Tetrahedron Letters, Vol.22, No.24, pp 2289 - 2290, 1981
Printed in Great Britain

0040-4039/81/242289-02$02.00/0

COMPOSITE CONSTITUENTS: FOUR NEW TRITERPENOIDS, NEOLUPENOL, TAROLUPENOL AND THEIR ACETATES ISOLATED FROM ROOTS OF A JAPANESE DANDELION, TARAXACUM JAPONICUM

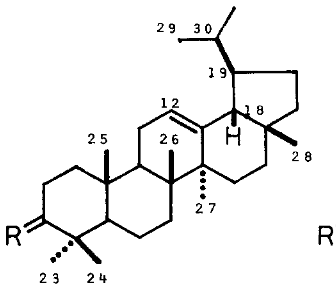
H. Ageta*, K. Shiojima, K. Masuda and T. Lin

Showa College of Pharmaceutical Sciences, 5-1-8 Tsurumaki, Setagaya-ku, Tokyo, JAPAN 154

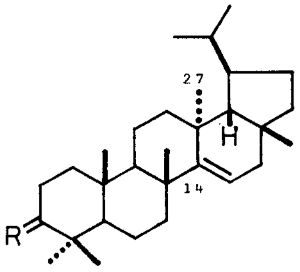
Abstract Neolupenyl acetate (Ia), tarolupenyl acetate (IIa) and their corresponding alcohols (Ib and IIb) were isolated from the roots of *Taraxacum japonicum*, and their structures were established as the members of migrated lupane series.

A Japanese crude drug "Hokoei-kon", the dried roots of *Taraxacum japonicum* KOIDZ. (Kansai-tampopo, Compositae),[1] is very rich in triterpenoid like those of *T. officinale* WEBER.[2] Hexane extraction of the crude drugs followed by silica-gel chromatography afforded fatty acid esters (0.14% of the drugs), acetates (0.62%) and mono-ols (0.19%) of triterpenoids. The acetates consisted of taraxasteryl acetate (29.8% of the acetates), α-amyrin acetate (16.0%), β-amyrin acetate (18.3%), lupenyl acetate (4.2%), taraxeryl acetate (3.7%) and two new compounds, named neolupenyl acetate (7.7%) and tarolupenyl acetate (13.3%). This communication concerns the characterization of the latter two compounds.

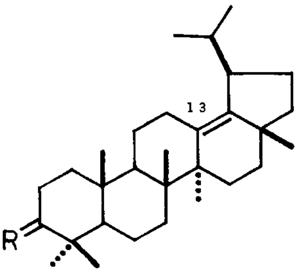
Neolupenyl acetate (Ia), m.p. 195.5-197°, $[\alpha]_D$ +71.4°($CHCl_3$), IR cm^{-1} 1742,1250,1022; 826, 816, was hydrolysed to give neolupenol (Ib), m.p. 208-209°, $[\alpha]_D$ +115.5°, IR cm^{-1} 3480,1042,1028; 826,808, which was also found in the mono-ols fraction. CrO_3 oxidation of Ib afforded neolupenone (Ic),[3] m.p. 163-164°, IR cm^{-1} 1708; 826,816, which gave neolupene (Id), m.p. 129-130°, IR cm^{-1} 823,812, on Wolff-Kishner reduction. MS spectrum of Ia, m/z M^+ 468.3956 ($C_{32}H_{52}O_2$; 11% of base peak), 408 (M^+-60; 12), 365 (M^+-60-C_3H_7; 8), 284(4), 218(99), 203(88) and 189(100), as well as those of Ic and Id, clearly showed the compound to be a pentacyclic triterpenoid having Δ^{12}-double bond and an isopropyl group. 100MHz ^1H-NMR spectra of Ia-Id (TABLE) suggested the compounds have 3β-acetoxyl in Ia, 3β-hydroxyl in Ib and 3-oxo in Ic (typical splitting pattern of 3α-H in Ia and Ib, and the chemical shifts of C(23)-C(26) methyl protons in Ia-Ic in comparison with those in Id), Δ^{12}double bond (triplet like dd signal of olefinec proton and the shifts of C(25)-C(28) methyl signals in Ia-Id), and 18βH, 19αH structure of the migrated lupane skeleton (one of the signals of isopropyl methyls remarkably shifted to high field in Ia-Id). Final proof of the structure of Ia



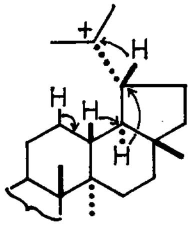
Ia R = α-H, β-OAc
Ib R = α-H, β-OH
Ic R = O
Id R = H_2



