3.2. *Überführung von* **9** *in 1,3,7,7-Tetramethyl-4-methoxymethyl-2-oxa-bicyclo*[4.4.0]*deca-3,5-dien* (**15**). Zu 225 mg (1,01 mmol) **9** in 5 ml abs. Methanol wurde bei –25° unter starkem Rühren eine Spatelspitze *p*-Toluolsulfonsäure gegeben. Das Gemisch wurde 30 Min. bei –25° gerührt, die leicht rote Lösung mit festem Natriumcarbonat versetzt, über *Celite* filtriert und im Wasserstrahlvakuum eingedampft. Beim Aufnehmen des öligen Rückstandes in Äther bildete sich ein flockiger Niederschlag. Das Gemisch wurde im Kugelrohr destilliert, und das bei 100–110°/0,01 Torr erhaltene gelbe Öl (193 mg) an Al_2O_3-neutral der Aktivitätsstufe III (*Woelm*) mit Pentan/Äther 9:1 in 15 mg eines nicht näher untersuchten Zweikomponentengemisches und 192 mg (68%) Äther **15** (Sdp. 100°/0,01 Torr) getrennt. – MS. (*m/e*): 252 (0,5, M^+, $C_{15}H_{24}O_2$), 237 (1), *221* (100), 189 (3), 181 (2), 165 (2), 43 (9). – IR. (CCl_4): 3040*w* (S), 2970*s*, 2930*s*, 2890*s* (S), 2870*s*, 2850*s* (S), 2818*m*, 1669*s*, 1602*w*, 1461*s*, 1450*m* (S), 1382*m*, 1365*s*, 1402*m*, 1390*w*, 1241*m*, 1228*m*, 1188*m*, 1172*w*, 1155*m* (S), 1145*m*, 1105*s*, 1085*s*, 1058*m*, 1020*m*, 1015*m* (S), 1000*w*, 980*w*, 958*w*, 945*w*, 905*m*, 900*w*, 865*m*. – ^{1}H-NMR. (CCl_4): 1,10, 1,18 (2*s*, 2 H_3C–C(7)); 1,31 (*s*, H_3C–C(1)); 1,80 (*s*, H_3C–C(3)); 1,20–2,00 (*m*, 2 H–C(8), 2 H–C(9), 2 H–C(10)); 3,17 (*s*, H_3C–O); 3,82 (*s*, H_2C–C(4)); 5,60 (*s*, H–C(5)). – ^{13}C-NMR. ($CDCl_3$): 16,33, 24,16, 30,58, 30,98, 56,89 (5 *q*, 2 H_3C–C(7), H_3C–C(1), H_3C–O, H_3C–C(3)); 19,02, 39,48, 40,11, (3 *t*, C(9), C(10), C(8)); 70,79 (*t*, H_2C–C(4)); 116,81 (*d*, C(5)); 34,85 (*s*, C(7)); 77,54 (*s*, C(1)); 107,18, 139,70, 148,49 (3 *s*, C(6), C(4), C(3)). – UV. (*n*-Pentan): 286 (4606).

Die Elementaranalysen wurden im mikroanalytischen Laboratorium (Leitung: *W. Manser*) ausgeführt. Für die Aufnahme der ^{1}H-NMR.-Spektren (100 MHz) und ^{13}C-NMR.-Spektren unter der Leitung von Herrn Prof. Dr. *J. F. M. Oth* danken wir Frl. *B. Brandenberg* und Herrn *K. Hiltbrunner*. Die massenspektroskopischen Analysen verdanken wir Herrn Prof. Dr. *J. Seibl* und seinen Mitarbeitern.

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76. A Chemical Investigation of the Volatile Constituents of East Indian Sandalwood Oil (*Santalum album* L.)

by **Edouard Demole, Cécile Demole,** and **Paul Enggist**

Firmenich SA, Research Department, 1211 Geneva 8

(5. II. 76)

Summary. Distillation foreruns from East Indian sandalwood oil (*Santalum album* L.), representing 5–8% of the oil, have been investigated using fractional distillation, preparative column chromatography, gas liquid chromatography (GLC.), and chemical treatments. This allowed the isolation and characterization by their spectral data of 46 compounds. 32 of them were newly identified sandalwood oil constituents including 4 novel substances: santalone (**2**), 4-methylcyclohexa-1,3-dien-1-yl methyl ketone (**4**), 5,6-dimethyl-5-norbornen-*exo*-2-ol (**7**), and (*E*)-5-(2,3-dimethyl-3-nortricyclyl)-pent-3-en-2-one (**20**). The other constituents identified were 1-furfuryl-

pyrrole (**10**) and 10 phenols accompanied by 17 terpene and sesquiterpene derivatives. *Endo*-2, *endo*-3-dimethyl-norbornan-*exo*-2-ol (**6**), an α-santenol (**z**) precursor, was present in the last group of constituents. The compounds **2**, **4**, **6**, **7**, **20** have been synthesized as well as another novel constituent, *endo*-2-methyl-3-methylidene-norbornan-*exo*-2-ol (**5**).

