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TERPENOIDS FROM *JUNIPERUS SABINA**

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Key Word Index—*Juniperus sabina*, Cupressaceae, diterpenoids, sesquiterpenoids, chemotaxonomy

Abstract—Twenty-two diterpenoids with labdane, pimarane and abietane skeletons and two sesquiterpenoids were isolated or identified from the hexane extract of berries of *Juniperus sabina*

INTRODUCTION

Juniperus sabina is a shrub or small tree that grows between 1 400 and 2 300 m in Europe, Asia and North America and is known as 'common sabine' and 'savin' The composition of its leaves has been studied, podophyllotoxin and savinin [1, 2], the constituents of the essential oil [3], and recently the coumarins [4] have been reported We have studied the essential oil of the berries [5] and in this paper we describe the non-volatile components of its hexane extract

RESULTS AND DISCUSSION

The acidic fraction was esterified with diazomethane and after chromatography yielded methyl callitrisate (**1a**), methyl 4-epi-abietate (**2a**), methyl 4-epi-neoabietate (**3**) [6], methyl myrcecommunate (isocommunate) (**5**), methyl *cis*-communate (**6**), methyl sandaracopimarate (**4a**), methyl *trans*-communate (**7a**) and two oxygenated derivatives of **1a**, methyl 7-oxo-callitrisate (**1d**) and methyl 7α-hydroxycallitrisate (**1e**) The latter two compounds may be autoxidation products of **1a** because they were isolated after some time from a less polar chromatographic fraction which initially did not demonstrate hydroxyl or conjugated carbonyl absorptions in the IR spectrum

The neutral fraction after several chromatographic separations yielded (a) the hydrocarbons abieta-7, 13-diene (**2b**) and *trans*-biformene (**7b**) [7], (b) the aldehydes 4-epi-dehydroabietal (**1b**), 4-epi-abietal (**2c**), *trans*-communal (**7c**), sandaracopimaral (**4b**) and 4-epi-palustral (**8**), (c) the ketones abieta-7, 13-dien-3-one (**9**) and abieta-7, 11, 13-trien-3-one (**10**), (d) the alcohols 4-epi-dehydroabietol (**1c**), 4-epi-abietol (**2d**), sandaracopimarol (**4c**), abietol (**2e**) [8], labd-*E*-13-ene-8, 15-diol (**11**) [9], and (e) the sesquiterpenoids oplopanone (**12**) and oplopenone (**13**) [10]

Compounds **1a**–**1e**, **2a**–**2d**, **4a**–**4c**, **5**, **6**, **7a**, **7c**, **9** and **12** were identified through direct comparison with samples previously obtained by us in other studies on *Juniperus* [11–14] Compound **8** was identified in a mixture with **2b** by its ^{1}H NMR signals at δ 9 60 (axial CHO-4), 5 30 (H-14) and 0 88 (Me-10) Compound **10** is an oil, $[\alpha]_D = -130\ 6°$, whose IR spectrum shows carbonyl (1715 cm^{-1}) and aromatic ring (1600, 1510, 840 cm^{-1}) bands Its ^{1}H NMR spectrum contains signals of the three aromatic protons (δ 6 78, 6 84 and 7 05) in a relative 1,2,4 arrangement, of an isopropyl group (δ 1 05) and of two other methyl groups (δ 1 13 and 1 26) Compound **13** was identical with the dehydration product of **12**

Table 1 Proportions of the isomeric $\Delta^{13(16)}$, *cis*- and *trans*-communic acids in *Juniperus* sp

Section	Species	$\Delta^{13(16)}$	*cis*-	*trans*-
Oxycedrus	*J oxycedrus*	98	1	1
	J communis	48	36	15
Sabina	*J sabina*	2	12	86
	J thurifera	1	62	37
	J phoenicea	2	51	47

As a considerable amount of work on the composition of berries of several *Juniperus* sp has been done [11–14], some chemotaxonomic relationships have been observed Thus, the relative proportions of the three isomeric communic acids (Table 1) may serve to differentiate the oxycedrus and sabina sections of the genus *Juniperus* Also, the ocurrence of acidic abietane derivatives in species of the sabina section and their absence in the oxycedrus section may be useful

EXPERIMENTAL

IR film ^{1}H NMR 60 MHz, $CDCl_3$ with TMS as int standard Optical rotations were determined in $CHCl_3$

Dry berries (360 g) of *Juniperus sabina* L were triturated and extracted in a Soxhlet with hexane for 12 hr The soln was left to stand overnight after which insoluble materials were removed

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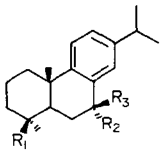
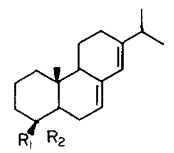
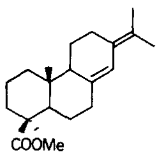
* For the preceding paper in this series see ref [4]



1a R_1 = COOMe, R_2 = R_3 = H
1b R_1 = CHO, R_2 = R_3 = H
1c R_1 = CH_2OH, R_2 = R_3 = H
1d R_1 = COOMe, R_2, R_3 = O
1e R_1 = COOMe, R_2 = OH, R_3 = H



2a R_1 = COOMe, R_2 = Me
2b R_1 = Me, R_2 = Me
2c R_1 = CHO, R_2 = Me
2d R_1 = CH_2OH, R_2 = Me
2e R_1 = Me, R_2 = CH_2OH



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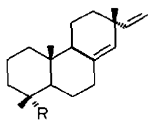

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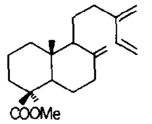
4b R = CHO
4c R = CH_2OH



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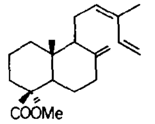

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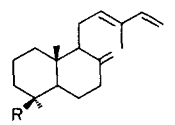
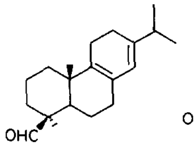


7a R = COOMe
7b R = Me
7c R = CHO



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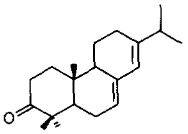

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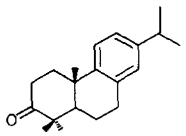

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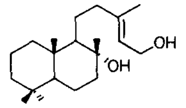

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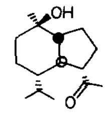

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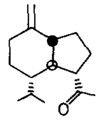

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The extract was defatted by pptation with MeOH and fractionated by aq NaOH (4 %) extraction The acidic fraction (19 g) was esterified with ethereal CH_2N_2 and its components were separated by repeated chromatography on Si gel–$AgNO_3$ and Al_2O_3–$AgNO_3$ columns to yield **1a** (160 mg), **2a** (544 mg), **3** (186 mg), **4a** (250 mg), **5** (200 mg), **6** (4 9 g), **7a** (10 5 g), **1d** (7 mg) and **1e** (13 mg) The neutral fraction (29 1 g) was saponified with KOH–MeOH and the unsaponifiable fraction treated with hexane The soluble part in hexane (9 7 g) after several chromatographic separations gave **2b** (360 mg), **7b** (85 mg), **1b** (398 mg), **2c** (357 mg), **8** plus **2c** (28 mg), **4b** (31 mg), **7c** (185 mg), **9** (250 mg), **10** (26 mg), **1c** (54 mg), **2d** (274 mg), **2d** plus **2e** (181 mg), **4c** (162 mg), **11** (70 mg), **12** (62 mg), **13** (15 mg), sitosterol (230 mg) and 10-nonacosanol (70 mg)

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