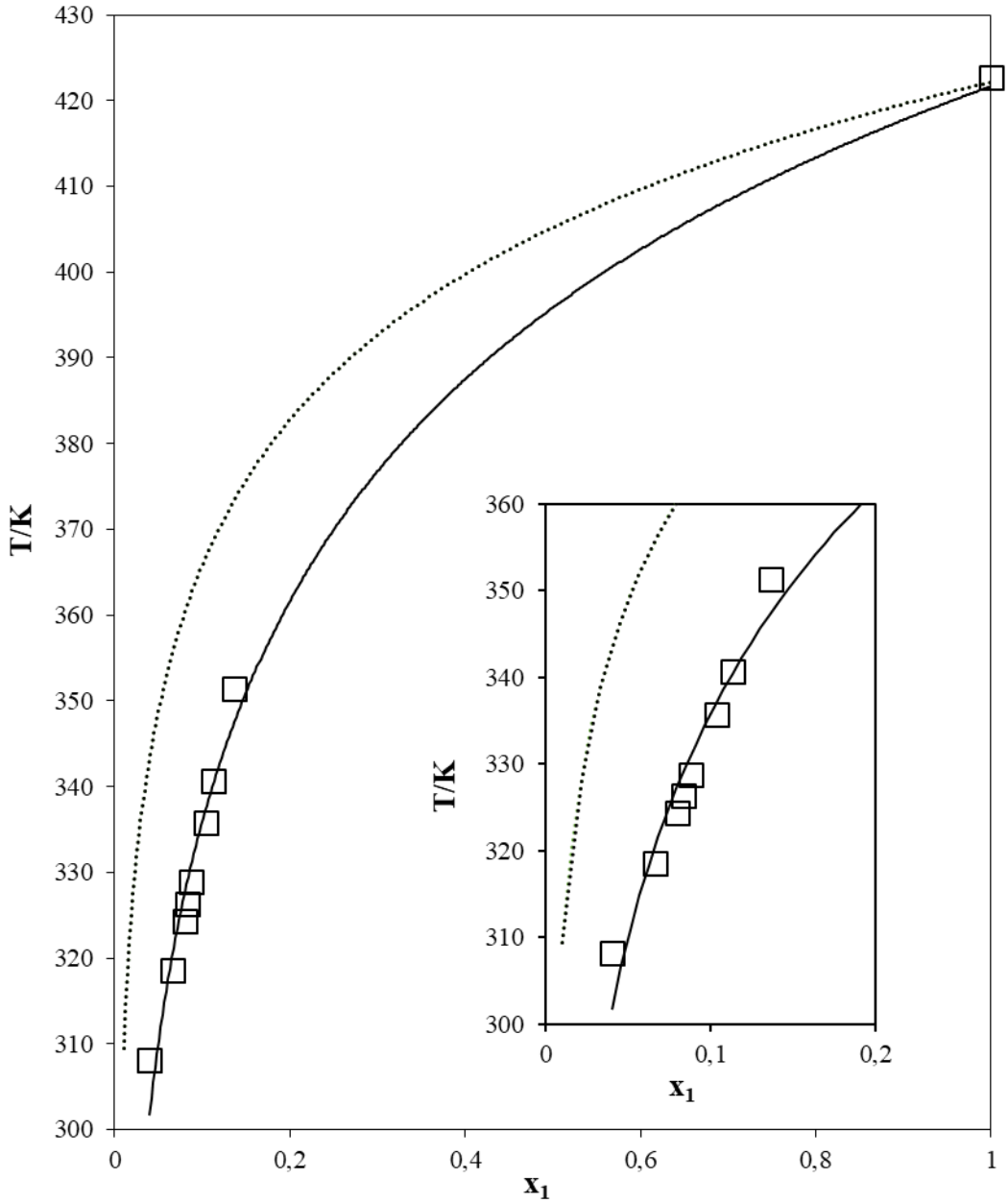


Figure S5. Experimental and calculated solubility of {DTAA (1) + water (2)} binary systems. Solid lines have been designated by the Wilson equation for water; the dotted line represents ideal solubility.