Although most of the characteristic fragrance of the valued East Indian sandalwood oil (*Santalum album* L.) is traditionally attributed to its high α-santalol (**A**)[1]) and β-santalol (**N**) contents (about 90%) [1], the odoriferous contribution due to the other minor constituents present in the oil should not be neglected. These minor constituents include sesquiterpene hydrocarbons (α-santalene (**B**) [1], β-santalene (**C**) [1] [2], *epi*-β-santalene (**D**) [3], α-curcumene (**E**) [4], β-curcumene [4], and possibly β-farnesene [4]) as well as minute amounts of relatively volatile and more fragrant substances. Several of the latter were characterized long ago [1]: santene (**F**), santenol[2]), santenone, teresantalol (**G**), teresantalic acid (**H**), nortricyclo-*eka*-santalal (**I**), borneol (**J**), and isovaleraldehyde. Other similar constituents escaped identification until relatively recently (tricyclo-*eka*-santalal (**K**) [5], *exo*-norbicyclo-*eka*-santalal (**L**) [6], and 11-methyl-7-oxa-tetracyclo[6.3.1.$0^{1,6}$.$0^{4,11}$]dodecane (**M**) [5]).

Nevertheless, it is amazing that none of the foregoing volatile constituents can truly account for the very peculiar and attractive fragrance displayed by the distillation foreruns obtained on distilling crude sandalwood oil. Consequently, we have carried out the present investigation of these foreruns with the hope of isolating novel and valuable perfumery compounds.

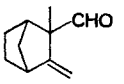
A. General, chromatographic investigation of the sandalwood oil foreruns. – The material used for this study resulted from a customary vacuum distillation of the commercial sandalwood oil, and represented about 5–8% of it. According to *Scheme 1* 1 kg of such foreruns was distilled twice at 10 Torr affording 40.3 g of a volatile fraction that was once more fractionated through a Teflon spinning band distillation column. Each of the five more volatile subfractions obtained (subfractions A–E, total weight 13.6 g, b.p. 30–117°/10 Torr) was then subjected to a chromatographic separation as well as subfraction F together with fraction 2b. This allowed the isolation of the compounds shown in *Table 1*, among which **1**–**15** are novel sandalwood oil constituents deserving the following comments.

1. *Teresantalal*[3]) (**1**). IR. (CCl_4, bands with decreasing intensities): 1715, 1185, 1445, 850, 3060, 2700 cm^{-1}. – MS.[4]) (*m/e* (% relative abundance)): 43 (32), 55 (16), 67 (18), 79 (52), 93 (100), 105 (32), 121 (68), 150 (M^+, 68). – NMR.[5]): 0.94 (*s*, 3H); 1.13 (*s*, 3H); (0.8–2.3 *m*, 7H); 9.83 (*s*, 1H). Teresantalal (**1**) undergoes facile auto-oxidation and

[1]) See formulas **A**–**M** in Table 1 and formula **N** in Table 2.

[2]) See formula **z** in *Section C* for α-santenol.

[3]) Some experimental evidence was obtained suggesting that the bicyclic teresantalal isomer **1a** also occurs in the sandalwood oil foreruns.

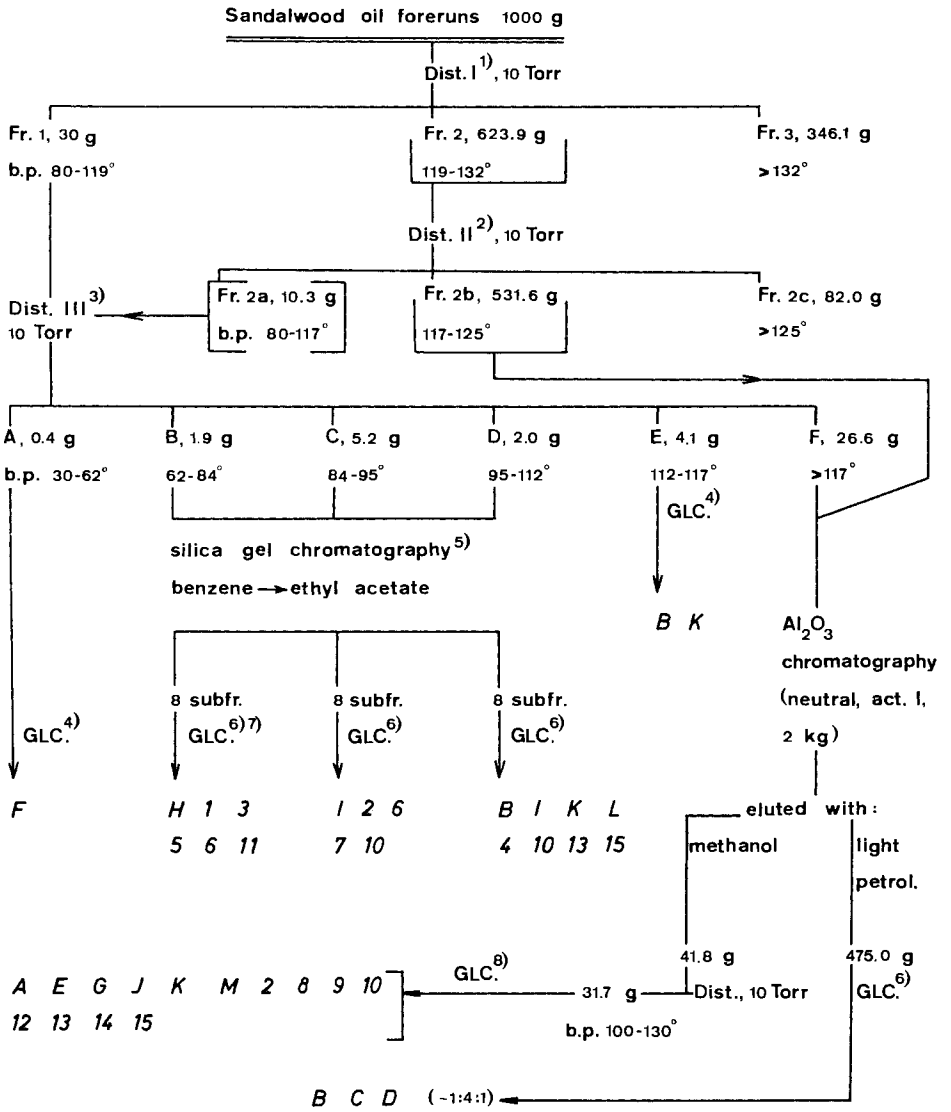


1a

[4]) Measured at 70 eV.

