

Studies on Triterpenoid Corticomimetics (III)

Determination of Acetyl-11-keto- β -boswellic Acid and 11-Keto- β -boswellic Acid in Olibanum

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Abstract □ From olibanum, acetylboswellic acid (I) and boswellic acid (II) were isolated as mixed crystals of α - and β -forms in the ratio of 1 to 2 and 1 to 4, respectively. And acetyl-11-keto- β -boswellic acid (III) and 11-keto- β -boswellic acid (IV) were also isolated and their α -forms were not found in olibanum by GC/selected ion monitoring MS technique. Contents of four compounds were determined.

Keywords □ olibanum, α - and β -boswellic acid, α - and β -boswellic acid acetate, 11-keto- β -boswellic acid, 11-keto- β -boswellic acid acetate, contents of boswellic acid and its derivatives in olibanum.

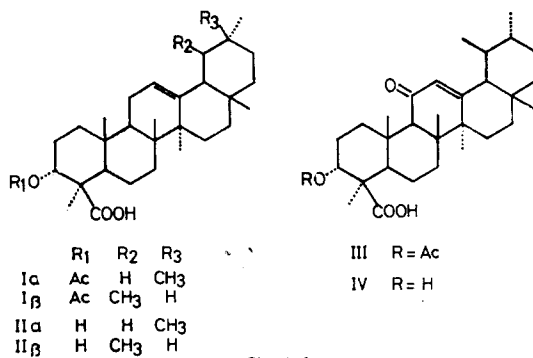


Chart 1

α -forms.

Thus, we also isolated four triterpenoids from olibanum. By their spectral data and GC/MS analysis, it was found that acetyl-11-keto-BA and 11-keto-BA which were occurred naturally and derived synthetically from BA or acetyl-BA, were all β -forms, and that α -forms of acetyl-11-keto-BA and 11-keto-BA did not occur in olibanum. On the other hand, acetyl-BA and BA isolated were turned to be mixtures of α and β with the ratio of 1 to 2 and 1 to 4, respectively. The present studies also determined the contents of the triterpenoids in olibanum.

EXPERIMENTAL METHODS

Materials

Olibanum was purchased from a market, Cho-

We have prepared 11-oxo-derivatives of some pentacyclic triterpenoids with Δ^{12} -ene skeleton for their corticoid-like activities.¹⁻⁴⁾ In order to investigate the effects of the alterations of functional groups on the corticomimetic activities, we attempted to obtain the 11-keto-derivatives of boswellic acid (BA) which contains one carboxy group at C₄ and one α -hydroxyl group at C₃.

It is well known that BA mainly occurs as the acetate in olibanum from *Boswellia carterii*, Burseraceae, and β -form (ursene type) is predominant and is accompanied by small amounts of α -BA (oleanene type).⁵⁻⁹⁾ Recently, Indian workers reported that acetyl-11-keto- β -BA and 11-keto- β -BA in addition to acetyl- β -BA and β -BA were isolated from *B. serrata*.⁹⁾ However, they did not mention the co-occurrence of the

ngno Street, Seoul. Other reagents were the first grade.

Isolation

Olibanum (3kg) was extracted with ether to yield an extract (950g). The extract was partitioned into ether and 5% NaOH. After usual work up, an ether-soluble acidic fraction (380g) was yielded.

The fraction (128g) was chromatographed over silica gel (1.5kg, size 9.2×100 cm) using hexane/ethylacetate (7:1) as eluant. Compounds I to IV were obtained in the order of elution. Each was recrystallized from methanol to yield I 2.7g, II 0.6g, III 0.26g and IV 0.41g. After repeatedly undertaking the above procedure, total amounts of the samples obtained were as follows; I 19.5g(0.65%), II 1.6g(0.05%), III 0.5g(0.02%) and IV 0.76g(0.03%).

Compound I(colorless needles), mp: 250° , IR $\nu_{\max}^{\text{KBr}} \text{cm}^{-1}$: 3100, 1700(COOH), 1730, 1235(OCOCH₃), PMR $\delta_{\text{ppm}}^{\text{TMS}}(\text{CDCl}_3)$: 0.81, 0.84, 0.88, 0.99, 1.01, 1.05, 1.09, 1.12, 1.17, 1.19, 1.24(CH₃), 2.09(3H, s, $1 \times \text{OCOCH}_3$), 5.14(1H, m, C₁₂-H), 5.28(1H, m, C₃-H), MS(m/z): 498(M⁺, 0.9%), 438(M⁺-CH₃COOH, 1.8%), 423(M⁺-CH₃COOH-CH₃, 1.0%), 394(1.8%), 219(20%), 218(base peak), 203(35.9%).