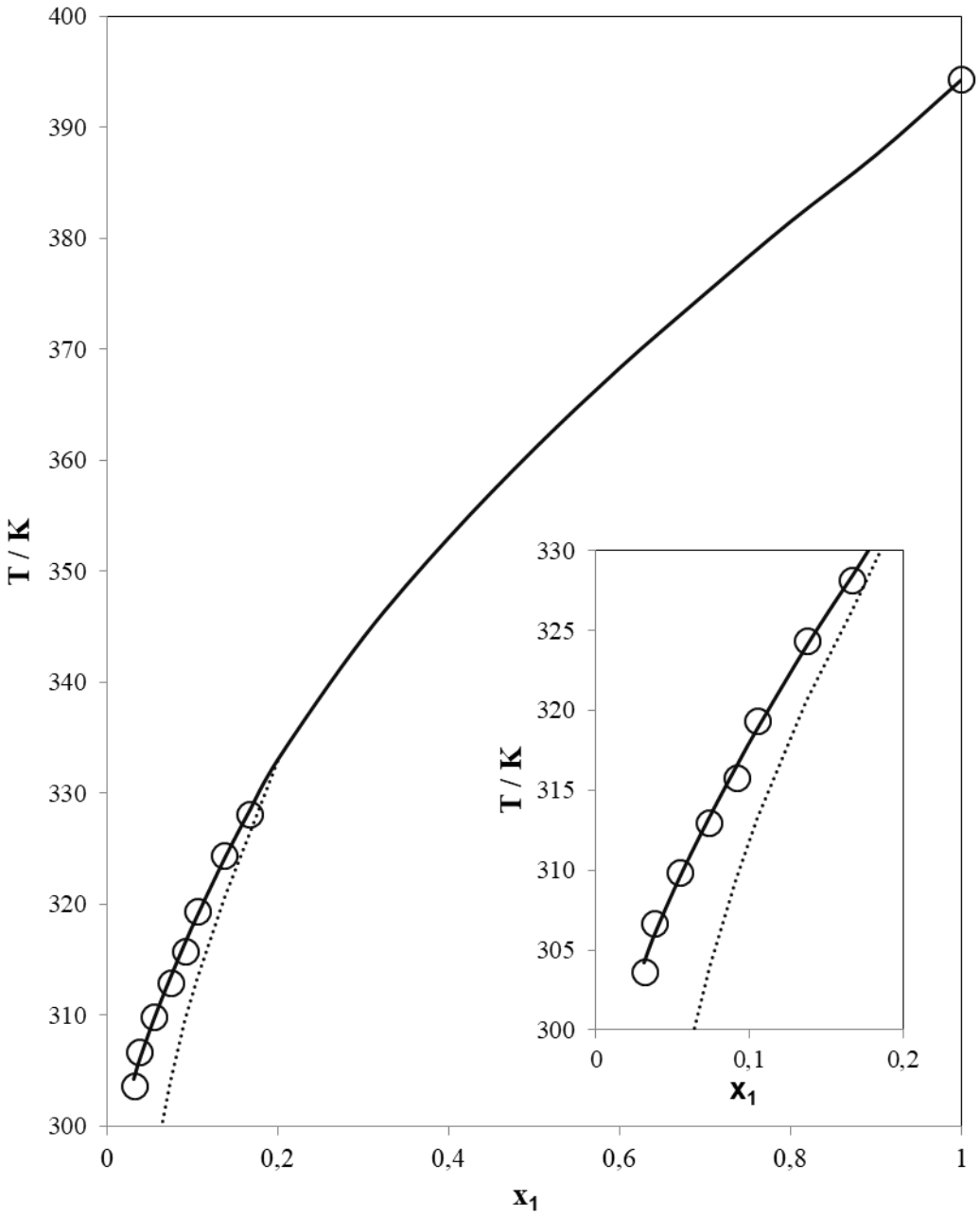


Figure S6. Experimental and calculated solubility of {TER (1) + water (2)} binary systems. Solid lines have been designated by the Wilson equation for water; the dotted line represents ideal solubility.