[5]) The NMR. spectra were measured in CCl_4 (δ-values).

Scheme 1. *Investigation of the sandalwood oil foreruns by chromatography*



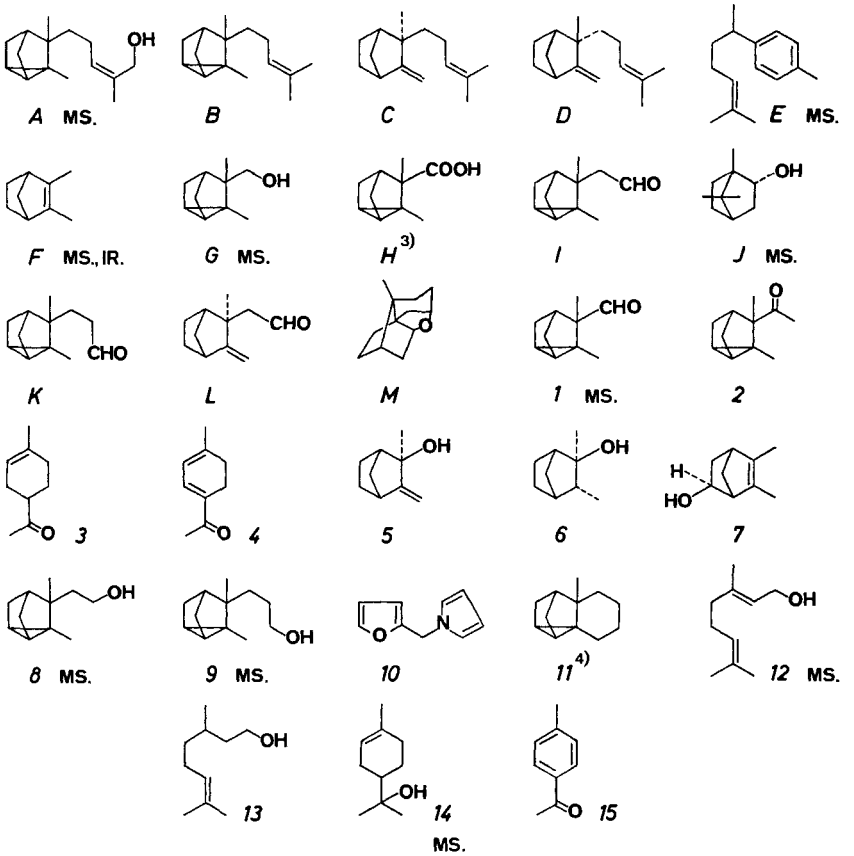
1) Using a 30 cm *Vigreux* column without refluxing head.
2) Using a 30 cm *Vigreux* column with refluxing head.
3) Using the 'Auto-annular teflon spinning band distillation system', *Nester/Faust Corp.*, Newark, Delaware, USA.
4) 15% Carbowax, 200°, 5 m column.
5) All liquid chromatographic separations were carried out on 30 parts of silica gel (*Mallinckrodt*, 100 mesh, analytical reagent).
6) 15% Silicone oil, 200°, 5 m column.
7) 5% Carbowax, 150°, 5 m column.
8) 15% Silicone oil and 5–15% Carbowax, 160–200°, 2.5 m columns.

usually contains some teresantalic acid (**H**). It can be prepared in moderate yield by chromic acid oxidation of teresantalol (**G**) [7].

2. *Santalone* (**2**). IR. (neat): 1695, 1350, 1275, 1450, 1070, 3050 cm^{-1}. – MS.: 43 (50), 79 (27), 93 (100), 105 (20), 121 (72), 164 (M^+, 59). – NMR.: 0.78 (*m*, 1H); 1.04 (*s*, 3H); 1.20 (*s*, 3H); 0.9–2.2 (*m*, 6H); 2.00 (*s*, 3H). The name *santalone* was already coined by *Müller* [8] in 1900 for an unknown $C_{11}H_{16}O$ ketone he isolated from sandalwood oil, a result confirmed ten years later by *Schimmel*'s chemists [9]. We use the same name for our compound **2** because it is probably identical with *Müller*'s ketone. Santalone (**2**) can be synthesized by reaction of teresantalic acid (**H**) with methyl-lithium (yield 94.5%, see exper. part, *Section 1*).

3. *4-Methyl-cyclohex-3-en-1-yl methyl ketone* (**3**). This compound has formerly been encountered in nature, *e.g.* in the wood of *Brazilian Cabreuva* tree [10]. An easy

Table 1. *Constituents of sandalwood oil foreruns isolated by chromatography*[1)2)]



1) All compounds have been identified by IR., NMR., and mass spectra unless otherwise stated
2) The absolute configurations shown have been arbitrarily chosen.
3) Identified as auto-oxidation product of **1**.
4) Tentative structure.

