Tetrahedron Letters No.42, pp. 3777-3781, 1965. Pergamon Press Ltd.
Printed in Great Britain.

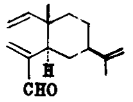
NEW CONSTITUENTS OF *THUJOPSIS DOLABRATA*

Shô Itô, Katsuya Endo, Hinako Honma and Koji Ota
Department of Chemistry, Tohoku University
Sendai, Japan

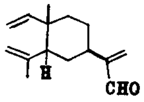
(Received 16 August 1965)

During the course of the analysis of terpenic constituents of *Thujopsis dolabrata* Sieb. et Zucc., we have isolated three new compounds; elemenal, γ-cuparenol and a ketone of fourteen carbon skeleton. The evidence for their structural assignment is described in this paper together with the identification of two other compound, α-1), and β-costal, the presence of which in nature has not been reported up to the present.

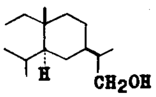
Elemenal Ib, $C_{15}H_{22}O$, $[\alpha]_{600}$ -11° 2); 2,4-dinitrophenylhydrazone, m.p. 180°, displayed the following spectroscopic properties similar to those of β-elemene and suggestive of a vinyl, an isopropenyl and a β-substituted α,β-unsaturated aldehyde group; λmax 218 mμ (ε 7600), 282 (239); νmax 2695, 1681 (CHO), 3067, 1626, 1403, 1000, 935, 909, 897 cm^{-1}(-CH=CH$_2$, C=CH$_2$); δ 1.01 (3H s.), 1.69 (3H br.s.), 4.56-4.97 (4H three m., -CH=C$\underline{H}_2$, C=C$\underline{H}_2$), 5.58-6.04 (1H q., -C$\underline{H}$=CH$_2$), 5.89, 6.18 and 9.53 (each 1H s., C$\underline{H}_2$=C-C$\underline{H}$O). Of the two alternative structures, Ia and Ib, deduced from the above spectroscopic data, Ib was proved to be the correct oneby the synthesis of its octahydro derivative II, b.p. 90-100°(external)/0.5 mmHg, $[\alpha]_D^{30}$ -3.2°; νmax 3370, 1240, 1128, 1076, 1033, 1003, 970 cm^{-1}: Tetrahydroelemol III 3a) was dehydrated and then oxidized by SeO$_2$ to give 2,3-secoselin-11(13)-en-12-al IV,



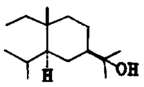
Ia



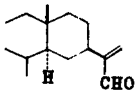
Ib



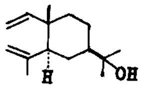
II



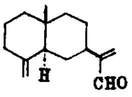
III



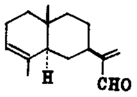
IV



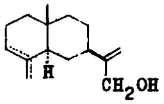
V



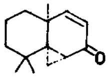
VIa



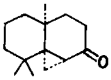
VIb



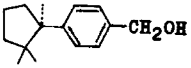
VII



VIII



IX



X

$[\alpha]_D^{27}$ -15°; λmax 218 mμ (ε 8000); νmax 2705, 1693, 1010, 943, 905 cm^{-1}; δ 0.70-0.96, (4Me several signals), 5,82, 6.12, 9.45 (each 1H s. H_2C-C=CHO); 2,4-DNP, m.p. 173°. IV was further hydrogenated to 2,3-secoselinan-12-ol, which was identical with II. On the other hand, elemen-14-al, b.p.100-110°(ext.)/0.5 mmHg, $[\alpha]_D^{27}$ -3.2°; λmax 218 mμ; νmax 3020, 2670, 1680, 1633, 996, 940, 900,882; δ 0.94 (3H s. Me-C-), 1.73 (3H br. s. $C\underline{H}_3$-C=CH_2), 2.83 (1H t. -C$\underline{H}$-CH_2-), 4.50-4.85 (4H m. $C\underline{H}_2$=C-), 5.41-5.87 (1H sx. -C$\underline{H}$=CH_2), 5.96, 6.07, 9.27 (each 1H s. $C\underline{H}_2$=C-C$\underline{H}$O), prepared from elemol V[3] by SeO_2 oxidation (product, m.p. 110-111°) followed by dehydration, was not identical with the natural elemal.

