Volatile Constituents of Blood and Blond Orange Juices: A Comparison[1]

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ABSTRACT: The volatile constituents obtained by solvent extraction of the juices of both blood and blond sweet oranges (*Citrus sinensis* (L.) Osbeck) were studied. Some known compounds are reported in orange juice for the first time. The spectral data of four new sesquiterpenoids (valencene hydrate [**1**], γ-selinene hydrate [**2**], selina-3,11-dien-5-ol [**3**], epoxy-valencene [**4**] and of a sulfur-containing compound (S,S'-ethylidene dithioacetate [**9**]) identified for the first time in a natural product, are given and an olfactive comparison is included.

KEY WORD INDEX: *Citrus sinensis*, Rutaceae, blood orange juice, blond orange juice, juice volatiles, olfactive analysis, valencene hydrate, γ-selinene hydrate, selina-3,11-dien-5-ol, epoxy-valencene, S,S'-ethylidene dithioacetate.

INTRODUCTION: Blood oranges and blond oranges are varieties of the sweet oranges (*Citrus sinensis* L. Osbeck). Whereas the cultivation of blond oranges is widespread, the conditions to grow blood oranges are limited: to develop the special flavor and the typical red pigmentation, cool night temperatures are required. The most important areas of production are Sicily and Spain. To our knowledge, only one analytical study on the volatile constituents of blood orange juice has been published: Schreier et al. (1) described the aroma compounds in Sanguinella oranges and their changes during juice processing. Dugo et al. (2) compared the compounds found in blond and blood orange peel oils in an extensive analysis. Lee et al. (3) studied juices of Moro blood oranges from Florida and California to characterize the sugars, nonvolatile acids, flavanoids and pigments, mostly composed of carotenoids and anthocyanins, which are responsible for the attractive burgundy color. Mouly et al. (4) mentioned blood oranges in an investigation of flavanone glycosides in various citrus juices. Di Giacomo et al. (5) measured the sugar, mineral salt, organic acid and flavanoid contents in different kinds of pigmented oranges.

In the present study, the juices of blood and blond oranges are analyzed, compounds never described in orange juice are listed, new compounds are characterized and an olfactive comparison is attempted.

EXPERIMENTAL: ***Choice of the Starting Material and Preparation of the Juices***—The brand of oranges was chosen according to their organoleptic properties. "Salamita Barcellona" (Sicily) was judged to have the typical flavor of blood oranges, whereas the variety "Washington"

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Table I. Relative intensities of the volatile constituents of a liquid-liquid extract of blood orange juice and blond orange juice

Compound	Blood	Blond	Compound	Blood	Blond
ethanol	0.82	0.75	nootkatene	0.13	0.19
α-pinene	0.61	0.46	α-terpinyl acetate	0.05	0.02
ethyl butyrate	0.51	1.18	benzyl alcohol	0.10	-
sabinene	0.30	0.16	theaspirenone	0.10	0.16
butanol	0.30	0.05	C_{21}	0.19	0.20
myrcene	2.15	1.80	4-vinyl-guaiacol	0.59	0.61
limonene	50.45	47.53	2-me-C_{22}	3.30	3.38
β-phellandrene	0.68	0.58	intermedeol	0.23	0.20
(E)-2-hexenal	0.05	0.90	C_{23}	4.01	4.01
hexanol	0.10	0.10	2-me-C_{23}	0.87	0.91
(Z)-3-hexanol	0.08	0.29	3-me-C_{23}	2.66	2.35
ethyl octanoate	0.01	0.01	C_{24}	1.60	1.57
octyl acetate	0.18	0.32	2-me-C_{24}	3.46	3.18
α-copaene	0.16	0.05	3-me-C_{24}	0.59	0.20
linalool	0.17	0.25	C_{25}	3.71	3.74
β-copaene	0.05	0.05	nootkatone	1.71	0.92
β-elemene	0.13	0.15	3-me-C_{25}	2.93	1.78
β-caryophyllene	0.16	0.15	2-me-C_{26}	0.80	0.50
α-humulene	0.19	0.18	3-me-C_{26}	0.10	0.10
ethyl 3-hydroxy-hexanoate	0.25	1.95	C_{27}	0.59	0.39
β-selinene	0.20	0.22	2-me-C_{27}	0.05	0.05
valencene	4.90	10.47	3-me-C_{27}	0.36	0.23
α-selinene	0.42	0.82	C_{28}	0.01	0.01
δ-cadinene	0.19	0.25	2-me-C_{28}	0.16	0.11
epi-α-selinene	0.42	0.70	3-me-C_{28}	0.01	0.01

Supelcowax 60 m, 50°-220°C, 5 min isotherm, 5°C min, 1.2 kg He, Shimadzu CR3A integrator

(Sicily) was representative of a good blond orange. Both varieties were said to come from biological cultures, which diminished the risk of sample contamination by fertilizers, insecticides and fungicides. 20 kg of each variety were cut into halves and the juice was squeezed out by means of an electrical citrus household press to afford 8.7 L of juice.