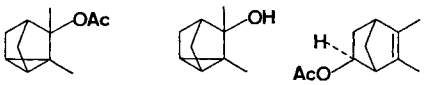
synthesis of **3** involves the regio-selective cycloaddition of isoprene to methyl vinyl ketone [11] [12].

4. *4-Methyl-cyclohexa-1,3-dien-1-yl methyl ketone* (**4**). IR. (neat): 1645, 1570, 1265, 1385, 1220, 825 cm^{-1}. – MS.: 43 (100), 77 (41), 91 (36), 93 (27), 121 (67), 136 (M^+, 28). – NMR.: 1.87 (*s*, 3H); 2.17 (*s*, 3H); 1.9–2.4 (*m*, 4H); 5.78 (*d*, J = 5.5, 1H); 6.75 (*d*, J = 5.5, 1H). This ketone can be synthesized by regio-selective cycloaddition of 1-diethylamino-3-methyl-buta-1,3-diene to methyl vinyl ketone, followed by acidic hydrolysis [13] (yield 44.5%, see exper. part, *Section 2*).

5. endo-*2-Methyl-3-methylidene-norbornan*-exo-*2-ol* (**5**). IR. (neat): 890, 1095, 1110, 920, 3400, 3070, 1660, 1785 cm^{-1}. – MS.: 43 (100), 55 (11), 67 (22), 79 (10), 95 (42), 109 (75), 123 (23), 138 (M^+, 14). – NMR.: 1.27 (*s*, 3H); 1.0–2.2 (*m*, 7H); 2.65 (narr. *m*, 1H); 2.80 (*s*, 1H, OH); 4.80 (*s*, 2H). This alcohol, formerly synthesized from dehydro-santene by *Alder* & *Grell* [14], can also be efficiently prepared *via dye-sensitized photo-oxygenation of santene* (**F**) (yield 71%, see exper. part, *Section 3*).

6. endo-*2*,endo-*3-Dimethyl-norbornan*-exo-*2-ol* (**6**). IR. (KBr): 3300, 1140, 920, 1380, 1110, 890 cm^{-1}. – MS.: 43 (100), 55 (49), 71 (82), 72 (79), 79 (16), 97 (34), 111 (14), 125 (9), 140 (M^+, 2). – NMR.: 0.83 (*d*, J = 7, 3H); 1.06 (*s*, 3H); 0.8–2.1 (*m*, 9H); 3.17 (*s*, 1H, OH). This alcohol, m.p. 102–103° (racemate), can be prepared from santene (**F**) either by addition of HCl followed by alkaline hydrolysis of the resulting hydrochloride [14], or more efficiently by *hydroboration* [15] (yield 94%, see exper. part, *Section 4*). All four stereoisomeric 2,3-dimethyl-norbornan-2-ols are known [16].

7. *5,6-Dimethyl-5-norbornen*-exo-*2-ol* (**7**). IR. (neat): 3350, 980, 1075, 1045, 1025, 1440 cm^{-1}. – MS.: 79 (84), 94 (100), 138 (M^+, 9). – NMR.: 1.55 (*s*, 6H); 1.2–1.8 (*m*, 4H); 2.37 (narr. *m*, 2H); 3.70 (*m*, 1H); 4.15 (*s*, 1H, OH). This alcohol can be synthesized from teresantalic acid (**H**) *via* oxidative decarboxylation with $Pb(OAc)_4$ [17], reduction of the resulting acetate **y** by $LiAlH_4$, cyclopropylmethyl-homoallylic rearrangement [18] of alcohol **y'** to the acetate **y''**, and reduction of the latter (overall yield 35%, see exper. part, *Section 5*).



y *y'* *y''*

8. *Nortricyclo*-eka-*santalol* (**8**). MS.: 41 (25), 55 (15), 67 (10), 79 (27), 93 (100), 98 (29), 105 (25), 121 (41), 151 (3), 166 (M^+, 2). – NMR.: 0.83 (*s*, 3H); 1.04 (*s*, 3H); 0.7–1.9 (*m*, 9H); 3.53 (*t*, J = 8, 2H); 4.13 (*s*, 1H, OH). *Semmler* & *Zaar* [19] synthesized this alcohol by reduction of methyl nortricyclo-*eka*-santalate.

9. *Tricyclo*-eka-*santalol* (**9**). IR. (neat): 1055, 3340, 1455, 3050, 850, 1375 cm^{-1}. – MS.: 41 (22), 55 (14), 79 (24), 93 (100), 105 (19), 121 (73), 165 (2), 180 (M^+, 17). – NMR.: 0.82 (*s*, 3H); 1.01 (*s*, 3H); 0.75–1.80 (*m*, 11H); 3.50 (*m*, 2H); 4.20 (*s*, 1H, OH). This alcohol was synthesized by *Semmler* & *Bode* [20].

