New Compounds with Sandalwood Odor

By J. Gora and J. Gibka, Institute of General Food Chemistry, Technical University of Lodz, Poland

Sandalwood oil is an essential component of many good perfume compositions, but its scarcity and high price have prompted searches for other compounds with sandalwood odor.[1-3] One of these compounds is dimethylnorbornane, which was described in the chemical literature by Ohloff,[4-6] Demole[7,8] and Brunke.[9,10] The present authors have synthesized certain dimethylnorbornane cyclic alcohol derivatives which are potential carriers of the sandalwood odor.[11]

Synthesis

The two-stage process for synthesis of these derivatives is shown in Figure 1. In the first stage, cyclic ketones **[6]**-**[9]** are produced, and are used in turn in the second stage

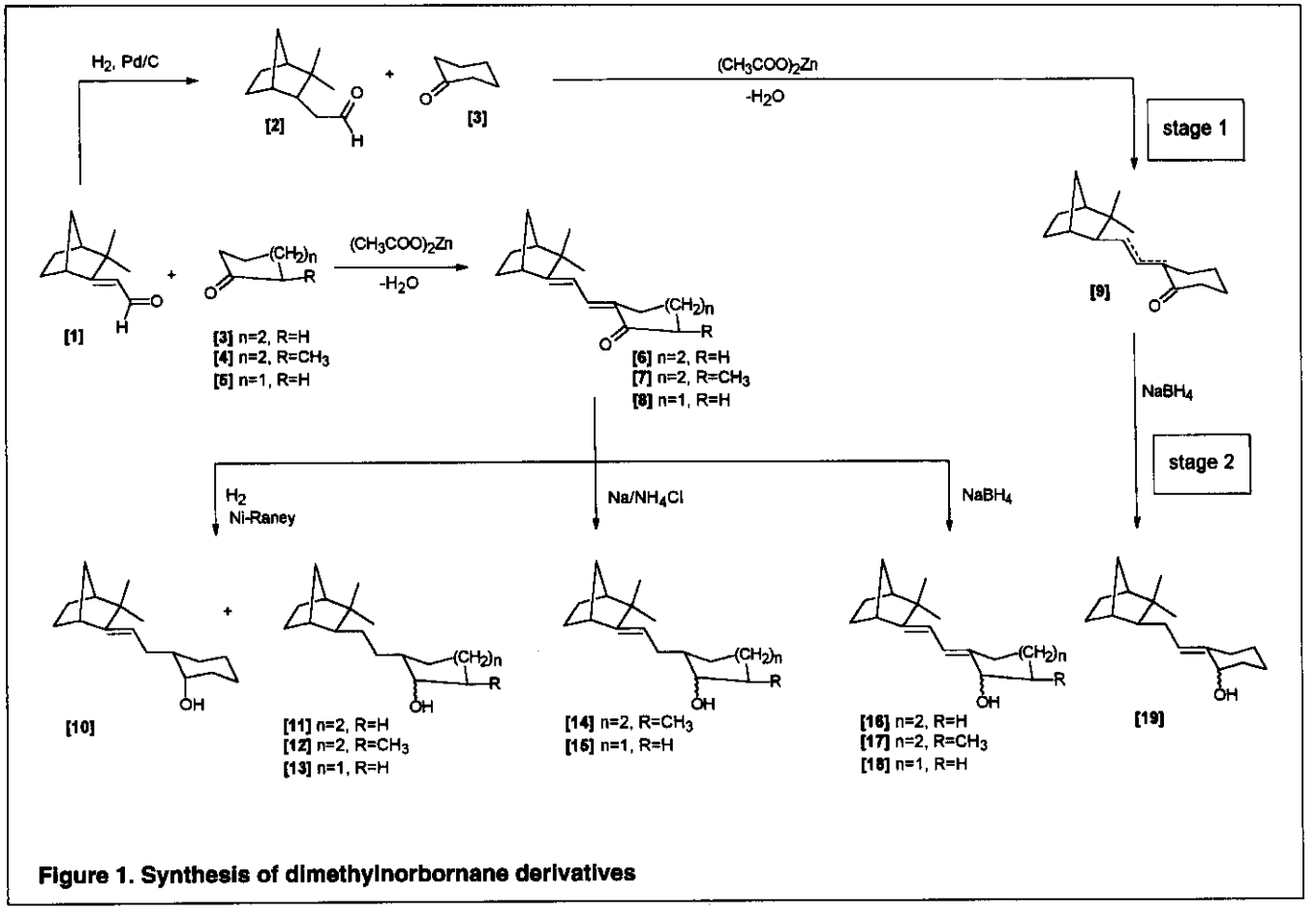

Figure 1. Synthesis of dimethylnorbornane derivatives

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to synthesize the saturated and unsaturated alcohols **[10]-[19]**.

The ketones **[6]-[9]** were obtained with a yield of 45-68% from the Croton condensation of 8-formylcamphene **[1]** with cyclohexanone **[3]**, 2-methylcyclohexanone **[4]**, cyclopentanone **[5]** and dihiydro-8-formylcamphene **[2]** with cyclohexanone **[3]** in the presence of zinc acetate.

The cyclic alcohols **[10]-[19]** were synthesized in the second stage via total or selective reduction by catalytic hydrogenation (Raney-Ni), sodium in saturated aqueous solution of ammonium chloride, and with sodium borohydride. The yield of these reduction reactions varied between 75% and 83%.