Extraction Method—Because any method to prepare the extracts by application of increased temperature was excluded, in order to preserve the fresh, authentic juice flavor, our method of choice was the continuous liquid-liquid extraction. The juice was diluted 1/1 with demineralized water and extracted for 4 h with diethyl ether. After careful evaporation of the solvent using a Vigreux column, the extracts exhibited the representative flavor of the two fresh juices: juicy, fresh, fruity, slightly astringent, spicy and slightly phenolic and meaty for the blood orange juice in contrast to the fresh, green, sweet, juicy notes of the juice of blond oranges. These extracts were preferred to the volatile isolates prepared by steam distillation at reduced pressure (50°C, 11 mmHg).

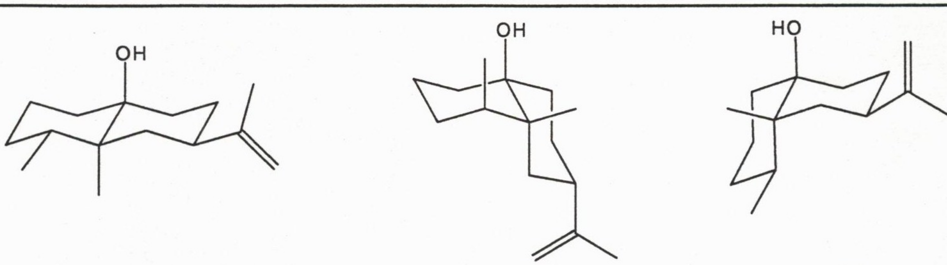
Fractionation—The extracts were fractionated by flash chromatograhy on SiO_2 into 14 fractions, using as eluent a mixture of pentane/ether = 9/1; the detector was the skilled human nose.

Analytical Methods—The total extracts and the individual fractions were analyzed by GC/MS (HP-MS-Engine, Supelcowax, 60 m, 0.25 mm or SPB-1, 60 m, 0.25 mm). The identifications were made by use of MS libraries (inhouse and Wiley) and by comparison of retention times with those of authentic samples. MS are given as m/z (% most abundant fragment) at 70 eV. The NMR spectra were measured with a Bruker WH 360 instrument, $CDCl_3$, with tetramethylsilane as internal standard, δ = 0.00 ppm).

RESULTS AND DISCUSSION: Table I and II present the volatile constituents in the order of elution on the polar GC-column. Table I gives the quantitative data of the total juice extracts calculated by integration of the surface areas of all the peaks and represent relative abundances. The comparison is valid as the procedures of the preparation of the juices, their extractions, their acquisitions by GC/MS and the integrations are identical. Our unusual results are due to the methods chosen for both extraction and analysis, which favor the identification of compounds covering a large range of volatility as well as polarity. In contrast to the data reported, the terpenoids, traditionally most important for citrus flavors, are part of a complex mixture of degradation compounds of the sugars, lipids, acids, flavanoids, pigments, proteins. The totality of these volatile stimulants, together with the nonvolatile ingredients, create the impression of flavor and taste. The paraffins might act as fixatives for the very volatile constituents.

Table II reports the trace components identified in both blood and blond sweet orange juice which have not been previously reported in (1-7). Crosses indicate, in which extract, blood or blond, the compound was identified. Literature references are given for some of the more uncommon structures. Quantitative data are omitted, due to unavoidable experimental errors created by the absorption on SiO_2 and Carbowax. The phenols and the 4-prenyloxy-phenyl-alcohols were identified on an apolar column (SPB-1), as they were absorbed on Carbowax. Among the compounds detected, three sesquiterpenoids are new compounds: valencene hydrate [**1**], γ-selinene hydrate [**2**] and compound [**3**]; epoxy-valencene [**4**] and S,S'-ethylidene dithioacetate [**9**] are found for the first time in nature. The indicated stereochemistry of these compounds refers to relative configurations.

