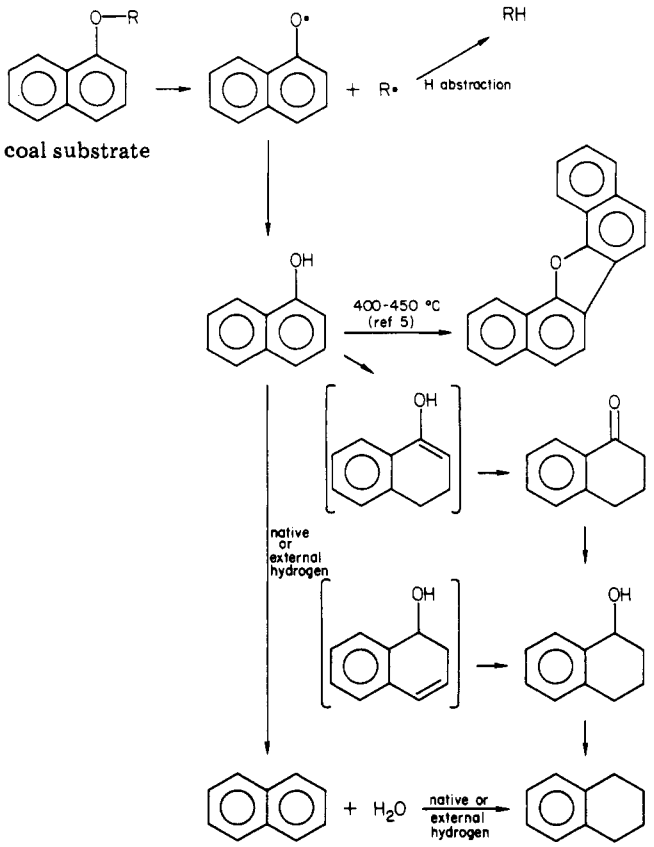
Scheme I. Proposed Sequential Conversion of Coal's Native Ethers to Aromatic and Hydroaromatic Hydrocarbons



our moderate hydrogen pressure conditions, the pathway proposed by Poutsma and Dyer[5] is superseded by reduction of the hydroxyl-containing ring. We calculate a rate constant (for the disappearance of 1-naphthol) of 2.2×10^{-3} s^{-1} at 450 °C under hydrogen vs. a rate constant of 1.3×10^{-4} s^{-1} determined at 400 °C without added hydrogen. The dramatic movement of our product slate to two-ring (vs. five-ring) and naphthenoaromatics (vs. oxygenates) using 1000 psi of hydrogen and no catalyst is a surprising result.

Scheme I provides a series of thermal steps which can account for the initial generation of phenolics, then aromatics, and finally hydroaromatics under hydropyrolysis conditions starting from alkyl aryl ether moieties (functionalities determined to be important for lignins[6] and for low-rank coals[7]). In contrast, when the naphthol is generated without external sources of hydrogen, the dominant pathway, even at 400 °C, is one of condensation to make a dimeric furan.[5] Since in a coal system there will be some available hydrogen (native to the coal), even a pyrolysis under an inert atmosphere will lead to some formation of aromatic and hydroaromatic compounds following the initial ether conversion to phenols. This interpretation is consistent with a report by Collins that 1-naphthol-^{14}C plus Illinois No. 6 coal at 400 °C for 20 h gave some small amount of naphthalene-^{14}C.[8]

Experimental Section

1-Naphthol (Aldrich) was used as received (capillary GC analysis showed 1-naphthol purity of >99%). The six batch reactors employed were constructed of 316 stainless steel and have been described in detail.[9] The reactors were each charged with 2.0 g of 1-naphthol and 3.5 MPa of H_2 (500 psi), held on a rack, and plunged into a preheated fluidized sand bath and moderately agitated. Individual reactors were removed from the hot sand bath at various times and rapidly cooled by plunging them into a water bath. Product analyses were carried out by capillary GC. Use of an external standard (hexadecane) allowed identification of >90% by weight of charged material.

