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THE CONSTITUENTS OF ARCTIUM LAPPA L

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Ten components including two new sesquiterpenes have been isolated from the leaves of Arctium lappa L. The new compounds, dehydrofukinone (I) and arctiol (II) proved to be $\Delta^{9(10)}$-fukinone and 8α-hydroxyeudesmol respectively.

Arctium lappa L. (Gobō in Japanese) of the family Compositae is a perennial herb and has been cultivated from long ago as a vegetable. We report the isolation and structural determination of the components from the leaves of the plant. From the methanol extract we isolated ten components by a combination of vacuum distillation and column chromatography. They were sesqui- and triterpenes, and consisted of eight known and two new substances. The known compounds were identified as eremophilene,[1)] fukinone,[2)] petasitolone,[3)] fukinanolide,[4)] β-eudesmol,[5)] taraxasterol[6)] and its esters, acetate and palmitate. The two new compounds were named dehydrofukinone (I) and arctiol (II) respectively. These structures were established as follows.

Dehydrofukinone (I), $C_{15}H_{22}O$, a fragrant oil, was obtained by preparative glc (PEG-20M, 2 m; column temp, 170°; H_2, 35 ml/min). It showed IR: 1660 (α,β-unsaturated ketone), 1620, 850 cm^{-1} (double bond) and λ_{max}^{hexane} 239 mμ (ε, 11870), 266mμ (ε, 6140). This compound was identical in all respects with dehydrofukinone I prepared by dehydrogenation of fukinone with DDQ.[2)]

Arctiol (II), $C_{15}H_{26}O_2$, mp 157.5-159.0°, $[\alpha]_D$ +84.0° (c, 1.0, MeOH) showed IR: 3300, 3250 (OH), 3070, 1642, 890 cm^{-1} (end-methylene) and δ^{CDCl_3}: 0.75 (s, C-Me), 1.30 (s, -O-CMe_2), 4.04 (dt, J=5.0, 10.0 Hz, W½=14 Hz, -O-CH), 4.07 (s, 2xOH), 4.46 and 4.76 (s each, C=CH_2). Jones' oxidation of arctiol II gave a ketol (III), $C_{15}H_{24}O_2$, mp 95.0-96.0°, which showed IR: 3475, 1157 (OH), 1698 cm^{-1} (C=O), indicating the presence of a hydrogen-bonded keto-group. Hydrogenation of II with Pt-EtOH gave dihydroarctiol (IV), $C_{15}H_{28}O_2$, mp 129.0-131.0°, which showed the absence of an end-methylene group in the IR and a new methyl signal at δ^{CCl_4}: 0.87 (d, J=6.3 Hz, CH-Me). Treatment of II with Ac_2O-pyridine afforded the monoacetate (V), $C_{17}H_{28}O_3$, mp 98.0-99.0°, $[\alpha]_D$ +108.0° (c, 1.24, MeOH), which showed IR bands at 3510, 1160, 1150 cm^{-1} for a tert-OH group.

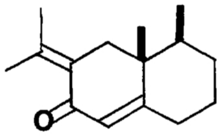
The above results suggest that arctiol II is a bicyclic sesquiterpene having an end-methylene, a secondary OH and a tertiary OH groups.

In order to clarify the carbon skeleton, dihydroarctiol IV was transformed into a hydrocarbon by the following route. Jones' oxidation of IV gave a saturated ketol (VI), $C_{15}H_{26}O_2$, IR: 3500 (OH), 1698 cm^{-1} (C=O), which was treated with $POCl_3$ to afford an α,β-unsaturated ketone (VII), $C_{15}H_{24}O$, bp 90-105° (bath temp)/

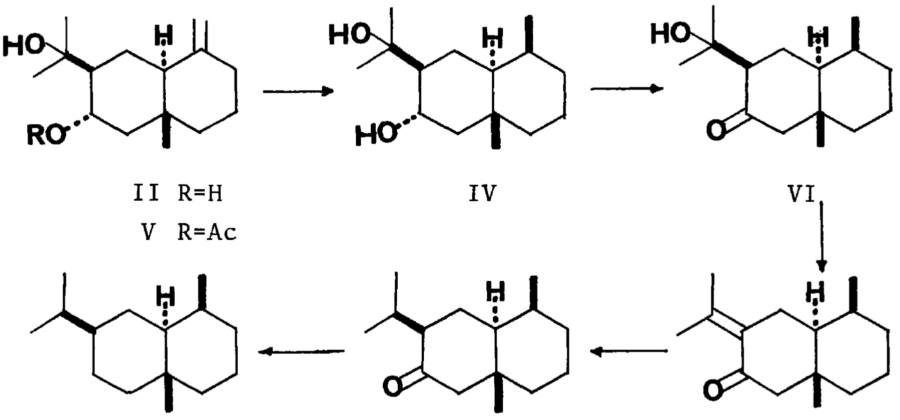
0.3 mm, $[\alpha]_D$ +24.7° (c, 0.82, MeOH); λ_{max}^{MeOH} 254 mμ (ε, 6600); IR: 1680, 1605 cm^{-1}; δ^{CCl_4}: 1.78 (s, $C{=}CMe_2$). This suggests 1,3-relationship between the two OH groups of arctiol II. Hydrogenation of the ketone VII with Pt-EtOH gave a saturated ketone (VIII), $C_{15}H_{26}O$, bp 98-115° (bath temp)/0.1 mm, $[\alpha]_D$ -26.4° (c, 1.23, MeOH), IR: 1705 cm^{-1} (C=O). Wolff-Kishner reduction of VIII furnished a hydrocarbon (IX), $C_{15}H_{28}$, bp 93-96° (bath temp)/2.0 mm, $[\alpha]_D$ +16.0° (c, 1.48, $CHCl_3$); m/e: M^+ 208, base peak 109; glc: PEG-20M, 2 m, column temp 110°, H_2 25 ml/min, rt=10.6 min, whose IR curve was fully superimposable with that of the known (+)-selinane IX.[7] The ORD curve of the saturated ketone VIII showed (-)-Cotton effect, suggesting the presence of the keto-group at C-8 on (+)-selinane IX.

The above evidence, therefore, demonstrated that the two OH groups of arctiol II should be located at C-8 and C-11 respectively, and the configuration of the secondary OH group should be 8α(eq)-orientation on the basis of the half-band width of the C-8 proton signal (14 Hz) in the NMR of II.

Thus arctiol can be represented by the stereoformula II.



I



II R=H
V R=Ac

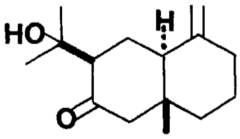
IV

VI

VII

VIII

IX



III

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