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Synthesis and GC–MS analysis of angelates and tiglates as an aid to identification of these components in essential oils

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ABSTRACT: One-hundred-and-forty-one angelates and tiglates were synthesized and their Kováts retention indices and mass spectra are presented. It is anticipated that the publication of these data will aid in the identification of angelates and tiglates from natural sources. Copyright © 2009 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: angelates; tiglates; flavor components; Kovats retention indices; GCMS spectra

Introduction

The angelates and the tiglates can contribute significantly to the composition of some essential oils.[1–3] The importance of the relative intensities of *m/z* 82 and 83 as well as 100 and 101 peaks in their mass spectra has been applied towards the differentiation of angelates from tiglates.[4] This method seems to be satisfactory primarily in distinguishing lower molecular weight angelates from tiglates. The limitations of its common use in this regard becomes limited when *m/z* 100 and 101 peaks are either absent or are of very low intensity. In addition, any distinction within the angelate isomers or the tiglate isomers also becomes difficult to ascertain. A combination of Kováts retention indices and mass spectral data still remains the most useful tool in the identification of these esters. Unfortunately, such data for the angelates and the tiglates derived from some of the most common primary and secondary alcohols as well as phenols is lacking in the literature. In this paper we report the mass spectra and Kováts retention indices, determined on two columns of different polarities, for angelates and tiglates prepared from >60 alcohols and phenols that are encountered among the essential oils.

Materials and Methods

Preparation of Esters

The preparation of angelic acid from commercial tiglic acid and the conversion of angelic acid to angeloyl chloride utilized methods from the literature.[5–7] The conversion of tiglic acid to tigloyl chloride was made using standard protocols.[6,7] The unpurified solutions of angeloyl chloride and tigloyl chloride were stored in hexane in a desiccator. The angeloyl chloride solution was ca. 1.2 M and the tigloyl chloride was ca. 1.6 M. The alcohols and phenols were available from a collection by the authors. Most of the alcohols and phenols subjected to conversion to esters were soluble in hexanes. For those not soluble in hexane, anhydrous THF was used as the solvent. A solution of 0.1 mM of the alcohol or the phenol was prepared in 500 µl of the appropriate solvent and added dropwise with a syringe to a stirred ice-cold suspension of 5 mg (ca. 0.1 mM) of 60% NaH suspension in mineral oil in a 10 ml vial fitted with a septum and N_2 inlet. The mixture was stirred for 1 h. To this, an appropriate volume of the solution containing ca. 2 mM of the acid chloride was added dropwise and the mixture stirred for another 1 h. Those reaction mixtures having hexanes as the solvent were first washed three times with 2 ml portions of 5% ice cold NaOH solution, followed by three washings with saturated NaCl solution and dried over anhydrous Na_2SO_4. To the reaction mixtures in THF, 4 ml hexane was added and then the previously described extraction procedure was followed. In the case of the reaction of orcinol with the acid chloride, the reaction mixture was first washed three times with 2 ml portions of 5% ice-cold solution of HCl, followed by washings with saturated NaCl, and subsequently dried over anhydrous Na_2SO_4. The dried hexane solutions were then subjected to gas chroamtography–mass spectrometry (GC–MS) data acquisition.

GC–MS Analyses

The samples were analysed on a HP5971 MSD mass spectrometer (scan time, 1/s), directly coupled to a HP 5890 gas chromatograph, using a J&W DB-5 (bonded methyl silicone), 0.26 mm i.d. × 30 m (0.25 µm coating thickness) fused silica capillary column, and separately analysed on a Restek Stabilwax® (cross-bonded Carbowax® polyethylene glycol), 0.25 mm i.d. ×30 m (0.25 µm coating thickness) fused capillary column. Analysis conditions (for both columns): injector, 220°C; transfer line temperature, 240°C; oven temperature, linear programmed from 60°C to 246°C at 3°C/min; carrier gas, He at 34.96 cm/s or 1.02 ml/min (at 210°C); injection volume, 0.1 µl (ca. 1% solution); split, 1:20, ca. 50 ng/on column. Typical tuning values for MSD operation[8] were: EM, 2400 V; X-ray, 44.0; emission, on; AMU gain, 88; AMU offset, 60; mass gain, 52; mass offset, 14; repellor, 10.20; ion focus, 0.0; ent

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Table 1. Angelates and tiglates with KIs on DB-5 and PEG (Restek Stabilwax)