Compound II(colorless scales), mp: 248° , IR $\nu_{\max}^{\text{KBr}} \text{cm}^{-1}$: 3420(OH), 3100, 1690(COOH), PMR $\delta_{\text{ppm}}^{\text{TMS}}(\text{CDCl}_3)$: 0.80, 0.88, 1.03, 1.08, 1.33(CH₃), 4.05(1H, m, C₃-H), 5.14(1H, m, C₁₂-H), MS(m/z): 456(M⁺, 2.2%), 219(19%), 218(base peak), 203(51%).

Compound III(colorless needles), mp; $264-268^\circ$, UV(λ_{\max} in methanol): 251nm(ϵ 8,870), IR $\nu_{\max}^{\text{KBr}} \text{cm}^{-1}$: 3100, 1700(COOH), 1735, 1230(OCOCH₃), 1660, 1610(α, β -unsaturated ketone and olefin), PMR $\delta_{\text{ppm}}^{\text{TMS}}(\text{CDCl}_3)$: 0.80, 0.91,

1.11, 1.16, 1.20, 1.32(CH₃), 2.05(3H, s, OCOCH₃), 2.39(1H, br. s, C₉-H), 5.27(1H, m, C₃-H), 5.53(1H, s, C₁₂-H), MS(m/z): 512(M⁺, 1.9%), 452(1.0%), 273(39%), 232(57%), 135(base peak).

Compound IV (colorless needles), mp: $266-270^\circ$, UV(λ_{\max} in methanol): 251(ϵ 7,550), IR $\nu_{\max}^{\text{KBr}} \text{cm}^{-1}$: 3420(OH), 3100, 1695(COOH), 1655, 1605(α, β -unsaturated ketone and olefin), PMR $\delta_{\text{ppm}}^{\text{TMS}}(\text{CDCl}_3)$: 0.79, 0.91, 1.10, 1.15, 1.30(CH₃), 2.40(1H, br. s, C₉-H), 4.05(1H, m, C₃-H), 5.52(1H, s, C₁₂-H), MS(m/z): 470(M⁺, 15%), 273(base peak), 232(74%).

Synthesis

Compound I (0.5g) in methanol (15ml) was treated with diazomethane to give its methyl ester(V). Recrystallized from methanol. (0.4g) mp: 195° , IR $\nu_{\max}^{\text{KBr}} \text{cm}^{-1}$: 1740, 1720(ester), PMR $\delta_{\text{ppm}}^{\text{TMS}}(\text{CDCl}_3)$: 2.08(3H, s, OCOCH₃), 3.67(CO-OCH₃), 5.15(1H, m, C₁₂-H), 5.32(1H, m, C₃-H).

Compound I (6g) in acetic acid (50ml) and dichloromethane (30ml) was treated with chromium trioxide (6g) in acetic acid (50ml). The reaction mixture was stirred at room temp. for 3hrs, and poured into ice water, and the product was extracted with chloroform. The extract was washed with water, dried over sodium sulfate anhydrous, and freed from solvent. The residue was chromatographed on a silica gel column eluting with hexane/ethylacetate (3:1), and crystallized from methanol to yield III. (1.5g).

Compound II (4.6g) was deacetylated with 5% sodium hydroxide under refluxing for 4hrs. After cooling, the reaction mixture was acidified to pH about 3 with *d*-HCl, extracted with chloroform. The extract was dried over sodium sulfate anhydrous, and freed from solvent. The residue was crystallized from methanol to give

IV. (3.3g).

Compound IV (2.3g) in methanol (50ml) was treated with diazomethane to yield its methyl ester (VI). Recrystallized from chloroform/methanol. (2.0g) mp: 214°, UV(λ_{\max} in methanol): 251nm (ϵ 6,230), IR ν_{\max}^{KBr} cm⁻¹: 1730(ester), 1660, 1640(α , β -unsaturated ketone and olefin), PMR $\delta_{\text{ppm}}^{\text{MS}}$ (CDCl₃): 2.40(1H, s, C₉-H), 3.66(3H, s, COOCH₃), 4.09(1H, m, C₃-H), 5.54(1H, s, C₁₂-H), MS(m/z): 484(M⁺, 3.3%), 4.25(1.0%), 273(37.6%), 232(76.5%).