IIa R = α-H, β-OAc
IIb R = α-H, β-OH
IId R = H_2



IIIa R = α-H, β-OAc
IIId R = H_2



IV

TABLE. Chemical Shifts (δ) for $CDCl_3$ solution (JEOL JNM-FX-100)$^{a)}$

	C( ) methyl protons							olefinic proton	3α-proton$^{c)}$
	23	24	25	26	27	28	29, 30$^{b)}$		
Ia	0.875	0.875	0.975	0.953	1.110	0.928	0.768d, 0.875d	5.159dd$^{d)}$	4.509dd
Ib	1.000	0.796	0.951	0.951	1.105	0.928	0.765d, 0.865d	5.162dd	3.224dd
Ic	1.098	1.056	1.076	1.000	1.110	0.928	0.768d, 0.870d	5.184dd	
Id	0.870	0.823	0.948	0.948	1.115	0.928	0.764d, 0.868d	5.162dd	
IIa	0.850	0.850	0.870	1.046	0.975	0.821	0.986d, 1.008d	5.325ddd$^{e)}$	4.484dd
IIb	0.982	0.774	0.850	1.049	0.982	0.826	0.991d, 1.016d	5.333ddd	
IId	0.848	0.803	0.848	1.049	0.990	0.823	0.989d, 1.016d	5.324ddd	
IIIa	0.867	0.848	0.887	0.916	1.084	0.970	0.882d, 0.919d		4.504dd
IIId	0.867	0.808	0.867	0.921	1.105	0.975	0.884d, 0.923d		

a) Assignments were confirmed by $CDCl_3$-C_6D_6 solvents shifts and Lanthanide shifts. Coupling constants observed were: b) 6.6-6.9 Hz, c) 9.2-10.3 and 5.4-6.8 Hz, d) 3.4-3.7 Hz, and e) 3.0, 2.8 and 1.4 Hz.

was given by identifying neolup-13(18)-en-3β-yl acetate (IIIa), m.p. 184-185°, derived from Ia by treatment with $2N-H_2SO_4$-benzene AcOH at 50°, with the corresponding specimen derived from lupenyl acetate by known process.$^{4)}$ Biogenetic consideration of the formation of Ia and Ib from prelupenyl cation (IV) by concerted 1,2-shifts of hydrogen (19βH → 20, 18αH → 19α, 13βH → 18β) also supports the stereochemistry of Ia and Ib.

Tarolupenyl acetate (IIa), m.p. 221-223°, $[\alpha]_D$ +70.6°($CHCl_3$), IR cm^{-1} 1744, 1241, 1021; 808, gave tarolupenol (IIb), m.p. 207-208°, $[\alpha]_D$ +135.7°, IR cm^{-1} 3280,1039; 808 on hydrolysis. The latter was also found in the mono-ols fraction in a small amount. CrO_3 oxidation of IIb followed by Wolff-Kishner reduction afforded tarolupene (IId), m.p. 163.5-164.5°, $[\alpha]_D$ +64.5°, IR cm^{-1} 3080,1616; 808. MS spectrum of IIa, m/z M^+ 468.3960 ($C_{32}H_{52}O_2$; 2), 408 (M^+-60; 52), 393 (M^+-60-CH_3; 35), 365 (M^+-60-C_3H_7; 68), 325(11), 229(30), 204(56), 189(100), as well as that of IId, suggested the compound to be a pentacyclic triterpenoid having Δ^{14}-double bond and an isopropyl group. ^{1}H-NMR spectra of IIa, IIb and IId (TABLE) showed the compounds have 3β-oxygen function in IIa and IIb, and Δ^{14}-double bond (one trisubstituted olefinic proton signal and the chemical shifts of C(25)-C(28) methyl signals). Treatment of IIa with $2N-H_2SO_4$ in benzene-AcOH at 20° gave a mixture (1:1) of Ia and IIIa. The facts mentioned above established the structures of tarolupenyl acetate and its derivatives to be formulated as IIa, IIb and IId.

Ia, Ib and IIa, IIb are two groups of the migrated lupane triterpenoids first isolated from natural source. Considering recent studies on cymbopogone,$^{5)}$ all the groups of migrated lupane series could be expected to be isolated like those of hopane and oleanane series.

References and Notes

1) "Hokoei-kon" used in this investigation was purchased at Tokyo market supposed to be a native of Chugoku area. Ia and IIa were also isolated from the fresh roots of *Taraxacum japonicum* KOIDS., *T. platycarpum* DAHLST., *T. longeappendiculatum* NAKAI and *T. hondoense* NAKAI, but little from *T. albidum* DAHLST. and *T. officinale* WEBER (natualized in Japan).
2) S.Burrows, J.C.E.Simpson, J.C.S.,1938,2042; T.R.Ames, J.L.Beton, A.Bowers, T.G.Halsall, E.R.H. Jones, *ibid.*,1954,1905; J.M.Beaton, F.S.Spring, R.Stevenson, J.L.Stewart, *ibid.*,1955,2131.
3) Recently 18β,19αH-lup-12-en-3-one was synthesized from friedelin (Y.Yokoyama, Y.Moriyama, T. Tsuyuki, T.Takahashi, Chemistry Lett.,1980,67; Bull.Chem.Soc.Jpn.,1981,54,234). The identity of the compound with Ic was confirmed by comparisons of their ^{1}H-NMR and MS spectra. Thanks are due to Prof. T.Takahashi for sending the data.
4) S.P.Adhikary, W.Lawrie, J.McLean, J.C.S.(C),1970,1030.
5) M.Crawford, S.W.Hanson, M.E.S.Koker, Tetrahedron Lett.,1975,3090; Y.Yokoyama, T.Tsuyuki, N. Nakamura, T.Takahashi, S.W.Hanson, K.Matsushita, *ibid.*,1980,3701.

(Received in Japan 7 March 1981)