Nor-diterpenoids from the Bark of *Pinus silvestris* L.*

**TORBJÖRN NORIN and BJÖRN WINELL**

Swedish Forest Products Research Laboratory, Box 5604, S-11486 Stockholm, Sweden

Three nor-diterpenoids have been isolated from the light petroleum soluble extractives of the bark of *Pinus silvestris* L. One of the compounds has been characterised as 19-norpimara-8(14),15-dien-3-one (1 a). Structures of the other two have been assigned to 19-norisopimara-8(14),15-dien-3-one (2 a), and 19-norisopimara-7,15-dien-3-one (3 a).

In connection with a detailed study of the lipophilic extractives of pine bark (*Pinus silvestris*)¹ a neutral light petroleum soluble fraction was obtained, which upon consecutive chromatography on silica gel and silver nitrate impregnated silica yielded the nor-diterpenoid A(C₁₉H₂₆O; MW 272, determined by mass spectrometry; [α]_D +99.6º, c 0.5 in chloroform; m.p. 85 – 86º, recrystallised from methanol) and a crystalline mixture of the nor-diterpenoids B and C. The characterisations of these compounds are described below.

A Wolff-Kishner reduction ² was performed on compound A (I a). The product was hydrogenated over platinum, and a mixture of saturated hydrocarbons was obtained. A decarboxylation ³ of pimaric acid (I b), followed by a catalytic hydrogenation over platinum, yielded the same hydrocarbons (GLC/MS), but in different relative proportions. This experiment thus establishes the 19(or 18)-norpimarane skeleton of compound A.

The characteristic groupings of compound A (I a) are assigned from spectral data. The NMR spectrum of the compound (see Experimental) exhibits three signals corresponding to three methyl groups. One of these signals is a doublet (J = 7 cps) and assigned to the secondary 4-methyl group. The olefinic part of the NMR spectrum shows a significant signal pattern, which is almost identical to that of pimara-8(14),15-diene groupings, but different from those of isopimara-8(14),15-dienes and isopimara-7,15-dienes.⁴ The strong positive rotation and the shape of the ORD curve of compound A (I a) at the low wavelength region ([α]_222 +30500º) is characteristic of pimara-8(14),15-dienes.⁵ Isopimara-8(14),15-dienes exhibit a corresponding strong negative rotation, whereas the corresponding A³,15-derivatives have much lower

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rotations at this wavelength region. The NMR and ORD data thus relate compound A to the normal pimara-8(14),15-diene skeleton.

The presence of a keto-group in compound A was shown by IR-data (1700 cm\(^{-1}\)). The compound exhibited a positive Cotton effect (\(\alpha = +35\) in methanol). A similar positive Cotton effect is also exhibited by 19-norisopimara-8(14),15-dien-3-one (2a), a diterpene degradation product described by Grant and Munro. These data suggest that compound A possesses a 3-keto-function, which was further confirmed by a positive Zimmermann reaction. According to Cohen and Rock the angular 19-methyl signals in steroids are shifted 0.23 \(\tau\) downfield by an introduction of a 3-keto function. The angular 20-methyl signal for norpimaradiene (1c) appears at 9.05 \(\tau\), and in compound A (1a) at 8.98 \(\tau\). The difference (0.07 \(\tau\)) is slightly less than the corresponding values for steroids (0.14 \(\tau\), probably due to slightly different anisotropic effects operating in the two types of compounds. However, this difference may be taken as indicative of a 3-keto group in compound A. Treatment of compound A with sulphuric acid gave no isomerisation of the 4-methyl group thus establishing the 4\(\alpha\)-configuration. The results presented above thus establish the 19-norpimara-8(14),15-dien-3-one structure (1a) of compound A.

Compounds B and C did not separate, using various TLC-conditions, but were easily separated by GLC. The mass spectra of the two compounds were obtained, using a combined GLC/MS technique. A comparison of the mass spectra of compounds A, B, and C with those of the methylesters of "pimaric" (1b) "sandaracopimaric" (2b) and "isopimaric" (3b) acids, respectively, reveals significant similarities (particularly peaks M–15 and M–29), indicating structural relationships in each pairs of compounds. Thus, compounds B and C have tentatively been formulated as 19-norisopimara-8(14),15-dien-3-one (2a) and 19-norisopimara-7,15-dien-3-one (3a) respectively.

Since a sample of 19-norisopimara-8(14),15-dien-3-one, previously prepared by Grant and Munro, was not available, a direct comparison with compound B could not be made.

From the bark of Croton oblongifolius, Seshadri et al. isolated oblongifoliol (4). From this diol it should be possible to obtain the enantiomer of 19-nor-
pimara-8(14),15-dien-3-one, using a retro-aldol reaction. Such a correlation of the two compounds is planned in collaboration with Professor Seshadri.