Compound VI (1.8g) in pyridine (10ml) was treated with a complex of chromium trioxide (1.8g) and pyridine (10ml) over night at room temp. The reaction mixture was pured into ice water. The product was extracted with ether. The ether layer was washed with *d*-HCl, then with water, dried over sodium sulfate anhydrous, and freed from solvent. The residue (1.5g) was chromatographed over silica gel using hexane/ethylacetate (5:1→2:1) as eluant to yield VII. Recrystallized from chloroform/methanol. (0.8g) mp: 202°, UV(λ_{\max} in methanol): 251nm(ϵ 8,600), IR ν_{\max}^{KBr} cm⁻¹: 1730(ester), 1715(ketone), 1650, 1620(α , β -unsaturated ketone and olefin), PMR $\delta_{\text{ppm}}^{\text{MS}}$ (CDCl₃): 2.35(1H, s, C₉-H), 3.68(3H, s, COOCH₃), 5.57(1H, s, C₁₂-H), MS(m/z): 482(M⁺, 9.3%), 467(2.8%), 423(2.5%), 273(41.4%), 232(93.7%), 135(base peak).

Instrumental Analysis

All melting points were taken on a Mitamura heat block apparatus and uncorrected. IR absorption spectra were obtained in KBr pellets on Perkin-Elmer Model 281B. NMR spectra were determined in CDCl₃ solution by a Varian Model FT80A NMR spectrometer with tetramethylsilane as an internal standard. (¹H:80MHz, ¹³C:20MHz) The chemical shifts are reported in δ . A recording spectrophotometer, Gilford

type 2600 was used for the measurements of UV/visible absorption spectra. Gas-liquid chromatograms were obtained on a Hewlett-Packard Model 5840A chromatograph. Mass spectra were obtained on a Hewlett-Packard GC/MS spectrometer(type 5985B) using an electron impact method. High performance liquid chromatograms were obtained with a Waters Liquid Chromatograph, attached with UV-spectrometer.

GC of Compound I and GC/MS of Its Methyl Ester (V)

GC of I and GC/MS of its methyl ester (V) were carried out under the following condition; OV-101 packed column (2mm i.d.×2m), detector: FID, injection temp: 250°, detection temp: 300°, carrier gas: helium ($\bar{\mu}$ =20cm/sec), scanning mass range: m/z 200~550, electron energy: 30eV.

Gas chromatogram of I showed two peaks at Rt 17.60 (peak-1) and 19.19 (peak-2) with the ratio of about 1 to 2. GC/MS of V also exhibited two peaks with the ratio of about 1 to 2.

Peak-1 (m/z): 512 (M⁺, 2.3%), 219 (19.5%), 218 (base peak), 203 (44.6%).

Peak-2 (m/z): 512 (M⁺, 3.3%), 219 (19.2%), 218 (base peak), 203 (16.8%).

Assay of Compounds I to IV

1. Preparation of test solution-Olibanum powdered (10g) was extracted three times with methanol (100ml) under refluxing, and the combined extracts were freed from solvent. The residue (4.97g) was partitioned into ether (100ml) and water (50ml). The extraction with ether was repeated more two times. The ether layers were combined and extracted with 5% NaOH (100ml). The aqueous layer was acidified to pH about 3 with *d*-HCl, and then extracted three times with ether (150ml). The ether extracts were combined, dried over sodium sulfate

anhydrous and freed from solvent. The residue (1.92g) was dissolved in methanol to make 100ml. The methanol solution was used as the test solution.

2. Analysis by GC-Five ml of the test solution was treated with diazomethane, and the reaction mixture was dried *in vacuo*. One mg of cholesterol as an internal reference was added to the residue. Trimethylsilylation was performed with 250 μ l of *N,O*-bis (trimethylsilyl) trifluoroacetamide at room temp. overnight. GC was carried out under the following condition: OV-1 fused silica capillary column (0.2mm i.d. \times 25m), injection temp.: 300 $^{\circ}$, detection temp.: 300 $^{\circ}$, detector: FID, oven temp. 1 : 270 $^{\circ}$ (rate, 1 $^{\circ}$ /min), temp. 2 : 300 $^{\circ}$, carrier gas: helium ($\bar{\mu}$ = 17cm/sec).