Acknowledgment. We gratefully acknowledge the counsel and encouragement of Dr. Martin L. Gorbaty and the helpful suggestions of Dr. William N. Olmstead.

Registry No. 1-Naphthol, 90-15-3.

(6) See, e.g.: Freudenberg, K. *Annu. Rev. Biochem.* **1938**, *8*, 88.
(7) Liotta, R. *J. Am. Chem. Soc.* **1981**, *103*, 1735.
(8) C. J. Collins, personal communication.
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Conjugate Addition–Cycloacylation of Acetylenic Diesters: Synthesis of Highly Functionalized Cyclopentenones

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Intramolecular trapping of anionic species generated by conjugate additions to unsaturated carbonyl compounds have recently provided some interesting new reaction sequences.[1-3] The majority of these reactions have involved 1,4-additions to α,β-ethylenic ketones and esters. Since nucleophilic conjugate additions to α,β-acetylenic esters followed by intermolecular capture of the intermediate anionic species have provided a wealth of useful methods for acyclic olefin synthesis,[4-11] we felt that intramolecular capture of the anion could serve to generate highly functionalized and substituted cyclic olefins. This report describes a conjugate addition–cycloacylation sequence on 1,6-hex-2-yne dioic esters **1**.

In order that the conjugate addition–cycloacylation might be attempted, we first required a short, efficient method for preparation of the acetylenic diester substrates and two sequences were tested (eq 1). Alkylation of the dianion[12] of isobutyric acid with propargyl bromide provided acetylenic acid **2**. Treatment of acetylene **2** with *n*-butyllithium (2 equiv) followed by quenching with CO_2,

(1) Little, R. D.; Dawson, J. R. *Tetrahedron Lett.* **1980**, *21*, 2608. Ratney, R.; English, J., Jr. *J. Org. Chem.* **1960**, *25*, 2213. Naf, F.; Decorzant, W.; Thommen, W. *Helv. Chim. Acta* **1975**, *58*, 1808. Posner, G. W.; Sterling, J. J.; Whitten, C. F.; Lentz, C. M.; Brunelle, D. T. *J. Am. Chem. Soc.* **1975**, *97*, 107 and references therein. McMurray, J. G.; Isser, S. J. *Ibid.* **1972**, *94*, 7132.
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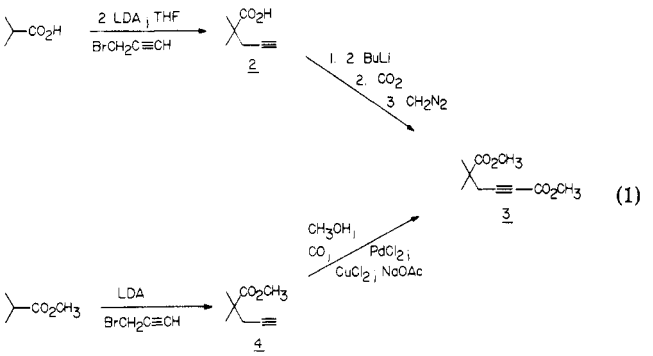
(11) Naf, F.; Degen, P. *Helv. Chim Acta* **1971**, *54*, 1939.
(12) Creger, P. L. *J. Org. Chem.* **1972**, *37*, 1907.
(13) Gregge, R. J.; Herrmann, J. L.; Lee, C. S.; Richman, J. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2425.

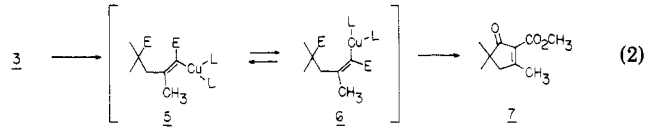
0022-3263/84/1949-3033$01.50/0



(1)

acidification, and esterification gave diester **3** in modest yield.[3] Alternatively, alkylation of the lithium enolate of methyl isobutyrate afforded 80% of **4** which was directly converted to **3** in 72% yield by the method of Tsuji[14] (CO, CH_3OH; $PdCl_2$; $CuCl_2$; NaOAc). We prefer the latter method because of its ease and efficiency.