10. *1-Furfuryl-pyrrole* (**10**) [21]. This constituent is known to occur in the flavour of miscellaneous roasted foodstuffs, *e.g.* in coffee aroma [22]. Because of its powerful

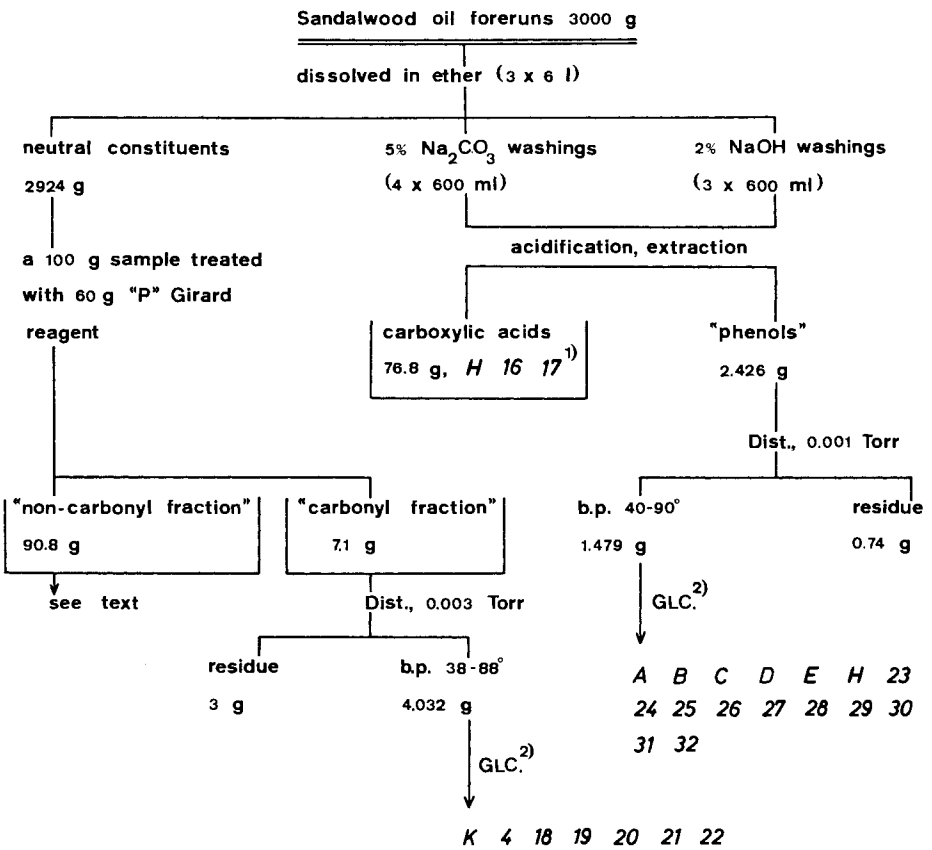
odour, **10** seems to play an important role in the whole fragrance of the sandalwood oil foreruns.

11. *Hydrocarbon* $C_{12}H_{18}$ (**11**). IR. (CCl_4): 1460, 1020, 3050, 1315, 1030, 1365 cm^{-1}. – MS.: 67 (23), 79 (47), 93 (100), 105 (27), 121 (53), 134 (56), 147 (22), 162 (M^+, 25). – NMR.: 0.4 (*m*, 1H); 0.74 (*s*, 3H + *m*, 1H); 0.9–2.2 (*m*, 13H). This practically odourless, solid constituent might be identical with a '$C_{11}H_{18}$' hydrocarbon isolated long ago from sandalwood oil [1]. Structure **11** rests only upon spectral evidence and requires further confirmation.

12. *Geraniol* (**12**), *citronellol* (**13**), *α-terpineol* (**14**), p-*methyl-acetophenone* (**15**). These common constituents require no comment, except that the occurrence of *p*-methyl-acetophenone (**15**) in the sandalwood oil foreruns is clearly related to that of ketones **3** and **4**.

B. Selective isolation of the acidic and carbonyl constituents of the sandalwood oil foreruns. – *Scheme 2* outlines the chemical procedure used to ob-

Scheme 2. *Chemical treatment of sandalwood oil foreruns*



1) **H**, m.p. 157°, is the major constituent (GLC. on 5% Carbowax, 200°, 2.5 m column).
2) 5% Carbowax, 150–210°, +10°/min, 2.5 m column.

tain fractions substantially enriched with respect to the acidic and carbonyl constituents occurring in the sandalwood oil foreruns. Thus, successive standard treatments of 3 kg of crude foreruns with inorganic bases and *Girard* 'P' reagent [23] afforded 2.5% carboxylic acids, < 0.1% 'phenols', 7.0% of a neutral 'carbonyl' fraction, and 90.4% of a neutral 'non-carbonyl' fraction. Subsequent GLC. separations of each of these mixtures led to the identification of the novel sandalwood oil constituents **16–32** shown in *Table 2.*

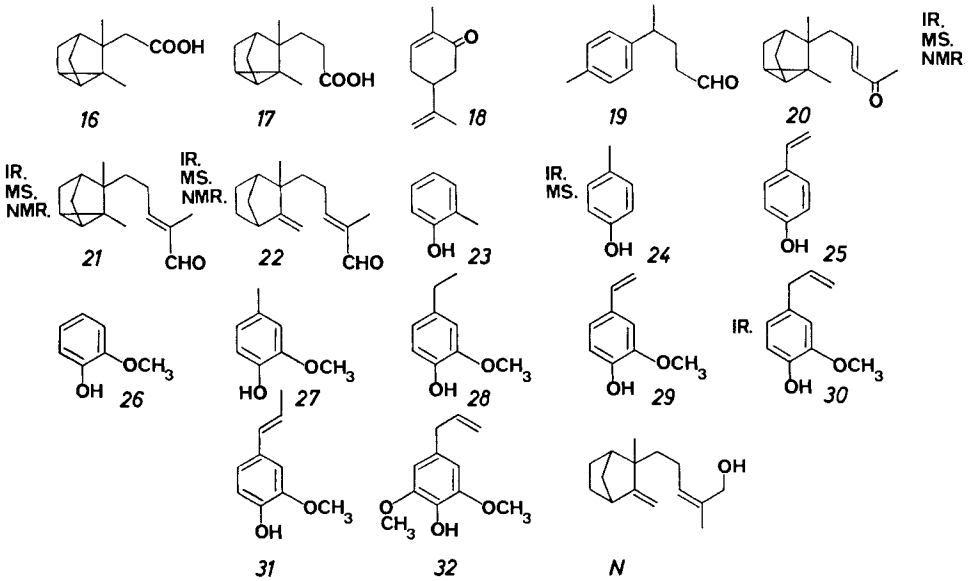
1. *Nortricyclo*-eka-*santalic acid* (**16**) [24]. MS.: 41 (27), 55 (10), 66 (18), 79 (23), 93 (100), 105 (35), 121 (32), 180 (M^+, 13). Could arise from the auto-oxidation of aldehyde **I**.