3. GC/Selected Ion Monitoring MS-The test sample which was methylated and trimethylsilylated was subjected to GC/MS for selected ion monitoring. GC was performed at the condition above described (OV-1 capillary column) and MS spectra were obtained at 30 eV electron energy. Mass fragments of the authentic samples were as follows;

The methyl ester of III; m/z 526 (M^+ , 47.0%), 273 (69.2%), 232 (base peak).

The Me_3Si derivative of the methyl ester of IV; m/z 556 (M^+ , 86.7%), 427 (base peak), 273 (62.8%), 232 (62.8%). Thus the ions of m/z 526, 556 and 273 were selected for MS-monitoring.

4. Analysis by HPLC-Methanol solution of III and IV (each 2mg/ml) were serially diluted and calibration curves were made under the following condition; column: μ Bondapak C_{18} , detector: UV (254nm), solvent: 80% methanol, flow rate: 1.5ml/min, injection volume: 5 μ l.

Chromatogram of the test solution showed two major peaks of R_t 6.25 and 7.96, correspond-

ing to IV and III, respectively.

RESULTS AND DISCUSSION

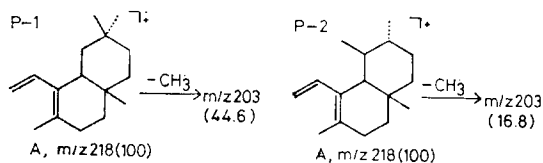
Characterization of Compounds I to IV

From the ether-soluble acidic fraction of olibanum, compounds I to IV were isolated by chromatography over silica gel, and each compound was recrystallized from methanol.

Compound I, mp 250 $^{\circ}$, was an acid acetate, as seen from its IR spectrum (3100, 1700; 1730), further confirmed by bands (1740, 1720) in IR spectrum of its methyl ester (V). NMR spectrum of I showed signals for one acetyl group at δ 2.09 (3H, s), one vinylic proton at δ 5.14 (1H, m, C_{12} -H) and a proton at δ 5.28 (1H, m, C_3 -H) on carbon carrying the acetyl function.

1H -NMR spectrum of the methyl ester (V) exhibited a peak at δ 3.67 (3H, s, $COOCH_3$) besides the signals mentioned above.

Mass spectrum of I showed the molecular ion peak at m/z 498, $C_{32}H_{50}O_4$, the base peak at m/z 218 due to an ion "A", arising as a result of characteristic retro-Diels-Alder fragmentation of ring-C of Δ^{12} -oleanene/ursene derivatives with no substituents on rings D and E¹⁰. On the basis of these observations, coupled with literature references,⁵⁻⁹ I was assumed to be α -and/or β -acetylboswellic acid. GC of I and GC/MS of its methyl ester (V) showed two peaks with the ratio of about 1 to 2. Mass fragmentation pattern of peak-1 and peak-2 were almost similar except the intensities of