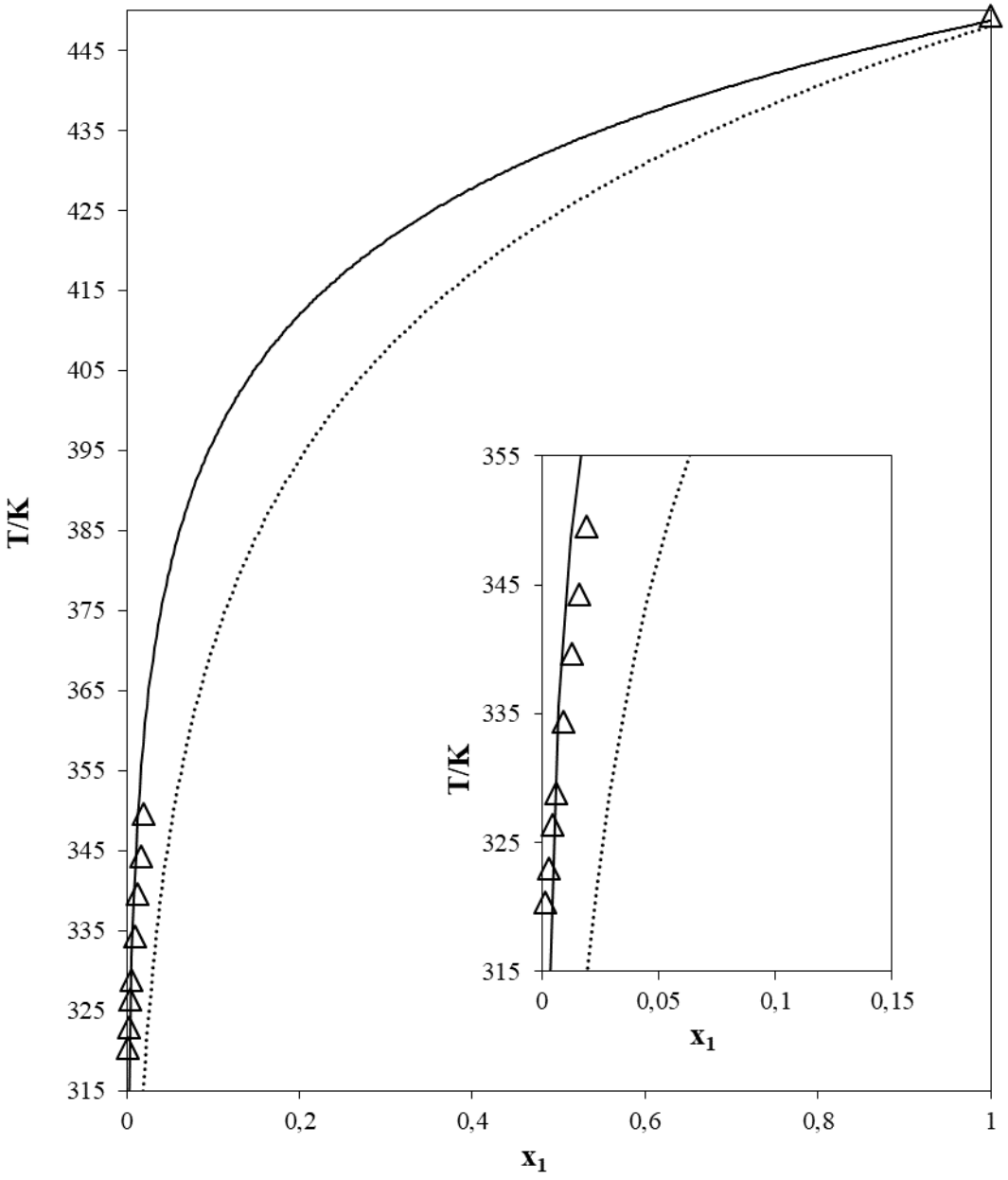


Figure S7. Experimental and calculated solubility of {PD (1) + water (2)} binary systems. Solid lines have been designated by the Wilson equation for water; the dotted line represents ideal solubility.