These alcohols belong to the group of homocamphanylocyclohexanol derivatives, but they differ in molecular structure, particularly in regard to the stereochemistry of the hydroxyl group, the number and position of the double bonds, and ring size. Their odors were determined, and the authors then made a thorough study of the relationship between compound structure and sandalwood aroma. Structures were determined by IR, NMR and MS analyses.

Products with the best sandalwood aroma were subjected to separation by preparative thin layer chromatography to identify which isomer possessed the sandalwood odor.

Discussion

The odor-structure relationships for the derivatives in Figure 1 are given in Table I. It shows that the typical, intensive sandalwood odor is characteristic for saturated alcohols **[11]** and **[13]** having a five- or six-membered ring and a hydroxyl group situated axially or quasi-axially. Ring size has no substantial influence on the odor of the molecule.

By examining the structures of

Table I. Odor characteristics of synthesized dimethylnorbornane derivatives

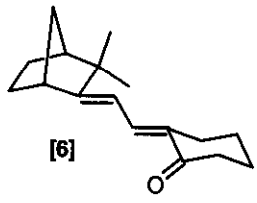
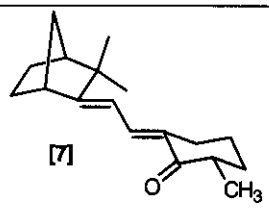
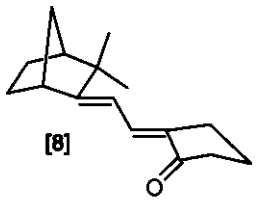
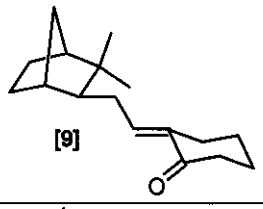
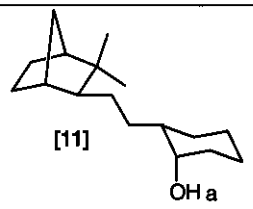
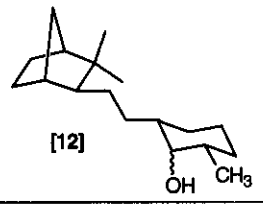
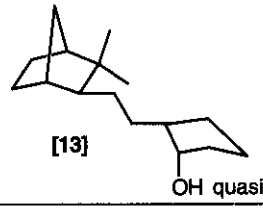
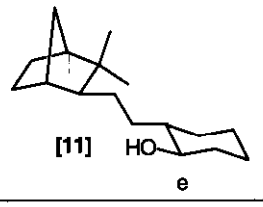
Structure	Formula	Molecular weight	Odor characteristics
 [6]	$C_{17}H_{24}O$	244.38	heavy sweet, fruit, with pineapple note
 [7]	$C_{18}H_{26}O$	258.45	unpleasant, pungent, heavy, animal
 [8]	$C_{16}H_{22}O$	230.34	unpleasant urinous
 [9]	$C_{17}H_{26}O$	246.39	sweet, heavy, fruit
 [11] OH a	$C_{17}H_{30}O$	250.42	strong sandalwood
 [12]	$C_{18}H_{32}O$	264.45	earthy with fresh menthol delicate note
 [13] OH quasi a	$C_{16}H_{28}O$	236.40	durable sandalwood
 [11] HO e	$C_{17}H_{30}O$	250.42	odorless