2. *Tricyclo*-eka-*santalic acid* (**17**) [20]. MS.: 41 (19), 55 (11), 66 (9), 79 (20), 93 (100), 105 (20), 121 (50), 151 (7), 194 (M^+, 14). Could arise from the auto-oxidation of aldehyde **K**.

3. *4-(p-Tolyl)-valeraldehyde* (**19**). MS.: 41 (6), 51 (2), 65 (4), 77 (6), 91 (17), 105 (9), 119 (72), 132 (100), 176 (M^+, 3). This constituent could have been formed in sandalwood oil by oxidation of α-curcumene (**E**). It can be synthesized according to *Büchi & Wüest* [25].

4. (E)-*5-(2,3-Dimethyl-3-nortricyclyl)-pent-3-en-2-one* (**20**). IR. (neat): 1675, 1250, 1695, 1625, 980, 1360, 3050 cm^{-1}. – MS.: 43 (22), 55 (5), 67 (3), 79 (13), 93 (61), 105 (10), 121 (100), 161 (< 1), 204 (M^+, < 1). – NMR.: 0.87 (*s*, 3H); 1.04 (*s*, 3H); 2.13

Table 2. *Constituents of sandalwood oil foreruns isolated* via *chemical treatment*[1])



[1]) All compounds have been identified by mass spectrometry unless otherwise stated.

(*s*, 3H); 0.7–2.2 (*m*, 9H); 5.93 (*d*, J = 15, 1H); 6.68 (*d*×*t*, J = 15, J' = 7.5, 1H). This novel compound can be synthesized in a *Horner-Wittig* reaction [26] between

nortricyclo-*eka*-santalal (**I**) and diethyl acetonyl-phosphonate (yield 55%, see exper. part, *Section 6*).

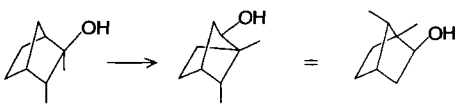
5. (E)-α-*Santalal* (**21**). IR. (neat): 1685, 1640, 1450, 3050, 850, 2700 cm^{-1}. – MS.: 41 (38), 55 (28), 79 (35), 93 (100), 107 (34), 121 (50), 151 (29), 218 (M^+, 21). – NMR.: 0.88 (*s*, 3H); 1.01 (*s*, 3H); 1.70 (*s*, 3H); 0.6–1.9 (*m*, 9H); 2.20 (*m*, 2H); 6.40 (*t*, J = 7.5, 1H); 9.33 (*s*, 1H). The (*E*)-configuration of the double bond, demonstrated by the NMR. signal at 9.33 ppm and due to the CHO proton [27], is the reverse of that of natural α-santalol (**A**) [28]. This fact appears to be unsignificant in so far as any (*Z*)-α-santalal eventually present in the sandalwood oil foreruns could have been isomerized to its (*E*)-counterpart during the acidic hydrolysis completing the treatment with *Girard* 'P' reagent [23] [29]. In this connection it is worth to point out that standard, neutral MnO_2 oxidation of the natural santalols essentially affords the expected (*Z*)-santalals, characterized by a CHO proton signal at 10.2 ppm in NMR. (CCl_4) [27]. Many years ago [30] the santalals were erroneously believed to represent major constituents of sandalwood oil. More recently *Bohlmann* & *Zdero* [31] have isolated (–)-(*E*)-α-santalal from *Piqueria trinerva*.

6. (E)-β-*Santalal* (**22**). IR. (CCl_4): 1690, 880, 1640, 3070, 2710 cm^{-1}. – MS.: 41 (56), 55 (37), 67 (40), 79 (74), 91 (53), 93 (98), 94 (100), 121 (49), 149 (20), 218 (M^+, 10). – NMR.: 1.05/1.09 (2*s*, 3H); 1.71 (*s*, 3H); 0.6–2.9 (*m*, 12H); 4.45 (*s*, 1H); 4.73 (*s*, 1H); 6.40 (*t*, J = 7.5, 1H); 9.34 (*s*, 1H). This aldehyde was clearly a mixture of *exo* and *endo* epimers as evidenced by the appearance of a two-fold signal for $H_3C-C\leqslant$ at 1.05 and 1.09 ppm in the NMR. spectrum. As in the case of isomer **21** the configuration of the trisubstituted double bond in **22** is the reverse of that of the related β-santalol (**N**) [32] (see comments in *Section 5* above).

7. *Phenols* **23–32**. These ten phenols appear to be mostly responsible for the 'smoky' note noticeable in the odour of the sandalwood oil foreruns. The presence of this type of constituent in sandalwood oil was suspected many years ago [33].