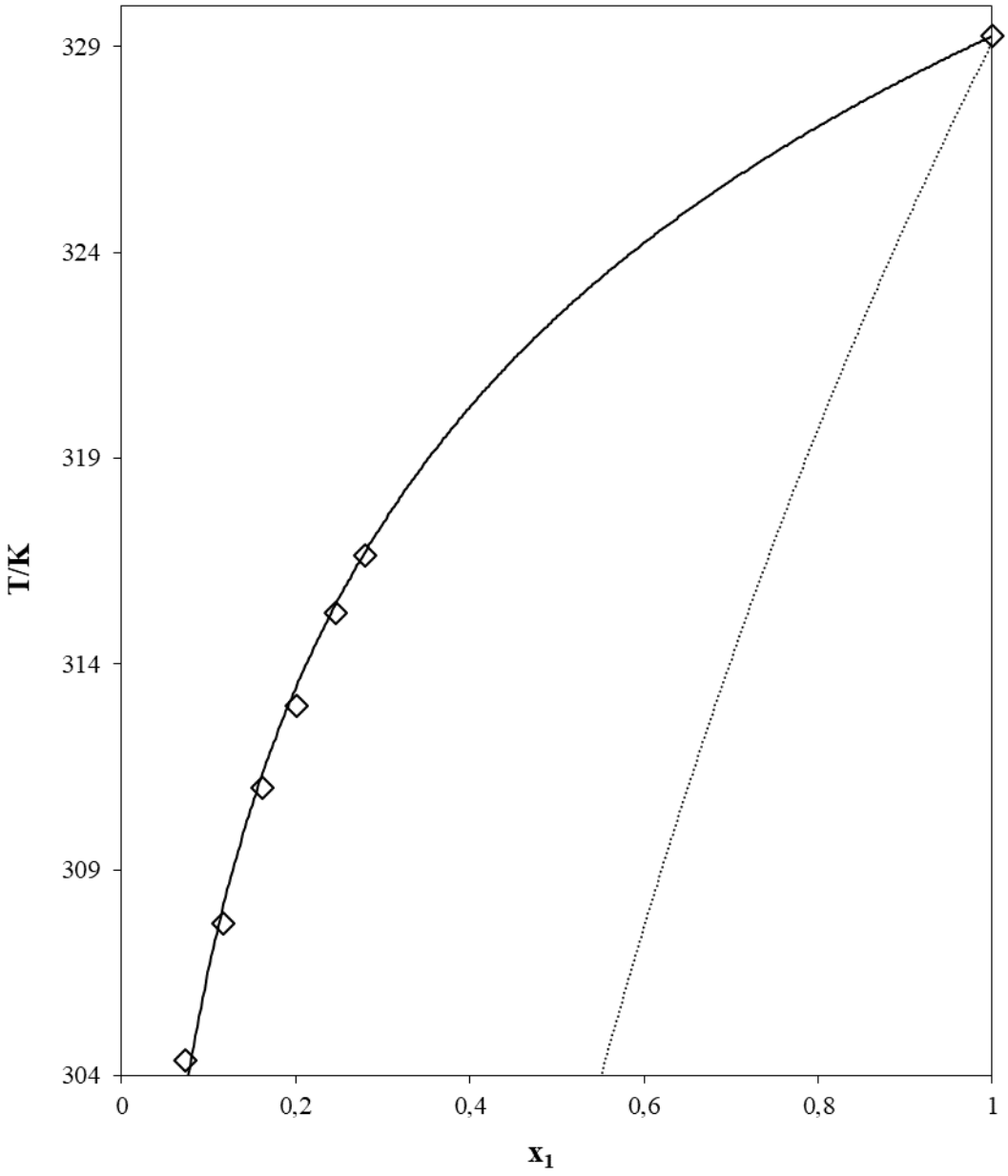


Table S4. Results of correlation of the experimental solubility data of the {α-pinene SOA acid (1) + water (2)} binary systems by means of the Wilson, NRTL, and UNIQUAC equations.

Compound	Parameters			Root-mean-square deviations		
	Wilson	NRTL	UNIQUAC	Wilson	NRTL	UNIQUAC
	$\Delta\lambda_{12}\Delta\lambda_{21}$ $J{\cdot}mol^{-1}$	$\Delta g_{12}\Delta g_{21}$ $J{\cdot}mol^{-1}$	$\Delta u_{12}\Delta g_{21}$ $J{\cdot}mol^{-1}$	δ_T K	δ_T K	δ_T K
MBTCA	-8188.0 218.63	-11906.22 5471.36	2241.76 -3875.52	2.24	2.53[a]	**2.21**
DTAA	754.33 4104.57	-741.01 5353.37	5398.52 1997.9	0.80	0.72[a]	**0.57**
TER	6373.79 3105.31	-1295.0 7415.67	1578.75 3967.94	**3.79**	10.98[c]	4.07
PD	641.97 8821.12	1739.30 5306.40	2383928.0 4181.7	**1.25**	1.89[b]	18.08

[a] $\alpha = 0.65$
[b] $\alpha = 0.60$
[c] $\alpha = 0.95$

7. Abbreviations used in the publication

a, activity; *D*, absorbance value; g_{ij}, molar energy of interaction between *i* and *j* (J mol^{-1}); ΔH, molar enthalpy (kJ mol^{-1}); *p*, pressure; p($a_H\gamma_{Cl}$), acidity function; p$K_{a,}$ constant acidity; *T*, equilibrium temperature (K); ΔT, estimated error of temperature (K); *x*, mole fraction;*V*, mole values ; *Greek letters* - α_{ij}, constant of the NRTL; τ_{ij}, binary interaction parameter in the NRTL model; $q_{i,}$ the surface parameter; λ_{ij}, cross interaction energy parameter for Wilson equation ($\lambda_{ij} - \lambda_{ii}$) (J/mol); λ_{Ji}, cross interaction energy parameter for Wilson equation ($\lambda_{jI} - \lambda_{ii}$) (J/mol); Λ_{ij}, Wilson parameter; γ, activity coefficient; σ_T, root-mean-square deviation in temperature; *Subscripts* – fus, fusion; i, j, component (i-solvent, j-solute); lit, literature data; *T*, temperature; tr, transition; *Superscript* - A^-, base value; cal, calculated value; exp, experimental value; lit, literature value; HA, acid value.

8. References:

1. Kostenidou, E.; Karnezi, E.; Kołodziejczyk, A.; Szmigielski, R.; Pandis, S. N. Physical and Chemical Properties of 3-Methyl-1,2,3-butanetricarboxylic Acid (MBTCA) Aerosol. *Environ. Sci. Technol.* **2018**, *52* (3), 1150-1155.