	KI (DB-5)	KI (PEG)		KI (DB-5)	KI (PEG)
Amyl angelate	1185	1446	Hexyl tiglate (in [8])	1332	1622
Amyl angelate, 4-methyl-	1249	1495	Hexyl tiglate, 2-	1246	1499
Amyl tiglate	1229	1525	Hydroxycitronellyl angelate	1744	2360
Amyl tiglate, 4-methyl-	1291	1576	Hydroxycitronellyl tiglate	1795	2451
Anisyl angelate, *meta*-	1673	2389	Ionyl angelate, methyl-*β*-(*E*)-	1837	2133
Anisyl angelate, *para*-	1692	2424	Ionyl tiglate, methyl-*β*-(*E*)-	1872	2185
Anisyl tiglate, *meta*-	1735	2514	Isobutyl angelate	1050	1293
Anisyl tiglate, *para*-	1755	2552	Isobutyl tiglate	1088	1364
Arbozyl angelate, endo-	1824	2209	Menth-1-en-9-yl angelate, *para*-	1694	2092
Arbozyl angelate, exo-	1855	2263	Menth-1-en-9-yl tiglate, *para*-	1746	2188
Arbozyl tiglate, endo-	1878	2305	Myrtenyl angelate	1608	1964
Arbozyl tiglate, exo-	1910	2364	Myrtenyl tiglate	1652	2050
Benzyl angelate	1439	1994	Nonadienyl angelate, (2*E*,4*E*)-	1644	2073
Benzyl tiglate (in [8])	1497	2110	Nonadienyl angelate, (2*E*,6*Z*)-	1575	1948
Butenyl angelate, 3-methyl-2- (in [8])	1190	1601	Nonadienyl angelate, (3*E*,6*Z*)-	1572	1937
Butenyl angelate, 3-methyl-3-	1336	1747	Nonadienyl tiglate, (2*E*,4*E*)-	1700	2183
Butenyl tiglate, 3-methyl-2-	1243	1872	Nonadienyl tiglate, (2*E*,6*Z*)-	1627	2046
Butenyl tiglate, 3-methyl-3-	1199	1828	Nonadienyl tiglate, (3*E*,6*Z*)-	1616	2011
Butyl angelate, 2-	1023	1254	Nonenyl angelate, (3*Z*)-	1561	1871
Butyl angelate, 2-methyl-1-	1152	1395	Nonenyl tiglate, (3*Z*)-	1606	1955
Butyl angelate, 3-methyl-2-	1092	1313	Nonenyl angelate, (2*E*)-	1577	1895
Butyl tiglate, 2-	1066	1327	Nonenyl angelate, (2*Z*)-	1564	1869
Butyl tiglate, 2-methyl-1-	1192	1472	Nonenyl angelate, (6*Z*)-	1576	1896
Butyl tiglate, 3-methyl-2-	1133	1384	Nonenyl tiglate, (2*E*)-	1633	1988
Carvyl angelate, *cis*-	1629	2024	Nonenyl tiglate, (2*Z*)-	1613	1958
Carvyl angelate, *trans*-	1585	1964	Nonenyl tiglate, (6*Z*)-	1620	1979
Carvyl tiglate, *cis*-	1680	2126	Nonyl angelate, 3-	1466	1673
Carvyl tiglate, *trans*-	1631	2055	Nonyl, tiglate 3-	1506	1750
Cinnamyl angelate, (*E*)-	1728	2432	Nopyl angelate	1705	1779
Cinnamyl tiglate, (*E*)-	1787	2556	Nopyl tiglate	1751	2149
Cumenyl angelate, *meta*-	1575	2082	Octadienyl angelate , (2*E*,4*E*)-	1541	1962
Cumenyl angelate, *ortho*-	1515	1992	Octadienyl tiglate, (2*E*,4*E*)-	1595	2069
Cumenyl tiglate, *meta*-	1642	2201	Octenyl angelate, (5*Z*)-	1476	1796
Cumenyl tiglate, *ortho*-	1568	2094	Octenyl tiglate, (5*Z*)-	1523	1880
Cymen-7-yl angelate, *para*-	1692	2195	Octyl angelate	1480	1745
Cymen-7-yl tiglate, *para*-	1757	2353	Octyl angelate, 2-	1389	1689
Dec-1-en-3-yl angelate	1553	1818	Octyl tiglate	1526	1827