Valencene hydrate [**1**] was confirmed by $LiAlH_4$-reduction of the epoxides [**4**] and [**5**] (27), prepared from valencene with m-chloroperbenzoic acid (Scheme 1); isomer [**6**] was isolated as a minor product. The isomer [**7**] has been described by Itokawa et al. (28). The unusual shifts of the methyl groups of [**1**], [**6**] and [**7**] were confirmed by Macromodel calculations (29): the isopropenyl group preferentially occupies the equatorial position and so the rings have to adapt to the consequent conformation. It follows that in [**6**], the 4a-hydroxy- and the 8-methyl-groups are forced to be in a diaxial orientation, shifting the ^{13}C-NMR signal from 15.1 to 17.7 ppm (γ-effect). The chemical shift of 19.0 ppm of the angular methyl group is due to high steric interactions (see Table V and Scheme 1).



{1} [6] [7]

Scheme 1. Most stable configurations of [**1**], [**6**] and [**7**], calculated with Macromodel (version 5.0)

The eudesmanoids [**2**] and [**3**] were first isolated from a still residue of orange essence oil and could be purified by preparative GC for the NMR-experiments (^{1}H- and ^{13}C-NMR, COSY, HMQC). The stereochemistry of [**2**] could be established by comparison with the NMR literature data (30) of its isomer [**8**], whereas the position of the hydroxy group in [**3**] is undetermined. The sulfur compound, S,S'-ethylidene dithioacetate [**9**], is a new natural product and its structure was confirmed by a one-pot synthesis (31).

Table II. New volatile constituents in orange juice

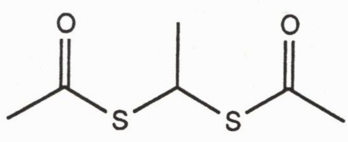
MW	Name	A	B	Ref
	Hydrocarbons			
150	(E)-4,8-dimethyl-1,3,7-nonatriene	X	X	(8)
150	(Z)-4,8-dimethyl-1,3,7-nonatriene	X		(8)
156	1,6-dimethyl-naphthalene	X	X	
168	1-dodecene	X	X	
196	1-tetradecene	X	X	
204	α-bergamotene*	X		
204	β-selinene	X	X	
204	α-selinene	X	X	
	2-methyl-alkanes C_{21}-C_{28}	X	X	
	n-alkanes C_{10}-C_{28}	X	X	
	3-methyl-alkanes C_{21}-C_{28}	X	X	
410	squalene	X	X	
	Ethers			
104	1-ethoxy-1-methoxy-ethane		X	
118	1,1-diethoxy-ethane		X	
152	3,9-epoxy-1-menthene (dill ether)	X		(9)
220	4,5-epoxy-caryophyllene	X	X	
220	1,2-epoxy-humulene	X	X	
220	1,10-epoxy-valencene [**4**]		X	
	Aldehydes			
70	(E)-2-butenal	X		
110	(E,E)-2,4-heptadienal	X	X	
110	(E,Z)-2,4-heptadienal	X	X	
112	(E)-2-heptenal		X	
126	(E)-2-octenal		X	
136	2,4,6-nonatrienal		X	
140	(E)-2-nonenal		X	
150	safranal	X		
152	β-cyclocitral		X	
152	vanillin	X	X	
154	(E)-2-decenal		X	
168	(E)-2-undecenal		X	
182	2-(4-hydroxy-2,6,6-trimethyl-1-cyclohexenyl)-acetaldehyde	X	X	(10)
226	pentadecanal	X		
240	hexadecanal	X		
254	heptadecanal	X		
268	octadecanal	X		
	Ketones			
88	3-hydroxy-2-butanone	X		
120	acetophenone	X	X	
124	(E)-6-methyl-3,5-heptadien-2-one	X	X	
124	(Z)-6-methyl-3,5-heptadien-2-one	X	X	
126	4-methyl-4-hydroxy-2-pentanone	X	X	
138	(4-methyl-3-cyclohexen-1-yl)-1-ethanone	X	X	
150	4,7-dimethylbicyclo[3.2.1]oct-3-en-2-one	X	X	(11)
150	verbenone	X		
150	3,5,5-trimethyl-4-methylene-2-cyclohexen-1-one		X	(10)
152	dihydrocarvone	X	X	
152	camphor	X	X	
152	oxophorone	X	X	(10)
154	4-hydroxy-2,6,6-trimethyl-2-cyclohexen-1-one		X	(10)
154	4-hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one		X	(10)
156	4-hydroxy-2,2,6-trimethyl-1-cyclohexanone	X	X	(10)
194	geranyl acetone	X	X	
206	dehydro-theaspirone	X	X	(12)
208	3-hydroxy-β-ionone		X	(10)
216	selina-3,5,11-trien-2-one	X	X	(13)
218	epi-α-cyperone	X	X	(13)
218	5α,7α,10β-selina-3,11-dien-2-one	X	X	(13)
218	5α,7α,10α-selina-3,11-dien-2-one	X		(13)
218	5β,7α,10α-selina-3,11-dien-2-one	X		(13)
220	1,10-dihydronootkatone	X	X	(13)
262	farnesylacetone*		X	
	Alcohols			
86	2-pentenol		X	
88	3-pentanol	X	X	
128	1-octen-3-ol	X	X	
128	(E)-2-octenol		X	
130	2-ethyl-hexanol	X		
134	cinnamic alcohol	X		
150	4-phenyl-2-butanol	X		(14)
206	2-(4-prenyloxy-phenyl)-ethanol	X		(15)
218	3-(4-prenyloxy-phenyl)-2-propenol	X		(16)
220	5β,7α,10α-selina-3,11-dien-5-ol [**3**]	X	X	
220	spathulenol	X	X	
220	nootkatol	X	X	(17)
220	3-(4-prenyloxy-phenyl)-propan-1-ol	X		(18)
222	valencene hydrate [**1**]	X	X	
222	4β,5β,7α,10α-selin-11-en-5-ol [**2**]	X	X	
222	farnesol*		X	