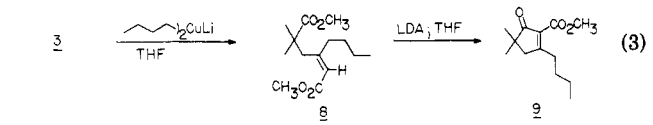
When diester **3** was added to a THF solution of lithium dimethylcopper at −78 °C and the solution was warmed to 25 °C, cyclopentenone **7** was obtained in 45% yield after flash chromatography. The reaction presumably takes the following course (see eq 2): initial syn[5,8] addition to provide



(2)

vinylcopper species **5** which is in equilibrium with **6**. Intermediate **6** then undergoes intramolecular acylation to produce **7**. The protonated forms of **5** and **6** have been isolated and similar olefinic species are always byproducts of the direct conjugate addition cycloacylation (method A). We have carried out a number of examples of this reaction using both lithium dialkyl cuprates and copper(I) iodide–Grignard complexes. These results are summarized in Table I.

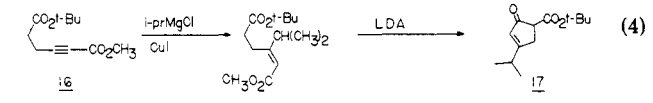
The efficiency of this one-step procedure can be improved in some cases by using a two-step method (method B) instead. If the intermediate vinylcopper species is protonated at low temperature (−78 °C), no cyclization occurs and the olefin **8** (eq 3) is isolated. If this acyclic



(3)

diester is then exposed to lithium diisopropylamide in THF (−78 °C to 0 °C), high yields (75% overall) of the cyclopentenone **9** can be realized.

If, however, the unsubstituted diester **16** is treated with isopropylmagnesium chloride according to method B, cyclization to produce keto ester **17** is observed (eq 4). Thus, cyclopentenones of a different substitution pattern can be obtained by this procedure.



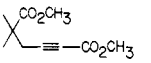
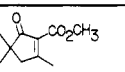
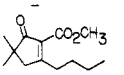
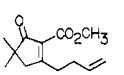
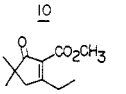
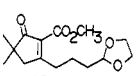
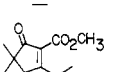
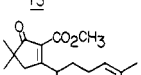
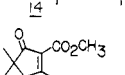
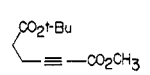
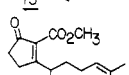
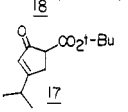
(4)

Experimental Section

Infrared spectra were recorded on a Beckman IR 4210. Nuclear magnetic resonance spectra were recorded either at 100 MHz on a Varian XL-100 or at 250 MHz on a Bruker WM-250 spectrometer. Microanalyses were performed by Galbraith Labs. Boiling points are uncorrected.

Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl immediately prior to use. Tetramethylethylenediamine (TMEDA) and hexamethylphosphoramide (HMPA) were dried by distillation from calcium hydride prior to use.

Table I. Synthesis of Highly Functionalized Cyclopentenones

diester	organometallic	product; yield, %, method a (b)
	$(CH_3)_2CuLi$	 45
		 41 (75)
		 43 (69)
	CH_3CH_2MgBr	 37 (53)
		 42 (61)
	$(CH_3)_2CHMgCl$	 35
		 48
		 40
		 48
	$(CH_3)_2CHMgCl$	 (52)