Another sesquiterpenic aldehyde isolated was the inseparable mixture (43:57) of α- VIa and β-costol VIb, $C_{15}H_{22}O$, $[\alpha]_{600}$ +13°; λmax 218 mμ (ε 16800), 282 (91); νmax 3086, 1639, 1611, 935, 911, 887, 790 (C=C), 2703, 1686 cm^{-1}(CHO); δ 0.75 (s. Me), 4.35 and 4.64 (m. $C\underline{H}_2$=C), 5.91, 6.20, and 9.52 (each s. $C\underline{H}_2$=C-CHO) for VIa; 0.82 (s. Me), 1.58 (br.s.), 5.27 (m.)($C\underline{H}_3$-C=CH-), 5.91, 6.20, and 9.52 (each s. $C\underline{H}_2$=C-CHO) for VIb; semicarbazone of VIa, m.p. 218°(d). The structure was established when VI was reduced with $NaBH_4$ to the mixture VII of the corresponding alcohols: IR and NMR spectra of VII were superimposable with those of sesquibenihiol (costol)4), except the presence of a band at 790 cm^{-1} and two signals at 0.81 and 5.25 ppm in the spectra of VII, all of these were attributed to β-sesquibenihiol, the endo-double bond isomer.

The new ketone VIII, $C_{14}H_{20}O$, m.p. 70°, $[\alpha]_D^{25}$ +259°, which was isolated and turned out to be identical with mayurone5), exhibited the following spectroscopic properties: λmax 217 mμ (ε 8700); ν_{max}^{KBr} 3070(CH), 1660 (conj.C=O), 1405 (CH-CO), 863, 803 cm^{-1}. In the NMR spectrum, VIII displayed three methyl signals at 0.67, 1.14 and 1.32 (all s.) and a pair of doublets at 5.94 and 5.43 ppm (J=10.3 c/s) attributable to the β-substituted α,β-unsaturated 6-membered carbonyl system6). The latter signal due to α-hydrogen is further splitted with J=1.3 c/s, showing the presence of α'-hydrogen oriented in the same plane with the unsaturated system7). The α'-hydrogen appears as an octet (apparent J=5.0, 9.0, and 1.3 c/s, X part of ABX system) at 1.95 ppm, fairly high field for the α-hydrogen of a carbonyl, hence the presence of a cyclopropane ring next to the carbonyl was implied. AB part of the ABX system was partly shown as four signals in 0.86-1.05 ppm and assigned as a methylene in cyclopropane ring. Spectra of the dihydro ketone IX, $C_{14}H_{22}O$, m.p. 108°; λmax 280 mμ; ν_{max}^{KBr} 3060 (cyclopropane), 1691 cm^{-1}(conj.C=O); δ 0.62, 1.11 1.18 (each 3H s.), 0.73-0.92 (four signals, CH_2 in cyclopropane), still showed conjugation to some extent although the ethylenic linkage had been reduced.

Appearance of one of the methyl signals in extremely high field, both in VIII and IX, implied that the methyl group suffer the diamagnetic anisotropy due to the cyclopropane[8)]. Furthermore, up-field shift of one of the other methyl signals upon hydrogenation suggested that the methyl was located at γ-carbon of the α,β-unsaturated system. These spectrocopic observations, when coupled with the analytical data, which indicate both VIII and IX to be tricyclic, suggest the formula VIII. This formula coincides with that deduced by Nozoe *et al*[9)] to the degradation product of thujopsene. Direct comparison proved their identity as well as the absolute configuration of VIII as the stereochemistry of thujopsene is rigorously established.[10)]