Table II. (Cont.)

MW	Name	A	B	Ref
Acids				
86	(E)-2-butenoic acid	X		
88	2-methyl-propanoic acid	X		
114	(E)-2-hexenoic acid	X	X	
144	2-ethyl-hexanoic acid	X		
148	cinnamic acid	X		
150	3-phenylpropanoic acid	X		
158	nonanoic acid	X	X	
166	perillic acid	X	X	
200	dodecanoic acid	X	X	
228	tetradecanoic acid	X	X	
242	pentadecanoic acid	X	X	
256	hexadecanoic acid	X	X	
280	(9Z,12Z)-octadeca-dienoic acid	X	X	
282	(9Z)-octadecenoic acid	X	X	
284	octadecanoic acid	X		
Esters				
114	ethyl (E)-2-butenoate	X	X	
130	propyl butyrate	X	X	
142	ethyl (E)-2-hexenoate	X	X	
142	butyl (E)-2-butenoate	X		
144	2-methylpropyl butyrate	X		
144	hexyl acetate	X	X	
150	benzyl acetate	X		
152	methyl salicylate		X	
158	3-methylbutyl butyrate	X		
158	propyl hexanoate	X		
164	ethyl 2-phenylacetate	X	X	
170	butyl (E)-2-hexenoate	X		
172	hexyl butanoate	X		
174	diethyl butanedioate	X		
174	propyl 3-hydroxy-hexanoate	X		
176	ethyl cinnamate	X		
178	ethyl 3-phenylpropionate	X	X	
188	butyl 3-hydroxy-hexanoate	X		
194	piperitenyl acetate	X	X	
194	perillyl acetate	X	X	
202	ethyl 3-acetoxyhexanoate		X	(19)
214	undecyl acetate	X		
226	5-dodecenyl acetate*	X		
228	dodecyl acetate	X		
266	3-(3,4,5-trimethoxy-phenyl)-(E)-2-propenyl acetate	X		(20)
268	3-(3,4,5-trimethoxyphenyl)-propyl acetate	X		(20)
292	methyl linolenate	X		
308	ethyl linoleate	X		
370	dioctyl hexanedioate	X		
Lactones				
114	γ-hexalactone	X	X	
114	δ-hexalactone		X	
184	3-methyl-4-decanolide	X		(21)
194	dehydrololiolide		X	(22)
196	loliolide	X	X	(23)
244	osthole	X		(24)
274	5-methoxy-osthol	X		(25)
Phenols				
120	p-vinyl-phenol	X		
150	p-vinyl-guaiacol	X	X	
164	eugenol		X	
194	3-(4-hydroxyphenyl)-propyl acetate	X		(26)
Miscellaneous				
133	4-hydroxy-phenylacetonitrile	X		
150	diisopropyl disulfide	X	X	
178	S,S'-ethylidene dithioacetate [**9**]	X		
182	diisopropyl trisulfide	X	X	

*correct isomer not identified
(A = Blood oranges; B = Blond oranges)

Tables III and IV summarize the constituents specifically identified in blood and blond orange juice respectively. In agreement with the overall description of the juices, constituents with terms like fruity, floral, balsamic, rosy, honey, sweet dominate in the blood orange, whereas green, fatty notes are characteristic of the blond orange flavor.