Table I. Odor characteristics of synthesized dimethylnorbornane derivatives

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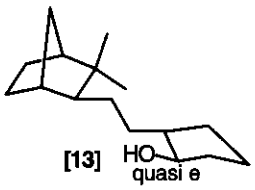
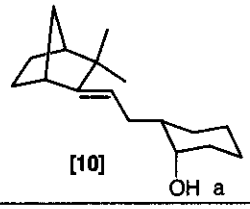
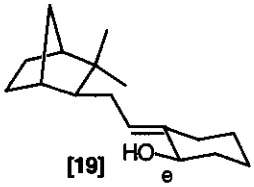
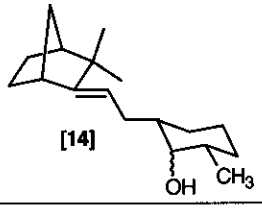
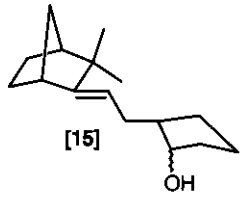
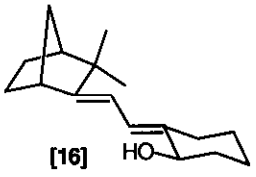
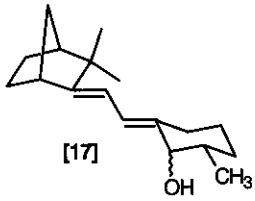
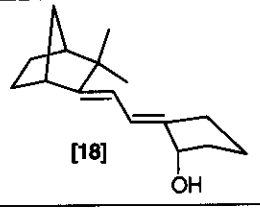
 [13] HO quasi e	$C_{16}H_{28}O$	236.40	earthy
 [10] OH a	$C_{17}H_{28}O$	248.41	woody; slightly sandalwood
 [19] HO e	$C_{17}H_{28}O$	248.41	woody with sandalwood note
 [14] OH CH_3	$C_{18}H_{30}O$	262.43	woody with chemical note
 [15] OH	$C_{16}H_{26}O$	234.38	woody; sandalwood with animal note
 [16] HO	$C_{17}H_{26}O$	246.39	slightly woody, nearly odorless
 [17] OH CH_3	$C_{18}H_{28}O$	260.41	woody; camphor with menthol note
 [18] OH	$C_{16}H_{24}O$	232.37	woody

alcohols **[11a]** and **[13a]**, it can be seen that the reason they have a strong sandalwood odor is their strong structural similarity with naturally occurring strong sandalwood-odored compounds.[4-9]

Unsaturated conformers with an equatorial hydroxyl **[11e]** or a quasi group **[13e]** have no sandalwood odor. The presence of one double bond C=C in alcohols **[10]**, **[15]** and **[19]** causes the sandalwood odor to disappear, leaving a general woody odor. The presence of a methyl group in the cyclohexane ring in the saturated alcohol **[12]** also causes the sandalwood odor to go away.

The size of the monocyclic ring has no influence on the odor of the alcohol. Finally, ketones **[6]**-**[9]** have no sandalwood odor.

References

Addresss correspondence to Prof. Dr. Josef Gora, Technical University of Lodz, Institute of General Food Chemistry, ul. Stefanowskiego 4/10, 90-924 Lodz, Poland.

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