A new alcohol, γ-cuparenol X, $C_{15}H_{22}O$, b.p. 110°(ext)/0.5 mmHg, $[\alpha]_D^{27}$ +92°; p-nitrobenzoate, m.p. 65°, was also isolated and the spectroscopic informations, λmax 252, 257, 263.5 272 mμ (ε 177-281); νmax 3350 (OH), 1508, 836, 805 (p-subst. benzene), 1407, 1007 cm^{-1}(CH_2OH); δ 0.54, 1.05, 1.23 (each 3H s. Me), 4.44 (2H s. $C\underline{H}_2$-O), 7.14 (4H s. benzene), especially the close similarity of the NMR spectrum with that of cuparene[11)] indicated it to be p-(α,β,β-trimethylcyclopentyl)-benzyl alcohol. In fact, the benzyl alcohol prepared by $LiAlH_4$ reduction of methyl cuparenate, νmax 1725, 1613, 1412, 1285, 711 cm^{-1}; δ 0.54, 1.07, 1.25, 3.82 (each 3H s. Me), 7.35 and 7.87 (each 1H d. J=8.5 c/s), was found to be identical with the natural γ-cuparenol.

We have also identified sesquibenihiol[4)], sesquibenihidiol[4)] and selinadiol[12)] in the same plant as well as thujopsene,[9)] cuparene,[11)] widdrol[13)], and elemol[14)]. Cooccurence of these biogenetically related compounds in the same plant is of interest from the chemotaxonomical point of view. Detail of the analysis will be published later.

We are indebted to Takasago Perfumery Co. for the extract and saw-

dust of the plant.

REFERENCES AND FOOTNOTE

1) V. Benesova, V. Herout, and F. Sorm, *Coll. Czech. Chem. Commun.*, **24**, 2365 (1959); A.S. Bawdekar, and G.R. Kelkar, *Tetrahedron*, **21**, 1521 (1965). This compound was also isolated recently by Nozoe *et al* from *Chamaecyparis formosensis* Matsum. T. Nozoe, Y.S. Chen, T. Toda, to be published.

2) UV, IR, and NMR spectra were measured in isooctane, liquid film, and carbon tetrachloride respectively. Rotations in chloroform.

3) a. A.D. Wagh, S.K. Paknikar, and S.C. Bhattacharyya, *Tetrahedron*, **20**, 2647 (1964). b. T.G. Halsall, D.W. Theobald, and K.B. Walshaw, *J. Chem. Soc.*, 1029 (1964).

4) S. Katsura, *Nippon Kagaku Zasshi*, **63**, 1460 (1942). V. Benesova, V. Sykora, V. Herout, and F. Sorm, *Chem. & Ind.*, 363 (1958).

5) After completion of this study, Dr. S. Dev, National Chemical Laboratory, Poona, India, informed us that he has also reached the structure VIII for mayurone he has previously reported (*Tetrahedron Letters*, 73 (1964)), although its elemental analysis indicated it be C_{15} compound. Cf. the preceding paper. Direct comparison carried out by Dr. Dev established the identity of these two compounds, hence the name is used in this paper.

6) *Inter al.*, O.L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2016 (1963).

7) Cf. Y. Sasaki, Y. Kondo, and G. Miyazima, *Yakugaku Zasshi*, **85**, 377 (1965).

8) S. Forsen, and T. Norin, *Tetrahedron Letters*, 2845 (1964).

9) T. Nozoe, H. Takeshita, S. Itô, T. Ôzeki, and S. Seto, *Chem. Pharm. Bull. Japan*, **8**, 936 (1960).

10) T. Norin, *Acta Chem. Scand.*, **17**, 738 (1963).

11) C. Enzell, and H. Erdtman, *Tetrahedron*, **4**, 361 (1958).

12) L. Dolejs, V. Herout, *Coll. Czech. Chem. Commun.*, **26**, 2045 (1961).

13) C. Enzell, *Acta Chem. Scand.*, **16**, 1553 (1962). S. Itô, K. Endo, and T. Nozoe, *Tetrahedron Letters*, 3375 (1964).

14) Also isolated by A. Yoshikoshi, Tohoku University, unpublished result.