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The Constitution of Diterpenoids from *Solidago elongata* Nutt[1]

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From an ethyl acetate extract of roots of *Solidago elongata* Nutt.[2] we have isolated several oily diterpenoids (see Table 1) by careful column and thin layer chromatography. Polar fractions from the columns, after methylation with diazomethane, have yielded three diterpenoid methyl esters, one of which is identical with an authentic sample of methyl kolavenate (*1*).[3] The close relationship of the other two esters to methyl kolavenate was indicated by their NMR spectra. Indeed, the only major differences are that the new compounds have the resonance of both quaternary methyl groups shifted to lower field and each shows evidence of additional oxygenation. Thus, one ester (*2*) has resonances attributable to a secondary acetate while, in the other (*3*), resonances arising from a secondary angelate are clearly visible (see Fig. 1). The location of these oxygen functions at C-6 in the methyl kolavenate skeleton was demonstrated as follows.

Major peaks in the mass spectra of compounds in this series result from cleavage of either the C-9,C-11 or the C-11,C-12 bonds. Thus, cleavage of the C-9,C-11 bond in methyl kolavenate (*1*) produces a peak at *m/e* 191, while cleavage of the C-11,C-12 bond with transfer of a hydrogen and subsequent loss of a methyl radical gives a peak at *m/e* 189. In the mass spectra of the acetate (*2*), angelate (*3*) and the derived alcohol (*4*), these peaks are two units

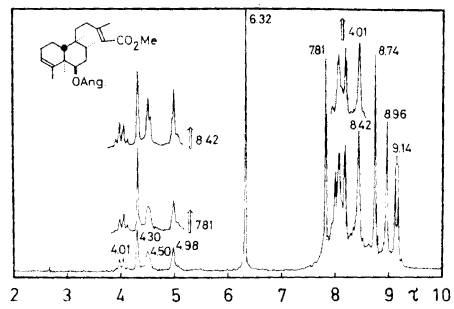

Fig. 1. NMR single and double resonance spectra at 100 Mc/s of methyl 6-angeloyloxykolavenate (*3*).

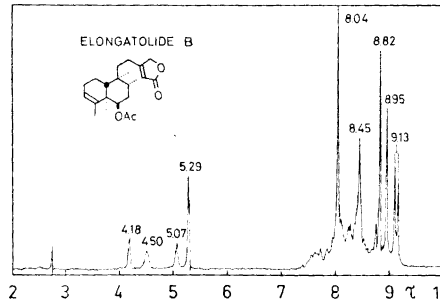

Fig. 2. NMR spectrum at 100 Mc/s of elongatolide B (*11*).

lower because of loss of ROH, while the corresponding ketone (*5*), m.p. 75—77°, gives a peak at *m/e* 205. These data exclude the possibility of the oxygen function being in the side chain.

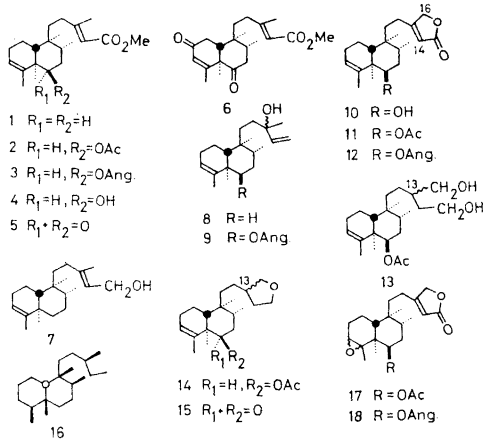

Table 1.

Compound No.	Name	Molecular formula	Methyl group resonances			
			C-13	C-4	C-8	C-9 and C-5
1	Methyl kolavenate	$C_{21}H_{34}O_2$	7.91	8.47	9.23	9.30, 9.05
2	Methyl 6-acetoxy-kolavenate	$C_{23}H_{36}O_4$	7.82	8.45	9.14	8.98, 8.79
3	Methyl 6-angeloyloxy-kolavenate	$C_{26}H_{40}O_4$			see Fig. 1	
7	Kolavenol	$C_{20}H_{34}O$	8.35	8.45	9.21	9.29, 9.03
8	Kolavelool	$C_{20}H_{34}O$	8.69	8.45	9.25	9.30, 9.03
9	6-Angeloyloxy-kolavelool	$C_{25}H_{40}O_3$	8.72	8.47	9.18	9.03, 8.79
10	Elongatolide A	$C_{20}H_{30}O_3$		8.28	9.10	8.87, 8.83
11	» B	$C_{22}H_{32}O_4$			see Fig. 2	
12	» C	$C_{25}H_{36}O_4$		8.44	9.14	8.96, 8.80
17	» D	$C_{22}H_{32}O_5$		8.74	9.12	8.98, 8.78
18	» E	$C_{25}H_{36}O_5$		8.74	9.12	8.98, 8.78