Methyl 2,2-Dimethylpent-4-ynoate (4). A solution of *n*-butyllithium (83 mL of a 2.6 M solution, 0.216 mol) in hexane was added dropwise to a cooled (0 °C), stirred solution of diisopropylamine (30.2 mL, 0.216 mol) in 200 mL of dry tetrahydrofuran. The solution was stirred 10 min and cooled to −78 °C whereupon a solution of methyl isobutyrate (20.0 g, 0.196 mol) in 20 mL of tetrahydrofuran was added dropwise. The solution was stirred for 1 h at −78 °C and a solution of propargyl bromide (24 mL, 80% by weight in toluene, 0.216 mol) in 37 mL of HMPA was added dropwise. After being stirred for 1 h at −78 °C, the mixture was quenched with saturated ammonium chloride and warmed to room temperature. The THF was removed in vacuo and the residue was dissolved in ether, washed 4 times with water, dried, concentrated, and distilled at reduced pressure to provide 21.79 g (80%) of a clear liquid: bp 48–50 °C (12 mm); 100-MHz ^1H NMR ($CDCl_3$, δ) 1.22 (s, 6 H) 1.88 (t, J = 3 Hz, 1 H), 2.34 (d, J = 3 Hz, 2 H), 3.58 (s, 3 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.63; H, 8.79.

Dimethyl 5,5-Dimethylhex-2-ynedioate (3). A mixture (initially heterogeneous) of acetylene **4** (21.8 g, 0.156 mol), palladium(II) chloride (200 mg, 1.30 mol), copper(II) chloride (42.1 g, 0.312 mol) and sodium acetate (25.8 g, 0.311 mol) in 650 mL of absolute methanol was stirred under an atmosphere of carbon monoxide for 3 h whereupon the mixture became homogeneous.

(14) Tsuji, J.; Takahashi, M.; Takahashi, T. *Tetrahedron Lett.* **1980**, *21*, 849.

The methanol was removed in vacuo and the residue was taken up in ether. The ether solution was washed with water, 50% aqueous ammonium hydroxide, and brine and then dried and concentrated. Distillation at reduced pressure gave 22.3 g (72%) of diester **3** as a clear liquid: bp 84–86 °C (1.0 mm); 100-MHz ^{1}H NMR ($CDCl_3$, δ) 1.31 (s, 6 H), 2.52 (s, 2 H), 3.62 (s, 3 H), 3.65 (s, 3 H).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.44; H, 7.06.

Typical Procedure for Conjugate Addition–Cyclizations. Method A. 2-Carbomethoxy-5,5-dimethyl-3-(2-methyl-2-hepten-6-yl)cyclopent-2-en-1-one (14). A solution of Grignard reagent [prepared from 2-chloro-6-methyl-5-heptene (10.0 g, 68.7 mmol) and magnesium (3.0 g, 125 mmol)] in 50 mL of dry tetrahydrofuran was added dropwise to a stirred mixture of dry copper(I) iodide (11.05 g, 68.7 mmol) and dry tetramethylenediamine (14.1 mL, 103.1 mmol) in 150 mL of dry THF at −78 °C. This mixture was stirred for 1 h at −78 °C, and a solution of diester **3** (6.0 g, 30.3 mmol) in 10 mL of dry THF was added dropwise. The mixture was stirred at −78 °C for 3 h and warmed to room temperature over 2 h. The reaction was quenched by slowly pouring the mixture into 10% HCl. The mixture was extracted with ether, and the ether layer was washed with saturated sodium bicarbonate, dried, and concentrated. Flash chromatography of the residue on 200 g of silica with 5% ethyl acetate/hexane gave 3.903 g (46%) of **14** as a pale yellow oil: 250-MHz ^{1}H NMR ($CDCl_3$, δ) 1.14 (s, 6 H), 1.17 (d, J = 6.5 Hz, 3 H), 1.53 (m, 2 H), 1.57 (br s, 3 H), 1.68 (br s, 3 H), 1.95 (m, 2 H), 2.51 (AB q, 2 H), 3.50 (tq, J = 6.5 Hz, 6.5 Hz, 1 H), 3.84 (s, 3 H), 5.08 (br t, J = 7 Hz, 1 H); IR (film) 1756, 1729, 1630, 1463, 1437, 1356 cm^{-1}.

Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.11; H, 9.45.