[**9**]

Table III. Constituents specific to blood oranges

Compound	Characteristics
dill ether	green, rose oxide, herbal
aldehydes C_{14} - C_{18}	
C_{15}	fresh, floral
C_{16}	mild, floral, waxy, orris
safranal	spicy, saffron, iodine
2-ethylhexanol	sweet, floral, rosy, fruity
benzyl alcohol	sweet, floral
cinnamic alcohol	cinnamic, balsamic, floral, sweet, fruity
4-phenyl-2-butanol	woody, powerful, green
perillic alcohol	floral, green, rosy, fruity
2-ethyl-hexanoic acid	fatty, herbal, green
cinnamic acid	honey-like, balsamic
3-phenylpropionic acid	warm, balsamic, sweet
ethyl 3-hydroxybutyrate	sweet, juicy, fruity
butyl 2-butenoate	
butyl 2-hexenoate	
butyl hexanoate	fruity, pear, banana
butyl 3-hydroxyhexanoate	
hexyl butyrate	lavender, fruity, pineapple
diethyl succinate	tart, fruity
nonyl acetate	fatty
undecyl acetate	fatty, fruity
5-dodecyl acetate	green, fruity, fatty
dodecyl acetate	fruity, green, fatty
benzyl acetate	sweet, floral, fresh, fruity
ethyl cinnamate	balsamic, fruity, cinnamic
ethyl 3-phenylpropionate	sweet, fruity, honey, floral
3-(4-hydroxyphenyl)-propyl acetate	
3-methyl-4-decanolide	lactonic, peach, coconut
osthol	
5-methoxy-osthol	
3-(4-hydroxyphenyl)-propyl acetate	weak
2-(4-prenyloxy-phenyl)-ethanol	weak
3-(4-prenyloxy-phenyl)-propanol	weak
3-(4-prenyloxy-phenyl)-2-propenol	weak
S,S'-ethylidene dithioacetate	alliaceous, transpiration

Spectral Data—8α,8aα-dimethyl-2β-isopropenyl-perhydronaphthalen-4aβ-ol [**1**]: *MS*: 222 (M^+, 2), 207(10), 204(78), 189(100), 175(20), 161(41), 162(40), 147(27), 133(31) , 123(41), 107(44), 95(39), 81(51), 69(48), 55(88), 41(66). *^{1}H-NMR*: 0.75 (d, J = 8, 3H); 0.91 (s, 3H); 1.32 (br. d, J = 12, 1H); 1.42 (d, J = 10, 1H); 1.73 (s, 3H); 2.23 (m, 1H); 4.69 and 4.71 (2s, 2H). *^{13}C-NMR*: see Table V.

Table IV. Constituents specific to blond oranges

Compound	Characteristics
1-ethoxy-1-methoxy-ethane	ethereal, green
1,1-diethoxy-ethane	refreshing, fruity, green
2-heptenal	green, fatty, apple
2-octenal	green, leafy
2,4,6-nonatrienal	fatty, broth
2-nonenal	green, fatty, oily, meaty
2-decenal	green, fennel
β-cyclocitral	powerful, green, minty
2-octenol	green, fatty, fruity, animal, nutty
carveol	fresh, herbaceous, minty
farnesol	sweet, floral, fresh, green, soft
methyl salicylate	sweet, fruity, rooty, pungent, green
ethyl 3-acetoxyhexanoate	fruity, pineapple, sweet