Two other possible points of attachment, C-1 and C-2, can be eliminated since, in the ketone (*5*) ν_{max} (1712 cm^{-1}), the Δ^3-olefinic bond is not conjugated to the carbonyl group nor does it migrate into conjugation when the ketone is passed over basic alumina. Further, a by-product from oxidation of the alcohol (*4*) to the ketone (*5*) was the dione (*6*) which contains both a conjugated (1665 cm^{-1}) and, more significantly, an *isolated* (1712 cm^{-1}) carbonyl group. Two alternative sites remain for consideration: C-6 and C-7. Spectroscopic data lead to choice of the former, the axial nature of the substituent being indicated by the width ($W_{\frac{1}{2}}=6$ cps) of the carbinyl proton. The proximity of the substituent and the Δ^3-olefinic bond produces significant changes in the chemical shift of H-3 and the C-4 methyl group on conversion of the acetate (*2*) (τ 4.48 and 8.45, respectively) into the alcohol (*4*) (τ 4.20 and 8.33) and the ketone (*5*) (τ 4.37 and 8.48). Moreover, in the IR of the alcohol (*4*), the hydroxyl group is intramolecularly hydrogen-bonded [ν_{max} 3620 (free) and 3560 cm^{-1} ($-OH\cdots\pi$, persists on dilution)]. In the mass spectrum of the ketone (*5*), the two most intense peaks are at *m/e* 108 and 109. They have shown by accurate mass measurements to be due to the ions $C_8H_{12}^+$ and $C_8H_{13}^+$ and probably result from cleavage of the C-9,C-10 and C-5,C-6 bonds, the latter process being enhanced by the presence of both the Δ^3-olefinic bond and the carbonyl group. Our conclusions concerning the location of the oxygen function at C-6 were reinforced by a study of the neutral diterpenoids from the roots. Of these (see Table 1) two, kolavenol (*7*) and kolavelool (*8*) have been obtained [3] previously. A new compound which appears to be a kolavelool bearing an angeloyloxy group is assigned the provisional structure (*9*) on spectral and biogenetic grounds. The remaining five new compounds, elongatolides A–E, have one outstanding structural feature in common, a β-substituted $\Delta^{\alpha\beta}$-butenolide ring [4] [IR 1786, 1756 cm^{-1}, UV 217 nm (EtOH), NMR 4.18 (H-14) and 5.29 (2 H-16) τ].

In three of them, the alcohol (*10*), the acetate (*11*) and the angelate (*12*), the Δ^3-olefinic bond and the 6β-oxygen substituent result in NMR data which parallel that of the kolavenate-related series. The acetate (*11*) was reduced with sodium borohydride to the C-13 epimeric diols (*13*) which, with dimethyl sulfoxide at 150° for 16 h,[5] gave the tetrahydrofuran (*14*). This compound, by hydrolysis and then oxidation, furnished the ketone (*15*) which is suitable for the study of benzene-induced solvent shifts because of the absence of additional carbonyl functions. On the basis of a clerodane (*16*) [6] skeleton, the values obtained [τ(benzene)$-\tau(CDCl_3)=-0.03$ (C-4-Me), -0.10 (C-5-Me), $+0.20$ (C-8-Me), and $+0.18$ ppm (C-9-Me)] accord [7] only with a C-6 carbonyl group and suggest that ring B is distorted into a twist-boat con-

formation. Spectral data allow assignment of provisional structures (*17*) and (*18*) to the remaining two compounds.

We have also isolated a polyacetylenic methyl ester (λ_{max} 246, 258, 272, 289, 309, 331 nm) and a sterol ($C_{29}H_{48}O$), m.p. 161–163°, from these roots. The latter also occurs [8] in *S. serotina* Ait. and its physical and spectral properties are very similar to a compound isolated[9] from *Aplopappus heterophyllus* Blake. *S. elongata* Nutt. has been classified by some authors as a subspecies of *S. canadensis* L. However, since the latter has been shown to be devoid of acetylenes [10] and to contain diterpenoids [11] which are markedly different from those reported in this communication, these plants are at least chemically distinct.

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NMR of Organophosphorus Compounds Tri-3-thienylphosphine

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As part of our studies on the determination of the magnitudes and signs of ^1H-^{31}P spin coupling constants in phosphorus substituted aromatic and heteroaromatic compounds we have recently analysed the NMR spectra of tri-2-thienylphosphine and some of its derivatives.[1]

In this note we wish to report the analysis of the ^1H NMR spectrum of the hitherto unknown 3-substituted isomer, tri-3-thienylphosphine (I), obtained by reaction of 3-thienyllithium with phosphorus tribromide. The proton magnetic resonance spectrum of (I) (Fig. 1) may be analysed as the ABC part of an ABCX

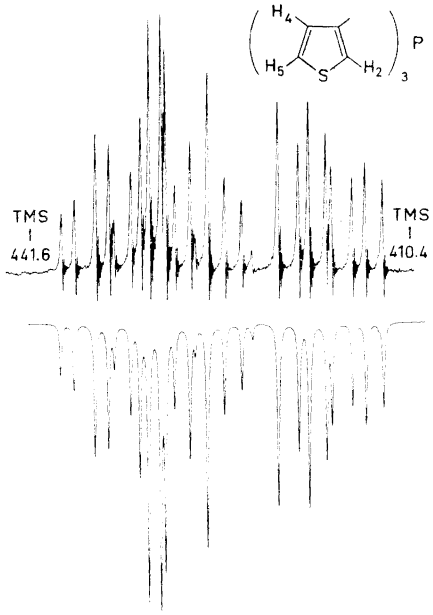

Fig. 1. Observed (above) and calculated (below) 60 MHz PMR spectrum of a 14 % w/w degassed solution of tri-3-thienylphosphine in CCl_4.