Method B. 2-Carbomethoxy-5,5-dimethyl-3-butylcyclopent-2-en-1-one (9). A solution of 1.65 M *n*-butyllithium in hexane (1.21 mL, 2.0 mmol) was added dropwise to a suspension of CuI (190 mg, 1.0 mmol) in 10 mL of dry THF at −78 °C. After being stirred for 15 min the mixture became homogeneous and diester **3** (198 mg, 1.0 mmol) in 5 mL of dry THF was added dropwise. The mixture was stirred for 30 min at −78 °C, quenched with saturated NH_4Cl, and diluted with ether. The organic layer was dried and concentrated to provide 255 mg (99%) of diester **8**: 100-MHz ^{1}H NMR ($CDCl_3$, δ) 0.90 (br t, 3 H), 1.22 (s, 6 H), 1.04–1.55 (band, 4 H), 1.95 (m, 2 H), 3.11 (s, 2 H), 3.69 (s, 6 H), 5.77 (s, 1 H).

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.90; H, 9.08.

A solution of 1.65 M *n*-butyllithium in hexane (0.710 mL, 1.17 mmol) was added dropwise to a solution of diisopropylamine (0.165 mL, 1.17 mmol) in 7 mL dry THF at 0 °C. The solution was stirred for 15 min at 0 °C and cooled to −78 °C whereupon a solution of diester **8** in 3 mL of dry THF was added dropwise. After 15 min at −78 °C the mixture was warmed to 25 °C over 30 min and quenched with 10% HCl and diluted with ether. The organic layer was washed with saturated $NaHCO_3$, dried, and concentrated. Flash chromatography (10% ethyl acetate/hexane) produced 100 mg (77%) of cyclopentenone **9** as a clear liquid: 100-MHz ^{1}H NMR ($CDCl_3$, δ) 0.95 (br t, 3 H), 1.24 (s, 6 H), 1.20–1.75 (band 4 H), 2.55 (s, 2 H), 2.66 (m, 2 H), 3.86 (s, 3 H); IR (film) 1758, 1730, 1632, 1477, 1442 cm^{-1}.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.25; H, 8.73.

2-Carbomethoxy-3,5,5-trimethylcyclopent-2-en-1-one (7): 100-MHz ^{1}H NMR ($CDCl_3$, δ), 1.14 (s, 6 H), 2.41 (s, 3 H), 2.57 (s, 2 H), 3.85 (s, 3 H); IR (film) 1745, 1720, 1633, 1436, 1344 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.79; H, 7.86.

3-(1-Buten-4-yl)-2-carbomethoxy-5,5-dimethylcyclopent-2-en-1-one (10): 100-MHz ^{1}H NMR ($CDCl_3$, δ) 1.14 (s, 6 H), 2.36 (m, 2 H), 2.57 (s, 2 H), 2.90 (m, 2 H), 3.85 (s, 3 H), 5.06 (m, 2 H), 5.79 (m, 1 H); IR (film) 1756, 1722, 1632, 1443, 1368 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.89; H, 8.27.

2-Carbomethoxy-5,5-dimethyl-3-ethylcyclopent-2-en-1-one (11): 100-MHz ^{1}H NMR ($CDCl_3$, δ) 1.13 (s, 6 H), 1.27 (t, J = 7 Hz, 3 H), 2.54 (s, 2 H), 2.73 (q, J = 7 Hz, 2 H), 3.82 (s, 3 H); IR (film) 1760, 1732, 1639, 1447, 1365 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.11; H, 8.05.

2-Carbomethoxy-5,5-dimethyl-3-[1-(2-dioxolanyl)prop-3-yl]cyclopent-2-en-1-one (12): 100-MHz ^{1}H NMR ($CDCl_3$, δ) 1.14 (s, 6 H), 1.74 (m, 4 H), 2.57 (s, 2 H), 2.83 (m, 2 H), 3.84 (s, 3 H), 3.91 (m, 4 H), 4.88 (t, J = 4 Hz); IR (film) 1758, 1726, 1618, 1434 cm^{-1}.