Nor-diterpenes have recently been isolated from the bark of some other conifer species. During the course of this work, Rowe et al.10 communicated the isolation of 18-nor-4α-hydroxypimara-8(14),15-diene (1 a) and 18-nor-4α-hydroxyabieta-8,11,13-triene (5 a) from the bark of P. banksiana. Recently, Quan and Swan11 reported the occurrence of 18-nor-4α-hydroxyisopimara-8(14),15-diene (2 c) and the corresponding 4β-derivative (2 d) in the bark of Thuja plicata Donn.

From the soil of a Pinus maritima forest, Biellman et al.12 recently isolated a microorganism which could metabolise dehydroabietic acid (5 b) to 19-norabieta-8,11,13-trien-3-one (5 c). In view of this finding it is an open question if the nor-diterpenoids from pine bark are products from the tree or artefacts as a result of microbial degradation of the corresponding resin acids which also occur in the bark.

EXPERIMENTAL

Light petroleum refers to a fraction with boiling range 40–60°C. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian A-60 instrument operating at 60 Mc/s (solvent, CDCl3; internal standard, TMS). Chemical shifts are given in δ units. Only characteristic spectral data are given.

The neutral light petroleum soluble part of the methylene chloride extract (21 g)1 of the bark was chromatographed on silica. Ether (10%) in light petroleum eluted a fraction (0.84 g) which was rechromatographed on silver nitrate impregnated silica with the same eluent yielding compound A (0.32 g, Rf = 0.37) and a mixture (0.11 g, Rf = 0.33) of compounds B and C.

**Compound A** (19-nor-pimara-8(14),15-dien-3-one (1 a)) was re-crystallised from methanol and had m.p. 85–86°C (C8H16O requires C 83.8%; H 10.4%. Found: C 83.9%; H 10.1%). It gave a positive Zimmermann13 colour reaction for 3-keto compounds. M. W. 272 (MS), IR (KBr): 1700 (C=O); 990, 915 (–CH=CH2); 850 (C=CH) cm–1. NMR: 4.20 τ, 1H (X-part of an ABX-spectrum, J = 17.5 and 10.5 cps); 4.80 τ, 1H, broad singlet, olefinic proton) 5.0 τ, 2H, (AB-part of an ABX-spectrum, J = 17.5, 10.5, and 2.5 cps); 7.4–8.8 τ, (methylene protons) 8.98 τ, 3H, doublet, J = 7 cps (CH3–CH); 9.82 τ, 3H, singlet (CH=CH2); 9.04 τ, 3H, singlet (CH3–C). ORD: [α]200 +525°, [α]195 +4380°, [α]170 + 875°, [α]123 + 30 500°; α + 35.

Compound A (1 mg) was dissolved in ethanol (1 ml). One drop of aqueous sulphuric acid (20%) was added and the mixture refluxed for 2 h. The starting material could be recovered unchanged (GLC, TLC and mixed m.p.).

A Wolff-Kishner reduction of compound A (1 a) was performed according to Nagata and Itazaki 4 (procedure A). The product (44% yield) was a colourless oil which was hydrogenated using a platinum catalyst in acetic acid. The saturated hydrocarbon mixture thus obtained was analysed by GLC/MS (1% XE60). Three main constituents were detected (rel. ret. times 1.00, 1.32, 1.52; rel. prop. 7:29:1).

The decarboxylation of pimaric acid was carried out according to the procedure previously described for A4(14)-dihydroabietic acid by Jensen and Johnson.5 The hydrocarbon mixture thus obtained was hydrogenated using a platinum catalyst in acetic acid yielding a mixture of saturated hydrocarbons which were analysed by GLC/MS. Four main constituents were detected (rel. ret. times 1.00, 1.16, 1.32, 1.52; rel. prop. 1:2:5:3:5). The mass spectra of the constituents with relative retention times 1.00, 1.32, and 1.52 were identical to those of the corresponding products derived from compound A.

*Added in proof. Professor Seshadri has now informed us that the proposed structure (4) of oblongifolil has to be revised.

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The proportions between compounds B and C were 1:3 (GLC). The mixture had the following properties. IR (thin film): 1700 (C=O); 3080, 1640, 995, 920, 910 (–CH=CH₂); 1660, 870, 830 (C=CH). NMR: 4.1–5.3 t, signal pattern characteristic for the olefinic part of an isopimara-7,15-diene or an isopimara-8(14),15-diene, 8.92–9.1 t; methyl groups. The mixture gave a positive Zimmermann colour reaction, indicating the presence of a 3-keto function.

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