Tetrahedron Letters No.55, pp.4879-4882, 1969. Pergamon Press. Printed in Great Britain.

ISOLATION OF NEW ACYCLIC C_{25}-ISOPRENYL ALCOHOL FROM POTATO LEAVES.

Masashi Toyoda, Masako Asahina, Hideaki Fukawa
and Toru Shimizu
Central Laboratory of Nisshin Flour Milling Co.,
Ohi, Iruma-gun Saitama, Japan

Received in Japan 8 October 1969; received in the U K for publication 28 October 1969

Recently two acyclic C_{25}-isoprenyl alcohol were reported, geranylfarnesol(1) from insect wax and geranylnerolidol(2) from phytopathogenic fungi which is responsible for the leaf spot disease of maize.

In this paper, we wish to report the isolation and characterization of a new acyclic C_{25}-isoprenyl alcohol from the unsaponifiable matter of potato (Solanum tuberosum) leaves.

The unsaponifiable matter obtained from lipid extract of dried potato leaves was chromatographed on the column of silica gel. Elution with 10 ~ 20% (v/v) ether in n-hexane yielded the fraction which contained mainly solanesol and the new isoprenyl alcohol. The acetone solution of this fraction was cooled to -30 C and then, a waxy crystal of solanesol was filtered off. Further purification was carried out by rechromatography of silica gel.

The new isoprenyl alcohol so far obtained was a pale yellow oil and gave a single spot on TLC and reversed phase PC in various solvents, n_D^{25}:1.4780, Anal. Found: C,81.28%; H,13.34%; Calcd. For $C_{25}H_{48}O$: C,82.33%; H,13.27%.

Its IR spectrum shows the structure of polyisoprenyl primary alcohol, ν_{max}^{film}, cm^{-1}: 3310(OH), 1660(C=C), 2900, 1460 and 1380(C-H), 1000(C-O stretching of allylic primary alcohol) and 835(C-H of trisubstituted olefin).

NMR data and assignments of the isoprenyl alcohol is presented in Table I.

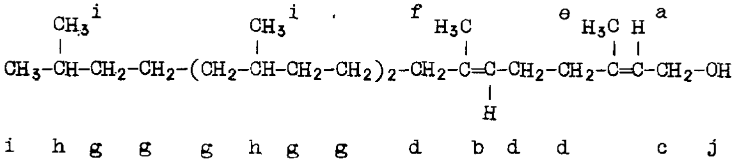
TABLE I

NMR Spectrum of the Isoprenyl Alcohol*

Peak Position (τ-Value)	Relative Areas Found	Relative Areas Expected	Assignment**
4.62	0.9	1	a
4.92	1.0	1	b
5.97	1.8	2	c
7.97	7.4	6 (+1)	d, (j)
8.29	3.0	3	e
8.45	3.0	3	f
8.84	20.0	16+1	g, h
9.20	12.6	12	i

* in $CDCl_3$ with TMS as internal reference at 60 Mc/S

**



$$\mathrm{CH_3\text{-}\overset{\overset{CH_3^{\,i}}{|}}{C}H\text{-}CH_2\text{-}CH_2\text{-}(CH_2\text{-}\overset{\overset{CH_3^{\,i}}{|}}{C}H\text{-}CH_2\text{-}CH_2)_2\text{-}CH_2\text{-}\overset{\overset{^{f}\,H_3C}{|}}{C}{=}\underset{\underset{H}{|}}{C}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{^{e}\,H_3C}{|}}{C}{=}\overset{\overset{H^{\,a}}{|}}{C}\text{-}CH_2\text{-}OH}$$

i h g g g h g g d b d d c j

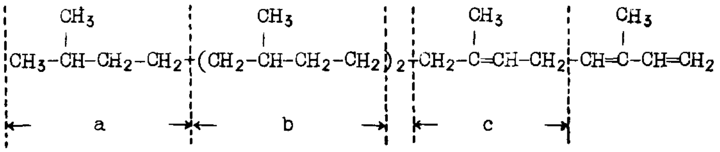
The result was consistent with the presence of three saturated isoprene units and two normal isoprene units to which a hydroxyl group is attached at the terminal unit. The signal of τ 8.45 and 8.29 are due to the methyl protons of a trans internal isoprene unit and a cis OH terminal isoprene unit, respectively. The signal of the α-methylenic protons to be attached to cis-bond are about 0.04 τ higher than those to trans bond. Those assignments were confirmed by geraniol, phytol and C_{55}-isoprenyl alcohol of mulberry(3).

The mass spectra of the isoprenyl acetate and the perhydroisoprenyl acetate, which was obtained by catalytic hydrogenation of the former, are shown in Table II.

TABLE II

(A) Mass Spectram of the Isoprenyl Alcohol

m/e	Assignment
67	M-(a+2b+c)
68	c
135	M-(a+2b)
138	b+c
140	2b
205	M-(a+b)
208	2b+c
278	(a+2b+c)-H
346	M

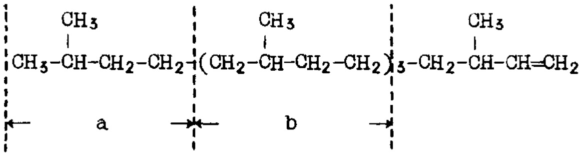


$CH_3-\overset{CH_3}{CH}-CH_2-CH_2-(CH_2-\overset{CH_3}{CH}-CH_2-CH_2)_2-CH_2-\overset{CH_3}{C}=CH-CH_2-CH=\overset{CH_3}{C}-CH=CH_2$

M $C_{25}H_{46}(346)$

(B) Mass Spectrum of the Perhydroisoprenyl Alcohol

m/e	Assignment
69	M-(a+3b)
70	b
140	2b
141	a+b
210	3b
211	a+2b
278	(M-a)-H
281	a+3b
350	M



$$\underbrace{CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2}_{a}-\underbrace{(CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2)_3}_{b}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH{=}CH_2$$

M $C_{25}H_{50}$ (350)

In both of those spectra, the peaks of (M-AcOH) were only observed instead of the parent peaks. But the major peaks in those spectra can readily be accomodated by the structure which is supposed with above results.

From ozonization followed by reductive cleavage of the ozonide, phyton and levulin aldehyde were only found as the 2,4-dinitrophenylhydrazones on TLC and reversed PC.

On the basis of the data outlined above, this isoprenyl alcohol has been identified as 3, 7, 11, 15, 19-pentamethyl-2-cis-6-trans-eicosadien-1-ol.

This is to say, this compound is the substance that one isoprene unit is attached to phytyl group. A biosynthesis of the isoprenyl alcohol by addition of a cis isoprene unit to hypothetical phytyl pyrophosphate is suggested.

Detailed results will be published elsewhere.

REFERENCES

(1) T. Rfos and S. Pérez C., Chem. Comm., 214 (1965).

(2) S. Nozoe, Tetrahedron Letters, 4457 (1968).

(3) H. Fukawa, M. Toyoda, T. Shimizu and M. Murohashi, ibid., 6209 (1966).