8. *Composition of the 'non-carbonyl' fraction* (see *Scheme 2*). Semi-preparative GLC. separations (15% silicone oil, 140–230°, program +10°/min, 2.5 m column) allowed the isolation and identification (MS.) of compounds **A**–**C**, **D** and **N** as major constituents of this fraction, together with a minor amount (~ 5%) of unknown sesquiterpenes (M^+ = 204).

C. Concluding remarks. – Most intriguing is the fact that we found no *santenol* (**z**, or stereoisomer thereof) throughout this investigation. Instead of this 'classical' sandalwood oil component [1], we isolated the novel constituent **6** that behaves as a specific α-santenol precursor in the presence of acids [14] (*Wagner-Meerwein* rearrangement **6** → **z**).



6 z

This raises the question as to whether α-santenol (**z**) is really a genuine sandalwood oil constituent, since it was originally isolated (probably as a stereoisomeric

mixture) after formic acid treatment of the oil [34]. In such conditions both **6** and santene (**F**) are expected to lead to the formate of **z**, although in a non-stereoselective way for the latter [35].

Apart from the 46 constituents mentioned in this communication, the sandalwood oil foreruns still contain several unknown C_{14}–C_{15} oxygenated sesquiterpenoids as well as unidentified sesquiterpenes ($M^+ = 204$).

Experimental Part

The spectra were measured on the following instruments: double-beam IR. spectrometer *Perkin-Elmer* Model 125; mass spectrometer *Atlas* CH4 IV 58 (*Atlas Werke AG.*); NMR. spectrometer *Varian* A-60 [internal standard $(CH_3)_4Si$]. The GLC. separations were carried out using gas chromatographs *Perkin-Elmer* Model 881 and *Aerograph* Model 1820-3 (*Varian Aerograph AG.*).

1. *Santalone* (**2**). A solution of teresantalic acid (**H**)[6] (9.6 g, 57 mmol) in anhydrous ether (25 ml) was added over 1 h at $-25°$ under N_2 to a stirred solution of methyl-lithium [prepared from 20.5 g (144 mmol) of methyl iodide and 2.03 g (293 mmol) of lithium in 80 ml of anhydrous ether]. The mixture was stirred for 30 min at $-20°$ and 2 h at 20°, and refluxed for 20 h. Usual work-up including alkaline extraction afforded 4.9 g of recovered teresantalic acid (**H**) and 4.4 g of *santalone* (**2**) (94.5% with respect to the consumed **H**). After purification by silica gel chromatography[7] (benzene/ethyl acetate 95:5) and GLC. this ketone exhibited the spectral properties described in the theor. part (*Section A 2*).

2. *4-Methyl-cyclohexa-1,3-dien-1-yl methyl ketone* (**4**). A solution of 3-methyl-but-2-enal [36] (13.6 g, 161 mmol) in anhydrous benzene (16.2 ml) was added over 20 min at $-10°$ to a stirred mixture of diethylamine (24.3 g, 332 mmol) and anhydrous potassium carbonate (6.5 g) [13]. The mixture was kept at 0° until it became clear, set aside for 4 h at 20°, and then distilled at 13 Torr in the presence of 97 mg of phenanthraquinone: Fr. 1, b.p. 60–70°, 12 g; Fr. 2, b.p. 71°, 11.0 g. The latter fraction represented a 49% yield of 1-diethylamino-3-methyl-buta-1,3-diene.

Methyl vinyl ketone (8.4 g, 120 mmol) in anhydrous benzene (10 ml) was slowly added at 10° to a solution of 1-diethylamino-3-methyl-buta-1,3-diene (11.0 g, 79 mmol) in 11 ml of the same solvent [13]. The mixture was kept for 24 h between 0° and 5°, when 10% cold hydrochloric acid was added (50 ml). After stirring at 0° (30 min), 10° (30 min), 15° (1 h), and 20° (3 h), the organic layer was separated, washed with water, and worked up as usual. Distillation of the product afforded 4.8 g (44.5%) of pure *4-methyl-cyclohexa-1,3-dien-1-yl methyl ketone* (**4**), b.p. 92°/10 Torr, $d_4^{20} = 0.979$, $n_D^{20} = 1.5369$. For the spectral data see theor. part, *Section A 4*.

3. endo-*2-Methyl-3-methylidene-norbornan*-exo-*2-ol* (**5**). A solution of santene (**F**) [37] (2.0 g, 16.4 mmol) and *Bengal red* (200 mg) in anhydrous methanol (200 ml) was irradiated[8] at 20° in the presence of a constant flow of dry oxygen (80 ml/min) [38]. After 2 h the mixture was concentrated *in vacuo* to 6 ml, sodium sulfite (5 g) in water (7 ml) was added, the solution was warmed to 50° and kept for $4^1/_2$ h at this temperature, set aside overnight at 20°, and worked up as usual (extraction with ether). Distillation of the product afforded 1.61 g (71%) of pure endo-*2-methyl-3-methylidene-norbornan*-exo-*2-ol* (**5**), b.p. 70°/10 Torr, $d_4^{20} = 0.998$, $n_D^{20} = 1.4975$. For the spectral data see theor. part, *Section A 5*.