Dec-1-en-3-yl tiglate	1598	1899	Octyl tiglate, 2-	1434	1737
Decadienyl angelate, (2*E*,4*E*)-	1745	2178	Orcinyl angelate	1753	2767
Decadienyl tiglate, (2*E*,4*E*)-	1802	2290	Orcinyl di-angelate	2094	2891
Decenyl angelate, (2*E*)-	1676	1992	Orcinyl di-tiglate	2171	3128
Decenyl angelate, (4*E*)-	1666	1974	Orcinyl tiglate	1812	2896
Decenyl angelate, (4*Z*)-	1654	1963	Penten-3-yl angelate, 1-	1093	1369
Decenyl tiglate, (2*E*)-	1728	2094	Penten-3-yl tiglate, 1-	1140	1447
Decenyl tiglate, (4*E*)-	1713	2063	Pentenyl angelate, (2*E*)-	1191	1492
Decenyl tiglate, (4*Z*)-	1697	2044	Pentenyl angelate, (2*Z*)-	1184	1511
Dihydrocitronellyl angelate	1584	1817	Pentenyl tiglate, (2*E*)-	1243	1602
Dihydrocitronellyl tiglate	1630	1898	Pentenyl tiglate, (2*Z*)-	1232	1578
Dodecadienyl angelate, (2*E*,4*E*)-	1946	2387	Perilla alcohol angelate	1709	2176
Dodecadienyl tiglate, (2*E*,4*E*)-	2004	2505	Perilla alcohol tiglate	1765	2286
Dodecyl angelate	1879	2153	Phenyl angelate, 2-(1*E*)-propenyl-	1619	2233
Dodecyl tiglate	1927	2241	Phenyl angelate, 2-(1*Z*)-propenyl-	1558	2109
Ethyl angelate	894	1169	Phenyl angelate, 2-allyl-	1550	2106
Ethyl tiglate (in [8])	936	1244	Phenyl ethyl angelate, 2-	1534	2095
Geranyl angelate	1648	2008	Phenyl ethyl tiglate, 2- (in [8])	1585	2188
Geranyl tiglate (in [8])	1696	2109	Phenyl tiglate, 2-(1*E*)-propenyl-	1674	2340
Guaiacyl angelate	1527	2219	Phenyl tiglate, 2-(1*Z*)-propenyl-	1610	2212
Guaiacyl tiglate	1584	2333	Phenyl tiglate, 2-allyl-	1597	2202
Heptadienyl angelate, (2*E*,4*E*)-	1442	1870	Pinocamphyl angelate, iso-	1577	1877
Heptadienyl tiglate, (2*E*,4*E*)-	1496	1969	Pinocamphyl tiglate, iso-	1628	1969
Heptenyl angelate, (4*Z*)-	1372	1688	Piperityl angelate, *cis*-	1573	1907
Heptenyl tiglate, (4*Z*)-	1418	1768	Piperityl angelate, *trans*-	1583	1928
Hepten-2-yl angelate, 6-methyl-5-	1383	1657	Piperityl tiglate, *cis*-	1627	2012
Hepten-2-yl tiglate, 6-methyl-5-	1427	1732	Piperityl tiglate, *trans*-	1640	2037
Heptenyl angelate, (3*Z*)-	1371	1679	Sesamyl angelate	1690	2526
Heptenyl tiglate, (3*Z*)-	1419	1763	Sesamyl tiglate	1751	2649
Heptyl angelate, 4-	1266	1467	Tridecenyl angelate, (2*E*)-	1972	2301
Heptyl tiglate, 4-	1309	1549	Tridecenyl tiglate, (2*E*)-	2024	2404
Hexadienyl angelate, (2*E*,4*E*)-	1345	1776	Undecenyl angelate, (2*E*)-	1774	2096
Hexadienyl tiglate, (2*E*,4*E*)-	1401	1874	Undecenyl angelate, 10-	1771	2105
Hexenyl angelate, (4*Z*)-	1292	1617	Undecenyl tiglate, (2*E*)-	1826	2197
Hexenyl tiglate, (4*Z*)-	1336	1693	Undecenyl tiglate, 10-	1818	2194
Hexyl angelate	1285	1544	Verbenyl angelate, *cis*-	1564	1654
Hexyl angelate, 2-	1199	1421			