Anal. Calcd for $C_{15}H_{25}O_5$: C, 63.81; H, 7.85. Found: C, 63.58; H, 8.65.

2-Carbomethoxy-5,5-dimethyl-3-isopropylcyclopent-2-en-1-one (13): 100-MHz ^{1}H NMR ($CDCl_3$, δ) 1.14 (s, 6 H), 1.18 (d, J = 7 Hz, 6 H), 2.52 (s, 2 H), 3.61 (m, 1 H), 3.85 (s, 3 H); IR (film) 1755, 1727, 1626, 1469, 1442 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.32; H, 8.65.

2-Carbomethoxy-5,5-dimethyl-3-propen-1-ylcyclopent-2-en-1-one (15): 100-MHz ^{1}H NMR ($CDCl_3$, δ) 1.17 (s, 6 H), 2.01 (dd, J = 7 Hz, 1.5 Hz, 3 H), 2.71 (br s, 2 H), 3.87 (s, 3 H), 6.62 (dq, J = 16 Hz, 7 Hz, 1 H), 7.31 (br d, J = 16 Hz, 1 H); IR (film) 1703, 1630, 1572, 1243, 1226 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.94; H, 7.70.

2-Carbomethoxy-3-(2-methyl-2-hepten-6-yl)cyclopent-2-en-1-one (18): 100-MHz ^{1}H NMR ($CDCl_3$, δ) 1.18 (d, J = 7 Hz, 3 H), 1.51 (m, 2 H), 1.58 (br s, 3 H), 1.68 (br s, 3 H), 1.93 (m, 2 H), 2.57 (m, 4 H), 3.45 (m, 1 H), 3.85 (s, 3 H), 5.07 (br t, J = 7 Hz, 1 H); IR (film) 1758, 1723, 1631, 1443, 1358 cm^{-1}.

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.58, H, 8.62.

5-Carbo-*tert*-butoxy-3-isopropylcyclopent-2-en-1-one (17): 100-MHz ^{1}H NMR ($CDCl_3$, δ) 1.22 (d, J = 7 Hz, 3 H), 1.48 (s, 9 H), 2.65 (m, 3 H), 3.35 (dd, J = 3 Hz, 6 Hz, 1 H), 5.88 (m, 1 H); IR (film) 1737, 1703, 1608, 1365 cm^{-1}.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61, H, 8.99. Found: C, 69.91, H, 9.22.

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Registry No. **3**, 90171-34-9; **4**, 86101-49-7; **7**, 91054-09-0; **8**, 91054-19-2; **9**, 91054-10-3; **10**, 91054-11-4; **11**, 91054-12-5; **12**, 91054-13-6; **13**, 91054-14-7; **14**, 91054-15-8; **15**, 91054-16-9; **17**, 91054-18-1; **18**, 91054-17-0; 3-dioxolan-2-ylpropylmagnesium bromide, 91083-05-5; methyl isobutyrate, 547-63-7; propargyl bromide, 106-96-7; $(CH_3)_2CuLi$, 15681-48-8; BuLi, 109-72-8; CH_2=$CHCH_2CH_2MgBr$, 7103-09-5; EtMgBr, 925-90-6; $(CH_3)_2CHMgCl$, 1068-55-9; CH_2=$CHCH_2MgCl$, 2622-05-1; *t*-BuOCO-$(CH_2)_2C$≡CCO_2CH_3, 91054-07-8; $(CH_3)_2C$=$CH(CH_2)_2CH(CH_3)MgCl$, 91054-08-9.

Synthesis of 9,10-Epoxy-9,10-secoabieta-8,11,13-triene[1]

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Of the several naturally occurring ring-B seco-tri- and tetracyclic diterpenoids which have been described in recent years, the simplest one is (+)-9,10-epoxy-9,10-secoabieta-8,11,13-triene (**1**) (Chart I) which was isolated in very small amount from the nonsaponifiable portion of Western White Pine bark.[2] As identification was based

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