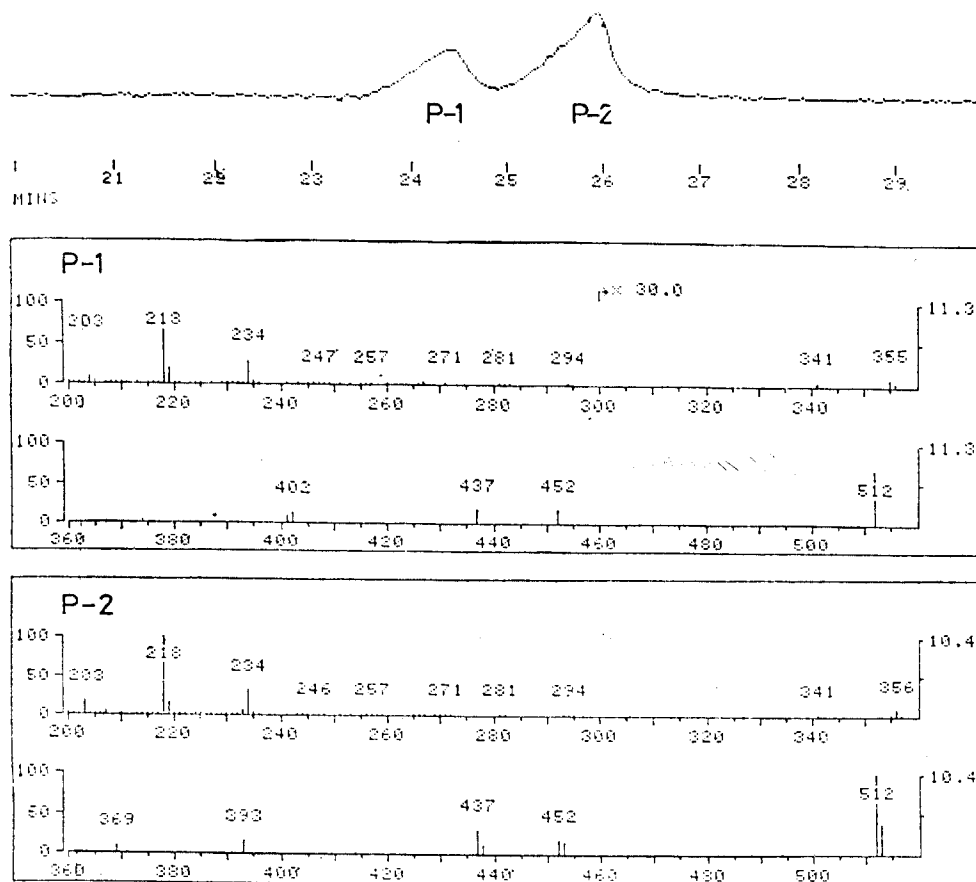


Fig. 1: GC/MS of acetyl boswellic acid methyl ester (V). Compound V showed two peaks with the ratio of about 1 to 2. Mass fragmentation patterns of the two peaks were almost similar except the intensities of peaks at m/z 203, which were 44.6 and 16.8%, respectively.

peaks at m/z 203, which were 44.6 and 16.8% respectively. (Fig. 1) The mass fragment of m/z 203 was thought to be one of $[A-CH_3]$, of which fragmentation tendency was known to be different between Δ^{12} -oleanene and Δ^{12} -ursene.¹⁰ Thus, we could assign P-1 and P-2 as acetyl- α -boswellic acid methyl ester and acetyl- β -boswellic acid methyl ester. Compound I was also obtained by acetylation of II.

Compound II, mp 248°, was a hydroxy acid as indicated by its IR spectrum (3420; 3100, 1690). PMR spectrum of II exhibited signals for one vinylic proton at δ 5.14(m, C_{12} -H) and

a proton at δ 4.05 (br. s, C_3 -H) on carbon carrying a hydroxyl function. Mass spectrum of II showed the molecular ion peak at m/z 456, $C_{30}H_{48}O_3$, and the base peak at m/z 218 due to the ion "A". This confirmed that II was a Δ^{12} -oleanene/ursene derivative with no substituents in rings D and E.

The CMR spectrum of II shown in Fig. 2 exhibited a signal for one carboxylic acid group at δ 183.7, two signals for C_{13} at δ 145.2 and 140.0, and two signals for C_{12} at δ 122.6 and 125.2. The ratio of two peaks for C_{13} or C_{12} was about 1 to 4. Two peaks at δ 145.2 and

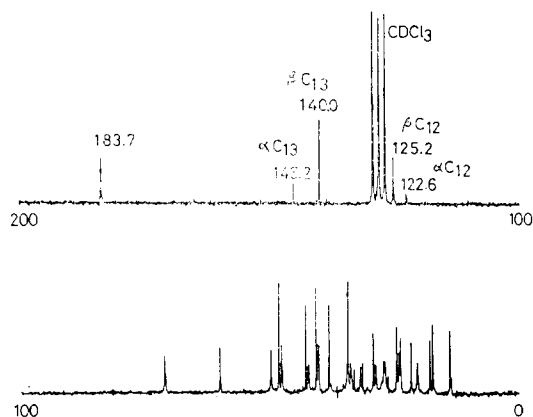
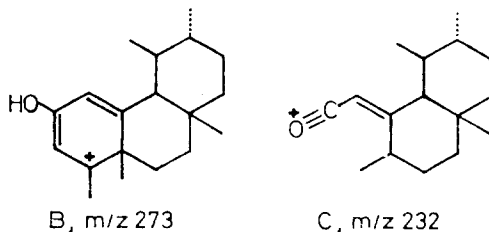


Fig. 2. ^{13}C -NMR spectrum of boswellic acid (II). This showed that II was the mixture of α - and β -boswellic acid with the ratio of about 1 to 4.