lens, 54; acquisition mode scan, scan range 41–415, 1 s/scan; solvent delay, 2.0 min.

Kováts indices (KI) were computed using the ARITHIND[8] program, based on the retention times of alkanes (C_4–C_{30}), run on both the DB-5 and PEG (Stabilwax) columns using the above-mentioned temperature programme.

Results and Discussion

The reaction of a suspension of the sodium salt of the alcohol or the phenol with the acid chloride in hexanes or in tetrahydrofuran (THF) resulted in the angelates and tiglate esters for 141 compounds (Table 1). A set of mass spectra for eight common

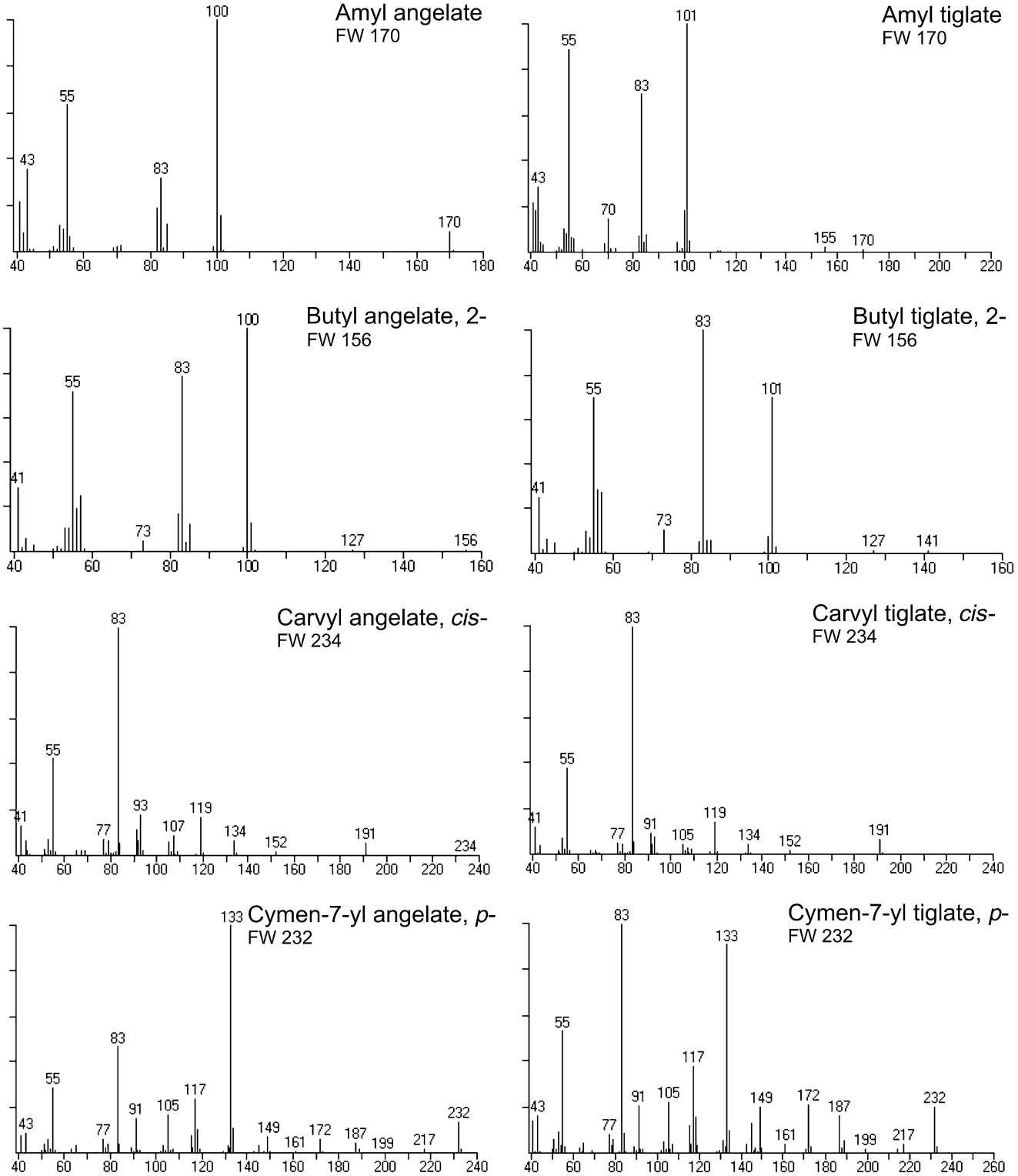

Figure 1. Representative mass spectra of eight common angelates and tiglates (see Supporting information on-line for the complete set of 141 mass spectra)

angelates and tiglates is shown in Figure 1 (see Supporting Information for the complete set of 141 mass spectra).

Supporting Information on the Internet

The following supporting information may be found in the online version of this article:

Figure S1. Complete set of 141 mass spectra

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