4. endo-*2*,endo-*3-Dimethyl-norbornan*-exo-*2-ol* (**6**). Diborane, formed from sodium borohydride (1.864 g, 49 mmol) and BF_3-etherate (13.5 ml) in diglyme (60 ml) [15], was introduced (N_2-stream) into a cold (0°) solution of santene (**F**) [37] (2.0 g, 16.4 mmol) in anhydrous tetrahydrofuran (6 ml). After standing for 2 h at 0° and 2 h at 20° the excess diborane was blown out by a N_2-stream for 1 h at 50°. Water (10 ml), 3N sodium hydroxide (4 ml), and 30% hydrogen peroxide (4 ml) were added to the cooled (0°) mixture, which was then saturated with sodium chloride and extracted with ether. The product resulting from usual work-up, purified by sublimation at 10 Torr, re-

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6) Natural **H**, obtained as indicated in *Scheme 2* and purified by crystallization and sublimation.
7) See footnote 5) in *Scheme 1*.
8) UV. lamp *Philips* HPK 125. All-glas (pyrex) apparatus.

presented 2.178 g (94%) of endo-*2*,endo-*3-dimethyl-norbornan*-exo-*2-ol* (**6**), m.p. 98°[9]. For the spectral data see theor. part, *Section A 6*.

5. *5,6-Dimethyl-5-norbornen*-exo-*2-ol* (**7**). Lead tetraacetate (48.9 g, 90% pure, 99 mmol) was added under N_2 to a stirred solution of teresantalic acid (**H**)[6] (8.2 g, 49.4 mmol) in anhydrous pyridine (5.86 g, 74.1 mmol) and benzene (100 ml) [17]. After 6–7 h refluxing the cooled mixture was chromatographed on silica gel[7] (250 g). Distillation of the product eluted with benzene (600 ml) gave 6.82 g (76%) of a 85:15 mixture of the acetate esters **y** and **y″**, b.p. 82°/10 Torr.

This acetate mixture (6.82 g, 37.9 mmol) was reduced with lithium aluminium hydride (1.3 g, 34 mmol) in refluxing ether (2 h). Usual work-up (quenching with ammonium chloride, extraction with ether) and distillation afforded 4.81 g (92%) of a 85:15 mixture of the alcohols **y′** and **7**, b.p. 67°/10 Torr (GLC., 15% Carbowax, 170°, 2.5 m column).

Acetic acid (4.0 g) containing concentrated sulfuric acid (12 drops) was added at 0° to a solution of the mixture of **y′** and **7** (4.0 g, 29 mmol) in acetic acid (4.0 g). The mixture was allowed to warm slowly to 20° over 5 h, and was set aside for a further 5 h at 20°. Usual work-up gave 3.11 g (59%) of 87% pure acetate **y″**. Standard reduction of **y″** by lithium aluminium hydride in refluxing ether afforded 2 g (97%) of *5,6-dimethyl-5-norbornen*-exo-*2-ol* (**7**), b.p. 87°/10 Torr, $d_4^{20} = 0.993$, $n_D^{20} = 1.4939$. For the spectral data see theor. part, *Section A 7*.

6. (E)-*5-(2,3-Dimethyl-3-nortricyclyl)-pent-3-en-2-one* (**20**). Diethyl acetonyl-phosphonate [39] (2.43 g, 12.5 mmol) in anhydrous 1,2-dimethoxy-ethane (DME, 2 ml) was added over 15 min at 10° to a stirred suspension of sodium hydride (300 mg, 12.5 mmol) in 15 ml of the same solvent [26] [40]. After 30 min stirring at 15° the mixture was warmed to 40°, and a solution of nortricyclo-*eka*-santalal (**I**)[10] (2.05 g, 12.5 mmol) in DME (2 ml) was added at this temperature. After stirring for 1 h at 50° and 1 h at 70°, the cooled mixture was poured into water (150 ml) and extracted twice with light petroleum. Distillation of the product afforded 2.35 g (92%) of (E)-*5-(2,3-dimethyl-3-nortricyclyl)-pent-3-en-2-one* (**20**), b.p. 65–68°/0.001 Torr. Pure **20** was obtained by silica gel chromatography[7] with benzene elution: 1.4 g (55%), b.p. 66–68°/0.001 Torr, $d_4^{20} = 0.982$, $n_D^{20} = 1.5043$. For the spectral data see theor. part, *Section B 4*.

$C_{14}H_{20}O$ (204.31) Calc. C 82.30 H 9.87% Found C 82.21 H 9.88%

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77. Synthesis and Some Reactions of 2,4,6-Cycloheptatrienethione[1])

by **Harry A. Dugger**[2]) and **André S. Dreiding**
Organisch-Chemisches Institut der Universität Zürich, Rämistrasse 76, 8001 Zürich

(12. XII. 75)

Summary. The synthesis of 2,4,6-cycloheptatrienethione (**1**) was accomplished by reaction of tropone and phosphorus pentasulfide. Although **1** proved to be extremely unstable in concentrated solution, its UV. spectrum was measured, the ε-values being determined indirectly by hydrolysis to tropone. The proof of structure rests on analytical data, conversion to tropone oxime on reaction with hydroxylamine and reaction with the sodium salt of malonitrile to give 2-amino-3-cyano-3a*H*-cyclohepta[*b*]thiophene (**4**) which rearranged on chromatography to give what is probably the corresponding 8*H*-compound (**5**). On dissolving **1** in 95% sulfuric acid, a large hypsochromic shift in the UV. spectrum was observed, which may be due to the mercaptotropylium ion.

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[2]) National Institutes of Health Postdoctoral Fellow 1962–1964. Present address is Drug Metabolism Section, Sandoz Pharmaceuticals, Sandoz, Inc., East Hanover, New Jersey 07936 USA.