122.6 were responsible for Δ^{12} -oleanene, and two peaks at δ 140.0 and 125.2 were for Δ^{12} -ursene¹¹⁾. Therefore, II was turned to be the mixture of α - and β -boswellic acid with the ratio of 1 to 4.

When the acetate of II was subjected to GC, it showed two peaks with the ratio of about 1 to 4, which were overlapped with two peaks of I. However, the acetate of II which was recrystallized from methanol, exhibited two peaks with the ratio of 1 to 2 in GC. Therefore, recrystallization of I and II yielded the mixtures of α - and β -forms in the ratio of 1 to 2 and 1 to 4, respectively.

Compound III, mp 264~266°, possesses α , β -unsaturated carbonyl, acetoxy, and carboxylic functions, as seen from its UV (251nm, ϵ 8870) and IR (1660, 1610; 1735, 1230; 3100, 1700) spectra. PMR spectrum of III showed signals for one acetyl group at δ 2.05 (3H, s), a methine proton at δ 2.39 (br. s, C_9 -H), and one vinylic proton at δ 5.53 (s, C_{12} -H), suggesting the presence of a 11-keto- Δ^{12} -system. Mass spectrum of II showed the molecular ion peak



at m/z 512, $\text{C}_{32}\text{H}_{48}\text{O}_5$. Peaks at m/z 273 and 232 were corresponding to ions B and C, respectively, arising as the results of characteristic retro-Diels-Alder and McLafferty fragmentation. Thus, III was thought to be acetyl-11-keto-boswellic acid. CMR data of III shown in Table I exhibited 32 peaks for 32 carbon atoms and two peaks for C_{29} and C_{30} at δ 17.3 and 20.5, respectively, indicating that III is ursene type. Therefore, III was established as acetyl-11-keto- β -boswellic acid.

Oxidation of I by chromium trioxide-acetic acid yielded III. Recrystallization of the synthetically obtained III only afforded β -form, of which PMR and CMR data were superimposed on the compound III naturally occurred.

Compound IV, mp 266~270°, contains hydroxyl, carboxyl and α , β -unsaturated carbonyl functions as seen from its IR spectrum (3420; 3100, 1695; 1655, 1605), UV absorption (λ_{max} at 215nm, ϵ 7,550) and PMR spectrum (1H on C_3 , m, 4.05; 1H on C_9 , br. s, 2.40; 1H on C_{12} , s, 5.52). Mass spectrum showed the molecular ion peak at m/z 470, $\text{C}_{30}\text{H}_{46}\text{O}_4$, and two ion peaks at m/z 273 (ion B) and 232 (ion C). De-acetate of III was identical with IV as judged from their mp and PMR spectra. CMR data of IV confirmed that IV was 11-keto- β -boswellic acid.

11-Keto- β -boswellic acid methyl ester (VI) was prepared by methylation of IV with diazomethane and also synthesized by oxidation of V with chromium trioxide-acetic acid, deacety-

Table I: ^{13}C -NMR data of 11-keto- β -boswellic acid (IV) and its acetate (III) in CDCl_3

Carbon	III	IV	Carbon	III	IV
1	40.9	41.0	16	27.2	27.3
2	23.6	26.3	17	33.9	34.0
3	73.2	70.5	18	50.5	49.0
4	46.5	47.4	19	39.3	39.4
5	59.1	59.2	20	39.3	39.4
6	18.8	18.9	21	30.9	31.0
7	32.9	33.1	22	34.7	34.0
8	43.8	43.9	23	28.8	28.9
9	60.4	60.6	24	181.2	182.3
10	37.4	37.6	25	13.2	13.3
11	199.2	199.4	26	18.4	18.5
12	130.4	130.6	27	21.1	21.1
13	164.6	164.8	28	23.7	24.3
14	45.1	45.2	29	17.3	17.4
15	27.3	27.6	30	20.5	20.6
			OCOCH ₃	21.1	
			O ₂ COCH ₃	170.1	

lation, and then recrystallization. 3, 11-Diketo- β -boswellic acid methyl ester (VII) was obtained by treatment of VI with a complex of chromium trioxide/pyridine. Methylation of the carboxyl

function of C_{24} was essential for preparing VII, since oxidation of IV with chromium trioxide/pyridine gave a nor-ketone.⁹⁾

The Absence of α -Forms of 11-Keto-boswellic acid and its Acetate in Olibanum.