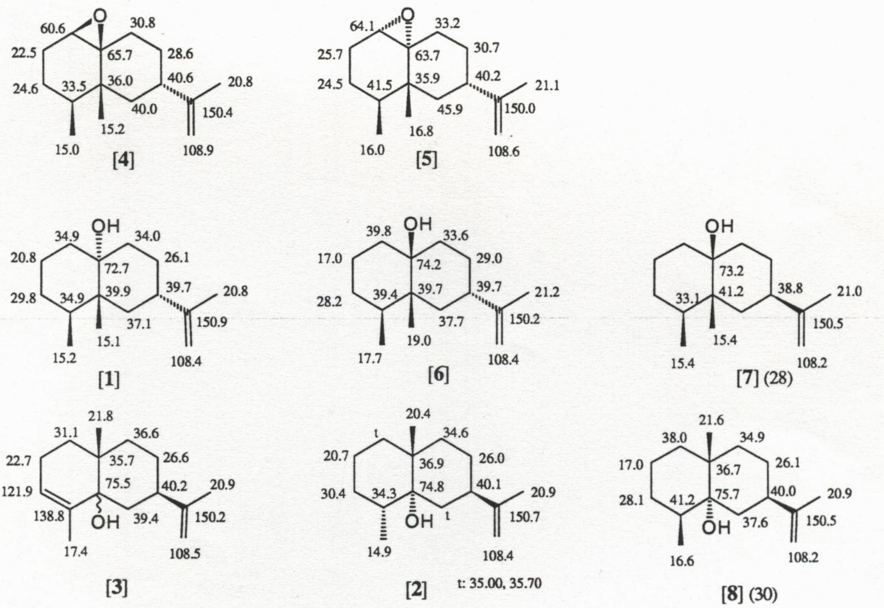


Table V. ^{13}C-NMR Assignments (90.55 MHz, $CDCl_3$)

8α,8aα-dimethyl-2β-isopropenyl-perhydronaphthalen-4aβ-ol [6]: *MS*: 222 (M^+, 2), 207(4), 204(26), 189(33), 178(11), 161(30), 147(24), 133(17), 126(39), 108(100), 97(39), 81(37), 69(40), 55(64), 41(53). *^{1}H-NMR*: 1.06 (s, 3H); 1.16 (d, J = 7.5 Hz, 3H); 1.73 (s, 3H); 2.28 (m, 1H); 4.70 (s, 2H). *^{13}C-NMR*: see Table V.

1,10-Epoxy-valencene (6,7-dimethyl-9-isopropenyl-2-oxa-tricyclo[5.4.0.$0^{1,3}$] undecane): [4] (Isomer 1): *MS*: 220 (M^+, 8), 205(19), 202(15), 187(16), 177(19), 161(40), 147(13), 135(46), 121(37), 107(72), 93(78), 81(50), 67(58), 55(67), 41(100). *^{1}H-NMR*: see (27) *^{13}C-NMR*: see Table V.

[**5**] (Isomer 2): *MS*: 220 (M^+,8), 205(13), 202(3), 187(8), 177(13), 161(18), 149(9), 135(31), 121(23), 107(59), 93(65), 81(44), 67(56), 55(63), 41(100). *^{1}H-NMR*: see (27). *^{13}C-NMR*: see Table V.

4β,5β,7α,10α-Selin-11-en-5-ol ([**2**], 4aα,8β-dimethyl-2α-isopropenyl-perhydronaphthalen-8aβ-ol): *MS*: 222 (M^+, 6), 207(3), 204(22), 189(17), 176(8), 161(21), 147(26), 133(13), 123(28), 109(82), 108(100), 95(36), 81(31), 69(27), 55(30), 41(20). *^{1}H-NMR*: 0.8 (d, J = 6.7 Hz, 3H); 1.03 (s, 3H); 1.74 (s, 3H); 2.41 (m, 1H); 4.70 (s, 1H); 4.72 (s, 1H). *^{13}C-NMR*: see Table V.

7α,10α-Selina-3,11-dien-5-ol ([**3**], 4aα,8-dimethyl-2α-isopropenyl-1,2,3,4,4a,5,6,8a-octahydro-naphthalen-8a-ol): *MS*: 220 (M^+ , 6), 205(3), 202(44), 187(12), 177(3), 164(6), 149(7), 136(10), 124(100), 123(80), 109(53), 95(20), 82(47), 67(25), 55(33), 41(59). *^{1}H-NMR*: 0.95 (s, 3H); 1.71 (s, 3H); 1.72 (s, 3H); 2.27 (b. t, 1H); 4.69 (b. s, 2H); 5.31 (b. s, 1H). *^{13}C-NMR*: see Table V.

S,S'-Ethylidene dithioacetate [**9**]: *MS*: 178 (M^+, 3), 163(0.5), 136(2), 135(13), 124(16), 118(2), 103(7), 93(4), 76(2), 61(8), 60(6), 59(13), 43(100). *^{1}H-NMR*: 1.70 (d, J = 8 Hz, 3H); 2.32 (s, 6H); 5.10 (q, J = 8 Hz,1H). *^{13}C-NMR*: 22.83 (q); 30.26 (q); 41.23 (d); 193.88 (s).

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