In order to examine whether α -forms of 11-keto-boswellic acid and its acetate were co-occurred with their β -forms or not, GC/selected ion monitoring MS were performed. The test sample of the ether-soluble acidic fraction of olibanum was methylated with diazomethane and trimethylsilylated. Mass ions of m/z 526 and 273 for acetyl-11-keto-boswellic acid methyl ester, and of m/z 556 and 273 for the trimethylsilyl derivative of 11-keto-boswellic acid methyl ester were selected for monitoring them, as shown in Fig. 3.

Any peaks corresponding to α -forms of the 11-keto compounds were not found by GC (Table II) and GC/MS (Fig. 3). Thus, only β -forms of the 11-keto compounds are occurred in olibanum.

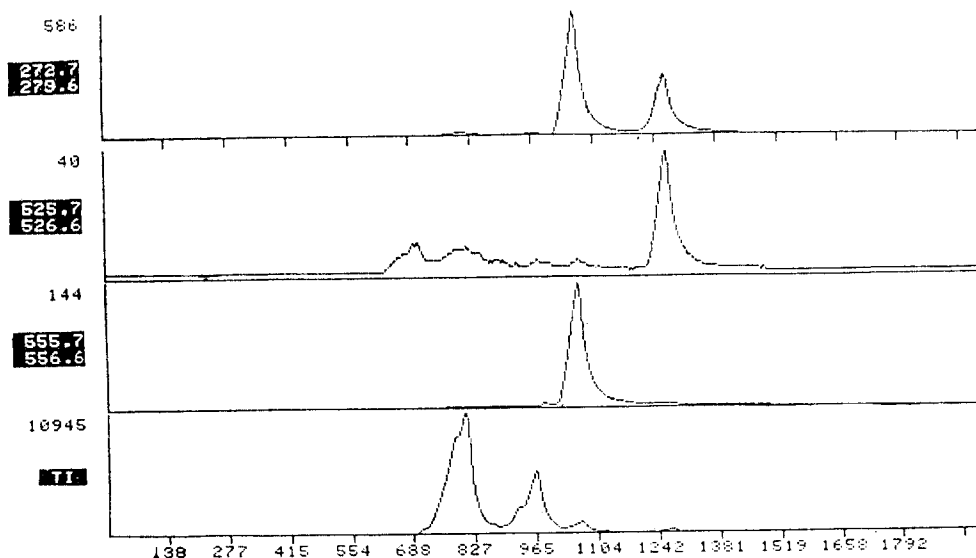


Fig. 3: GC/selected ion monitoring MS of the ether-soluble acidic fraction of olibanum. Mass ions of m/z 526 and 273 for acetyl-11-keto-boswellic acid methyl ester, and of m/z 556 and 273 for TMS derivative of 11-keto-boswellic acid methyl ester were selected for their monitoring. TI: Total ions.

Contents of Compounds I to IV in Olibanum

Acetylboswellic acid (I) and boswellic acid (II) were isolated and crystallized as mixtures of α - and β -forms in the ratio of 1 to 2 and 1 to 4, respectively, from olibanum. And acetyl-11-keto- β -boswellic acid (III) and 11-keto- β -boswellic acid (IV) were also isolated and their α forms were found to be absent in olibanum. In combination with GC and HPLC techniques, their contents in olibanum were determined as shown in Table II. Content ratio of α - and β -boswellic acid and their acetates were about 1 to 4 and 1 to 3, respectively.

Table II: Contents of compounds I to IV in olibanum

Compounds	Contents, % (Rt, min)	
	GC*	HPLC**
I α	1.59(17.34)	—
β	4.58(18.03)	—
II α	0.65(14.69)	—
β	2.70(17.24)	—
III (β)	0.86(23.74)	0.76(7.96)
IV (β)	1.72(19.60)	1.16(6.25)

* Analysis by GC. Cholesterol(Rt, 9.48) was used as internal reference. Details are described in "EXPERIMENTAL METHODS".

** Analysis by HPLC.

ACKNOWLEDGEMENTS

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